Elements of
PHYSICAL CHEMISTRY

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SECOND EDITION

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Preface

As its title implies, the purpose of this book is to present, in the words of Webster's Dictionary, "an outline regarded as containing the fundamental features" of physical chemistry. It is an introductory text intended not only for students who propose to specialize in chemistry, but also for those who require some knowledge of physical chemistry in connection with their studies of physics, engineering, metallurgy, biology, medicine, geology, etc.

In preparing this revised version, the objective has been essentially the same as was the case with the first edition, namely, to help the reader obtain an understanding of the basic principles and concepts of modern physical chemistry. The emphasis, as before, is on simplicity and clarity, so that average students can follow the presentation while those with exceptional ability will find that it provides a useful groundwork for further study.

In view of the developments in the teaching of physical chemistry that have taken place in recent years, a number of elementary topics, which are now covered in other courses, have been omitted and new material of a more advanced character has been added. Because of the basic importance of thermodynamics in physical chemistry, the first two laws are now introduced at an early stage, following a necessary discussion of the behavior of gases. The treatment of molecular properties and of nuclear chemistry has been enlarged so that these subjects now constitute separate chapters. In addition, the reading references have been extended to include articles published in chemical review journals as well as in the Journal of Chemical Education.

The completely new sets of problems are an important feature of the present edition. While a number of these are of a relatively straightforward nature, intended to illustrate the application of important equations in physical chemistry, many are of the type which present more of a challenge to the student. Their purpose is to encourage thought and arouse interest while teaching the fundamentals of the subject.

SAMUEL GLASSTONE
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I

Introduction

THE NATURE OF PHYSICAL CHEMISTRY

1a. The Scope of Physical Chemistry.—Although the nature of the problems that fall within the scope of **physical chemistry** is well recognized, it is nevertheless not an easy matter to give a simple and precise definition of this subject. Chemistry has been described as the science which deals with matter and its transformations, in contrast to physics which is concerned largely with energy and its transformations. Physical chemistry may be regarded as an intermediate field involving the study of the interactions between matter and energy. However, this definition is not complete enough to include all the topics that are generally regarded as being properly in the realm of physical chemistry, and the situation may well be considered from another point of view. Inorganic chemistry and organic chemistry deal primarily with the actual nature of the material changes occurring in chemical reactions. In physical chemistry, on the other hand, the influence of physical factors, such as temperature, pressure, concentration, electricity, light, etc., both on the reacting substances and on the reactions, is of primary interest; the objective is the understanding of the fundamental nature of chemical change. It is thus reasonable to describe physical chemistry as being concerned with *the elucidation or clarification of the principles underlying those transformations of matter known as chemical reactions*, through a study of the physical properties of the reacting substances and of the effect of physical changes on the reactions themselves.

The substances that take part in chemical reactions are generally encountered in the form of gas, liquid or solid, or perhaps in solution. Consequently, in the study of physical chemistry the properties of the various forms of matter, both in the pure state and in mixtures, are examined from various points of view. In this connection, two particular approaches are of interest. One of these involves the use of thermodynamics. This subject is based on two fundamental postulates which summarize actual experience with regard to the conversion of one form of energy into another. The conclusions drawn from thermodynamics are, however, independent of the nature of matter; that is to say, they take no account of the existence and structure of atoms and molecules. In the second approach, therefore, an attempt is made to apply atomic theory to interpret the properties and behavior of substances which might take part in chemical reactions. With the general background, derived from both thermodynamic and structural considerations, the student will be in a position to consider actual reactions, and to examine the factors which determine the direction, velocity and extent of a chemical change. In this manner it is hoped to justify the assertion that physical chemistry deals with the fundamental principles that underlie all chemical transformations, irrespective of whether inorganic or organic substances are involved.

1b. Scientific Method.—Before proceeding to the more detailed consideration of the various topics, as just outlined, it is desirable to say a few words about the methods of physical chemistry. Essentially, the study of this subject provides one of the best illustrations of the use of what is called the **scientific method.** To start with, experiments are performed, and the results of the observations, i.e., the empirical data, relating to a particular phenomenon are collected. An attempt is made to generalize these results in the form of a simple statement or mathematical expression known as a **law**; so long as further experiments bring to light no exceptions, the law is regarded as holding good. Sometimes, as in the case of the influence of temperature and pressure on the volume of a gas, more accurate observations show that the laws which were originally proposed are approximate and are applicable under certain restricted conditions only. In other instances, as, for example, with the laws of thermodynamics, no exceptions are known.

The next stage in the application of the scientific method is to put forward a **hypothesis** with the object of explaining the experimental observations, or of accounting for the general law which summarizes them. It is, of course, doubtful whether a complete "explanation" of observed phenomena is ever possible; after all, the fundamental concepts of matter and energy cannot really be "explained". What a hypothesis generally attempts, therefore, is *an interpretation of the experimental facts in terms of simpler or more easily understood phenomena.* In other words, the purpose of the hypothesis is to state the causes which lead to the observed effects. These causes themselves have underlying causes, and it is the object of science to trace them, step by step, as far back as possible; the ultimate aim is the unification of all phenomena into one scheme. This is being gradually achieved in chemistry, for example, by the use of the concepts of the electron, the proton and the neutron; even though the exact nature of these structural units cannot be explained, the resulting systematization has, nevertheless, proved of great value.

1c. Hypothesis and Theory.—It may happen that two or more alternative hypotheses are proposed to account for certain experimental facts. A familiar illustration is provided by the phenomenon of burning or combustion in air. Two hypotheses, one based on the supposed existence of "phlogiston" and the other on the idea of combination with oxygen, were suggested. In the course of time it became evident that the latter hypothesis offered a more satisfactory interpretation of the observations than did the former. The phlogiston hypothesis of combustion was consequently discarded, and it ceased to have any but historical interest. When a particular hypothesis has withstood the test of many experiments, while the others have been eliminated or proved to be unsatisfactory in one way or another, it is referred to as a **theory.**

Although a distinction should strictly be drawn between the terms *hypothesis* and *theory*, it is nevertheless the common practice to regard them as having the same significance. It is probably true to say that the use of the term "hypothesis" is decreasing in modern scientific writings, and the word "theory" is employed almost exclusively in this connection. One reason for this preference, in spite of its not being strictly correct, lies partly in the fact that the adjective "hypothetical" has acquired the significance of referring to something that is imaginary. The same objection, however, does not apply to the adjective "theoretical," and such expressions as the "theoretical treatment" of a subject, or the "theoretical approach" to a problem can be used without misunderstanding.

It should be apparent from what has been said that there is nothing that is necessarily permanent about a theory. A satisfactory theory must be able to correlate all the known facts concerning a particular phenomenon or set of phenomena, and also predict new ones. If there exist proven facts which are not in harmony with the theory, or the theory makes predictions which are later found to be incorrect, then that particular theory must be modified or discarded in favor of another. Sometimes an unsatisfactory theory has to be retained, simply because the necessary improvement or alternative is not immediately evident. This was the case, for example, in connection with certain properties of salt solutions, i.e., the strong electrolytes. In the course of time, however, suggestions were made for modifying the theory, which had been known for many years to be inadequate, so as to bring it into better agreement with the observed facts. Even now, in spite of the great advances that have been made, it is realized that the theory is still incomplete. Sometimes a theory can be modified, as just indicated, but in other cases it may have to be discarded altogether. In any event, a theory is retained only as long as it proves useful in the correlation and interpretation of experimental data, for that is its prime function in the operation of the methods of science.

Among the theories which have stood the test of time and which have found useful application in the development of physical chemistry, mention may be made of Dalton's atomic theory, the theory of atomic structure, the kinetic theory of gases, the theory of valence and molecular structure, quantum theory and the theory of electrolytic dissociation. Combination of many of these theories with the laws of thermodynamics, which are generalizations based on experience, has led to results of fundamental importance to chemistry, as will become apparent in the course of this book.

2

The Properties of Gases

THE GAS LAWS

2a. The States of Matter.—As a general rule, the chemist or physicist is unable to study the properties of individual molecules, but he deals rather with the aggregates of molecules as they occur in nature. It is the aggregations of molecules which come within the scope of human experience that constitute what is known as **matter.** The various kinds of substances that make up matter can be divided roughly into three categories, namely, gases, liquids and solids; these are often referred to as the three **states of matter.**

The gaseous state is characterized by a marked sensitivity of the volume to changes of temperature and pressure, and also by the fact that a gas normally has no bounding surface and so it tends to fill completely any available space. A liquid, like a gas, has no definite shape, and so it takes the shape of the vessel in which it is placed. There is, however, an important difference between a gas and a liquid; whereas the former has no surface at all, the latter has a surface which places a limit on the extent of space or volume it can occupy. It is this surface, as will be seen in Chapter 5, which is responsible for many of the characteristic properties of liquids. As a general rule, liquids are more dense, that is, they have a greater density, than gases, but there are certain conditions (§ 10b) under which the densities become similar in value. Solids differ markedly from liquids and gases in the respect that they have a definite shape; like liquids, however, their volumes do not alter greatly when subjected to changes of temperature and pressure. From their general behavior, it may be concluded that the properties of liquids are intermediate between those of gases and solids; the order of increasing complexity of the states of matter is thus: gas, liquid, solid. The gaseous state will, therefore, be treated first, and the other states will be considered in later chapters.

2b. Boyle's Law.—When the pressure on a gas is increased, at constant temperature, the volume decreases; a simple relationship between the volume and the pressure was discovered by R. Boyle (1662). He found, within the limits of error of his somewhat crude experiments, that *at constant temperature the volume of a definite mass of gas is inversely proportional to the pressure.* In other words, *the product of the pressure and volume of a given mass of gas is constant at a fixed temperature.* These are alternative statements of **Boyle's law,** which may also be written in the form of the equation

$$PV = \text{constant}, \tag{2.1}$$

where P is the pressure and V is the volume of a definite mass of gas at a constant temperature. The magnitude of the constant depends on the temperature and mass of the gas, and also upon its nature. The facts implied by equation (2.1) may be expressed in still another manner; thus, if V_1 is the volume of a given mass of gas when the pressure is P_1, and V_2 is the volume of the same mass of gas when the pressure is changed to P_2, at the same temperature, then

$$P_1V_1 = P_2V_2. \tag{2.2}$$

The value of Boyle's law lies in its usefulness for calculating the volume of a gas at any required pressure, if the volume at another pressure is known.

Example: A given mass of gas occupies a volume of 240 milliliters (ml) at a pressure of 1.25 atmospheres (atm); by how much would the volume change if the pressure were altered to 0.75 atm at the same temperature? What would be the volume of double the given mass of gas at the latter pressure?

Let V ml be the volume at 0.75 atm; then by Boyle's law, e.g., equation (2.2),

$$1.25 \times 240 = 0.75 \times V$$

$$V = \frac{1.25 \times 240}{0.75} = 400 \text{ ml.}$$

The volume has therefore increased by 400 − 240 160 ml as a result of the pressure change.

At a definite temperature and pressure, the volume of a gas is directly proportional to its mass; hence, doubling the mass would double the volume. The volume of double the given mass of gas at 0.75 atm would thus be 2 × 400 = 800 ml.

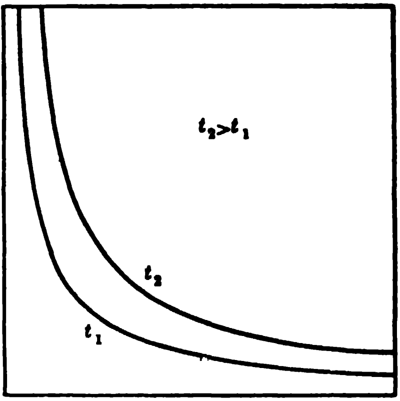

FIG. 2.1. Boyle's law isotherms for an ideal gas

The result of Boyle's law may be represented graphically by plotting the pressures as ordinates and the corresponding volumes, at constant temperature, as abscissae, as in Fig. 2.1. The curve drawn through the resulting points will then be a rectangular hyperbola, as shown, if Boyle's law is obeyed. The general term **isothermal** or **isotherm** is used to describe a curve, such as that in Fig. 2.1, which gives the variation of volume with pressure of a gas at constant temperature. According to Boyle's law, the isotherm for a definite mass of a given gas is a rectangular hyperbola. For each temperature a different hyperbola is obtained, as shown in Fig. 2.1, where the temperature t_2 is higher than t_1.

2c. Gay-Lussac's Law: Absolute Temperatures.—The variation of the volume of a gas with temperature, at constant pressure, is expressed by the generalization often called **Gay-Lussac's law** (J. L. Gay-Lussac, 1802); it is sometimes referred to as **Charles's law,** because similar results were obtained by J. A. C. Charles in 1787, although they were not published at that time. In its simplest form, the law states that *at constant pressure, the volume of a fixed mass of any gas increases by the same relative amount (or fraction) for every degree rise in temperature.* If V_0 is the volume of a definite mass of gas at 0°C (at a given pressure) then, according to Gay-Lussac's law, the volume V_t at the temperature t°C (at the same pressure) will be given by

$$V_t = V_0 + (\alpha_v V_0)t = V_0(1 + \alpha_v t), \tag{2.3}$$

where α_v, called the coefficient of expansion, should be the same for all gases. It will be seen shortly that α_v varies to some extent, although it approaches a constant value at low pressures and high temperatures (§ 2f). As a fair approximation, however, α_v may be taken as being equal to 1/273 per °C, so that equation (2.3) may be written as

$$V_t = V_0\left(1 + \frac{t}{273}\right). \tag{2.4}$$

If V_1 and V_2 are the volumes of the same mass of gas at the two temperatures t_1 and t_2, respectively, at a given pressure, then

$$V_1 = V_0\left(1 + \frac{t_1}{273}\right) \tag{2.5}$$

and

$$V_2 = V_0\left(1 + \frac{t_2}{273}\right). \tag{2.6}$$

Upon dividing equation (2.5) by (2.6) the result is

$$\frac{V_1}{V_2} = \frac{273 + t_1}{273 + t_2}. \tag{2.7}$$

Suppose a new scale of temperature is devised in which the degree has the same size as the Celsius degree,[*] but the zero is 273° below the zero on the Celsius scale; that is to say, the zero on the new scale is at −273°C. Temperatures T on the new scale are then obtained by adding 273° to the Celsius temperature t, viz.,

$$T = 273 + t.$$

The temperatures on the new scale, which is defined more exactly below, are called **absolute temperatures,** because there are reasons for believing that

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[*] By international agreement, the designation Celsius has been adopted in place of the term centigrade, formerly in common use.

the zero on this scale is the lowest conceivable temperature. The symbol °K, that is, "degrees Kelvin," is most frequently employed to represent absolute temperatures, in honor of Lord Kelvin (William Thomson) who derived an exactly equivalent scale from considerations of thermodynamics (§ 8i).

Making use of the definition of absolute temperature, equation (2.7) becomes

$$\frac{V_1}{V_2} = \frac{T_1}{T_2} \tag{2.8}$$

or

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \tag{2.9}$$

or

$$\frac{V}{T} = \text{constant.} \tag{2.10}$$

These are alternative expressions of Gay-Lussac's law, and their significance may be put into words in the form of the following statement of the law: *the volume of a given mass of gas at a definite pressure is directly proportional to the absolute temperature.* It may be noted that, according to the Gay-Lussac law, the volume of a gas should be zero at the absolute zero, i.e., at −273°C; however, apart from the fact that the gas will have liquefied and solidified before this temperature can be attained, it will be seen shortly that the law fails to hold at low temperatures.

A graphical representation of the variation, at constant pressure, of the volume of a gas with the absolute temperature, as required by Gay-Lussac's law, is given in Fig. 2.2. The straight lines, called **isobars** (Greek: *constant pressure*), which extrapolate to zero volume at 0°K, are shown for two pressures, P_2 being greater than P_1.

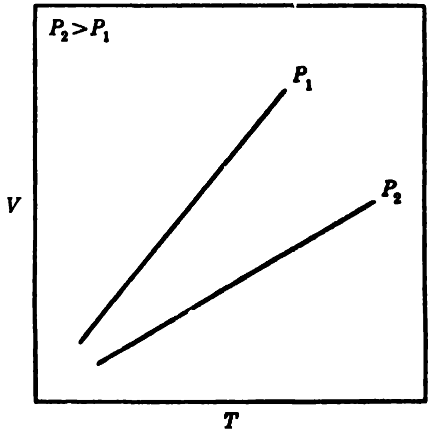

FIG. 2.2. Gay-Lussac's law isobars for an ideal gas

Example: The volume of a given mass of gas is 360 ml at 15°C; at what temperature will the volume be 480 ml, assuming constant pressure?

The absolute temperature corresponding to 15°C is 273 + 15 = 288°K; the volume is then 360 ml. Let T be the absolute temperature at which the volume is 480 ml; then according to Gay-Lussac's law, e.g., equation (2.9),

$$\frac{360}{288} = \frac{480}{T}$$

$$\frac{480 \times 288}{360} \quad 384°\text{K}.$$

The corresponding Celsius temperature is thus 384 − 273 = 111°C.

2d. Equation of State.—The results of the laws of Boyle and of Gay-Lussac may be combined in an expression which represents the relationship between the pressure, volume and temperature of a given mass of gas; such an expression is described as an **equation of state.** Suppose the gas has initially a volume V_1 at the pressure P_1 and temperature T_1; then when the pressure is changed to P_2 and the temperature to T_2, the volume will be V_2. The relationship between these quantities may be derived in the following manner. Suppose the temperature is maintained at T_1 while the pressure is changed from P_1 to P_2; if the accompanying volume change is from V_1 to V_1', then Boyle's law, equation (2.2), which is applicable since the temperature is constant, gives

$$P_1V_1 = P_2V_1'$$

$$V_1' = \frac{P_1V_1}{P_2}. \tag{2.11}$$

The pressure is now kept constant at P_2, and the temperature is altered from T_1 to T_2; the volume will then change from V_1' to the final value of V_2. Applying Gay-Lussac's law [equation (2.9)], at constant pressure, it follows that

$$\frac{V_1'}{T_1} = \frac{V_2}{T_2},$$

and upon introducing the value of V_1' from equation (2.11), it is seen that

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}. \tag{2.12}$$

An exactly similar result will be obtained for the volume V_3 at pressure P_3 and temperature T_3, and so on; hence,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = \frac{P_3V_3}{T_3} = \cdots$$

or, in general,

$$\frac{PV}{T} = \text{constant}, \tag{2.13}$$

for a given mass of gas. The equation (2.13) is thus a form of the equation of state for a gas which obeys Boyle's law and Gay-Lussac's law; it implies that, for a definite mass of gas, *any change of temperature and pressure will be accompanied by an adjustment of volume so that the quantity PV/T remains unaltered.*

Example: A given mass of gas occupies a volume of 250 ml at 21°C and a pressure of 1.40 atm. At what pressure will the volume be 300 ml when the temperature is raised to 49°C?

For this problem it is convenient to use equation (2.12); then

$P_1 = 1.40$ atm $V_1 = 250$ ml $T_1 = 273 + 21 = 294°$K
$P_2 = ?$ $V_2 = 300$ ml $T_2 = 273 + 49 = 322°$K

Consequently,

$$\frac{1.40 \times 250}{294} = \frac{P_2 \times 300}{322}$$

$$P_2 = \frac{1.40 \times 250 \times 322}{294 \times 300} = 1.28 \text{ atm.}$$

2e. Dependence of Pressure on Temperature: the Gas Thermometer.

—If the volume of a fixed mass of gas is maintained constant, it follows from equation (2.13) that

$$\frac{P}{T} = \text{constant.} \qquad (2.14)$$

In other words, the pressure of a given mass of gas, at constant volume, is directly proportional to the absolute temperature. This result is indicated graphically in Fig. 2.3; the straight lines, called **isochores** (Greek: *constant volume*), are for two different volumes V_1 and V_2, where V_2 is larger than V_1.

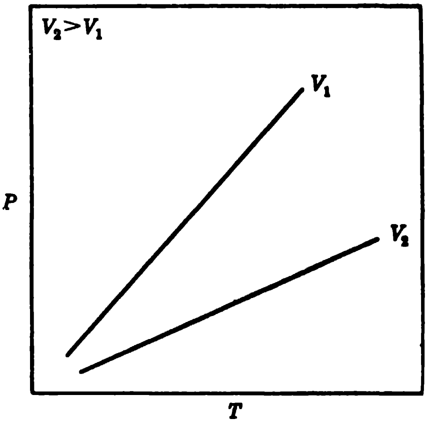

FIG. 2.3. Isochores for an ideal gas

The dependence of the pressure of a given mass of gas, at constant volume, on the temperature can also be represented by an expression similar to equation (2.3); thus,

$$P_t = P_0 + (\alpha_p P_0)t = P_0(1 + \alpha_p t), \qquad (2.15)$$

where P_t and P_0 are the pressures at the temperatures t and 0°C, respectively, and α_p is the coefficient of pressure change. By combining equations (2.14) and (2.15); it follows that

$$\frac{T_t}{T_0} = \frac{P_t}{P_0} = (1 + \alpha_p t),$$

and, similarly, from equations (2.3) and (2.8),

$$\frac{T_t}{T_0} = \frac{V_t}{V_0} = (1 + \alpha_v t).$$

Upon comparing these two results, it is seen that

$$\alpha_p = \alpha_v,$$

assuming Boyle's law. Hence, the relative (or fractional) change in pressure with temperature at constant volume is identical with the relative (or fractional) change in volume with temperature at constant pressure.

The variation of the volume or pressure of a fixed mass of gas as a function of temperature forms the basis of the system of temperature measurement. In the **constant volume gas thermometer,** for example, the pressure which must be applied to the gas at a given temperature to maintain the volume constant is measured. The temperature scale is established by determining the pressures at certain fixed points and assigning numerical values to them. Two temperatures in general use for this purpose are the ice point, i.e., the temperature of equilibrium between ice and air-saturated water at 1 atm pressure, which is assigned the value 0°C, and the steam point, i.e., the temperature of equilibrium between steam and water at 1 atm pressure, which is taken as 100°C. Let P_0 and P_{100} be the gas pressures measured, for constant volume, at these two fixed temperatures; then, if P_t is the pressure observed at any other temperature, that temperature is given by equation (2.15) as

$$t = \frac{100(P_t - P_0)}{P_{100} - P_0}.$$

Since the equations given above do not hold precisely for actual (or real) gases, the observed pressures must be corrected for deviations from ideal behavior. Helium is commonly employed in gas thermometry because it exhibits smaller deviations than other gases under similar conditions. For practical temperature measurement, however, the gas thermometer is inconvenient, and so mercury in glass thermometers, thermocouples and resistance thermometers are used. These are calibrated in terms of the gas thermometer temperature scale, as described above.

2f. The Ideal Gas Equation.—The value of the constant in equation (2.13) depends upon the mass and nature of the gas, but the introduction of **Avogadro's law** permits of a remarkable simplification. According to this law, equal numbers of molecules of different gases will occupy the same volume, at a given temperature and pressure. In other words, provided equal numbers of molecules are concerned, and P and T are the same, V will be the same for different gases; the constant in equation (2.13) will then obviously be independent of the nature of the gas. In accordance with its definition, one mole, i.e., one gram molecular weight, of any substance always contains the same number of molecules; hence, *provided one mole of gas is under consideration, PV/T will be equal to a universal constant R, known as the* **gas constant,** *which has the same value for all gases.* The general equation of state for any gas would then be

$$\frac{PV}{T} = R$$

or

$$PV = RT, \tag{2.16}$$

where V is the volume occupied by 1 mole, i.e., the **molar volume,** at the pressure P and the temperature T. At the same pressure and temperature, the volume of n *moles* would be n times as great as for 1 mole; if v is this volume,* then

$$Pv = nRT. \tag{2.17}$$

So far it has been tacitly assumed that gases do actually obey the laws of Boyle and Gay-Lussac; however, for real gases these laws can only be regarded as approximations applicable at relatively low gas pressures and moderately high temperatures. It will be seen later (§ 4a) that actual gases exhibit deviations from the gas laws, such deviations being greater the nearer the temperatures and pressures are to the conditions under which the gas can be condensed to a liquid. It appears, therefore, that equations (2.16) and (2.17), and all other equations based on Boyle's law and Gay-Lussac's law, as given in previous sections, cannot be regarded as correct for real gases. It is, nevertheless, very useful to postulate a hypothetical or imaginary **ideal gas,** or **perfect gas,** defined as a gas to which the laws of Boyle and Gay-Lussac are strictly applicable. For such a gas, too, the Avogadro law, from which actual gases show deviations, holds precisely, and so equations (2.16) and (2.17) are exact; these are consequently forms of the equation of state for an ideal gas. The equation (2.16) is thus frequently referred to as the **ideal gas equation** or the **ideal gas law equation** for one mole.

Since equations (2.16) and (2.17) do not apply to real gases, there immediately arises the problem of the evaluation of the ideal gas constant R, for it is only for ideal gases that R would be an exact constant. If the pressure P and volume V of 1 mole of an ideal gas were known at a definite temperature T, it would be a simple matter to evaluate R from equation (2.16), but as no gas behaves ideally, this procedure would appear to be ruled out. Fortunately, it is an experimental fact that all gases *approach* ideal behavior as the pressure is decreased. Hence, by making pressure, volume and temperature measurements on a real gas at a number of pressures, and extrapolating the results to zero pressure, it is possible to derive the properties of an ideal gas.

The data obtained in this manner, after extrapolation, should be independent of the actual gas employed for the experiments, and this expectation has been confirmed. From measurements of the effect of temperature on the volume of a gas at a number of constant pressures, the limiting (extrapolated) value of the coefficient of expansion at zero pressure is found to be 0.0036610 per °C. The absolute zero of temperature for an ideal gas on the Celsius scale is then

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* The convention which will be employed subsequently, as far as possible, is to use capital V for the volume of 1 mole, and a small v when the given volume contains the general number n moles.

$$0°\mathrm{K} = -\frac{1}{0.0036610} = -273.15°\mathrm{C}.$$

Strictly speaking, therefore, it is necessary to add 273.15 to the Celsius temperature to obtain that on the absolute (Kelvin) scale. For many purposes, however, it is sufficient to use the approximate value of −273°C for the absolute zero.

By measuring the volumes of gases at different pressures and constant temperature, and extrapolating the data to zero pressure to correct for departure from ideal behavior (Fig. 2.4), it has been found that the volume

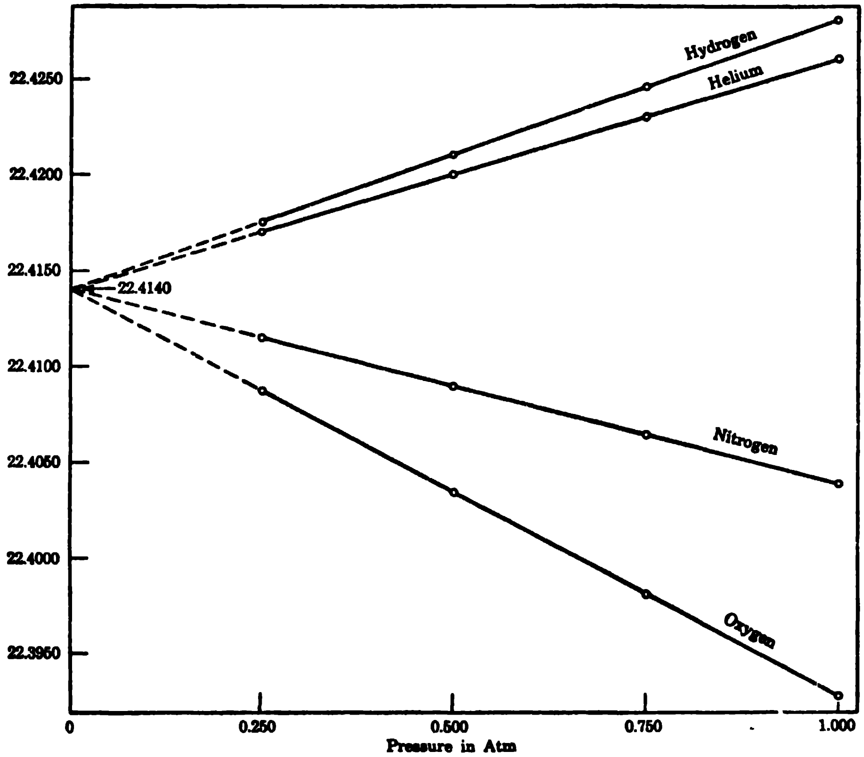

FIG. 2.4. Evaluation of the ideal gas pressure-volume product at 0°C

occupied by 1 mole of an ideal gas at standard temperature and pressure (S.T.P.), defined as 0°C, i.e., 273.15°K, and 1 atm, i.e., 76.0 cm of mercury, respectively, is 22.414 liters.

2g. Evaluation of the Gas Constant.—All the data are now available for calculating the ideal gas constant R, but before doing so it is necessary to consider the matter of the proper **units** to employ. The question of units is one that is of fundamental importance in many aspects of physical chemistry, and the evaluation of the gas constant will serve to illustrate some of the points involved.

The most general definition of R is given by equation (2.17) as

$$R = \frac{Pv}{Tn}, \tag{2.18}$$

and so the gas constant has the dimensions of pressure × volume divided by number of moles × temperature. The dimensions of pressure are force × $(\text{area})^{-1}$, i.e., pressure is force per unit area, and area is $(\text{length})^2$; hence,

$$\text{pressure} = \text{force} \times (\text{length})^{-2}.$$

Since volume has the dimensions of $(\text{length})^3$, and temperature is expressed in degrees, it follows from equation (2.18) that

$$R = \frac{\text{force} \times (\text{length})^{-2} \times (\text{length})^3}{\text{degrees} \times \text{no. of moles}}.$$

The product of force and length is energy, and so

$$R = \frac{\text{energy}}{\text{degrees} \times \text{no. of moles}}. \tag{2.19}$$

It is thus seen that *the proper dimensions for the expression of R are energy per degree per mole*, i.e., energy degree^{-1} mole^{-1}. It may be noted, incidentally, by comparing equations (2.18) and (2.19), that the product of pressure and volume has the dimensions of energy.

The temperature employed in the evaluation of the gas constant is generally the absolute temperature, based on the Celsius degree,* but the energy may be stated in various ways, of which three are most commonly used; these are (i) liter-atmospheres, (ii) ergs, and (iii) calories, which will be considered in turn.

I. Energy in Liter-Atmospheres.—For this purpose, the volume of the gas is expressed in liters and the pressure in atmospheres; the energy is then in liter-atmospheres. As seen above, 1 mole, i.e., $n = 1$, of an ideal gas occupies 22.414 liters at 1 atm pressure and a temperature of 273.15°K; hence,

$$R = \frac{PV}{T} = \frac{1 \times 22.414}{273.15}$$

$$= 0.082054 \text{ liter-atm degree}^{-1} \text{ mole}^{-1}.$$

II. Energy in Ergs.—The pressure must now be stated in cm-gram-sec (cgs) units, i.e., dynes per sq cm, and the volume in cubic centimeters. Since 1 atm is equivalent to 76.0 cm of mercury, the density of which is 13.595 g cm^{-3} at 0°C, it follows that

$$1 \text{ atm} = 76.0 \times 13.595 \times 980.66 \text{ dynes cm}^{-2},$$

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* Engineers frequently express absolute temperatures on a scale based on the Fahrenheit degree; these are called Rankine temperatures.

where 980.66 cm per sec per sec is the acceleration due to gravity. Upon multiplying out, it is found that

$$1 \text{ atm} = 1.0132 \times 10^6 \text{ dynes cm}^{-2}.$$

The volume of 1 mole of ideal gas at S.T.P. is 22,414 ml and since 1 ml is actually 1.000027 cc, this volume is 22,414.6 cc. The value of R is then given by

$$R = \frac{PV}{T} = \frac{1.0132 \times 10^6 \times 22{,}414.6}{273.15}$$

$$= 8.314 \times 10^7 \text{ ergs degree}^{-1} \text{ mole}^{-1}.$$

III. Energy in Calories.—The evaluation of the gas constant with the energy in calories is most readily made by utilizing the fact that a calorie is equivalent to 4.184×10^7 ergs (§ 6a). It follows then that

$$R = \frac{8.314 \times 10^7}{4.184 \times 10^7} = 1.987 \text{ cal degree}^{-1} \text{ mole}^{-1}.$$

It is seen that the gas constant is very close to 2 cal degree^{-1} mole^{-1}, i.e., 2 cal per degree per mole. This approximate value is frequently employed in calculations, but it must be clearly understood that this can only be done if the energy, i.e., the pressure-volume product, is expressed in calories. The necessity for exercising great care in the matter of the use of the proper units cannot be stressed too strongly; examples will be given from time to time illustrating the correct choice of units.

Example: How many moles of oxygen are contained in 10.0 liters of the gas at a pressure of 75.0 cm of mercury and a temperature of 27°C, assuming ideal behavior?

A pressure of 75.0 cm of mercury is equal to 75.0/76.0 atm, and since the volume is given in liters, it is convenient to express R in liter-atm, i.e., 0.082. The temperature T is $273 + 27 = 300$°K, and hence rearrangement of equation (2.17) gives

$$n = \frac{Pv}{RT} = \frac{(75.0/76.0) \times 10.0}{0.082 \times 300} = 0.401 \text{ mole}.$$

2h. Mixtures of Gases: Dalton's Law of Partial Pressures.—The connection between the total pressure of a mixture of gases and the pressures of the individual gases was expressed by J. Dalton (1801) in the form of the **law of partial pressures.** The **partial pressure** of each gas in a mixture is defined as *the pressure the gas would exert if it alone occupied the whole volume of the mixture at the same temperature.* According to Dalton's law of partial pressures, *the total pressure of a mixture of gases is equal to the sum of the partial pressures of the constituent gases.*

Consider a vessel of volume v containing three gases, the amounts being n_1, n_2 and n_3 moles, respectively. Suppose that if the vessel were occupied exclusively by the n_1 moles of the first gas, the pressure would be p_1; if it contained the n_2 moles of the second gas only, the pressure would be p_2; and if the n_3 moles of the third gas were the sole occupants of the vessel the pressure would be p_3, all at a definite temperature. If the total pressure when the three gases are present in the vessel is P, then by the law of partial pressures

$$P = p_1 + p_2 + p_3, \tag{2.20}$$

and so on, for any mixture of gases. For reasons which will appear shortly, the law of partial pressures suffers from the same limitations as do the other gas laws. The equation (2.20) is strictly applicable, therefore, to a mixture of ideal gases, although the deviations exhibited by actual gases are not large unless the conditions approach those under which liquefaction is possible.

If each of the gases present in the mixture behaves ideally, it is possible to write for each of the gases separately occupying the vessel of volume v,

$$p_1v = n_1RT \tag{2.21a}$$

$$p_2v = n_2RT \tag{2.21b}$$

$$p_3v = n_3RT, \text{ etc.,} \tag{2.21c}$$

and hence,

$$(p_1 + p_2 + p_3 + \cdots)v = (n_1 + n_2 + n_3 + \cdots)RT. \tag{2.22}$$

According to the law of partial pressures, represented by equation (2.20), the sum of the pressures p_1, p_2, p_3, etc., may be replaced by the total pressure P; consequently equation (2.22) becomes

$$Pv = (n_1 + n_2 + \cdots)RT = nRT, \tag{2.23}$$

where n, equal to $n_1 + n_2 + n_3 + \cdots$, is the total number of moles in the gas mixture. Upon dividing equation (2.21a) by (2.23) and rearranging, the result is

$$p_1 = \frac{n_1}{n}P. \tag{2.24a}$$

Similarly, from equations (2.21b) and (2.23),

$$p_2 = \frac{n_2}{n}P, \tag{2.24b}$$

and so on. The fractions n_1/n, n_2/n, etc., are called the **mole fractions** of the respective gases. The mole fraction of a constituent of any mixture—gaseous, liquid or solid—is defined as *the number of moles (or molecules) of that constituent divided by the total number of moles (or molecules) in the mixture.* If the symbol x is used to represent the mole fraction, it is seen that the equations (2.24) may be written as

$$p_1 = x_1P,\ p_2 = x_2P, \text{ etc.} \tag{2.25}$$

This result is an important consequence of Dalton's law, for it enables the partial pressure of any constituent of a mixture of ideal gases to be calculated from the total pressure, at the same temperature, if the mole fraction is known.

There are many useful applications of the law of partial pressures in physical chemistry; some of these are illustrated by the following examples.

Example: A gas collected over water at 25°C becomes saturated with water vapor; the measured volume is 190 ml at a total pressure of 740 mm of mercury. The partial pressure of the water vapor in the mixture, equal to the vapor pressure of water at 25°, is 24 mm. Calculate the volume the dry gas would occupy at a pressure of 760 mm, assuming the gas and the water vapor to behave ideally.

The partial pressure p of the dry gas is equal to the total pressure, i.e., 740 mm, minus the partial pressure of the water vapor, i.e., 24 mm; hence,

$$p = 740 - 24 = 716 \text{ mm}.$$

This is the pressure of the dry gas when it occupies the whole volume of 190 ml; the volume v of the dry gas at a pressure of 760 mm is then given by Boyle's law as

$$716 \times 190 = 760 \times v$$

$$v = \frac{716 \times 190}{760} = 179 \text{ ml}.$$

Example: A mixture consists of 0.495 gram of gas A of molecular weight 66.0, and 0.182 gram of a gas B of molecular weight 45.5; the total pressure is 76.2 cm of mercury. Calculate the partial pressures of the two gases.

$$\text{Number of moles of gas A is } \frac{0.495}{66.0} = 0.0075$$

$$\text{Number of moles of gas B is } \frac{0.182}{45.5} = 0.0040$$

$$\text{Total number of moles} = 0.0075 + 0.0040 = 0.0115.$$

The mole fraction of A is thus 0.0075/0.0115, and hence by equation (2.25),

$$\text{Partial pressure of A} = \frac{0.0075}{0.0115} \times 76.2 = 49.7 \text{ cm of mercury,}$$

and

$$\text{Partial pressure of B} = \frac{0.0040}{0.0115} \times 76.2 = 26.5 \text{ cm of mercury.}$$

Alternatively, the latter quantity can be obtained by subtracting 49.7 cm from the total pressure 76.2 cm.

Example: A volume of 125 ml of gas A measured at 0.60 atm, and 150 ml of a gas B at a pressure of 0.80 atm, are passed into a vessel whose capacity is 500 ml. What is the total pressure of the mixture in the vessel at the same temperature?

The partial pressure p_A of A is the pressure the gas would exert if it alone occupied the 500 ml vessel; since its pressure is 0.60 atm when it occupies 125 ml, it follows from Boyle's law that

$$p_A \times 500 = 0.60 \times 125,$$

$$p_A = \frac{0.60 \times 125}{500} = 0.15 \text{ atm}.$$

Similarly, the partial pressure p_B of B will be given by

$$p_B \times 500 = 0.80 \times 150,$$

$$p_B = \frac{0.80 \times 150}{500} = 0.24 \text{ atm.}$$

The total pressure, which is the sum of the two partial pressures, is then 0.15 + 0.24 = 0.39 atm.

2i. Diffusion of Gases: Graham's Law.—The phenomenon of **diffusion** may be described as *the tendency for any substance to spread uniformly throughout the space available to it.* Diffusion is exhibited by gases, liquids and even by solids, but it is most rapid with gases. If a wide-mouthed jar of hydrogen is placed mouth to mouth with a jar of oxygen, it will be found, after a short time, that the two gases have spread uniformly throughout the two jars. This will happen irrespective of whether the lighter gas is in the top or the bottom jar. It is true that gravity has some effect on the distribution of the gases, but this is quite negligible unless a long column of gas is under consideration, as in the earth's atmosphere.

The term diffusion is frequently applied, also, to the movement of gases through porous media, such as porous earthenware. If a porous pot, filled with hydrogen, for example, is left in air, the hydrogen will diffuse out of the interior and the air will diffuse in from the outside. A phenomenon that is probably related to this passage of gases through fine pores, is that which has been called **effusion**; this is the streaming of a gas through a small hole.

The rate at which a gas diffuses (or effuses) is dependent upon its density, and the connection is given by Graham's **law of diffusion** (T. Graham, 1829). According to this law, which, like the other gas laws, is approximate only, *the rate of diffusion (or effusion) of a gas is inversely proportional to the square root of its density.* If D_1 and D_2 represent the rates of diffusion of two gases whose densities under the given conditions are d_1 and d_2, respectively, then

$$\frac{D_1}{D_2} = \sqrt{\frac{d_2}{d_1}}. \tag{2.26}$$

Since the density of a gas is directly proportional to its molecular weight, equation (2.26) may be written as

$$\frac{D_1}{D_2} = \sqrt{\frac{M_2}{M_1}}, \tag{2.27}$$

where M_1 and M_2 are the molecular weights of the two gases.

It follows from Graham's law of diffusion that a light gas will diffuse more rapidly than a heavy one. This fact was utilized in the earliest attempts to separate the isotopes of neon (F. W. Aston, 1913), and diffusion methods have frequently been used for isotopic separations in more recent times. An outstanding example is the enrichment of uranium in the isotope uranium-235 which plays an important part in the release of atomic energy. The process *of gaseous diffusion (or effusion) used for this purpose is described in § 64d.*

The results of Graham's law of diffusion have been used to determine gas densities by measuring the time required for a definite volume of the gas to effuse through a small hole in a thin metal plate. The experiment is then repeated, under precisely the same conditions, with a gas of known density. The time required for the volume of gas to pass through the hole is inversely proportional to its rate of diffusion (or effusion); if the times for the two gases are t_1 and t_2, then by equations (2.26) and (2.27),

$$\frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}. \tag{2.28}$$

Hence, either the density or the molecular weight of the unknown gas can be determined, approximately, provided a comparison gas, of known density or molecular weight, is available. The effusion method was used by A. Debierne (1910) to obtain the molecular weight, and hence the atomic weight, of the radioactive gas radon.

Example: The time taken for a certain volume of gas to stream through a small hole was 1.44 min; under exactly the same conditions an equal volume of oxygen took 1.80 min to pass through. Calculate the approximate density of the gas relative to hydrogen.

The molecular weight of oxygen is 32, and hence its density d_1 relative to that of hydrogen (molecular weight = 2) is 16; the time t_1 of diffusion of oxygen is 1.80 min, while that, t_2, for the other gas is 1.44 min. If the density of the latter is d_2, then, by equation (2.28),

$$\frac{1.44}{1.80} = \sqrt{\frac{d_2}{16}}$$

$$d_2 = \left(\frac{1.44}{1.80}\right)^2 \times 16 = 10.2.$$

THE KINETIC THEORY OF GASES

3a. The Fundamentals of the Kinetic Theory.—Now that the general properties of gases, particularly ideal gases, have been described, it is of interest to develop a theory which permits the various laws of gaseous behavior to be coordinated. Such a theory is the **kinetic theory of gases.** The essential postulate of this theory is that *a gas consists of a large number of very small, perfectly elastic particles, which may be identified with the chemical molecules, moving about in all directions.* As a result of this continual movement, the molecules will frequently collide with each other and with the walls of the containing vessel; it is these elastic impacts on the walls of the vessel that are supposed to be responsible for the pressure exerted by the gas. Increase of temperature will result in a more vigorous movement of the molecules, so that if the volume is kept constant the pressure will increase. Further, if the molecules are made to occupy a smaller volume, they will strike the walls of the vessel more frequently, and so there will be an increase of pressure. These qualitative conclusions, drawn from the kinetic theory of gases, are, of course, in agreement with observation; it is more important, however, to see if the theory can predict quantitatively the behavior of gases.

For the present, the treatment will be restricted to an ideal gas; for such a substance, it is postulated that *the molecules are so small that their actual volume is negligible in comparison with the total volume of the gas.* Further, it is supposed that *the molecules exert no attraction upon one another.* With these simple assumptions, it is possible to develop an expression for the pressure of an ideal gas.

3b. Pressure of an Ideal Gas.—Several methods have been proposed for the calculation of gas pressure from the kinetic theory; the most exact are somewhat complicated, and so a simple, although approximate, derivation which leads to the correct result will be given here. Imagine a cube of l cm edge, containing n molecules, each having an actual mass of m gram. These molecules are moving at random in all directions, with velocities covering a considerable range of values. The velocity c cm per sec of any molecule may be resolved into three component velocities, designated x, y and z, in the three directions at right angles to each other, parallel to the edges of the cube (Fig. 3.1). The various velocities are then related by the expression

$$c^2 = x^2 + y^2 + z^2. \qquad (3.1)$$

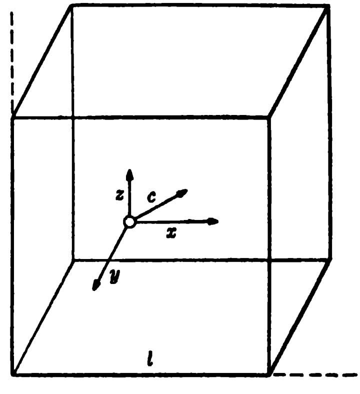

FIG. 3.1. Molecular velocity and its components

The total effect of the impact of the molecule of velocity c on the walls of the cube can now be obtained by summing the effects due to the three components x, y and z.

When a molecule strikes the wall and rebounds elastically, the component velocities remain unaltered in magnitude but reversed in sign because of the change in direction of motion. Thus, the velocity component x before impact becomes $-x$ after impact; correspondingly, the momentum component of the molecule mx becomes $-mx$, and similarly for the components in the other two directions. The momentum change in the x-direction is thus $2mx$ gram cm sec^{-1} for each impact of a molecule with the wall.

Since l cm is the edge length of the cube, the number of impacts per second on the walls perpendicular to the x-direction is x/l. The change of momentum per second (or rate of change of momentum) due to such impacts is therefore $2mx \times x/l = 2mx^2/l$ gram cm sec^{-2} (or dynes). Similarly, the rate of change of momentum accompanying impacts of a single molecule with the faces perpendicular to the other two directions will be $2my^2/l$ and $2mz^2/l$ dynes, respectively. The total rate of change of momentum for impacts of a single molecule with all six walls of the cube is thus $2m(x^2 + y^2 + z^2)/l$ or, in view of equation (3.1), $2mc^2/l$ dynes.

According to Newton's laws of motion, the rate of change of momentum is equal to the force acting; consequently,

$$\text{Force due to impacts of a single molecule} = \frac{2mc^2}{l} \text{ dynes.}$$

Each of the molecules in the cube will exert a similar force, so that

$$\text{Total force due to impacts of } n \text{ molecules} = \frac{2m}{l}(c_1^2 + c_2^2 + \cdots c_n^2) \text{ dynes,}$$

where $c_1, c_2, \cdots, c_n$ are the velocities of the individual molecules. The **mean square velocity** $\overline{c^2}$, which is the average of the squares of the velocities of the n molecules,* is defined by

$$\overline{c^2} = \frac{c_1^2 + c_2^2 + \cdots + c_n^2,}{n}$$

so that

$$\text{Total force due to impacts of } n \text{ molecules} = \frac{2nm\overline{c^2}}{l} \text{ dynes.}$$

As seen earlier (§ 2g), pressure is defined as force per unit area; since the total area of the walls of the cube is $6l^2$, the total pressure exerted by all the molecules is given by

$$\text{Pressure} = \frac{2nm\overline{c^2}}{l} \times \frac{1}{6l^2} = \frac{nm\overline{c^2}}{3l^3} \text{ dynes cm}^{-2}.$$

The quantity l^3 is equal to the volume v of the cube, and if the pressure is represented by P, it follows that

$$P = \frac{nm\overline{c^2}}{3v} \text{ dynes cm}^{-2}. \tag{3.2}$$

An expression has thus been derived from the kinetic theory which relates the gas pressure to the volume of the vessel and to the number, mass and velocities of the molecules.

3c. Derivations from Kinetic Theory.—The speeds of the molecules of a gas will increase with increasing temperature, and it is possible to define temperature, on the basis of the kinetic theory, as being proportional to the

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* The quantity $\overline{c^2}$ is equivalent to finding the squares of the velocities of all the molecules, adding these squares together, and taking the average. It must not be confused with the square of the mean velocity, i.e., $\bar{c}^2$, which would be obtained by evaluating the mean velocity of all the molecules and then squaring the result. The square root of the mean square velocity, i.e., $\sqrt{\overline{c^2}}$, is thus not equal to the mean velocity $\bar{c}$; the former is equal to 1.085, times the latter, as will be seen in § 3g.

mean kinetic energy $\frac{1}{2}m\overline{c^2}$ per molecule. This definition is in harmony with the theoretical deduction of J. Clerk Maxwell (1860) that *the mean kinetic energies of the molecules of all gases are the same at constant temperature.* It will be seen shortly that the temperature scale based on the mean kinetic energy is actually identical with the familiar absolute scale of temperature. In the meantime, however, use will be made of the conclusion, which follows from the definition, that at constant temperature the kinetic energy $\frac{1}{2}m\overline{c^2}$ is constant for any gas. If a definite mass of gas is under consideration, the total number of molecules n will evidently remain unchanged; hence, for a given mass of gas at constant temperature, the quantity $\frac{1}{3}nm\overline{c^2}$ will be constant. If, now, equation (3.2) is rewritten in the form

$$Pv = \tfrac{1}{3}nm\overline{c^2}, \tag{3.3}$$

it is apparent that, for a definite mass of gas at constant temperature, the right-hand side of equation (3.3) will remain constant; hence,

$$Pv = \text{constant},$$

in agreement with Boyle's law. The kinetic theory of gases, as applied to an ideal gas, thus provides a satisfactory basis for this law.

For any two gases, indicated by the subscripts 1 and 2, it is possible to write, in accordance with equation (3.3),

$$P_1v_1 = \tfrac{1}{3}n_1m_1\overline{c_1^2} \quad \text{and} \quad P_2v_2 = \tfrac{1}{3}n_2m_2\overline{c_2^2}. \tag{3.4}$$

If the two gases have the same pressure, i.e., $P_1 = P_2$, and occupy the same volume, i e., $v_1 = v_2$, it follows from the equations (3.4) that

$$\tfrac{1}{3}n_1m_1\overline{c_1^2} = \tfrac{1}{3}n_2m_2\overline{c_2^2}. \tag{3.5}$$

If the gases are also at the same temperature, the mean kinetic energies of the molecules will be the same, as mentioned above; that is,

$$\tfrac{1}{2}m_1\overline{c_1^2} = \tfrac{1}{2}m_2\overline{c_2^2}. \tag{3.6}$$

Combination of equations (3.5) and (3.6) then immediately leads to the result

$$n_1 = n_2.$$

In other words, it is seen that for two gases at the same pressure and temperature, equal volumes should contain equal numbers of molecules; this is, of course, Avogadro's law, which has thus been derived from the kinetic theory for an ideal gas.

3d. Kinetic Energy and Temperature.—As a result of introducing the postulate that the temperature T of the gas is proportional to the mean kinetic energy $\frac{1}{2}m\overline{c^2}$ of the molecules, it follows from equation (3.3) that

$$Pv = nkT, \tag{3.7}$$

where k is a proportionality constant that is the same for all gases. (The conclusion that k is a universal constant follows from Maxwell's proof that at a given temperature the mean kinetic energy is independent of the nature of the gas.) If the pressure P of a given mass of gas is maintained constant, it is evident from equation (3.7) that v will be proportional to T, since P, n and k are all constant; hence,

$$\frac{v}{T} = \text{constant.}$$

This result is identical with equation (2.10) which expresses the experimental facts of Gay-Lussac's law. It is seen, therefore, that the temperature scale defined in terms of the mean kinetic energy of the molecules is the same as the absolute scale derived from the expansion of an ideal gas (§ 2c).

According to definition, all substances contain the same number of molecules in 1 mole; this number, represented by the symbol N, is called the **Avogadro number.*** Hence, for 1 mole of gas, the number n of molecules in the given volume, now represented by V, is equal to N; equation (3.7) may then be written as

$$PV = NkT. \tag{3.8}$$

Further, since both N and k are universal constants, their product will have a constant value for 1 mole of any ideal gas; representing this by R, equation (3.8) becomes

$$PV = RT,$$

which is the same as the familiar equation of state for 1 mole of an ideal gas, R being the gas constant.

It may be noted, incidentally, that since k is equal to R/N, it may be regarded as the *gas constant per single molecule;* this quantity is known as the **Boltzmann constant.** It is usually expressed in ergs deg^{-1}; thus, since R is 8.314×10^{7} ergs deg^{-1} mole^{-1} (§ 2g, II), and N is 6.023×10^{23}, it follows that the value of the Boltzmann constant is 1.380×10^{-16} erg deg^{-1} molecule^{-1}.

Since $\frac{1}{2}m\overline{c^2}$ is the mean kinetic energy per molecule, $\frac{1}{2}Nm\overline{c^2}$ will be equal to the total kinetic energy of all the molecules in 1 mole of gas; if this is represented by E_K, then

$$E_K = \tfrac{1}{2}Nm\overline{c^2}.$$

For 1 mole of gas, containing N molecules, equation (3.3) may be expressed as

$$PV = \tfrac{1}{3}Nm\overline{c^2} = \tfrac{2}{3}\cdot\tfrac{1}{2}Nm\overline{c^2}, \tag{3.9}$$

and hence,

$$PV = \tfrac{2}{3}E_K. \tag{3.10}$$

Further, since PV is equal to RT for 1 mole,

$$E_K = \tfrac{3}{2}RT. \tag{3.11}$$

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* It will be seen in § 3k that N is 6.023×10^{23} molecules per mole.

The total kinetic energy of the molecules in 1 mole of an ideal gas is thus equal to $\frac{3}{2}RT$.

3e. The Law of Partial Pressures.—If n_1 molecules of a gas 1, each having a mass m_1 and a mean square velocity $\overline{c_1^2}$, occupied a volume v, the pressure p_1 exerted by these molecules would be given by the kinetic theory [equation (3.2)] as

$$p_1 = \frac{n_1 m_1 \overline{c_1^2}}{3v}. \tag{3.12}$$

Similarly, if n_2 molecules of gas 2 occupied the same volume v, to the exclusion of the other molecules, the pressure would be

$$p_2 = \frac{n_2 m_2 \overline{c_2^2}}{3v}, \tag{3.13}$$

where m_2 is the mass and $\overline{c_2^2}$ is the mean square velocity of these molecules. Analogous expressions can, of course, be derived for the pressures p_3, p_4, etc., for any molecular (gaseous) species occupying the same volume.

If all the gases 1, 2, 3, etc., were present in the vessel of volume v at the same time, then, provided the various molecules do not interact with one another, and they all behave ideally, the kinetic theory treatment would lead to the result

$$P = \frac{n_1 m_1 \overline{c_1^2}}{3v} + \frac{n_2 m_2 \overline{c_2^2}}{3v} + \frac{n_3 m_3 \overline{c_3^2}}{3v} + \cdots \tag{3.14}$$

for the total pressure P due to all the molecules. Upon introducing the results of equations (3.12), (3.13), etc., which give the values of the partial pressures of the constituents of the mixture, it is seen that

$$P = p_1 + p_2 + p_3 + \cdots,$$

which is Dalton's law of partial pressures [equation (2.20)]. This law, like the other laws applicable to ideal gases, may therefore be correlated with the simple kinetic theory of gases.

3f. Molecular Velocities: Diffusion.—For 1 mole of gas, the ideal gas law equation (2.16) and equation (3.9) yield the result

$$PV = RT = \tfrac{1}{3}Nm\overline{c^2},$$

and since the product of the Avogadro number N and the weight m of a single molecule is equal to the molecular weight M, it follows that

$$RT = \tfrac{1}{3}M\overline{c^2},$$

and consequently,

$$\sqrt{\overline{c^2}} = \sqrt{\frac{3RT}{M}}. \tag{3.15}$$

The square root of the mean square velocity is generally referred to as the

root mean square velocity, and this equation shows that *the root mean square velocity of the molecules is directly proportional to the square root of the absolute temperature and inversely to the square root of the molecular weight of the gas.* If the latter is known, the root mean square velocity can be calculated at any desired temperature, making use of the experimental value of R derived in § 2g.

Example: Calculate the root mean square velocity of oxygen molecules at 25°C.

If the velocity is to be expressed in cm per sec, i.e., in cgs units, the value of R must be in the same units, i.e., ergs deg^{-1} mole^{-1}, that is, 8.31×10^7. The absolute temperature T is $273 + 25 = 298°\text{K}$, and the molecular weight M of oxygen is 32; hence, by equation (3.15),

$$\sqrt{\overline{c^2}} = \sqrt{\frac{3 \times 8.31 \times 10^7 \times 298}{32}} = 4.82 \times 10^4 \text{ cm sec}^{-1}.$$

It will be seen shortly that the average (or mean) velocity of the molecules of a gas is somewhat smaller than the root mean square velocity. The average velocity of an oxygen molecule at 25°C is about 450 meters per sec, which is not very different from the velocity of sound in the gas at the same temperature. For a substance of higher molecular weight the average speed of the molecules would be less; for higher temperatures the velocities would be greater. Although the direct experimental determination of the speeds with which molecules travel is not an easy matter, a number of methods have been devised that make this possible. The results are not exact, but they are nevertheless in very satisfactory agreement with those calculated from the kinetic theory of gases.

Because of frequent collisions with one another, the molecules of a gas do not travel very far in a direct line; however, the resultant rate of progress in a particular direction may be expected to be dependent on the molecular velocity. If this is the case, the rate at which a gas diffuses should be proportional to the speeds of the molecules; thus, for two gases whose rates of diffusion are D_1 and D_2, it is reasonable to write

$$\frac{D_1}{D_2} = \frac{c_1}{c_2}, \tag{3.16}$$

where c_1 and c_2 are the mean velocities of the molecules of the two gases. Like the root mean square velocity, the mean velocity of the molecules of a gas is inversely proportional to the square root of the molecular weight; hence,

$$\frac{D_1}{D_2} = \sqrt{\frac{M_2}{M_1}}$$

at constant temperature. Comparison with equation (2.27) shows that this is a form of Graham's diffusion law, which has thus been derived from the kinetic theory of ideal gases.

The rate of the process of effusion, that is, the passage of gas through a small hole in a thin plate, depends on the number of molecules that strike the area occupied by the hole, in a given time. The conditions are then such that every molecule striking this area passes through the hole. It is possible to calculate from the kinetic theory the rate of effusion of a gas on this basis, and it is found to be inversely proportional to the square root of the molecular weight (or density); this has been confirmed experimentally.

3g. Distribution of Molecular Velocities.—The molecules of a gas do not all move with the same speed; because of the frequent collisions, there is a continual interchange of momentum between the molecules, and hence their velocities will vary. Even if all the molecules in a vessel were started off moving in parallel lines with the same velocity, the slightest disturbance of a single molecule, due to gravitational or other forces, would result in collisions and ultimately in the chaotic molecular movement that is believed to occur in a gas. The manner in which the molecules of a gas are distributed over the possible velocities, from zero to very high values, was first worked out by J. C. Maxwell (1860), using the theory of probability. The results are expressed as the **law of distribution of molecular velocities,** one form of which is

$$\frac{1}{n}\cdot\frac{dn}{dc} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} e^{-Mc^2/2RT}c^2. \tag{3.17}$$

In this expression, the left-hand side is virtually (although not exactly) the fraction of the total number of molecules (n) having a particular velocity c. This fraction can be readily calculated, for all the quantities on the right-hand side of equation (3.17) are known; thus, M is the molecular weight of the gas, R is the gas constant, which must be expressed in ergs deg^{-1} mole^{-1}, if the velocity c is in cm per sec; T is the absolute temperature and e is the base of natural logarithms. By deciding on any given gas of molecular weight M, at any desired temperature T, the fraction of the molecules having a particular velocity c can be determined.

The consequences of Maxwell's law are conveniently represented graphically, as in curve I in Fig. 3.2; the ordinates give the fraction of the molecules having velocities indicated by the abscissae. The actual curve will depend on the molecular weight of the gas and the temperature, but the general form is always the same. The maximum of the curve indicates the **most probable velocity,** which is the velocity possessed by more molecules than is any other velocity. An expression for this quantity can be obtained by differentiating equation (3.17) with respect to c and setting the result equal to zero, as required for a maximum. It is then found that

$$c \text{ (most probable)} = \sqrt{\frac{2RT}{M}}. \tag{3.18}$$

The **average** (or **mean**) **velocity** c of the molecules of a gas, defined by

$$\bar{c} = c_1 + c_2 + \cdots + c_n$$

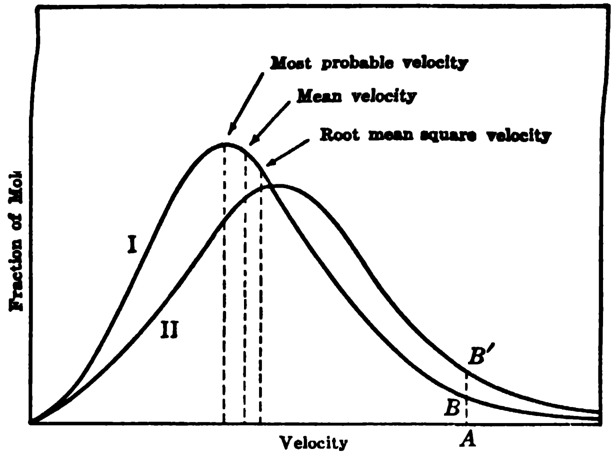

FIG. 3.2. Maxwell's law of the distribution of molecular velocities

can also be derived from equation (3.17); thus,

$$\bar{c} = \frac{1}{n}\int_0^\infty c\,dn = \sqrt{\frac{8RT}{\pi M}}. \tag{3.19}$$

From these two expressions, it is seen that the ratio of the mean velocity to the most probable velocity is $\sqrt{8/\pi}$ to $\sqrt{2}$, i.e., 1.128. Similarly, upon comparing equations (3.15) and (3.19), the ratio of the root mean square velocity to the mean velocity, i.e., $\sqrt{\bar{c^2}}$ to $\bar{c}$, is found to be $\sqrt{3}$ to $\sqrt{8/\pi}$ or 1.085.

It is evident from Fig. 3.2 that the majority of the molecules of the gas have speeds that are in the vicinity of the average or most probable velocities. Nevertheless, the important result to be noted is that there are always some molecules having very low and some with very high speeds at any given temperature.

As the temperature is raised, the general form of the distribution curve changes from I to II; the maximum is shifted to the right, corresponding to the increase of molecular velocity with increasing temperature. The flattening of the maximum indicates a wider distribution of velocities. The essential point to note, however, is that there is a pronounced increase in the number of molecules with speeds that are much higher than the average. Consider, for example, the velocity represented by the point A; the fraction of the molecules possessing this speed at the temperature I is equal to BA, but at the higher temperature II the fraction is increased to $B'A$. Further, the total fraction of molecules having speeds equal to or greater than the particular value at A is determined by the area under the curve from A to infinity; this obviously increases rapidly as the temperature is raised.

The marked effect of temperature in increasing the proportion of molecules having high velocities or, what comes to the same thing, high kinetic energies, is provided for by the presence of the *exponential factor* $e^{-Mc^2/2RT}$ *in the* Maxwell equation (3.17). The quantity $\frac{1}{2}Mc^2$ is equal to the kinetic energy of 1 mole of molecules each of which has the same velocity c; this may be replaced by E, representing the kinetic energy of these molecules, so that the exponential factor, frequently referred to as the **Boltzmann factor,** may be written as $e^{-E/RT}$. Because of the presence of the temperature T in the denominator of the negative exponent, this factor increases markedly with increasing temperature. The greater the value of E, the more rapid is the *relative* increase of the Boltzmann factor. This result is of particular importance in connection with the theory of reaction rates (Chapter 16).

It should be noted that the Maxwell equation is a particular case of a general expression which finds application in many aspects of physical chemistry. This expression, known as the **Boltzmann equation,** is

$$\frac{n_2}{n_1} = e^{-E/RT}, \tag{3.20}$$

where n_1 is the number of molecules in a given volume in any specified energy state 1, and n_2 is the number in the same volume in a state 2 in which the potential energy is E per mole in excess of that in state 1. Both states must, of course, be at the same temperature T.

3h. Mean Free Path and Viscosity.—*The average distance a molecule travels between two successive collisions* is called the **mean free path.** Its value is determined essentially by the number of molecules present in a given volume of gas, and by a property of the molecules known as the **collision diameter.** When two molecules approach one another a point is reached at which mutual repulsion becomes so great as to cause a reversal of direction of motion. *The distance between the centers of the molecules at this point of closest approach* is the collision diameter (Fig. 3.3), represented by the symbol σ (Greek, *sigma*). Even if the molecules are infinitesimally small, as has been postulated for an ideal gas (§ 3a), they would still have an effective collision diameter, because of their mutual repulsion.

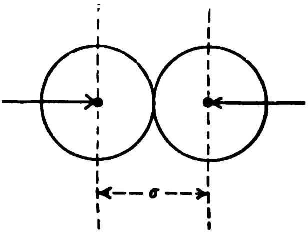

Fig. 3.3. Collision diameter of molecules

The mean free path of the molecules in a gas can be calculated by considering all but one of the molecules in a given volume to be stationary. If l' is the mean free path under these conditions, then the moving molecule will, on the average, collide with another molecule after it has traveled this distance (Fig. 3.4). It is evident from the diagram that there can be only one molecule in the cylindrical volume of length l' and diameter 2σ. Hence, each molecule inhabits an average volume of $\pi\sigma^2 l'$, so that if n is the number of molecules per unit volume,

$$n = \frac{1}{\pi\sigma^2 l'}$$

and

$$l' = \frac{1}{\pi n \sigma^2}$$

The mean free path l, when all the molecules are in motion, is less than l', for a single moving molecule, by a factor of $\sqrt{2}$, so that

$$l = \frac{1}{\sqrt{2}\pi n \sigma^2}. \tag{3.21}$$

Various relationships exist between the mean free path and other properties of a gas; one of these properties is the **viscosity.** Consider two layers of gas, one of which is streaming over the other; because of their continual movement, there will be an interchange of molecules between the two layers, with the result that some of the momentum of the streaming layer will be transferred to the stationary layer. The net effect will be a decrease of the relative rate of movement of one layer with respect to the other. *This retarding influence of a stationary layer of gas on a moving one* is the property referred to as viscosity; it may be described in simple terms as an internal friction or an internal resistance to motion. The **coefficient of viscosity** or, in brief, the **viscosity,** is defined as *the force in dynes that must be exerted between two parallel layers, 1 sq cm in area and 1 cm apart, in order to maintain a velocity of streaming of 1 cm per sec of one layer past the other.* In terms of these quantities (cgs units) the viscosity is expressed in dynes cm^{-2} sec units; this unit is called a **poise,** in honor of J. L. M. Poiseuille. In 1844, the latter derived the fundamental equation of viscosity for streamline (or nonturbulent) flow, namely

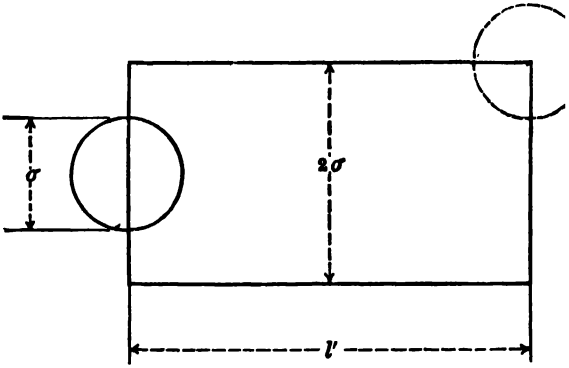

Fig. 3.4. Molecular collision and mean free path

$$\eta = \frac{\pi r^4 t p}{8 v L}, \tag{3.22}$$

relating the coefficient of viscosity η (Greek, *eta*) to the volume v cc of gas (or liquid) which will flow through a narrow tube of length L cm and radius r cm in the time t sec, when under the influence of a driving pressure of p dynes per cm^2. The experimental methods for the determination of viscosity are based on the Poiseuille equation.

Since gaseous viscosity may be ascribed to the interchange of molecules between two adjacent layers of gases, some connection between the coefficient of viscosity and the mean free path of the molecules is to be expected. For an ideal gas, the relationship

$$\eta = \tfrac{1}{3}\bar{c}dl, \tag{3.23}$$

where $\bar{c}$ is the mean velocity of the molecules, d is the density of the gas, and l is the mean free path, has been derived from the kinetic theory. The viscosity and density of a gas can be determined, and the mean velocity is given by equation (3.19); hence, it should be possible to calculate the value of the mean free path of the molecules under the given conditions.

Example: The viscosity of hydrogen gas at 0°C is 8.41×10^{-5} poise; determine the mean free path of the molecules at this temperature and 1 atm pressure.

If η in equation (3.23) is in poises, the density d must be in grams per cc; $\bar{c}$ must be in cm per sec, and l in cm. At 0°C and 1 atm pressure, 2.0 grams (1 mole) of hydrogen occupy 22,400 cc, and hence

$$d = \frac{2.0}{22{,}400} = 8.9 \times 10^{-5} \text{ gram cc}^{-1}.$$

The mean velocity $\bar{c}$, by equation (3.19), with R in cgs units, i.e., 8.31×10^7 ergs deg^{-1} mole^{-1}, is

$$\sqrt{\frac{8 \times 8.31 \times 10^7 \times 273}{3.14 \times 2.0}} = 1.70 \times 10^5 \text{ cm sec}^{-1}.$$

From equation (3.23), therefore

$$8.41 \times 10^{-5} = \tfrac{1}{3} \times 1.70 \times 10^5 \times 8.9 \times 10^{-5} \times l$$

$$l = 1.67 \times 10^{-5} \text{ cm}.$$

The mean free paths of most gases at atmospheric pressure and room temperatures are of the order of 10^{-5} cm; the reason for this approximate constancy may be seen from equation (3.21). At definite temperature and pressure, the number of molecules n in unit volume is constant, by Avogadro's law, and since nearly all molecules that are gaseous at ordinary temperatures and pressures have collision diameters of about 2×10^{-8} to 4×10^{-8} cm (see Table 3.1), it follows that the mean free path will not vary greatly from one gas to another.

The effects of temperature and pressure may also be derived from equation (3.21). It is seen from this equation that the product of n and l should be constant, provided the collision diameter does not change. At constant pressure, the number of molecules n in unit volume is inversely proportional to the absolute temperature, and so the mean free path l will be *directly proportional* to this temperature. On the other hand, at constant temperature, n is directly proportional to the pressure, and hence l will be inversely proportional to the latter; thus,

$$\frac{l}{T} = \text{constant, at constant pressure}$$

and

$$l \times P = \text{constant, at constant temperature.}$$

Since the value of l is about 10^{-5} cm at ordinary temperature and 1 atm pressure, it follows that it would be necessary to decrease the pressure to about 10^{-5} atm in order to make the mean free path about 1 cm.

To show the effect of temperature and pressure on the viscosity of a gas, equations (3.19) and (3.21) for $\bar{c}$ and l, respectively, are first substituted in equation (3.23). Next, since n is the number of molecules in unit volume of the gas, the density d may be replaced by Mn/N, where N is the Avogadro number. The result is

$$\eta = \frac{2}{3N\pi\sigma^2}\sqrt{MRT}$$

so that the viscosity of an ideal gas is independent of pressure but increases in proportion to the square root of the absolute temperature. For a real gas, the viscosity increases more rapidly than this due to the cohesive forces between the molecules (§ 4c). That the viscosity of a gas should increase with temperature can be derived qualitatively from the kinetic theory. Since the velocity of the gas molecules increases with temperature, the rate of transfer of momentum between streaming and stationary layers increases and, hence, so also does the viscosity.

3i. Collision Numbers.—In accordance with the definition of the mean free path, a gas molecule travels the very small distance of about 10^{-5} cm between collisions at 1 atm pressure and normal temperatures; the total number of such collisions between molecules in unit time must therefore be very large. Since $\bar{c}$, the mean velocity, is the average distance a molecule travels per sec and l is the mean distance between collisions, the average number of collisions a molecule makes per sec is $\bar{c}/l$. The total number of collisions for the n molecules in unit volume would appear, at first thought, to be $n\bar{c}/l$ per sec. However, this number is too large by a factor of two, since a collision between molecule 1 and molecule 2 is regarded as different from a collision between molecule 2 and molecule 1, whereas they are, of course, the same. Hence, the collision number Z, i.e., the number of collisions in unit volume per sec, is $\frac{1}{2}n\bar{c}/l$. Utilizing equation (3.19) for $\bar{c}$ and equation (3.21) for l, it is found that

$$Z = 2n^2\sigma^2\sqrt{\frac{\pi RT}{M}}, \tag{3.24}$$

where all the symbols have the same significance as before.

In order to utilize this equation to calculate the number of collisions, it is necessary to know n and σ; the former can be obtained from the Avogadro number, and the latter is most simply derived from the viscosity. By combining equations (3.21) and (3.23), so as to eliminate l, the result is

$$\sigma^2 = \frac{\bar{c}d}{3\sqrt{2}\pi\eta n}. \tag{3.25}$$

It is not actually necessary to evaluate σ^2, for upon introduction of equation (3.25) into (3.24), and making use of equation (3.19) for $\bar{c}$, it follows that

$$Z = \frac{4nd}{3\pi\eta} \cdot \frac{RT}{M}. \tag{3.26}$$

Example: Utilizing the data of the preceding example, calculate the number of collisions taking place in 1 sec between hydrogen molecules in 1 cc of gas at 0°C and 1 atm pressure.

To obtain the number of collisions per sec in 1 cc, i.e., collisions $\text{sec}^{-1}\ \text{cc}^{-1}$, all the data must be expressed in cgs units. The values of d and of η are given in the previous example, viz., 8.9×10^{-5} g cc^{-1} and 8.41×10^{-5} poise, respectively; R is 8.31×10^7 ergs deg^{-1} mole^{-1}, T is 273°K and M is 2.0; only n remains to be estimated. At 0°C and 1 atm, 1 mole of gas occupies 22,400 cc, and since 1 mole of any substance contains 6.02×10^{23}, i.e., the Avogadro number (§ 3k), individual molecules, the number n of molecules per cc is $6.02 \times 10^{23}/22{,}400 = 2.69 \times 10^{19}$. Hence, from equation (3.26)

$$\begin{aligned} Z &= \frac{4 \times 2.69 \times 10^{19} \times 8.9 \times 10^{-5}}{3 \times 3.14 \times 8.41 \times 10^{-5}} \times \frac{8.31 \times 10^7 \times 273}{2.0} \\ &= 14 \times 10^{28} \text{ molecular collisions sec}^{-1}\ \text{cc}^{-1}. \end{aligned}$$

The number of collisions between molecules at ordinary temperatures and pressures is of the enormous order of 10^{28} per second in 1 ml (or 1 cc) of gas. That the value does not vary greatly with the molecular weight may be seen from equation (3.24), since an increase of M is usually accompanied by a compensating increase of σ. Further, at constant pressure, temperature has a relatively small effect, since it is the square root of the absolute temperature that appears in equation (3.24); in any event, there is some compensation due to the decrease in the value of n. The number of collisions is, however, seen to be proportional to the square of the number of molecules in unit volume, i.e., to n^2, by equation (3.24); it is consequently proportional to the square of the pressure, at constant temperature. Increase of pressure thus has a marked effect in increasing the number of collisions.

In a mixture of gases A and B, the number of collisions $Z_{A,B}$, each involving an A molecule and a B molecule, taking place per second in 1 cc, may be calculated from the equation

$$Z_{A,B} = n_A n_B \sigma_{A,B}^2 \left(8\pi RT \frac{M_A + M_B}{M_A M_B}\right)^{1/2}, \tag{3.27}$$

where n_A and n_B are the respective numbers of molecules in unit volume, and M_A and M_B are the molecular weights of the two gases. The mean collision diameter $\sigma_{A,B}$ is equal to $\frac{1}{2}(\sigma_A + \sigma_B)$. This equation reduces to equation (3.24) when A and B are the same, provided the result is divided by 2, to avoid counting each collision twice; otherwise, each molecule would be treated as colliding with itself, as well as with other molecules.

3j. Collision Diameters.—Although the concept of collision diameters has been used in the foregoing sections, there has been no necessity to calculate the values of these diameters. The results are nevertheless of interest, because they give a measure of the effective dimensions of molecules, at least in collisions. One way of determining the collision diameter is to utilize equation (3.25), after inserting the expression for $\bar{c}$; thus,

$$\sigma^2 = \frac{2d}{3\pi\eta n}\sqrt{\frac{RT}{\pi M}}, \tag{3.28}$$

so that the collision diameter σ can be evaluated if the viscosity η of the gas is known.

Example: Calculate the collision diameter of hydrogen, using the viscosity and other data from the two preceding examples.

Again cgs units must be used throughout to obtain σ in cm; thus, d is 8.9×10^{-5} gram cc^{-1}, n is 2.7×10^{19} molecules cc^{-1}, η is 8.41×10^{-5} poise and R is 8.31×10^{7} ergs deg^{-1} mole^{-1}; hence

$$\begin{aligned}\sigma^2 &= \frac{2 \times 8.9 \times 10^{-5}}{3 \times 3.14 \times 8.41 \times 10^{-5} \times 2.7 \times 10^{19}}\sqrt{\frac{8.31 \times 10^{7} \times 273}{3.14 \times 2.0}}\\ &= 5.0 \times 10^{-16}\ \text{cm}^2.\\ \sigma &= 2.2 \times 10^{-8}\ \text{cm}.\end{aligned}$$

The collision diameters of most gaseous molecules are found to lie in the range of 2×10^{-8} to 4×10^{-8} cm. Since distances of the order of 10^{-8} cm appear frequently in chemistry, e.g., molecular and atomic dimensions, and in physics, e.g., wave lengths of X-rays, the term **angstrom unit** and the symbol A are used to represent a length of 10^{-8} cm. Consequently, it may be stated that the collision diameters are generally from 2 A to 4 A for molecules of gaseous substances. Some actual results, obtained from viscosity measurements, after applying certain corrections for nonideal behavior, are given in Table 3.1. Similar values have been derived from other physical properties of gases, such as heat conductivity and diffusion, which also depend on the

TABLE 3.1. COLLISION DIAMETERS FROM VISCOSITY MEASUREMENTS

Substance	σ	Substance	σ
Hydrogen	2.45 A	Hydrogen chloride	2.86 A
Helium	2.18	Hydrogen bromide	3.16
Nitrogen	3.50	Hydrogen iodide	3.50
Oxygen	3.40	Carbon dioxide	4.20
Chlorine	4.50	Ammonia	3.05

mean free path of the molecules and, hence, on the collision diameter. It may be mentioned that the collision diameters do not differ greatly from the actual diameters obtained in other ways not depending on the kinetic theory of gases; as a general rule, the former are larger than the latter by about 1 A, so that molecular dimensions are of the order of 10^{-8} cm (see Chapter 7).

3k. The Real Existence of Molecules: The Avogadro Number.—The general agreement between the experimental facts and the conclusions drawn from the kinetic theory provides strong support for this theory, but it would obviously be important if more direct evidence were available for the real existence of molecules. Such evidence was obtained by J. Perrin (1908) from a study of the phenomenon known as the **Brownian movement.** In 1827, the botanist R. Brown noticed that pollen grains when suspended in water exhibited continual and haphazard motion in all directions. This Brownian movement has been observed with small particles of all kinds; it is quite independent of the nature of the particles or of the medium in which they are suspended. It is generally accepted that *the movement is caused by the continual bombardment of the suspended particles by the molecules of the medium.* The increasing and erratic motion of the particles is thus a direct result of the movements of the molecules surrounding them; in fact, the Brownian movement may be regarded as providing a magnified picture of the motion of the molecules themselves.

Because of the influence of gravity, the molecules in a column of gas are not distributed uniformly; there are more molecules at lower than at higher levels. This fact is illustrated by the decrease of atmospheric pressure at increasing elevations. The vertical distribution of the gas molecules can be derived from the Boltzmann equation (3.20). The difference in potential energy between molecules at heights h_1 and h_2, due to the difference in the gravitational forces, is $mg(h_2 - h_1)$ per molecule, m being the mass of a molecule and g the acceleration of gravity. The potential energy difference per mole is thus Nmg $(h_2 - h_1)$, where N is the Avogadro number; this is equivalent to E in equation (3.20). Hence, if the numbers of molecules (per unit volume) at these heights are n_1 and n_2, respectively, it follows that

$$\frac{n_2}{n_1} = e^{-Nmg(h_2-h_1)/RT}.$$

Upon taking (natural) logarithms of both sides it is found that

$$\ln \frac{n_1}{n_2} = \frac{Nmg(h_2 - h_1)}{RT}, \tag{3.29}$$

where "ln," sometimes written "$\log_e$," is the symbol for natural logarithms.*

In his treatment of the Brownian motion, Perrin made certain postulates concerning the similarity between suspended particles and gas molecules

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* The relationship between natural and common logarithms, i.e., to the base of 10, is given by the expressions

$$\ln x = 2.303 \log x \quad \text{or} \quad 0.4343 \ln x = \log x.$$

which were equivalent to implying that the vertical distribution of particles in a suspension is also given by equation (3.29). The only modification necessary is the introduction of the factor $(1 - d'/d)$ on the right-hand side to allow for the buoyancy of the particles of density d suspended in a liquid of density d'; thus,

$$\ln \frac{n_1}{n_2} = \frac{Nmg(h_2 - h_1)}{RT}\left(1 - \frac{d'}{d}\right), \tag{3.30}$$

m being now the mass of a suspended particle. If the latter is spherical, then m is equal to $\frac{4}{3}\pi r^3 d$, where r is the radius of the particle and d is its density. Making this substitution for m in equation (3.30), and rearranging, the result is

$$\frac{RT}{N} \ln \frac{n_1}{n_2} = \frac{4}{3}\pi r^3 g(h_2 - h_1)(d - d'). \tag{3.31}$$

By working with suspensions in water of spherical particles of gamboge and mastic, which are visible in the microscope, Perrin was able to count the numbers of particles n_1 and n_2 at different levels, and to determine their radius r and density d. Since d', the density of water, is known, all the information necessary to calculate the Avogadro number N by means of equation (3.31) was obtained. As the result of many experiments made under a wide variety of conditions, Perrin found the value of N to be about 6×10^{23}, and a similar figure was obtained from other measurements with suspended particles.

In addition to the methods which depend directly or indirectly on the kinetic theory of gases, several procedures are available for the calculation of the Avogadro number which are quite independent of the kinetic theory. Two examples of such methods may be given here. The volume of helium gas, measured at S.T.P., liberated from radium in its disintegration is 0.043 ml per gram of radium per year; the number of α-particles emitted in the same time by the same amount of radium, calculated from direct observations, is 11.6×10^{17}. Each α-particle should yield one atom or one molecule of helium, since for this element the atom and molecule are identical; it follows, therefore, that 0.043 ml should contain 11.6×10^{17} individual molecules. One mole of gas occupies 22,400 ml, and consequently the number of molecules in 1 mole, which is the Avogadro number, is given by

$$N = \frac{11.6 \times 10^{17} \times 22{,}400}{0.043} = 6.05 \times 10^{23}.$$

The remarkable agreement between this result and those derived from a study of the Brownian movement provides very strong evidence for the real existence of molecules.

The most accurate method for the determination of the Avogadro number is based on the diffraction of X-rays by crystals, to be considered in Chapter 7. By measuring the angles of diffraction, the spacing of certain planes of atoms in the crystal can be determined, provided the wave length of the X-rays is known. The crystal spacing can then be related to the known molecular weight and density of the solid and to the Avogadro number, e.g., by equation (18.4). Hence, from measurements of the wave length of X-rays and their diffraction by a crystal, the Avogadro number can be determined. The accepted value of the Avogadro number, derived from such measurements, e.g., with calcite crystals, which can be obtained in a pure state and of perfect form, is 6.023×10^{23} molecules per (chemical) mole.*

31. Heat Capacity and the Kinetic Theory.—The **heat capacity** of any system is *the quantity of heat required to raise the temperature of the system by one degree.* If the weight of the material is 1 gram, the heat capacity is then called the **specific heat** of the substance. In physical chemistry, the quantity considered is frequently 1 mole, and so the heat capacity is referred to as the **molar heat capacity,** or sometimes as the **molecular heat.** Heat capacities are generally expressed in **calories,** where the "15° calorie" is the amount of heat required to raise the temperature of 1 gram of water from 14.5° to 15.5°C. Because of the uncertainty in the isotopic composition of water, it has been recommended that the calorie be defined as 4.1840 absolute joules, i.e., 4.1840×10^7 ergs;† this value is only very slightly different from that of the 15° calorie.

For all substances, and particularly for gases, the heat capacity depends on whether both the pressure and volume are allowed to vary or not. In order to obtain definite results, therefore, it is necessary to specify the conditions; two such conditions are in general use. First, it can be specified that the volume is maintained constant while the temperature is being raised, and the pressure is consequently allowed to increase; this is the **heat capacity at constant volume.** Second, the pressure may be maintained constant, and the volume permitted to change, thus giving the **heat capacity at constant pressure.** The specific heats at constant volume and constant pressure are designated c_V and c_P, respectively, whereas the molar heat capacities are represented by C_V and C_P, respectively. The latter symbols are also frequently used for heat capacities in general, where the amount of the substance, or substances, concerned is not stated explicitly.

Suppose the molecules of a gas possess one kind of energy only, namely kinetic energy of translation, sometimes called **translational energy;** this is the energy whose value has been already calculated by means of the kinetic theory of gases. If the temperature of the gas is raised, *at constant volume,* the heat supplied goes merely to increase the kinetic energy of the molecules. This fact makes it immediately possible to calculate the heat capacity of such a gas from the kinetic theory. From equation (3.11), the kinetic energy of the molecules in 1 mole of ideal gas is equal to $\frac{3}{2}RT$ at the temperature T.

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* The distinction between the chemical mole, which is the ordinary chemical gram molecular weight, and the physical mole will be apparent in § 64c.

† Prior to 1948, the calorie was defined as 4.1833 international joules, where 1 international joule is 1.0002×10^7 ergs.

If the temperature is raised by 1° to $T + 1$, the kinetic energy becomes $\frac{3}{2}R(T + 1)$, so that

$$\begin{aligned}\text{Increase of kinetic energy per degree} &= \tfrac{3}{2}R(T + 1) - \tfrac{3}{2}RT \\ &= \tfrac{3}{2}R.\end{aligned}$$

Since, as postulated above, the heat supplied to the gas at constant volume is used up entirely for increasing the translational kinetic energy, it follows that the heat capacity per mole, which is the heat required to raise the temperature by 1°, is given by

$$C_V = \tfrac{3}{2}R. \qquad (3.32)$$

The value of R is 1.987 cal deg^{-1} mole^{-1} (§ 2g); hence, the molar heat capacity at constant volume of a gas possessing translational energy only should be 2.98 cal deg^{-1} mole^{-1}. It is of interest to note that results close to 3 cal deg^{-1} mole^{-1} have been recorded for helium, neon and other gases of Group 0 of the periodic table, and also for the vapors of mercury, potassium and other metals. There are many reasons for believing that in all these substances the molecules are *monatomic*, i.e., the molecule contains but one atom. Such molecules would be expected to possess translational energy as the only, or essential, form of energy. At very low temperatures the value of C_V of hydrogen, which is not monatomic, also approaches 3 cal deg^{-1} mole^{-1}. However, whereas for helium, neon, etc., the heat capacity remains almost constant, that for hydrogen increases rapidly as the temperature is raised. The reason for this, as will be seen below, is that the hydrogen molecules can possess other forms of energy, in addition to translational, and these become apparent with increasing temperature.

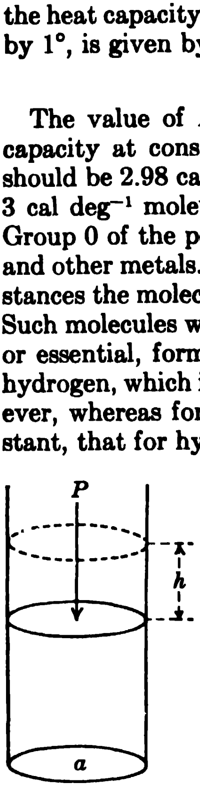

FIG. 3.5. Work done in expansion against an external pressure

When a gas, or in fact any substance, expands it has to do work against the external pressure, generally the pressure of the atmosphere. Consequently, when the temperature of a gas is raised at constant pressure, and the volume increases, heat must be supplied to perform the external work, in addition to that required to increase the kinetic energy of the molecules. The value of the work done by the gas when it expands against a constant external pressure may be obtained in the following manner. Consider any substance contained in a cylinder of cross section a sq cm, fitted with a piston upon which is exerted a constant pressure of P dynes per sq cm. The total force acting on the piston is equal to the pressure multiplied by the area, i.e., to Pa dynes. Suppose the substance in the cylinder expands, *the external pressure remaining constant;* the piston is raised through a height h cm (Fig. 3.5). The work done against the external pressure is equal to the product of the force acting and the displacement of the point of application; it follows, therefore, that

$$\text{External work done in expansion} = Pa \times h \text{ ergs.}$$

The quantity $a \times h$ represents the increase in volume during expansion, and this may be replaced by ΔV, so that

$$\text{External work done in expansion} = P\Delta V. \qquad (3.33)$$

This result holds for any system, gaseous, liquid or solid; hence, *the external work done is always equal to the product of the (constant) external pressure and the change of volume.*

For 1 mole of an ideal gas at a temperature T,

$$PV = RT,$$

and if the temperature is raised by 1° at constant pressure, the volume increases by ΔV to $V + \Delta V$, so that

$$P(V + \Delta V) = R(T + 1).$$

Upon subtraction of these two equations, it is seen that

$$P\Delta V = R.$$

It follows, therefore, that when the temperature of 1 mole of an ideal gas is raised by 1° at constant pressure, the work done on account of expansion is equal to the value of the gas constant R. This gives the contribution to the molar heat capacity due to the external work, and if it is added to the heat required to increase the kinetic energy of the molecules, i.e., $C_V = \frac{3}{2}R$, the total is the molar heat capacity of the gas at constant pressure; thus,

$$\begin{aligned} C_P = C_V + R &= \tfrac{3}{2}R + R \\ &= \tfrac{5}{2}R. \end{aligned} \qquad (3.34)$$

There are two important consequences of the foregoing arguments; first, *the difference between the molar heat capacities of a gas at constant volume and at constant pressure should be equal to R;* thus,

$$C_P - C_V = R = 1.987 \text{ cal deg}^{-1} \text{ mole}^{-1}, \qquad (3.35)$$

i.e., approximately 2 cal deg^{-1} mole^{-1}. Second, *the ratio of the two heat capacities for any ideal gas possessing translational energy only should be $\frac{5}{3}$, i.e., 1.667;* thus, representing this ratio by the symbol γ, it follows from equations (3.32) and (3.34) that

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = 1.667. \qquad (3.36)$$

It may be noted that the former of these conclusions, i.e., equation (3.35), may be expected to hold, *at least approximately*, for any gas, but the latter, i.e., equation (3.36), will be applicable to a gas whose molecules possess translational energy only. This is particularly the case for monatomic gases, at all temperatures; as indicated above, hydrogen gas has this property at low, but not at higher, temperatures. The results in Table 3.2, for some gases and vapors which are believed to be monatomic, are in agreement with expectation. The values are essentially independent of temperature.

TABLE 3.2. MOLAR HEAT CAPACITIES OF MONATOMIC GASES

Gas	C_P (cal deg^{-1})	C_V (cal deg^{-1})	$C_P - C_V$ (cal deg^{-1})	γ
Helium	5.00	3.02	1.98	1.66
Argon	4.98	2.99	1.99	1.67
Mercury	4.97	2.98	1.99	1.67
Iodine (atomic)	5.0	3.0	2.0	1.67

3m. Heat Capacities of Polyatomic Molecules.—If the heat capacities of gases which contain two or more atoms in the molecule, that is, of polyatomic gases, are studied, it is found that although $C_P - C_V$ is approximately equal to 2 cal per deg per mole, the actual values of the heat capacities are usually greater than $\frac{5}{2}R$ and $\frac{3}{2}R$ for C_P and C_V, respectively; for polyatomic molecules, therefore,

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{5}{2}R + c}{\frac{3}{2}R + c} < 1.667,$$

so that the ratio of the heat capacities is less than 1.667. The cause of this discrepancy lies in the fact that when it contains more than one atom, the molecule possesses other forms of energy, in addition to translational, which can increase as the temperature is raised and thus contribute to the heat capacity. These forms of energy are **rotational energy** and **vibrational energy.** The rotational energy is due to the rotation of the molecule as a whole about three axes at right angles to one another, whereas the vibrational energy is associated with the oscillations of the atoms within the molecule. As in all vibrational systems, the energy has both kinetic and potential components. According to the classical **principle of the equipartition of energy,** each form of energy manifested by a molecule contributes $\frac{1}{2}R$ to the heat capacity of a gas. Thus, the heat capacity of any molecule should be the sum of $\frac{3}{2}R$ for the three translational components, $\frac{1}{2}R$ for each type of rotation, and $2 \times \frac{1}{2}R$, i.e., R, for each mode of vibration.

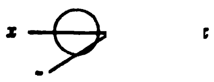

FIG. 3.6. Diatomic molecule

A diatomic molecule may be pictured as a small dumbbell, as in Fig. 3.6. The molecule as a whole will have translational components parallel to the x, y and z directions (§ 3b). In addition, it can rotate about the axes y and z. Rotation about the x-axis, if it occurs, is unaffected by temperature change and so does not contribute to the heat capacity. Further, if the temperature is high enough, the atoms will vibrate along the line connecting their centers. As a result of all these motions, the maximum heat capacity of the diatomic molecules at constant volume may be expected to be $\frac{3}{2}R + 2 \times \frac{1}{2}R + R = \frac{7}{2}R$, i.e., about 7 cal deg^{-1} mole^{-1}. At ordinary temperatures, most diatomic molecules, e.g., hydrogen, oxygen, nitrogen, carbon monoxide, hydrogen chloride, etc., have values of C_V of about 5 cal deg^{-1} mole^{-1}, but there is a definite increase with increasing temperature. This is most marked with chlorine, the molecule of which is also diatomic; at 0°C the molar heat capacity at constant volume is 5.95 and it reaches a value of about 7 cal deg^{-1} mole^{-1} at 700°C, there being little change above this temperature.

Although the classical theory of equipartition of energy is inadequate to interpret these results, the quantum theory provides the explanation. It appears that all forms of energy are quantized; that is to say, the molecule does not take up its energy in a continuous manner, but only in the form of definite amounts or quanta (§ 15b). The translational quanta are very small, rotational quanta are somewhat larger, and vibrational quanta much larger. At temperatures above the absolute zero, all molecules possess translational energy; at ordinary temperatures all possess rotational energy, but only at high (or moderately high) temperatures do molecules absorb enough energy to raise them out of the lowest vibrational quantum level.* Hence, for most diatomic gases at ordinary temperatures the vibrational energy does not affect the heat capacity. The molar heat capacity at constant volume is then the sum of $\frac{3}{2}R$ for the kinetic energy and $2 \times \frac{1}{2}R$ for the rotational energy, making a total of $\frac{5}{2}R$, i.e., 5 cal deg^{-1} mole^{-1}, in agreement with experiment. The value of γ for many diatomic gases is consequently $(\frac{5}{2}R + R)/\frac{5}{2}R = 1.40$, at ordinary temperatures.

As the temperature is raised, increasing numbers of molecules acquire various quanta of vibrational energy, with the result that the contribution to the heat capacity increases toward the classical value of R for each mode of vibration. This explains why the C_V values of diatomic gases increase steadily to about 7 cal deg^{-1} mole^{-1} as the temperature is raised (Table 3.3).

TABLE 3.3. MOLAR HEAT CAPACITIES OF DIATOMIC GASES AT CONSTANT VOL

Gas	0°	100°	200°	500°	1200°	2000°C
H_2	4.87	4.93	5.05	5.16	5.67	6.28 cal deg^{-1}
N_2, O_2, CO	4.99	5.05	5.15	5.26	5.75	6.3
HCl	5.00	5.09	5.27	5.46	6.13	6.9
Cl_2	5.95	6.3	6.7	6.9	7.1	7.2

With chlorine, the vibrational energy quanta are not too large, and so an appreciable number of molecules have such quanta even at ordinary temperatures; hence, the molar heat capacity of chlorine at constant volume already exceeds $\frac{5}{2}R$ at 0°C.

If the foregoing arguments are correct, it is to be expected that at sufficiently low temperatures the rotational contribution to the heat capacity should fall off to zero. This condition has been realized with ordinary hydrogen gas, for at a temperature of 50°K, i.e., −223°C, its heat capacity has decreased to 3 cal deg^{-1} mole^{-1}, which is the value for a monatomic gas. At these low temperatures, translational energy only, and no rotational

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* It is of interest to mention that even in its lowest vibrational energy state a molecule still possesses some energy of vibration; this is known as the **zero-point energy**, and is $\frac{1}{2}h\nu$ per molecule for each mode of vibration, h being the Planck constant and ν the frequency of vibration (cf. § 15b). The presence of zero-point energy, even at the absolute zero, is of fundamental importance in certain aspects of the chemistry and physics of molecules.

energy, contributes to the heat capacity. For other gases, liquefaction has occurred before the temperature is reached at which the rotational contribution ceases.

A linear polyatomic molecule, i.e., one containing more than two atoms that lie in a straight line, has only two types of rotation exactly like a diatomic molecule. In the case of a nonlinear (or bent) molecule, rotation about a third axis becomes possible. In each case the molecule possesses the usual three translational degrees of freedom. The number of modes of vibration which the molecule will exhibit may be derived in the following manner. To specify the location in space of n separate atoms requires $3n$ coordinates, i.e., $x_1y_1z_1$, $x_2y_2z_2$, $\cdots$, $x_ny_nz_n$; when combined to form a molecule, the atoms no longer behave independently, and their locations are determined by the translational, rotational and vibrational motions which the molecule undergoes.

For a linear molecule there are five kinds of motion due to translation and rotation; the molecule must then have $3n - 5$ modes of vibration. A bent molecule, on the other hand, will have $3n - 6$ vibrational modes, since it has six kinds of modes of motion due to translation and rotation. The maximum (limiting) heat capacity at constant volume for a linear molecule thus consists of $\frac{3}{2}R$ for translation, $\frac{2}{2}R$ for rotation and $(3n - 5)R$ for vibration, making a total of $(3n - \frac{5}{2})R$, whereas for a nonlinear (or bent) molecule the value will be $\frac{3}{2}R$ for translation, $\frac{3}{2}R$ for rotation and $(3n - 6)R$ for vibration, or a total of $(3n - 3)R$. These values are approached at sufficiently high temperatures. In each case the heat capacity at constant pressure is greater by R, approximately.

Example: Calculate the maximum high temperature molar heat capacity at constant volume to be expected for (i) acetylene (C_2H_2), which is a linear molecule, and (ii) ammonia, which is nonlinear.

(i) For acetylene, n is 4, so that there are $3n - 5 = (3 \times 4) - 5 = 7$ modes of vibration; these can contribute up to $7R$ to the heat capacity. There are two types of rotation, and these can contribute $2 \times \frac{1}{2}R$, i.e., R. Translation contributes $\frac{3}{2}R$, and so the total maximum C_V is $9\frac{1}{2}R$, i.e., 19 cal deg^{-1} mole^{-1}.

(ii) For ammonia, n is 4, but as the molecule is nonlinear, there are $3n - 6 = (3 \times 4) - 6 = 6$ modes of vibration, contributing a maximum of $6R$; the three types of rotation add $3 \times \frac{1}{2}R$, i.e., $\frac{3}{2}R$, and translation a further $\frac{3}{2}R$, making a total maximum C_V of $9R$, i.e., 18 cal deg^{-1} mole^{-1}. (The actual value is 6.6 cal deg^{-1} mole^{-1} at 0°C increasing to 11.4 at 1200°C; it is seen therefore that at 0° the rotational and translational contributions account for most of the heat capacity. Because of decomposition at high temperatures the limiting heat capacity has not been observed.)

REAL GASES

4a. Deviations from Ideal Behavior.—As already indicated (§ 2f), real gases do not obey the ideal gas laws exactly. At low pressures and moderately high temperatures the laws of Boyle, Gay-Lussac and Avogadro, as expressed in the form of the equation $PV = RT$ for 1 mole of gas, are obeyed approximately, but as the pressure is increased or the temperature decreased, marked departure from ideal behavior becomes apparent. The magnitude and nature of these deviations from Boyle's law may be seen from an examination of the product of pressure and volume for various pressures, at constant temperature; if Boyle's law were obeyed the values would be constant. The data for hydrogen and nitrogen at 0°C, and for carbon dioxide at 40°C, are given in Table 4.1 and are plotted in Fig. 4.1; the value of PV at 1 atm pressure is taken as unity in each case. For an ideal gas, obeying Boyle's law, the effect of pressure on the pressure-volume product is represented by the horizontal dotted straight line in Fig. 4.1. It is obvious from this figure,

TABLE 4.1. VARIATION OF THE PRESSURE-VOLUME PRODUCT WITH PRESSURE

Pressure	Hydrogen	Nitrogen	Carbon Dioxide
1 atm	1.000	1.000	1.000
50	1.033	0.985	0.741
100	1.064	0.985	0.270
200	1.134	1.037	0.409
400	1.277	1.256	0.718
800	1.566	1.796	1.299

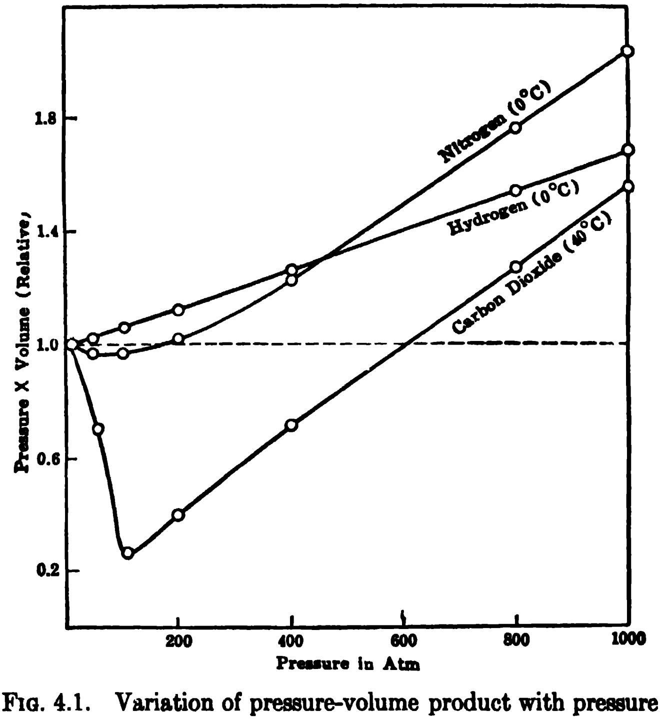

FIG. 4.1. Variation of pressure-volume product with pressure

as well as from the results in Table 4.1, that real gases show considerable deviations from ideal behavior, especially at high pressures. At pressures of the order of 1 atm, or less, the departure from Boyle's law is usually small.

An examination of Fig. 4.1 reveals the fact that whereas the value of *PV* for hydrogen increases continuously as the pressure is increased, with the other gases there is at first a decrease, followed by an increase. Helium and neon are similar to hydrogen in their behavior at ordinary temperatures. However, if the temperature is lowered, the shape of the curve changes, and in each case it eventually becomes like that for nitrogen or carbon dioxide in Fig. 4.1. On the other hand, at sufficiently high temperatures, the pressure-volume product curves of these and other gases become like those for hydrogen, helium and neon at ordinary temperatures. The curves in Fig. 4.2 show the relative values of *PV* for nitrogen plotted against the pressure for a number of temperatures; the change in the shape of the curves with in-

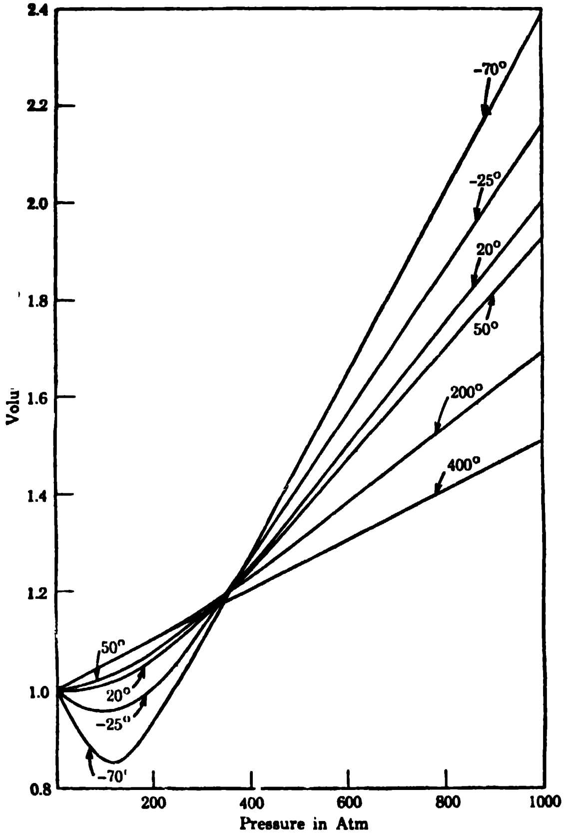

FIG. 4.2. Variation of pressure-volume product of nitrogen

creasing temperature is clearly seen. It appears, therefore, that the general nature of the deviations from ideal behavior does not depend on the gas, but rather on the temperature. Actually, the determining factor is the temperature relative to the critical temperature (§ 10a) of the particular gas; when near this point the PV curves are like that for carbon dioxide, but when far away the curves are like that for hydrogen in Fig. 4.1.

In addition to the deviations from Boyle's law, real gases exhibit departures from Gay-Lussac's law; this is apparent from the fact that the shape of the PV curves, e.g., in Fig. 4.2, changes with temperature. In general, the discrepancies are greater the higher the pressure and the closer the temperature is to that at which liquefaction is possible.

The accuracy of Avogadro's law may be tested by determining the volume occupied by 1 mole of a gas at 0°C and 1 atm pressure. If the law were strictly true, the volume would be independent of the nature of the gas, but the results in Table 4.2 show that this is not the case. As before, the largest deviations are shown by the most easily liquefiable gases, e.g., ammonia and ethyl chloride; the departure from ideal behavior increases with decreasing temperature and increasing pressure. By measuring the volume occupied by 1 mole of gas at 0°C and various pressures, and extrapolating the pressure-volume product to zero pressure, the volume of 1 mole of an ideal gas at 0° and 1 atm has been found to be 22.414 liters, as mentioned earlier.

TABLE 4.2. TEST OF AVOGADRO'S LAW

Gas	Molecular Weight	Volume of 1 Mole at 0°C and 1 Atm
Hydrogen	2.016	22.427 liters
Nitrogen	28.02	22.405
Oxygen	32.00	22.394
Carbon dioxide	44.01	22.264
Ammonia	17.03	22.084
Ethyl chloride	50.49	21.879

Provided the pressure is of the order of 1 atm or less, and the temperature is not too near the point of liquefaction, the deviations from the ideal gas laws are not more than a few per cent. Under these conditions, therefore, the equation $PV = RT$, and related expressions, may be used for approximate calculations, at least. The lower the pressure and the higher the temperature, the more reliable are the results obtained in this manner.

4b. Causes of Deviations from Ideal Gas Law.—The ideal gas laws were derived from the kinetic theory on the basis of two important assumptions; these were that the volume of the molecules is negligible in comparison with the total volume of the gas, and that the molecules exert no attraction upon one another (§ 3a). It is because neither of these assumptions can be regarded as applicable to real gases that the latter show departure from ideal behavior. The fact that even the simple kinetic theory leads to the necessity for postulating a collision diameter, representing the distance of closest approach of two molecules in a collision, shows the molecule must possess an *effective volume*. Further, the volume of a gas can be reduced by increasing the pressure and cooling until liquefaction and eventually solidification occur. In the solid state, however, there is a considerable resistance to any further attempt at compression. It is apparent, therefore, that the molecules of a gas must have an appreciable volume, which is probably of the same order as the volume occupied by the given molecules in the solid state.

If the molecules of a gas did not attract one another, it is doubtful whether gases could ever be liquefied; actually, any gas can be converted into a liquid by the use of low temperatures and high pressures (§ 10a). One of the essential properties of a liquid is that of cohesion, which is attributed to the attraction between the molecules. This molecular attraction is presumably manifested in the gas as well as in the liquid. More direct evidence for the existence of this attractive force was obtained by J. P. Joule and W. Thomson (Lord Kelvin) in the course of experiments carried out between 1852 and 1862. A stream of gas at constant pressure was passed through a tube into which was fixed a porous plug of absorbent cotton or silk; the gas emerging from the plug was found to be, in general, appreciably cooler than the entering gas. The change of temperature, known as the **Joule-Thomson effect,** is due to a decrease of the speed, and hence of the kinetic energy, of the molecules; this occurs because energy must be supplied in order to overcome the molecular attractive forces when the gas expands in passing through the porous plug.

In addition to attracting each other, it can be shown that there must be forces of repulsion exerted between molecules. This is evident from the existence of a more or less definite collision diameter; the latter represents the distance at which the repulsive force becomes so great that the direction of motion of the molecules is reversed, i.e., from toward one another to away from one another. However, the forces of repulsion fall off extremely rapidly with increasing distance of separation of the molecules, much more rapidly than do the forces of attraction. As a result there is a net attraction between a pair of molecules when they are an appreciable distance apart, and a net repulsion when they are very close together.

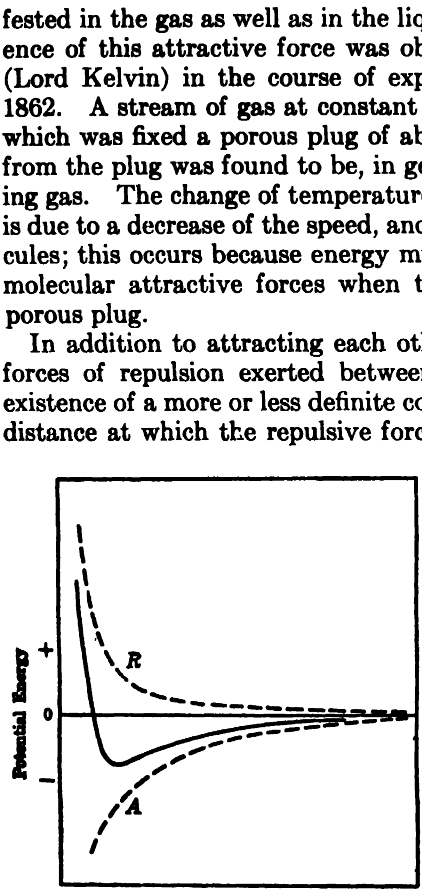

FIG. 4.3. Potential energy diagram of two gaseous molecules

The forces between molecules (or atoms) are frequently represented by means of a **potential energy diagram,** such as that in Fig. 4.3, in which the mutual potential energy of two gas molecules is plotted as a function of their distance apart. Although the attractive and repulsive forces between molecules operate at the same time, it is instructive, as a first step, to consider them separately. In Fig.

4.3, the dotted curve marked *R* shows the effect of repulsion; in order to bring two molecules closer together, work must be done against the repulsive force and so the potential energy of the system increases. Below a certain distance the curve is seen to rise steeply, indicating a rapid increase in the repulsive energy. The effect of attraction on the potential energy is shown by the dotted curve *A*; because of the increase in the attractive force, the potential energy now becomes increasingly negative as the molecules are brought closer together. It follows from the shape of the curves that, in general, the contribution of the attractive forces increases less rapidly with closeness of approach of the molecules than does that of the repulsive forces.

The net mutual potential energy of the two molecules, as shown by the full curve in Fig. 4.3, is the sum of the repulsive and attractive contributions. The quantitative details of this curve vary from one molecular species to another, but the general form is always like that shown. At relatively large distances of separation, the potential energy is negative, so that the attractive effect predominates. The net attractive energy increases, at first, as the molecules come closer together. Subsequently, at intermolecular distances closer than the minimum of the curve, the repulsive effect becomes apparent and the net attractive energy decreases with decreasing distance between the molecules. Eventually, at small intermolecular distances, the net potential energy is seen to increase rapidly and become positive, indicating that the repulsive forces are now dominant. The distance between the molecules at which the potential energy is zero, i.e., at which the attractive and repulsive forces just balance each other, is the collision diameter.

4c. The van der Waals Equation.—In order to adapt the ideal gas law equation to the behavior of real gases allowance should be made for the attractive and repulsive forces between molecules. One of the simplest and most useful attempts in this direction was made by J. D. van der Waals (1873) somewhat along the following lines. Consider a molecule in the interior of a gas; it is surrounded by other molecules equally distributed in all directions (Fig. 4.4, A), so that they exert no *resultant* attractive force on the molecule under consideration. As the latter approaches the wall of the containing vessel, however, the uniform average distribution of the molecules changes to one in which gas molecules are present on one side only (Fig. 4.4, B), so that a force is exerted tending to pull the molecule inwards. It appears, therefore, that at the instant any molecule is about to strike the containing vessel, and thus contribute its share toward the total gas pressure, the molecules in the bulk of the gas exert a force having the effect of pulling the molecule away from the wall. The measured pressure *P* is thus less than the ideal pressure required by the simple kinetic theory. It is conse-

FIG. 4.4. Molecular attractions: (A) in the interior of gas, (B) at the wall

quently necessary to *add* a correction term to the observed pressure in order to obtain the ideal pressure, that is, the pressure an ideal gas would exert under the same conditions.

The attractive force exerted on a single molecule about to strike the wall is proportional to the number n of molecules per unit volume in the bulk of the gas. Further, the number of molecules striking the walls is also proportional to this number, so that the total attractive force, which is related to the correction term to be added to the measured pressure, is proportional to n^2. If V is the volume occupied by 1 mole of gas, then n is inversely proportional to V, and hence the attractive force will vary as $1/V^2$. The correction term may then be represented by a/V^2, where a is a constant; thus,

$$\text{Corrected (ideal) pressure} = P + \frac{a}{V^2},$$

where P is the actual (observed) gas pressure.

The effect of combined repulsive and attractive forces is to give the molecules an appreciable size, and hence the space available for their movement is less than the actual measured volume V of the gas. In order to obtain the ideal volume, therefore, it is necessary to *subtract* an appropriate correction term from the total volume. This correction term, which has been shown in various ways to be equal to four times the actual volume of the molecules, is given the symbol b, and is called the **covolume.** It is seen, consequently, that

$$\text{Corrected (ideal) volume} = V - b.$$

The product of the ideal pressure and ideal volume derived in this manner may be expected to be equal to RT, as for an ideal gas; hence, it is reasonable to write

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{4.1}$$

for 1 mole of an actual (real) gas. This is the **van der Waals equation,** one of the best known and simplest of the equations of state proposed for real gases.

The values of the van der Waals constants a and b, the former giving a measure of the molecular attraction and the latter of the volume of the molecules, may be obtained in several ways. The one generally used is based on the critical temperature, pressure and volume of the gas (§ 10c). Actually, the so-called constants vary to some extent with temperature, and this shows that the van der Waals equation is not a complete solution of the problem of real gases. Nevertheless, it is possible to ascribe values to the van der Waals constants a and b which provide a useful, if not exact, means for correcting for departure from ideal behavior. The values of a and b depend on the units employed for expressing P and V; the results in Table 4.3 are based on V in liters per mole of gas and P in atm. The most easily liquefiable gases, such as those on the right-hand side of the table, exhibit the largest values of a; this is to be expected if a is a measure of the attractive forces between the molecules of a gas.

TABLE 4.3. VAN DER WAALS CONSTANTS

Gas	a (liter^2-atm mole^{-2})	b (liter mole^{-1})	Gas	a (liter^2-atm mole^{-2})	b (liter mole^{-1})
Hydrogen	0.245	2.67×10^{-2}	Hydrogen chloride	3.8	4.1×10^{-2}
Helium	0.034	2.36	Ammonia	4.0	3.6
Nitrogen	1.38	3.94	Acetylene	4.4	5.1
Oxygen	1.32	3.12	Ethylene	4.5	5.6
Carbon monoxide	1.49	4.00	Chlorine	5.5	4.9
Carbon dioxide	3.60	4.28	Sulfur dioxide	6.7	5.6

Example: One mole of carbon dioxide was found to occupy a volume of 1.32 liters at 48°C and a pressure of 18.40 atm. Calculate the pressure that would have been expected (i) from the ideal gas equation, (ii) from the van der Waals equation.

(i) Making use of the ideal gas equation, for 1 mole, in the form $P = RT/V$, with V in liters and P in atm, then R is 0.0820 liter-atm deg^{-1} mole^{-1}, and T is $273 + 48 = 321$°K; hence, since V is 1.32 liters,

$$P = \frac{0.0820 \times 321}{1.32} = 19.9 \text{ atm.}$$

(ii) For this purpose the van der Waals equation may be written

$$P = \frac{RT}{V - b} - \frac{a}{V^2},$$

and since $a = 3.60$ liter^2-atm mole^{-2} and $b = 4.28 \times 10^{-2}$ liter mole^{-1} (Table 4.3), it follows that

$$P = \frac{0.0820 \times 321}{1.32 - 0.043} - \frac{3.60}{(1.32)^2} = 18.5 \text{ atm.}$$

4d. Applicability of the van der Waals Equation.—As indicated above, the van der Waals equation does not reproduce the exact behavior of real gases, but it is certainly a great improvement on the ideal gas equation. That it is in agreement with the general properties of gases, as represented by Fig. 4.1, may be seen in the following manner. Upon multiplying out equation (4.1) and rearranging it is found that

$$PV = RT + Pb - \frac{a}{V} + \frac{ab}{V^2}. \tag{4.2}$$

At low pressures, so that P is small and V is large, the terms Pb and ab/V^2 may be neglected in comparison with a/V, so that equation (4.2) reduces to

$$PV = RT - \frac{a}{V}. \tag{4.3}$$

Under these conditions, therefore, PV should be less than RT, the difference, which is equal to a/V, increasing as V decreases, that is, as the pressure increases. The dip in the plot of PV against P in Fig. 4.1, for nitrogen and carbon dioxide, can thus be correlated with the effect of the a/V^2, i.e., molecular attraction, term of the van der Waals equation. This is in agreement with the statement made earlier that when the molecules are relatively far apart, as at low pressures, the attractive predominate over the repulsive forces.

At high pressures, the last two terms on the right of equation (4.2), being of opposite sign and approximately equal magnitude, may be neglected in comparison with the other two terms; the van der Waals equation then becomes

$$PV = RT + Pb. \tag{4.4}$$

It is seen that PV is now greater than RT, and that it increases in a linear manner with the pressure; this accounts for the rising part of the three curves in Fig. 4.1, which is largely due to the influence of the b term, i.e., the volume of the molecules or the repulsive forces.

For most gases, *at ordinary temperatures*, the effect of the a/V^2 term in the van der Waals equation is dominant at low pressures, while that of b is most important at high pressures. With hydrogen, helium and neon, however, the values of a, i.e., the molecular attractions, are so small (see Table 4.3) that the b, i.e., volume of molecules, effect predominates even at low pressures. It is for this reason that the PV curve for hydrogen shows no dip at ordinary temperatures (Fig. 4.1).

At extremely low pressures, when V is very large, both a/V^2 and b are small in comparison with P and V, respectively; the van der Waals equation then reduces to the ideal gas equation, $PV = RT$. Under these conditions, therefore, all real gases should obey the ideal gas laws, and consequently these laws may be regarded as representing the limiting behavior of gases at infinitesimally small pressures, as implied in previous sections. The physical basis of this result is that at small pressures there are so few molecules in unit volume that the attractive force between them may be ignored; further, the volume of the gas is then so large that the actual volume of the molecules is negligible in comparison. The real gas consequently behaves as if it consisted of point molecules which do not attract one another, that is, as an ideal gas.

4e. Other Equations of State.—Something like one hundred different equations of state for gases have been proposed from time to time. The majority of these depend on the same principles as does the van der Waals equation, corrections being applied to the ideal gas equation to allow for the volume of the molecules and their mutual attraction. Most of these equations of state achieve an improvement by the introduction, in addition to a and b, of further empirical constants derived from experimental data. Such equations contribute little to the underlying theory of the behavior of real gases, but they are useful as a means of expressing the observed pressure-volume-temperature relationships of a gas in the form of an equation. The chief function of these equations is for the interpolation or extrapolation of experimental data. Mention may be made in this connection of two modifications of the van der Waals equation which have at least a partial theoretical basis; these are the **Keyes equation** (1917) and the **Beattie and Bridgeman equation** (1927). The former has four empirical constants, in addition to R, while the latter has five such constants. Over the temperature interval from 0° to 200°C and up to 250 atm pressure, the Beattie-Bridgeman equation, with a suitable choice of constants, agrees with experimental values for many gases, to within 0.5 per cent.

In recent years increasing use has been made of the **virial equation** (virial: Greek, *force*) of H. K. Onnes (1901); this is a very general equation of the form

$$PV = RT\left(1 + \frac{B}{V} + \frac{C}{V^2} + \cdots\right), \tag{4.5}$$

where the coefficients B, C, etc., which vary with temperature, are called the second, third, etc., **virial coefficients.** An equation of this type is useful for extrapolation purposes, the values of the coefficients B, C, etc., being calculated from the experimental pressure-volume-temperature measurements. In general, the coefficient B is negative at low (or moderately low) temperatures, becoming zero and then positive as the temperature is increased. The temperature at which B is zero is called the **Boyle temperature,** since the gas then obeys Boyle's law, to a fair degree of approximation, over a moderately wide range of pressures.

By using enough terms, the pressure or volume values calculated from equation (4.5) can be made to agree with experiment as closely as desired. However, it is important to point out that the virial equation is more than a mere empirical expression for representing the P-V-T relationships of a gas. Theoretical methods are being developed for calculating the virial coefficients from the forces of intermolecular attraction and repulsion, so that ultimately this is likely to provide the most complete approach to the problem of real gases.

4f. Origin of Molecular Attraction and Repulsion.—The existence of forces of repulsion between molecules can be readily understood. They probably arise from the interaction of the electron cloud or field of one molecule with that of another, when they are close together. The explanation of the origin of the physical forces of molecular attraction, generally known as **van der Waals forces,** however, presented a difficulty for many years. For polar molecules, that is, those possessing resultant or permanent dipole moments (§ 16g), it might be possible to account for the molecular forces by the electrical interaction of the dipoles.* However, van der Waals forces occur between nonpolar molecules, such as hydrogen, oxygen, nitrogen, etc., and even between monatomic molecules, such as helium, neon, etc. It was suggested by F. London (1930) that in molecules (and atoms) of all kinds, the positively charged nuclei and the negatively charged electrons must be regarded as un-

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* A polar molecule is one in which the centers of positive and negative electric charge do not coincide. The magnitude of the permanent dipole moment is then equal to the product of the electronic charge and the relative displacement of the positive and negative electrical centers.

dergoing some kind of oscillations with respect to each other; as a result of this displacement of positive and negative charges, every molecule behaves as an **oscillating dipole.** It is the electrostatic attraction between these dipoles and corresponding dipoles induced in adjacent molecules that is the cause of molecular attraction. The forces due to these oscillating dipole interactions are called **dispersion forces,** because the dispersion of light is also related to these dipoles. For nonpolar molecules, the dispersion forces constitute the whole of the van der Waals attractive forces, but for polar molecules, possessing permanent dipole moments, in addition to those due to the oscillating dipoles, other electrostatic forces contribute to the total molecular attraction.

GAS DENSITIES AND MOLECULAR WEIGHTS

5a. Limiting Densities.—The equation of state for an ideal gas system containing n moles in a volume v is given by equation (2.17), viz.,

$$Pv = nRT. \tag{5.1}$$

If w is the weight of the gas and M is its molecular weight, the number of moles n is equal to w/M; hence, equation (5.1) may be written as

$$Pv = \frac{w}{M} RT, \tag{5.2}$$

$$M = \frac{wRT}{Pv} = \frac{w}{v} \cdot \frac{RT}{P}. \tag{5.3}$$

The quantity w/v is equal to the density d of the gas, generally expressed in grams per liter, at the temperature T and pressure P; equation (5.3) for an ideal gas then becomes

$$M = \frac{d}{P} RT. \tag{5.4}$$

It is evident from this equation that if the density of the gas is measured at a series of pressures, at constant temperature, the ratio d/P should be constant, since M, R and T are constant.

Experiments have shown that for a real gas this ratio is not constant but varies with the pressure. However, if the values of d/P for various pressures are extrapolated to zero pressure, the limiting value, designated by $(d/P)_0$, should correspond to that to be expected if the gas behaved ideally. It is possible, therefore, to write equation (5.4), for an actual gas, in the form

$$M = \left(\frac{d}{P}\right)_0 RT. \tag{5.5}$$

Since R is known, e.g., from similar experiments with oxygen whose molecular weight is taken to be 32.0000, the molecular weight of a gas can be determined from density measurements with the aid of equation (5.5). This is known as the **method of limiting densities.**

The extrapolation of d/P to zero pressure is, of course, a device for correcting for departure from ideal behavior, and this correction has been applied in various ways. The simplest is based on the actual plot of d/P against P, as shown in Fig. 5.1 for ammonia gas at 0°C. At pressures below 1 atm this plot is very close to a straight line for most gases, and so accurate extrapolation to zero pressure is possible without the necessity of making measurements at very low pressures. From Fig. 5.1 it is found that $(d/P)_0$ for ammonia at 0°C is 0.75988 gram liter^{-1} atm^{-1}, the volume being expressed in liters and the pressure in atm; hence, with R equal to 0.082054 liter-atm deg^{-1} mole^{-1}, it follows from equation (5.5) that

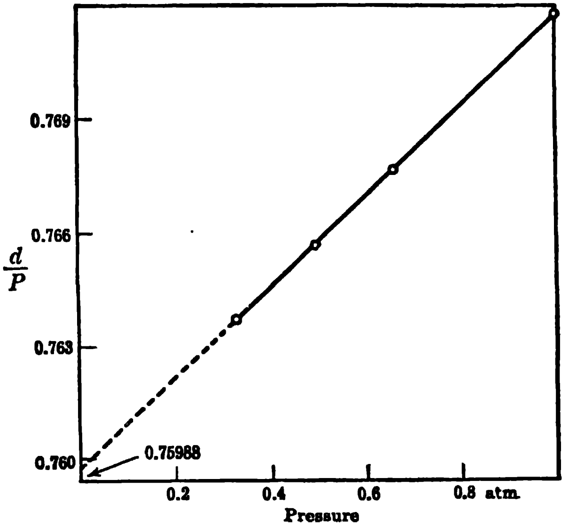

FIG. 5.1. Extrapolation of gas densities

$$M = 0.75988 \times 0.082054 \times 273.15 = 17.034.$$

The accurate molecular weights of gases determined by the method of limiting densities have been used for the evaluation of atomic weights, particularly of nonmetallic elements, such as carbon, nitrogen, fluorine, etc., that do not form easily analyzable compounds, and of the inert gases of Group 0 that form no stable compounds at all. From the results given above, the molecular weight of ammonia (NH_3) is found to be 17.034, and since the atomic weight of hydrogen is 1.0080, it follows that

$$\text{Atomic weight of nitrogen} = 17.034 - 3 \times 1.0080 = 14.010.$$

The accepted value of the atomic weight of nitrogen at the present time is 14.008.

5b. Limiting Pressures.—A modification of the method of limiting densities, for use in connection with the buoyancy balance (see § 5c), is known as the **method of limiting pressures.** Consider two gases, of molecular weights M_1 and M_2; by means of the buoyancy balance, these gases are found to have exactly the same density d at the pressures P_1 and P_2, respectively, at a given temperature. It follows then from equation (5.4) that

$$\frac{M_2}{M_1} = \frac{P_1}{P_2}. \tag{5.6}$$

For actual gases this equation is not strictly correct, but if the experimental ratio P_1/P_2 of the two pressures, for a series of densities, is plotted against one of the pressures, e.g., P_1, and the plot is extrapolated to zero pressure, the limiting pressure ratio $(P_1/P_2)_0$ corresponds to the ideal gas value; hence, for real gases

$$\frac{M_2}{M_1} = \left(\frac{P_1}{P_2}\right)_0 \tag{5.7}$$

If the molecular weight M_1 of one of the gases, e.g., oxygen, is known, the molecular weight M_2 of the other can thus be determined.

5c. Determination of Gas Densities.—Three chief methods have been used for the experimental determination or comparison of gas densities. In the **Regnault method,** a glass globe or bulb of about 500 ml capacity is dried, evacuated and weighed; it is then filled with the gas to be studied at a known pressure and reweighed. The difference between the two weights gives the weight of the gas filling the bulb at the particular temperature and pressure. The volume of the bulb is then found by filling it with water and weighing again. Various corrections must be applied to obtain accurate results.

In the **volumeter method,** the gas is liberated from a suitable generating apparatus, and its weight is determined by the change in weight of the apparatus. The gas is collected in a globe (or globes) of known volume at a definite temperature, and the pressure is measured by a manometer. In this way the mass, volume, pressure and temperature of the gas are found, thus providing all the data necessary for the evaluation of the density at the particular temperature and pressure. In a modification of this method, the weight of the gas is obtained by pumping it out of the globes and absorbing it in a convenient reagent.

Instead of actually measuring the density at a given pressure, in the **buoyancy method** the pressure is determined at which the density has a particular value. The buoyancy balance consists of a small evacuated bulb A suspended by a fine quartz fiber from one end of a beam B, the other end having a suitable counterweight C attached (Fig. 5.2). The balance, which is quite small in size, is enclosed in a tube of 2 to 3 cm diameter and 8 to 10 cm in length. The tube is evacuated and the first gas is gradually admitted; the suspended bulb rises, because of its buoyancy, and the pressure is measured when a pointer F attached to the counterweight reaches a certain level. The gas is then pumped out, and the observation is repeated with the second gas.

The two pressures measured are those at which the two gases have precisely the same density at the temperature of the experiment. By replacing the suspended bulb with one having a different weight, the measurements may be carried out at a series of pressures, as required for the application of the method of limiting densities described above.

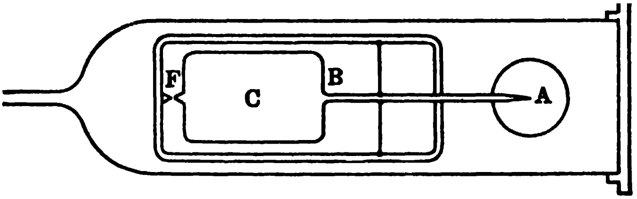

FIG. 5.2. Buoyancy microbalance (seen from above)

5d. Vapor Densities and Molecular Weights.—The vapors of volatile substances which are solid or liquid at ordinary temperatures deviate so considerably from ideal behavior that no great accuracy could be expected from the molecular weights obtained from density measurements. It is useful, nevertheless, to have methods whereby approximate molecular weights of such substances can be determined with fair rapidity. These are generally referred to as **vapor density methods,** because they involve measurement of the weight and volume of the vapor, at a known temperature and pressure. The approximation is made of supposing the ideal gas laws to be applicable, and then the approximate molecular weight of the vapor is given by equation (5.3); thus,

$$M = \frac{wRT}{Pv}. \tag{5.8}$$

The various experimental procedures that have been used involve different means for the determination of the weight w, the volume v, and the pressure P of the vapor. Three of the more important of these methods will be described briefly.

In the **Dumas method** (1826), the substance to be studied, usually a liquid, is introduced into a weighed glass bulb, about 250 ml capacity, having a narrow outlet tube that can either be sealed off or closed by a stopcock. The bulb is heated in a constant temperature bath, about 20° above the boiling point of the experimental liquid. The heating is continued until the whole of the liquid has been converted into vapor and the air is completely expelled from the bulb. The latter is thus filled with the vapor at atmospheric pressure P and the temperature T of the heating bath. The bulb is now closed off, cooled and weighed; the difference between this weight and the weight of the "empty" bulb, after allowing for the air contained in the latter, gives the weight w of the vapor. The volume v of the bulb may be obtained in the familiar manner by filling with water and weighing.

Example: *Calculate the molecular weight of chloroform from the following data obtained with the Dumas method: weight of bulb with air = 52.30 g; weight of bulb filled with vapor = 52.96 g; weight of bulb filled with water at 20°C = 302 g; temperature of heating bath, 100°C; atmospheric pressure, 752 mm of mercury. (The density of air at ordinary temperatures and pressures may be taken as 1.29 g liter^{-1}.)*

The weight of water filling the bulb is 302 − 52.3 = 250 g, and taking the density as approximately unity, the volume v is 250 ml. The density of air is 1.29 g liter^{-1}, and so this volume of air will weigh 0.32 g; hence, the weight w of the vapor is 52.96 − (52.30 − 0.32) = 0.98 g. Expressing v in liters, i.e., 0.25 l, the pressure P in atm, i.e., 752/760 atm, and R in liter-atm deg^{-1} mole^{-1} units, i.e., 0.082, with $T = 273 + 100 = 373°$, it follows from equation (5.8) that

$$M = \frac{wRT}{Pv} = \frac{0.98 \times 0.082 \times 373}{(752/760) \times 0.25} = 120.$$

The **Hofmann method** (1868) utilizes a graduated barometer tube containing mercury, surrounded by a jacket for maintaining a suitable constant temperature by means of the vapor of a boiling liquid. A weighed quantity, e.g., 0.1 to 0.3 gram, of the experimental substance is enclosed in a tiny stoppered (Hofmann) bottle and introduced into the apparatus by allowing it to rise through the mercury. The liquid vaporizes into the space above the mercury so that the level of the latter falls; this lowering gives the pressure P of the vapor, and its volume v is read off from the graduations on the tube. Since the temperature of the heating jacket is known, all the information is available for the determination of the approximate molecular weight. The chief advantage of the Hofmann method is that vaporization occurs under reduced pressure in the space above the mercury in the barometer tube. This means that the temperature can be well below the normal boiling point (see § 11b), and so it is possible to work with materials which may decompose on heating.

The most familiar of the vapor density methods is the **Victor Meyer method** (1878). The apparatus consists of a long vertical tube widening out into an elongated bulb at its lower end, and having a side-tube near the top. The side-tube is connected to a gas buret containing water or mercury, or to any convenient device for measuring the volume of air expelled from the apparatus. The vertical tube and bulb are surrounded by a jacket kept at a constant temperature, about 20° or 30° above the boiling point of the material being studied, by vapor from a boiling liquid. A weighed quantity of the experimental substance, contained in a small (Hofmann) bottle, is dropped into the apparatus; vaporization occurs immediately and an equal volume of air at the temperature of the bulb is expelled. This is cooled to room temperature, however, in the measuring apparatus, and the volume recorded is that which the vapor would occupy at atmospheric pressure if determined at the temperature of the gas buret. The assumption made here is that the air and the vapor have the same coefficient of expansion, as would be the case if they both behaved as ideal gases. Since the Victor Meyer method is an approximate one, in any case, the error is not serious. As the weight of the material is known, and the volume of its vapor, at the atmospheric temperature and pressure, have been measured, the molecular weight can be calculated. One advantage of the method is that the volume is obtained at atmospheric temperature, and so the temperature of the heating bath need not be known.

Example: In a Victor Meyer experiment, 0.241 gram of chloroform expelled 47.9 ml of air, collected over mercury, measured at 23°C and 764 mm pressure. Calculate the approximate molecular weight of chloroform.

It is again convenient to express v in liters, i.e., 0.0479, and P in atm, i.e., 764/760, so that R is 0.082 liter-atm deg^{-1} mole^{-1}; T is $273 + 23 = 296°$; w is 0.241 g. Hence,

$$M = \frac{wRT}{Pv} = \frac{0.241 \times 0.082 \times 296}{(764/760) \times 0.0479} = 120.$$

If the displaced air is collected over water, it will become saturated with water vapor. If the air in the Victor Meyer tube was originally dry, or almost dry, it is necessary to correct for the presence of the water vapor. This is done by making use of Dalton's law of partial pressures (see § 2h); the actual pressure of the dry air is equal to the total (atmospheric) pressure minus the pressure of the water vapor at the temperature of the gas-collecting device.

A modification of the Victor Meyer apparatus, employing a small bulb made of porcelain or iridium, has been used for determinations of molecular weights at temperatures up to 2000°C.

5e. Molecular Weights of Elements.—Molecular weight determinations based on density methods, i.e., on pressure, volume and temperature measurements of a given mass of gas or vapor, have given results that are generally in agreement with those expected from ordinary chemical considerations. In addition a number of facts of special interest and importance have come to light. For example, it has been found that in the vapor state the molecular weights of many metals, e.g., sodium, zinc, cadmium, mercury, thallium and lead, are almost the same as the atomic weights. This means that the molecules of the metal vapors are mainly monatomic, the atom and the molecule being identical.

At moderate temperatures the gaseous nonmetals, such as hydrogen, nitrogen, oxygen and the halogens have molecular weights which are twice the respective atomic weights; these substances are consequently diatomic. There is evidence, however, that at elevated temperatures the diatomic molecules, particularly those of the heavier halogens, break up to some extent and that free atoms, i.e., monatomic molecules, can exist. Provided the temperatures are not too high, the molecules of phosphorus, arsenic and antimony each contain four atoms in the vapor state, i.e., P_4, As_4 and Sb_4, while sulfur and selenium vapors consist largely of molecules containing eight atoms, i.e., S_8 and Se_8. In every case, however, increase of temperature results in a simplification of the molecules, so that at very high temperatures a considerable proportion are monatomic.

5f. Molecular Association.—It has been observed that a number of compounds have molecular weights in the vapor state that are appreciably higher than those to be anticipated from simple valence considerations. Structural organic chemistry leads to the view that the formula of acetic acid is CH_3COOH, so that the molecular weight should be 60.0; nevertheless, actual measurements made just above the boiling point at atmospheric pressure give a value of about 100. The result varies with the temperature and pressure of the vapor; the observed molecular weight approaches a limiting value of 120, i.e., twice the theoretical molecular weight, as the temperature is lowered. It appears, therefore, that acetic acid vapor contains a large number of double molecules, i.e., $(CH_3COOH)_2$; these molecules split up into single molecules as the temperature is raised or the pressure lowered. Similar results have been obtained with formic acid and with other carboxylic acids.

Substances which have molecular weights that are larger than those expected for the simple molecules are said to be **associated,** and to exhibit the phenomenon of molecular **association.** Acetic acid and other carboxylic acids are thus associated in the vapor state. It is probable that these acids are almost completely associated to form double molecules in the liquid state, and are also associated to some extent in solution (§ 26a) as well as in the vapor. It should be noted, however, that other hydroxylic substances, such as water, alcohols and phenols, which undoubtedly form associated molecules in the liquid state and in certain solutions, are not associated in the vapor state. Vapor density determinations show that the vapors of these compounds consist of single molecules. This difference between the behavior of carboxylic acids, on the one hand, and hydroxylic compounds, such as water, alcohols and phenols, on the other hand, is in accord with the different types of hydrogen bonds in the two cases (§ 16i). With the former the resulting molecular association is of a specific character, leading to the production of double molecules, but with the latter the association is more general in nature. Thus, in the carboxylic acids the double molecules exist as units in the liquid and vaporize as such; with water, etc., only single molecules, which break away from their general attachment with other molecules, escape into the vapor under normal conditions.

5g. Thermal Dissociation.—In contrast to the behavior just described, certain substances give molecular weights that are less than expected, the value decreasing towards a limit as the temperature is raised. This is undoubtedly due to the splitting up of a relatively complex molecule into simpler molecules when the substance is heated and vaporized. The phenomenon is known as **thermal dissociation,** and it may be described as *the decomposition of a molecule into simpler parts on heating, these parts recombining to form the original molecule on cooling.* The vapors of ammonium chloride, and of other ammonium salts, and of phosphorus pentachloride, for example, exhibit molecular weights that approach one-half the chemical values as the temperature is raised; in these cases there is chemical evidence for the dissociations

$$NH_4Cl = NH_3 + HCl \qquad \text{and} \qquad PCl_5 = PCl_3 + Cl_2.$$

Since each molecule of the original substance can split up into two molecules of product, when the dissociation is complete, the actual number of molecules present in the vapor will be about twice as great as the value that would have been observed if there had been no dissociation. As a result the volume is doubled, and hence the density and the approximate molecular weight will be about one-half the theoretical value. The occurrence of dissociation upon vaporization is thus able to account for the observed molecular weight being lower than would otherwise have been anticipated.

It is important to point out that whereas a low vapor density or molecular weight implies dissociation, the process of dissociation is not always accompanied by a decrease of density. Such a decrease is observed only when there is an increase in the number of molecules as a result of the dissociation. If there is no change in the number of molecules as, for example, when gaseous hydrogen iodide dissociates to form hydrogen gas and iodine vapor, i.e.,

$$2HI = H_2 + I_2,$$

the volume, density and molecular weight are unaffected.

When thermal dissociation is accompanied by a change in the number of molecules and, hence, in the vapor density, measurement of the density at any given temperature and pressure can then be used to determine the extent of dissociation, i.e., the fraction of the molecules dissociated, under the specified conditions. The method employed and its application to the study of chemical equilibria in thermal dissociation reactions will be discussed in Chapter 10.

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PROBLEMS

1. A quantity of an ideal gas weighing 1.531 g occupies a volume of 612 ml at 10°C and 2 atm pressure. At what pressure, in cm of mercury, will 0.218 g of this gas occupy 150 ml at 25°C?

2. Calculate the density, in g per liter, of an equimolar mixture of CH_4 and C_2H_6 at 100°C and 700 mm pressure.

3. A 300 ml bomb at 27°C is filled with 1 atm CH_4 and 4 atm O_2 and the mixture is exploded. Calculate the pressure if the final temperature is (*a*) 150°C, (*b*) 27°C. (The vapor pressure of water is 26.7 mm at 27°C.)

4. The density of a mixture of argon and helium is 1.1656 g per liter at 20°C and 1 atm pressure. What is the composition of the mixture (*a*) by weight, (*b*) in mole %?

5. Calculate the number of molecules of air (21% oxygen, 79% nitrogen) which, in

one second, strike a sphere of 10 cm radius when the temperature is (*a*) 0°C, (*b*) 100°C, the pressure being 1 atm in each case.

6. A balloon of one million liters capacity was filled with helium at 770 mm pressure and 27°C. Upon ascending, the temperature fell to −13°C, while the external pressure decreased to 125 mm. What weight of helium would have to be released to keep the volume of the balloon constant?

7. Determine the temperature of the melting point of ice (0°C) on the Kelvin scale from the following data on the coefficient of expansion of nitrogen:

p(m Hg)	0.99828	0.74966	0.59959	0.44942	0.33311
$\alpha_v \times 10^7$ °C^{-1}	36740	36707	36686	36667	36652

8. A 1 liter container is evacuated from atmospheric pressure of 740 mm to 10^{-6} mm at 20°C. Calculate (*a*) the weight of air removed, (*b*) the number of molecules left. (The molecular weight of air may be taken as 28.9.)

9. A liter flask contains 10^{20} molecules of helium at 27°C. Approximately how many will have (*a*) the average kinetic energy, (*b*) 10 times the average, (*c*) 100 times the average?

10. Calculate the weight of propane (C_3H_8) in a 5 liter steel cylinder at 125°C and 100 atm pressure using the van der Waals equation. Compare the result with the value calculated by the ideal gas equation. The van der Waals constants for propane are: $a = 8.66$, $b = 8.47 \times 10^{-2}$.

11. The density of dry air at 25°C and 1 atm pressure is 1.184 mg ml^{-1}. What will be the density if the humidity of the air is (*a*) 50%, (*b*) 100%? The vapor pressure of water at 25°C is 23.76 mm.

12. A 1 liter vessel at 27°C contains 10 g of oxygen and 0.6 g of H_2O. (*a*) Neglecting the volume occupied by the portion of the H_2O which is liquid, calculate the pressure in the vessel. (*b*) What would be the volume and pressure if the mixture were expanded at constant temperature until the water was just completely vaporized?

13. The following results have been obtained for the density of nitrous oxide in grams per liter at several pressures at 0°C:

p	1	$\frac{2}{3}$	$\frac{1}{2}$	$\frac{1}{3}$ atm
d	1.9804	1.3164	0.9861	0.6565

Determine the molecular weight of nitrous oxide and the atomic weight of nitrogen.

14. The following data were obtained for the pressures at which a buoyancy balance was in equilibrium when filled with oxygen and benzene (C_6H_6) vapor at 22.00°C:

p_{O_2} (mm)	169.201	131.764	114.531	81.880	47.103
$p_{C_6H_6}$ (mm)	68.949	53.759	46.753	33.457	19.269

Calculate the molecular weight of benzene vapor and the atomic weight of carbon.

15. At what temperature will molecules of oxygen have the same root-mean-square velocity as molecules of nitrogen at 0°C?

16. The viscosity of methane at 20°C and 1 atm pressure is 1.09×10^{-4} poise. Calculate (*a*) the mean free path, (*b*) the mean collision diameter, (*c*) the number of collisions per sec in 1 ml of the gas at 0°C and 0.1 atm pressure (assume the collision diameter to remain constant).

17. It takes 110 sec for 50 ml of oxygen to pass through a small hole. (*a*) How long will it take the same volume of ethyl ether $(C_2H_5)_2O$ vapor to pass through the same hole? (*b*) What volume of chlorine will pass through the hole in 5 min?

18. Calculate the Avogadro number from the distribution under gravity of gamboge particles, of radius 2.12×10^{-5} cm and density 1.206 g ml^{-1}, suspended in water at

15°C. The average numbers of particles observed over a period of time at four equidistant heights were:

Height in 10^{-4} cm	5	35	65	95
Average no. of particles	4.00	1.88	0.90	0.48

19. Calculate the limiting value of γ, the ratio of the heat capacities at constant pressure and volume, for the linear, triatomic molecule, nitrous oxide. The value of γ is 1.30 at 15°C. Account for the discrepancy.

3

Thermodynamics and Thermochemistry

THE FIRST LAW OF THERMODYNAMICS

6a. Thermodynamics and Energy.—The **energy** of a body may be defined broadly as its capacity for doing work. This energy may take various forms, such as kinetic energy of the body in motion, potential energy due to position, heat energy as measured by the temperature, electrical energy, chemical energy, etc. Chemical and physical processes are almost invariably accompanied by energy changes, and results of considerable importance have been obtained by studying the laws underlying these changes. It is this study of energy transformation which constitutes the subject matter of **thermodynamics.** Although thermodynamics may appear to be somewhat theoretical in nature, its two laws have led to results of fundamental importance to chemistry, as well as to physics and engineering.

All forms of energy have the dimensions of mass × $(\text{length})^2 \times (\text{time})^{-2}$ and they can be expressed in terms of the same units, viz., ergs, joules or calories. The unit of energy in the cgs system is the **erg**; it is equal to the work done when a force of 1 dyne acts through a distance of 1 cm, the dyne being the force which acting on a mass of 1 gram gives it an acceleration of 1 cm per sec per sec. Since the erg is so small, a subsidiary unit, the **absolute joule,** is defined as 10^7 ergs. The **international joule,** which is based on electrical measurements (§ 47a), differs slightly from the absolute joule; it is equivalent to 1.0002×10^7 ergs.

There is a natural tendency for other forms of energy ultimately to change into heat, e.g., chemical energy may change into heat as the result of a chemical reaction, electrical energy is converted into heat when an electric current is passed through a resistance, mechanical energy is transformed into heat by friction, and so on. It is, therefore, convenient to express the values of other forms of energy in terms of the unit of heat energy, that is, in terms of calories. Careful experiments initiated by J. P. Joule, between 1848 and 1873, have shown that *when a definite amount of any form of energy, particularly mechanical and electrical energy, is converted into heat, a perfectly definite number of calories of heat is always produced.* There is thus an exact relationship between heat and other forms of energy; this is known as the **mechanical equivalent of heat.** In fact, as stated in § 31, the calorie is defined in terms of its equivalent in mechanical work; thus, *1 calorie is taken as equal to 4.1840 absolute joules, i.e.,* 4.1840×10^7 *ergs.*

Example: Calculate the energy in calories required to increase the volume of a substance by 1 cc against a pressure of 1 atm.

As seen in § 31, the work done in the expansion is equal to $P\Delta V$, where ΔV is the increase of volume. In the present case, the values of both pressure and the volume change should first be expressed in cgs units; 1 atm pressure is equivalent to 1.013×10^6 dynes cm^{-2} (§ 2g, II), and since ΔV is 1 cc, it follows that

$$\text{Work done} = 1.013 \times 10^6 \times 1 = 1.013 \times 10^6 \text{ dynes cm, i.e., ergs.}$$

To convert into calories, this is divided by 4.184×10^7; the result is 0.0242 cal.

6b. Conservation of Energy: The First Law of Thermodynamics.—Many attempts have been made from time to time to realize "perpetual motion," that is, the continuous production of mechanical work without supplying an equivalent amount of energy from another source. The failure of all such efforts has led to the universal acceptance of the **principle of conservation of energy.** This principle has been stated in many forms, but essentially they amount to the fact that *although energy can be converted from one form to another, it cannot be created or destroyed* or, alternatively, *whenever a quantity of one kind of energy is produced, an exactly equivalent amount of other kinds must disappear.* It is evident that perpetual motion, in the generally accepted sense of the term, would be contrary to this principle, for it would involve the creation of energy. Further, the exact equivalence of mechanical or electrical work and heat, as found by Joule and others, is a necessary consequence of the same principle.

The law of conservation of energy is purely the result of experience, no exception to it having as yet been found. The assumption that it is of universal applicability is the basis of the **first law of thermodynamics.** This law can be stated in any of the ways given above for the principle of the conservation of energy, or else it may be put in the following form. *The total energy of a system* and its surroundings must remain constant, although it may be changed from one form to another.*

Attention may be called to the equivalence of mass and energy expressed by the Einstein equation, $E = mc^2$, where E is the energy equivalent of the mass m and c is the velocity of light (§ 65g). A net decrease of mass accompanying a particular process will thus be associated with the release of a definite amount of energy. This situation introduces an apparent limitation upon the principle of the conservation of energy, for energy can be produced by the destruction of mass. Strictly speaking the laws of conservation of mass and of conservation of energy are part of a comprehensive law, according to which the combined mass and energy of an isolated system remains constant. One form of energy may be changed into another form, and mass may be converted into energy, or vice versa, but the total mass and energy equivalents must be unchanged. In the problems treated by thermodynamics there is no measurable conversion of mass into energy, and so the simple form of the principle of conservation of energy may be regarded as adequate.

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* The term "system" refers to the specified portion of matter under consideration.

6c. Thermodynamic Quantities.—The energy of a system depends upon its pressure, volume, temperature, mass and composition. These five quantities are always related, at least in principle, by an equation of state, so that if any four are specified, the fifth is automatically fixed. Hence, for a system of definite (constant) mass and composition, only two of the quantities, e.g., pressure and volume, need be given, since the temperature is thereby determined. Consider any such system—gas, liquid or solid—represented by the point A in Fig. 6.1, where the coordinates are the pressure and volume; these may be regarded as defining the state (and energy) of the system.

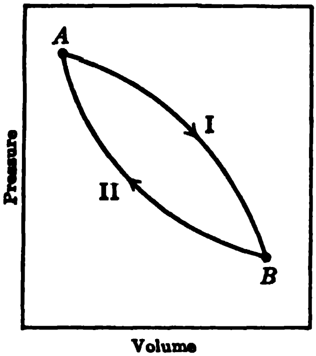

FIG. 6.1. Energy change independent of path

Suppose the conditions are now altered so that the system moves to B by the path I, and is then brought back again to the state A by a different path II. It is a direct consequence of the first law of thermodynamics that the total energy change in path I must be identical with that in path II; if it were not, perpetual motion would be possible. Imagine, for instance, that the increase in energy involved in path I were greater than the decrease in returning by II; then by carrying out the process $A \rightarrow B$ by path I and $B \rightarrow A$ by path II, the system would be brought back to its original state, but there would be a net gain of energy. In other words, energy would have been created without the disappearance of an equivalent amount of another kind. Since this is contrary to all human experience, it must be concluded that the resultant energy in passing from the state A to the state B depends only on the initial and final conditions, and is independent of the path followed in going from A to B.

According to the foregoing arguments, it is possible to ascribe a definite amount of energy to any given state of a system, which is determined only by the state itself, and not by its previous history. If E_A represents the energy in the state A and E_B that in the state B, then the change in energy ΔE in passing from A to B is given by

$$\Delta E = E_B - E_A, \qquad (6.1)$$

and is independent of the path taken. The same conclusion is sometimes expressed in mathematical language by stating that in an infinitesimal process the small change dE is a **complete** or **exact differential.** The quantity E, which depends on pressure, volume and temperature, is generally called the **internal energy** or, in brief, the energy of the system; it includes all forms of energy, other than those resulting from the position of the system in space, for this is assumed to remain constant. The *actual* value of the internal energy is generally not known, but this is of no significance, for thermodynamics is concerned primarily with *changes* in energy, and these are measurable quantities.

Any experimental quantity which has an exact differential is called a **thermodynamic variable** (or **thermodynamic coordinate**). Whenever possible such quantities are used in describing processes, since no knowledge of the history of the process is necessary; all that needs to be known is the net change in that quantity that has occurred during the process. In addition to the internal energy, pressure, volume and temperature, which are thermodynamic variables, others will be defined below as further aspects of thermodynamics are developed.

The properties of a system may be distinguished as being either extensive or intensive. An **extensive property** is one that is dependent upon the amount (or amounts) of the substance (or substances) present in the system. If the quantity of material in the system is changed, the extensive property is changed in a proportionate manner. Volume and mass are simple illustrations of extensive properties, and internal energy is another example of such a property. An **intensive property**, on the other hand, is a specific characteristic of the system and is independent of the amount of material concerned. Thus, temperature, density, surface tension, refractive index, viscosity, etc., are intensive properties.

6d. Internal Energy, Work and Heat Changes.—When a system changes from one state to another, it may perform some kind of external work, such as mechanical work of expansion, electrical work, etc.; this work is represented by the symbol w. If work is done *by* the system, e.g., as in the expansion of a gas, the value of w is positive, but if work is done *on* the system, e.g., as in compression of a gas, the value is negative. Further, the system may absorb or evolve heat in the course of the change, and this quantity of heat is indicated by q. If the system *absorbs* heat q is positive, but if heat is *evolved* the value is negative. It is seen, therefore, that when a system changes from the state A to the state B, its internal energy changes by ΔE, while at the same time the system does work w and absorbs heat q.

According to the first law of thermodynamics the *total* energy of system and surroundings must remain unaltered as the system changes from A to B. Hence the change ΔE in the internal energy of the system must be exactly equivalent to the energy q absorbed from the surroundings in the form of heat, less the energy w lost to the surroundings in the form of external work done by the system; thus,

$$\Delta E = q - w. \tag{6.2}$$

For an infinitesimal stage in a change which the system is undergoing, equation (6.2) may be written in the form

$$dE = \delta q - \delta w, \tag{6.3}$$

where dE represents the small change in the internal energy, δq is the small quantity of heat absorbed, and δw is the small amount of external work done at the same time by the system. It was seen above that dE is a complete or exact differential, for the change in E depends only on the final and initial states of the system and is independent of the path taken between them;

however, δq and δw are not exact differentials, for their values generally depend on the nature of the path. This fact is represented in equation (6.3) by writing δw and δq instead of dw and dq. Although δq and δw are inexact differentials, their difference must nevertheless be an exact differential.

To clarify the statement that δw and δq are inexact differentials, consider the work done in passing from state A to state B by different paths. As seen in § 31, the work done in expansion (or contraction) is equal to the product of the external pressure and the volume change. When the external pressure changes during the process, the work done is the sum (or integral) of a series of PdV terms, where P is the external pressure. In other words, the value of w will be equal to the area under the curve representing the process on a diagram in which the volume is plotted against the external pressure; this is shown by the shaded regions in Fig. 6.2 for two paths. It is evident that

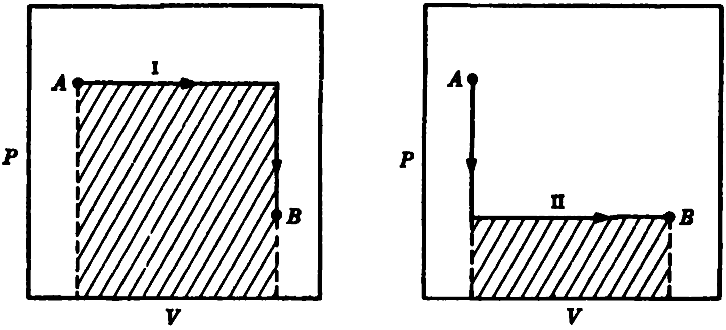

FIG. 6.2. Work depends on path

the work done in passing from A to B by path I is greater than that done by path II. Hence, unless the path is specified, the work done in the process is indeterminate and δw is an inexact differential; however, a definite amount of work corresponds to each distinct path. Since ΔE is the same in each case, being independent of the path, $q - w$ will be the same for all paths; the heat absorbed, q, will therefore vary with the path. That is to say, δq will be inexact until the path is specified.

6e. Heat Changes at Constant Pressure and Constant Volume.—There are certain simple conditions under which the heat absorbed in a particular process becomes a definite quantity, depending only on the initial and final states. Writing equation (6.2) in the form

$$q = \Delta E + w,$$

it will be supposed, as in the case of most thermodynamic changes which do not involve electrical processes, that the work w is only mechanical work of expansion or contraction. It is then possible to replace w in general by $P\Delta V$, where P is the constant external pressure and ΔV is the increase of volume, so that

$$q = \Delta E + P\Delta V. \tag{6.4}$$

For a process occurring at constant volume ΔV is zero, and then equation (6.4) becomes

$$q_V = \Delta E, \tag{6.5}$$

so that the heat absorbed in a constant volume process is equal to the increase of internal energy in that process. Since the latter depends only on the initial and final states of the system, the same must apply to the heat change at constant volume.

At constant pressure, equation (6.4) is written as

$$q_P = \Delta E + P\Delta V. \tag{6.6}$$

The increase of internal energy ΔE is equal to $E_2 - E_1$, where the subscripts 1 and 2 are used to indicate initial and final states, respectively; similarly, the volume increase ΔV may be replaced by $V_2 - V_1$, so that

$$\begin{aligned} q_P &= (E_2 - E_1) + P(V_2 - V_1) \\ &= (E_2 + PV_2) - (E_1 + PV_1). \end{aligned} \tag{6.7}$$

Since P and V are thermodynamic properties of the system, it follows that the quantity $E + PV$, like the internal energy E, is dependent only on the state of the system, and not on its previous history. This extensive thermodynamic property is called the **enthalpy** (Greek: *warm*)* and is represented by the symbol H, i.e.,

$$H = E + PV,$$

so that

$$H_2 - H_1 = \Delta H = \Delta E + \Delta(PV).$$

When P is constant, this becomes

$$\Delta H = \Delta E + P\Delta V, \tag{6.8}$$

and comparison with equation (6.6) shows that

$$q_P = \Delta H. \tag{6.9}$$

The increase ΔH in the enthalpy of the system at constant pressure is thus equal to the heat absorbed under these conditions; the latter quantity, like ΔH, will consequently depend on the initial and final states of the system, and not on the path taken in the process.

By combining equations (6.5) and (6.6), the result is

$$q_P = q_V + P\Delta V. \tag{6.10}$$

It is seen from this equation that the heat absorbed in a process occurring at constant pressure exceeds that for the same process taking place at constant volume by the amount $P\Delta V$, where P is the constant pressure and ΔV is the

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* It is also referred to as the "heat content," but this name is apt to be misleading and so it will not be used in this book.

accompanying increase of volume. *The reason for this difference lies in the* fact that when the volume is constant the system does no external mechanical work of expansion or compression; the heat absorbed q_V is then merely equal to the increase ΔE in the internal energy of the system. If the pressure is kept constant, however, there may be a volume change and external work may be done; in this event the heat absorbed q_P will not only go to increase the internal energy but an additional amount, equivalent to the work done, i.e., $P\Delta V$, will be required.

It should be noted that equations (6.8) and (6.10), like other thermodynamic equations, automatically include proper allowance for the signs of the various quantities involved. For example, if the process at constant pressure is accompanied by a *decrease* of volume, ΔV will be negative and ΔH (or q_P) will then be less than ΔE (or q_V). Because of the contraction in volume at constant pressure work is done *on* the system, which thus gains energy; hence, a smaller amount of heat q_P will be required from an outside source at constant pressure than the amount q_V required at constant volume. As will be seen shortly, in some processes there is no volume change even when they are carried out at constant pressure; in such cases $P\Delta V$ is zero, and ΔE and ΔH, that is, q_V and q_P, are then identical. The foregoing considerations apply to processes of all kinds, both physical and chemical, provided the external work is only mechanical work due to a volume change.

It must be emphasized that changes in E and H may occur in *any* kind of process. The foregoing discussion has indicated the conditions under which ΔE and ΔH are most easily determined, namely, when the process is performed at constant volume or constant pressure, respectively.

6f. Reversible Changes: Maximum Work.—A system can be changed from a particular state A to another state B under a great variety of conditions. In every case the energy change is definite, but the heat and work changes may or may not be so. From the thermodynamic standpoint one of the most important of such conditions is that *the change be carried out infinitesimally slowly, so that the system is always in temperature and pressure equilibrium with its surroundings.* A change carried out in this manner is said to be **thermodynamically reversible,*** for it may be reversed by an appropriate infinitesimal change in any of the thermodynamic variables. It may be remarked that a reversible change is to be regarded as a hypothetical or imaginary ideal process, for in actual practice complete thermodynamic reversibility cannot be realized. Nevertheless, in spite of its hypothetical nature, the concept is of great value. It makes possible the expression of energy exchange between a system and its surroundings in terms of experimentally measured properties of the system alone.

As a simple illustration of a thermodynamically reversible change, imagine a liquid in equilibrium with its vapor in a vessel closed by a frictionless piston and placed in a constant temperature bath. The pressure on the

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* The term "reversible" as applied to a thermodynamic process must not be confused with the use of the same adjective in connection with the so-called reversible chemical reactions.

piston will then be equal to the vapor pressure of the liquid at the given temperature. If the external pressure is increased by an infinitesimally small amount the vapor will condense, but the condensation will occur so slowly that the heat evolved will be readily taken up by the bath; the temperature of the system will not rise and the pressure above the liquid will remain constant. Although condensation of the vapor is taking place, the system at every instant may be considered to be essentially in a state of equilibrium. Similarly, if the external pressure is made just smaller than the vapor pressure, the liquid will vaporize at a very slow rate, and again the temperature and pressure will remain constant. Although the system is changing, since evaporation is occurring, the changes may be regarded as a series of equilibrium states. Rapid evaporation or condensation, resulting from rapid expansion or compression, will lead to temperature changes and to considerable disturbance of equilibrium; such processes are not thermodynamically reversible.

The work done in reversible vaporization or condensation is a definite quantity which can be readily calculated, since it is equal to the product of the external pressure and the change of volume. In the case under consideration p, the vapor pressure of the liquid at the given temperature, may be taken as the external pressure, since it is only infinitesimally different, and this remains constant throughout the process. If ΔV is the change of volume in the course of the reversible evaporation, then the work done by the system is equal to $p\Delta V$. For the corresponding condensation, the same amount of work would be done on the system. Since ΔE and w have definite values, it follows that q must also be definite for reversible evaporation or condensation; this is actually equal to the heat of vaporization (or condensation) at the specified temperature.

An important characteristic of infinitesimally slow or reversible changes is that if they take place at constant temperature, i.e., if they are **isothermal,** such as is the case for reversible evaporation, the work obtainable from the system not only has a definite value, it is also the **maximum work** possible for the given change. If, for example, in the evaporation process just considered, the external pressure had been released suddenly, instead of extremely slowly, the work done by the system would have been less than $p\Delta V$, since the pressure against which the expansion occurred would be smaller than the vapor pressure p. In other words, since the external pressure p_{ext} is less than the vapor pressure p, the work done, which is $p_{ext}\Delta V$, is less than $p\Delta V$. Similarly, rapid condensation can be brought about by applying an external pressure larger than p, so that $p_{ext}\Delta V$ will be greater than $p\Delta V$ for the reversible process. In condensation (and other compression processes), the reversible process requires the *minimum* work. Any real process, however, must occur at a finite rate and so cannot be reversible; hence the work obtainable in expansion will be less than the maximum work and that done in compression will be more than the minimum.

6g. Maximum Work in Isothermal Expansion of a Gas.—In the course of the reversible evaporation process considered in the preceding section, the pressure of the vapor remained constant because it was always in equilibrium with the liquid. When a gas expands at constant temperature the pressure must decrease during the course of the expansion. In order to carry out such a change in a reversible manner, it must be supposed that *the external pressure continuously adjusts itself so as to be always less than the pressure of the gas by an infinitesimally small amount.* Under these ideal conditions the expansion takes place infinitesimally slowly, and the work done by the gas is the reversible work of expansion for the given process.

If P is the pressure of the gas at any stage in the expansion, the external pressure will then be $P - dP$, where dP is a very small quantity. The work δw done, when the gas increases its volume by an extremely small amount dV, is then equal to the product of the external pressure $P - dP$ by this volume change; thus,

$$\delta w = (P - dP)dV.$$

Neglecting the very small product $dPdV$, it follows that

$$\delta w = PdV. \tag{6.11}$$

The total work w done in the expansion will be the sum of a continuous series of PdV terms, with the value of P decreasing steadily, and the volume increasing, from the initial state to that in the final state. The result may be expressed mathematically by means of the integral

$$w = \int_{V_1}^{V_2} PdV, \tag{6.12}$$

where V_1 is the initial volume of the gas and V_2 is the final volume after expansion; this is the general equation for the reversible work of expansion.

The work done in a reversible change may be determined graphically, as in Fig. 6.2, by the area under the P-V curve representing the particular path followed in the process. However, P may now be taken as the actual pressure of the gas, as in Fig. 6.1. If, as a consequence of a series of reversible changes, the system is returned to its original state, the resultant work done is equal to the area on the P-V curve enclosed by the paths of the changes. Thus, in Fig. 6.1, this would be the area enclosed by the paths I and II, if they were reversible.

The reversible work integral in equation (6.12) may be evaluated if the relationship between pressure and volume is known. For example, if the system consists of *1 mole of an ideal gas*, then $PV = RT$, and P is equal to RT/V; hence, if the expansion is isothermal, i.e., the temperature remains constant, insertion of this result in equation (6.12) gives

$$w = RT \int_{V_1}^{V_2} \frac{dV}{V} = RT \ln \frac{V_2}{V_1}. \tag{6.13}$$

Since the *isothermal, reversible work* is also the maximum work it is a simple matter to calculate the maximum work done by 1 mole of an ideal gas in expanding between two prescribed volumes. It is obvious from equation

(6.13) that the result depends only on the final and initial volumes, apart from the constant temperature, and is independent of the path, provided it is a reversible one.

Example: Calculate the maximum work in ergs for the expansion of 1 mole of an ideal gas from a volume of 10 liters to 20 liters (exactly) at 25°C.

Since V_2/V_1 in equation (6.13) is a ratio it is independent of the units of volume; the value of w is then given in the same units as R (strictly RT). The maximum work is required in ergs mole^{-1}, and so R is taken as 8.314×10^7 ergs deg^{-1} mole^{-1}. The absolute temperature T is $273.2 + 25.0 = 298.2°K$, and hence,

$$\begin{aligned} w &= 8.314 \times 10^7 \times 298.2 \ln \tfrac{2}{1} \\ &= 8.314 \times 10^7 \times 298.2 \times 2.303 \log 2 = 1.719 \times 10^{10} \text{ ergs mole}^{-1}. \end{aligned}$$

An alternative form of equation (6.13) is often convenient; since the gas is supposed to be ideal, $P_1V_1 = P_2V_2$ at constant temperature, and so V_2/V_1 is equal to P_1/P_2. If the appropriate substitution is made in equation (6.13), the maximum work of isothermal expansion for 1 mole of an ideal gas is given by

$$w = RT \ln \frac{P_1}{P_2}. \tag{6.14}$$

6h. Maximum Work in Phase Change.

—A phase change, e.g., vaporization of a liquid, melting of a solid, or the transition from one solid form to another, at a given temperature, can be carried out reversibly. Such a process can be performed at constant temperature and pressure. As shown in § 6f, the maximum work is then $p\Delta V$, where p is the equilibrium (or vapor) pressure of the system and ΔV is the volume change. If the process is isothermal vaporization, ΔV is equal to $v_v - v_l$, where v_v is the volume of vapor produced by the vaporization of volume v_l of liquid. If the temperature is not too near the critical point, v_l can be neglected in comparison with v_v, so that the maximum work of isothermal vaporization is

$$w = pv_v. \tag{6.15}$$

At sufficiently high temperatures, the vapor may be assumed to obey the ideal gas law, so that $v_v = nRT/p$. Upon substituting this into equation (6.15), the result is

$$w = p \times \frac{nRT}{p} = nRT,$$

where n is the number of moles of liquid vaporized (or of vapor formed) in the process.

The method given above can also be applied to the vaporization (or sublimation) of a solid, since the volume of the solid vaporized is considerably smaller than that of the vapor produced. But for solid-liquid or solid-solid transitions, the volumes of the two phases are not very different, so that neither can be neglected in comparison with the other.

6i. Internal Energy of an Ideal Gas.—An ideal gas possesses an important property which may be considered here. Experiments with actual gases show that as a gas approaches ideal behavior the Joule-Thomson effect (§ 4b) becomes less marked, and it is possible to state that an ideal gas will show no Joule-Thomson effect at any temperature. This is to be expected, since the molecules of an ideal gas are supposed not to attract one another or to have appreciable volume. Since the Joule-Thomson effect is zero, there is no absorption or liberation of heat, i.e., $q = 0$, when an ideal gas is allowed to expand into a vacuum.* At the same time, no work is done, i.e., $w = 0$, since the external pressure, in the vacuum, is zero. It follows, therefore, from the first law equation (6.2), that ΔE will then also be zero. In other words, the expansion of an ideal gas, at constant temperature, is accompanied by no change in the internal energy. This result, which constitutes an alternative definition of an ideal gas, can be generalized in the statement that, *at any constant temperature, the internal energy of a given quantity of an ideal gas is independent of its volume.*

For an ideal gas, therefore, *ΔE is zero for any isothermal expansion or compression*, irrespective of whether it takes place into a vacuum or in any other way; hence, it follows from equation (6.2) that for such processes

$$\Delta E = q - w = 0,$$

and

$$q = w, \tag{6.16}$$

so that the heat absorbed is equal to the work done by the ideal gas. Combination of equation (6.16) with equations (6.13) and (6.14) thus gives

$$q = RT \ln \frac{V_2}{V_1} = RT \ln \frac{P_1}{P_2} \tag{6.17}$$

for the heat absorbed in the isothermal, reversible expansion or compression of 1 mole of an ideal gas from the state 1 to the state 2.

6j. Heat Capacities at Constant Pressure and Constant Volume.—It was seen in § 3l that the heat capacity of a system is defined as the heat required to raise the temperature of the system by one degree. Since the heat capacity C may vary with temperature, it is preferable to define it in the differential form, viz.,

$$C = \frac{\delta q}{dT},$$

where δq may be regarded as the heat absorbed when the temperature is raised by dT degrees. Since δq, as already seen, is not in general an exact differential, the heat capacity will be an indefinite quantity unless certain

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* This experiment, with an actual gas, was carried out by J. L. Gay-Lussac (1807) and by J. P. Joule (1845), who observed no detectable temperature change. A small change would have been detected, however, if the apparatus had been sensitive enough, since a real gas (not an ideal one) was used.

conditions, particularly constant volume or constant pressure, are specified. The heat capacity at constant volume is then given by

$$C_V = \frac{\delta q_V}{dT}, \tag{6.18}$$

while for constant pressure,

$$C_P = \frac{\delta q_P}{dT}. \tag{6.19}$$

According to equation (6.5), the heat q_V absorbed at constant volume is equal to the increase ΔE in the internal energy under the same conditions; for a small change the corresponding quantities are δq_V and dE_V, and so the heat capacity at constant volume, defined by equation (6.18), may be written as

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V. \tag{6.20}$$

The internal energy E, as seen in § 6c, is a function of both pressure and volume, and so the subscript V is used to indicate that in this case the volume is maintained constant. The heat capacity at constant volume is consequently equal to the rate of increase of the internal energy with temperature, also at constant volume. For an ideal gas, E is independent of the volume, as was seen above. It is, therefore, permissible to drop the subscript V implying constant volume on the right of equation (6.20) and to write

$$C_V \text{ (ideal gas)} = \frac{dE}{dT}. \tag{6.21}$$

In an exactly similar manner, utilizing the fact that q_P, the heat absorbed, is equal to ΔH at constant pressure, by equation (6.9), and applying equation (6.19) for the heat capacity, it follows that

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P. \tag{6.22}$$

The heat capacity of a system at constant pressure is consequently represented by the rate of increase of the enthalpy with temperature at constant pressure. For an ideal gas it is not necessary to specify constant pressure, so that

$$C_P \text{ (ideal gas)} = \frac{dH}{dT}. \tag{6.23}$$

The value of $C_P - C_V$ for an ideal gas can be readily determined from the first law of thermodynamics, starting with equation (6.3) in the form

$$\delta q = \delta w + dE. \tag{6.24}$$

Suppose 1 mole of an ideal gas undergoes an infinitesimal reversible change in which the work done is pressure-volume work only, i.e., due to expansion or contraction. Then, by equation (6.11), $\delta w = PdV$, where P is the pressure of the gas, and by equation (6.21), $dE = C_V dT$, where C_V is the molar heat capacity; if these values are substituted into equation (6.24), the result

$$\delta q = PdV + C_V dT. \tag{6.25}$$

Upon differentiating the equation of state for an ideal gas, i.e., $PV = RT$, at *constant pressure*, it is found that

$$PdV = RdT.$$

Substitution of this into equation (6.25) and division by dT give

$$\frac{\delta q_P}{dT} = C_V + R,$$

the subscript in δq_P being required by the stipulation of constant pressure. By equation (6.19), $\delta q_P/dT = C_P$, so that for 1 mole of ideal gas

$$C_P = C_V + R, \tag{6.26}$$

in agreement with the result obtained in a different manner in § 3l. Although a reversible process has been assumed in the derivation, equation (6.26) is quite general, since C_P and C_V are properties of the system which are independent of its history.

6k. Adiabatic Changes.—A special type of process which can be carried out reversibly is that known as an **adiabatic change** (Greek: *not passing through*); such a change is *one in which no heat enters or leaves the system.* In the adiabatic expansion or compression of a gas, for example, the temperature and volume are supposed to adjust themselves automatically to the proper equilibrium values as the pressure is changed; the process is then thermodynamically reversible. The essential difference between isothermal and adiabatic processes is that in the former case the temperature remains constant and the system exchanges heat with its surroundings, while in the latter case there must be no heat exchange and so the temperature will be altered. In an adiabatic expansion of a gas the system does external work, and since no heat can be taken up, the necessary energy comes from the kinetic energy of the molecules; the decrease in the value of the latter means that there is a fall in the temperature. Similarly, in an adiabatic compression the temperature of the gas will rise.

In mathematical terms, the characteristic of an infinitesimal adiabatic change is that $-\delta q$, the heat absorbed, is zero; hence, by equation (6.2),

$$dE = -\delta w. \tag{6.27}$$

The work $-\delta w$ done *on* the system in an adiabatic process is thus equal to the change of internal energy, and hence it is a definite quantity that is independent of the path, provided it is adiabatic in nature. An adiabatic expansion (w positive) is accompanied by a decrease in internal energy, whereas a compression (w negative) produces an increase.

It was seen in § 6j that, for an infinitesimal reversible process with an ideal gas, $\delta w = PdV$ and $dE = C_V dT$; substitution into equation (6.27) then shows that for a reversible adiabatic process

$$C_V dT = -PdV, \qquad (6.28)$$

where P is the pressure of the gas. For 1 mole of an ideal gas $P = RT/V$, so that introduction into equation (6.28) and rearrangement yield

$$C_V \frac{dT}{T} = -R\frac{dV}{V}.$$

If C_V is assumed to be independent of temperature then, since R is constant, integration gives

$$C_V \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V},$$

where V_1 and V_2 are the initial and final molar volumes, respectively, of the ideal gas undergoing the adiabatic process; T_1 and T_2 are the corresponding temperatures. Upon performing the indicated integrations, the result is

$$C_V \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1}$$

or

$$C_V \log \frac{T_2}{T_1} = -R \log \frac{V_2}{V_1}. \qquad (6.29)$$

Since V_2 is greater than V_1, the left side of equation (6.29) is negative; hence, in an adiabatic expansion, T_2 is less than T_1, i.e., the temperature will fall. Conversely, in an adiabatic compression, the temperature will rise. Since the internal energy of an ideal gas depends on the temperature alone, it follows that a reversible adiabatic expansion is accompanied by a decrease in internal energy.

For an ideal gas,

$$\frac{T_2}{T_1} = \frac{P_2V_2}{P_1V_1}$$

and substitution for T_2/T_1, together with equation (6.26), into equation (6.29) leads to

$$C_V \log \frac{P_2}{P_1} = C_P \log \frac{V_1}{V_2}$$

or

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{C_P/C_V}.$$

so that

$$P_1V_1^\gamma = P_2V_2^\gamma, \qquad (6.30)$$

where, as in § 31, $\gamma = C_P/C_V$. This result, which is quite general, is the characteristic equation for any adiabatic change with an ideal gas. It may be compared with $P_1V_1 = P_2V_2$ for an isothermal change with such a gas.

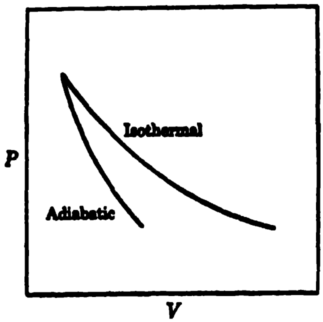

FIG. 6.3. Isothermal and adiabatic changes

The difference in the P-V relationships for isothermal and adiabatic changes is shown by the curves in Fig. 6.3. Since γ is greater than unity, the slope of the adiabatic curve must be greater than that of the isothermal curve. As a consequence, a given decrease in pressure in an adiabatic expansion, for example, would be accompanied by a smaller volume increase than in an isothermal process from the same initial state, as is apparent from Fig. 6.3. This is, of course, to be expected since the temperature decreases in the adiabatic process.

THERMOCHEMISTRY

7a. Heat Changes in Chemical Reactions.—The subject of **thermochemistry** *deals with the heat changes accompanying chemical reactions.* As will be seen shortly, the laws of thermochemistry are based largely on the principle of the conservation of energy or the first law of thermodynamics. Different substances have different amounts of internal (chemical) energy, and so the total energy of the products of a reaction is generally different from that of the reactants; hence, the chemical change will be accompanied by the liberation or absorption of energy, which may appear in the form of heat. If heat is liberated in the reaction the process is said to be **exothermic,** but if heat is absorbed it is described as **endothermic.** The majority of, although not all, chemical reactions which go to virtual completion at ordinary temperatures are exothermic in character, since they are accompanied by an evolution of heat.

If a chemical reaction is associated with a volume change, as is particularly the case for many processes involving the combination of gases, the magnitude of the heat change will depend on whether the reaction is carried out at constant pressure or at constant volume, as seen in § 6e. Since many reactions normally occur at constant (atmospheric) pressure it is the usual practice to record heat changes by quoting the value of q_P, the heat absorbed at constant pressure; this may, of course, be identified with ΔH, the increase of enthalpy under the same conditions. This quantity is often referred to as the **heat of reaction;** it represents *the difference in the enthalpies of the reaction products and of the reactants, at constant pressure, and at a definite temperature, with every substance in a definite physical state.* From the value of q_P (or ΔH) the value of q_V (or ΔE) can be readily determined if the volume change ΔV at the constant pressure P is known, as will be seen below.

The heat change accompanying a reaction, for example, that between solid carbon (graphite) and gaseous oxygen to yield carbon dioxide gas at 25°C or 298°K, is represented in the form of a thermochemical equation, as follows:

$$\text{C(graphite)} + \text{O}_2(g) = \text{CO}_2(g) \qquad \Delta H_{298} = -94.05 \text{ kcal.}$$

This means that when 12.01 grams of solid carbon (graphite) and 32 grams of gaseous oxygen react completely at 25°C to yield 44.01 grams of gaseous carbon dioxide, at constant pressure, there is a *decrease* in enthalpy, since ΔH is negative, of 94.05 kilocalories (kcal), i.e., 94,050 calories. It is the general practice in modern thermochemical work to express results in kilocalories because the statement of heat changes in calories implies an accuracy greater than is usually attainable experimentally. It should be noted, incidentally, that the ΔH (or ΔE) values always refer to *completed* reactions, appropriate allowance having been made, if necessary, if the process does not normally go to completion. Further, the results are for the reaction taking place with all the reactants and products *at a definite temperature*, which should always be specified (see § 7h). The symbols g, l and c, placed in parentheses after the formula, indicate whether the substance taking part in the reaction is gas, liquid or crystalline solid, respectively. Reactions taking place in aqueous solution are indicated by the symbol *aq;* thus,

$$\text{HCl}(aq) + \text{NaOH}(aq) = \text{NaCl}(aq) + \text{H}_2\text{O} \qquad \Delta H_{293} = -13.70 \text{ kcal.}$$

Strictly speaking the use of *aq* implies that the reaction occurs in such dilute solution that the addition of further water causes no detectable heat change.

A negative value of ΔH, as in the two instances quoted above, means that the reaction is accompanied by a decrease in enthalpy; that is to say, the enthalpy of the products is less than that of the reactants, at the specified temperature. In other words, the reaction, at the given temperature, is associated with an evolution of heat. It follows, therefore, that when ΔH is negative the reaction is exothermic; similarly, if ΔH is positive the process is endothermic. The same conclusions can be reached directly, of course, from the fact that q_P, which is equal to ΔH, is the *heat absorbed* in the reaction; hence, when ΔH is negative heat is actually evolved.

7b. Heats of Reaction at Constant Pressure and Constant Volume.—The relationship between heats of reaction at constant pressure and at constant volume is given by equation (6.8); thus,

$$\Delta H = \Delta E + P\Delta V, \tag{7.1}$$

where ΔV is the increase of volume when the reaction occurs at the constant pressure P. As explained previously, $P\Delta V$ represents the external work done by the system when the reaction is carried out at constant pressure. For a process involving solids or liquids only, the volume change ΔV is generally so small that it can be neglected, and ΔH and ΔE may be taken as being equal, within the limits of experimental error. If gases are concerned, however, the change in volume may be quite large; in this case the difference between

ΔH and ΔE may be readily calculated with sufficient accuracy in the following manner. If n_A is the number of moles of gaseous reactants, i.e., in the initial state of the reaction, and n_B is the number of moles of gaseous products, i.e., in the final state, the process is accompanied by a change of $n_B - n_A = \Delta n$ moles of gas. If V is the volume of 1 mole of any gas, at the given temperature and pressure, then the total change of volume ΔV in the reaction will be equal to $V\Delta n$; equation (7.1) may therefore be written as

$$\Delta H = \Delta E + PV\Delta n.$$

If the gases are assumed to behave ideally, PV is equal to RT, and hence

$$\Delta H = \Delta E + RT\Delta n. \tag{7.2}$$

From this expression the difference between ΔH and ΔE can be obtained without difficulty.

Example: When 1 mole of liquid benzene is completely burnt in oxygen to form liquid water and carbon dioxide gas, ΔH is -781.0 kcal at 25°C (298°K). Calculate the heat of this reaction at constant volume at the same temperature.

For this reaction,

$$C_6H_6(l) + 7\tfrac{1}{2}O_2(g) = 3H_2O(l) + 6CO_2(g) \qquad \Delta H_{298} = -781.0 \text{ kcal}.$$

The number of moles n_A of gaseous reactants is 7.5, while the number of moles n_B of gaseous products is 6, so that $\Delta n = n_B - n_A = -1.5$. The temperature T is 298°K, and R may be taken as 2 cal (or 2×10^{-3} kcal) deg^{-1} mole^{-1}; hence,

$$\Delta H = \Delta E - (2 \times 10^{-3} \times 298 \times 1.5)$$

$$-781.0 = \Delta E - 0.9$$

$$\Delta E_{298} = -780.1 \text{ kcal}.$$

This is the heat (absorbed) of reaction at constant volume. (Combustion reactions, such as that of benzene, are generally studied at constant volume; the calculation given above is then reversed so as to derive ΔH from ΔE.)

For reactions involving solids or liquids only, such as

$$Al(c) + Fe_2O_3(c) = Al_2O_3(c) + 2Fe(c)$$

$$Na(c) + \tfrac{1}{2}Br(l) = NaBr(c),$$

and for reactions in which the same number of gaseous molecules occur on both sides of the equation, e.g.,

$$C(c) + O_2(g) = CO_2(g)$$

$$H_2(g) + Cl_2(g) = 2HCl(g),$$

the change of volume is negligible, and hence the heats of reaction at constant pressure and constant volume may be taken as identical.

7c. Heat of Formation.—The **heat of formation** of a compound is usually defined as *the increase of enthalpy when 1 mole of the substance is formed* *from its elements.* It is generally postulated that the elements are in their so-called **standard states**, that is, in their stable forms at ordinary temperature and 1 atm pressure. Thermodynamic quantities relating to processes occurring under standard state conditions are always identified by the superscript ^{0}, e.g., ΔHf^0 for the standard heat of formation. From the data already given for the reaction between carbon and oxygen to form carbon dioxide, it is evident that the standard heat of formation of this gas is -94.05 kcal at 25°C. It may be noted in this connection that graphite is the stable form of carbon, and hence it represents the standard state of this element. The heat of formation of gaseous hydrogen iodide may be obtained from the thermochemical equation

$$H_2(g) + I_2(c) = 2HI(g) \qquad \Delta H^0_{298} \quad 12.40 \text{ kcal.}$$

Since two moles of hydrogen iodide are formed, the heat of formation is 6.20 kcal. The standard heats of formation of a number of compounds at 25°C are recorded in Table 7.1.

TABLE 7.1. STANDARD HEATS OF FORMATION IN KCAL PER MOLE AT 25°C

Substance	ΔHf^0_{298} (kcal)	Substance	ΔHf^0_{298} (kcal)
$H_2O(l)$	-68.3174	$C_2H_4(g)$	$+12.496$
$H_2O(g)$	-57.7979	$C_2H_6(g)$	-20.236
$HCl(g)$	-22.063	$C_2H_2(g)$	$+54.194$
$HBr(g)$	-8.66	$CH_3OH(l)$	-57.02
$HI(g)$	$+6.20$	$C_2H_5OH(l)$	-66.356
$CO(g)$	-26.4157	$CH_3COOH(l)$	-116.4
$CO_2(g)$	-94.0518	$C_6H_6(l)$	$+11.718$
$NH_3(g)$	-11.04	$PbO(c, \text{red})$	-52.40
$NO(g)$	$+21.600$	$HgO(c, \text{red})$	-21.68
$H_2S(g)$	-4.815	$HgO(c, \text{yellow})$	-21.56
$SO_2(g)$	-70.96	$AgCl(c)$	-30.362
$CH_4(g)$	-17.889	$NaCl(c)$	-98.232

The heats of formation of the compounds taking part in a chemical reaction have an important connection with the heat of reaction. For purposes of calculation the following convention is adopted: *The enthalpies of all elements in their standard states are arbitrarily taken to be zero at all temperatures. The enthalpy of a compound is then equal to the heat of formation* ΔHf^0, as may be seen by considering a simple case. The formation of hydrogen chloride from its elements is represented by

$$H_2(g) + Cl_2(g) = 2HCl(g) \qquad \Delta H^0_{298} = -44.12 \text{ kcal}$$

or, dividing through by two,

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) = HCl(g) \qquad \Delta Hf^0_{298} = -22.06 \text{ kcal.}$$

There is here a decrease of 22.06 kcal in the enthalpy of the system when 1 mole of hydrogen chloride is formed from its elements. If the enthalpies of the latter are taken as zero, in accordance with the convention, the enthalpy of hydrogen chloride must obviously be −22.06 kcal, in agreement with the statement made above. It should be clearly understood that since thermochemical quantities are always *differences* in enthalpy, i.e., ΔH, it is quite immaterial what basis of reference is chosen for calculation purposes, *provided it is always the same.* The one given above has the great merit of simplicity and convenience, but *it does not imply that the enthalpies of elements are actually zero.*

By means of the two rules, viz., the enthalpy of an element is zero and that of a compound is equal to its heat of formation, the heat change in a reaction can be readily calculated. Considering the chemical change

$$\begin{array}{cccc} CH_4(g) + & 2O_2(g) = & CO_2(g) + & 2H_2O(l), \\ -17.9 & 0 & -94.1 & 2(-68.3) \end{array}$$

and writing the enthalpy of each species below its formula, it is seen that the total enthalpy of the products is $-94.1 + 2(-68.3)$, and that of the reactants is $-17.9 + 0$; the increase ΔH^0 of the enthalpy in the reaction is thus given by the difference between these two quantities, viz.,

$$\Delta H^0_{298} = [-94.1 + 2(-68.3)] - (-17.9 + 0) = -212.8 \text{ kcal.}$$

Instead of using the heats of formation to calculate the heat of reaction, the procedure may be reversed; the heat of formation of a compound taking part in a reaction can be calculated, provided the values for all the other compounds and the heat of reaction are known.*

Example: The enthalpy change of the reaction

$$Al_2Cl_6(c) + 6Na(c) = 2Al(c) + 6NaCl(c)$$

is −256.8 kcal. The heat of formation of solid NaCl is −98.2 kcal; calculate the heat of formation of solid Al_2Cl_6.

The enthalpies of the reactants and products may be written as follows:

$$\begin{array}{cccc} Al_2Cl_6 + & 6Na = & 2Al + & 6NaCl \\ x & 0 & 0 & 6(-98.2) \end{array}$$

where x is the enthalpy, and hence the heat of formation, of Al_2Cl_6. For the whole reaction ΔH is −256.8 kcal; consequently,

$$-256.8 = [0 + 6(-98.2)] - (x + 0)$$

$$x = -332.4 \text{ kcal.}$$

7d. Heat of Combustion.—Organic compounds containing carbon, hydrogen and oxygen can be burnt in oxygen to give carbon dioxide and water as the sole products; *the enthalpy change accompanying the complete combustion of*

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* Many heats of reaction are small numbers obtained by subtracting large numbers. Consequently, a small uncertainty in the large numbers becomes a large uncertainty in the smaller one. It is only rarely that heats of reaction are known with an accuracy better than ±0.01 kcal. It is for this reason that the values given in the tables are frequently rounded off in solving problems.

1 mole of a compound is called the **heat of combustion.** If the substances concerned are all in their respective standard states, the result is represented by the symbol ΔHc^0 with the temperature as subscript. From data given in preceding sections, it will be seen that the standard heat of combustion of benzene is −781.0 kcal, and that of methane is −212.8 kcal. The values for a number of familiar compounds are quoted in Table 7.2; the products are gaseous carbon dioxide and liquid water in each case.

TABLE 7.2. STANDARD HEATS

Substance	ΔHc^0_{298} (kcal)	Substance	ΔHc^0_{298} (kcal)
Methane (*g*)	−212.80	Acetic acid (*l*)	−208.34
Ethylene (*g*)	−337.23	Ethyl acetate (*l*)	−539.1
Ethane (*g*)	−372.82	Benzene (*l*)	−780.98
Acetylene (*g*)	−310.62	Benzoic acid (*c*)	−771.72
Methanol (*l*)	−173.65	Naphthalene (*c*)	−1231.6
Ethanol (*l*)	−326.70	Sucrose (*c*)	−1348.9

The heats of combustion of both liquid and gaseous hydrocarbons are important from the industrial standpoint, and the term **calorific value** is frequently used for the heat of combustion of a substance used as a fuel. The heats of combustion of fat, carbohydrate and protein, which are the essential energy constituents of food, are of significance in nutritional studies.

The heat of combustion of a compound may be used to calculate its heat of formation, utilizing the procedure described in § 7c; this fact is of particular value, for the heats of formation of many organic compounds cannot be determined by direct experiment.

Example: The standard heat of combustion of liquid ethanol is −326.70 kcal at 25°C; calculate its heat of formation from the elements in their standard states at this temperature.

The equation for the combustion may be written out, and the conventional enthalpies of oxygen, gaseous carbon dioxide and liquid water may be inserted in the usual manner; thus,

$$\begin{array}{ccccccc} C_2H_5OH(l) & + & 3O_2(g) & = & 2CO_2(g) & + & 3H_2O(l) \\ x & & 0 & & 2(-94.05) & & 3(-68.32) \end{array}$$

For the overall reaction, $\Delta H = -326.70$ kcal; hence,

$$-326.70 = [2(-94.05) + 3(-68.32)] - (x + 0)$$

$$x = -66.36 \text{ kcal.}$$

Thus,

$$2C(c) + 3H_2(g) + \tfrac{1}{2}O_2(g) = C_2H_5OH(l) \qquad \Delta Hf^0_{298} = -66.36 \text{ kcal.}$$

7e. Thermochemical Laws.—The calculation of heats of reaction and of heats of formation given above have all been tacitly based on the principle of conservation of energy, and hence on the first law of thermodynamics. Two important thermochemical laws are based on the same fundamental principle. According to the observations of A. L. Lavoisier and P. S. Laplace (1780), *the* *quantity of heat which must be supplied to decompose a compound into its elements is equal to the heat evolved when that compound is formed from its elements.* In other words, the heat of decomposition of a compound is numerically equal to its heat of formation but of opposite sign. This experimental result is, of course, in direct agreement with the first law of thermodynamics, for otherwise it would be possible to create heat energy by making a compound from its elements and then decomposing it, or vice versa. An important consequence of the law of Lavoisier and Laplace is that thermochemical equations can be reversed, provided the sign of the heat term is changed, its numerical value remaining the same. This rule applies not only to reactions involving a compound and its constituent elements, e.g.,

$$\mathrm{S}(c) + \mathrm{O_2}(g) = \mathrm{SO_2}(g) \qquad \Delta H^0_{298} = -70.96 \text{ kcal}$$

$$\mathrm{SO_2}(g) = \mathrm{S}(c) + \mathrm{O_2}(g) \qquad \Delta H^0_{298} = 70.96 \text{ kcal},$$

it can be extended to reactions of all types, thus

$$\mathrm{CO_2}(g) + \mathrm{H_2}(g) = \mathrm{CO}(g) + \mathrm{H_2O}(g) \qquad \Delta H^0_{298} = -0.68 \text{ kcal}$$

$$\mathrm{H_2O}(g) + \mathrm{CO}(g) = \mathrm{CO_2}(g) + \mathrm{H_2}(g) \qquad \Delta H^0_{298} = 0.68 \text{ kcal}.$$

The second important law of thermochemistry was discovered experimentally by G. H. Hess (1840); it is known as **Hess's law** or **the law of constant heat summation.** This law states that *the resultant heat change in a chemical reaction carried out either at constant pressure or constant volume is the same whether it takes place in one or several stages.* This means that the *net* heat of reaction, *at constant pressure or constant volume*, depends only on the initial and final states, and not on the intermediate states through which the system may pass. The law of Hess is thus a direct consequence of the first law of thermodynamics. It has been seen that according to this law the quantities ΔE and ΔH, which are equal to the heats of reaction at constant volume and constant pressure, respectively, are dependent only on the initial and final states of the system, and are independent of the path connecting them.

The great practical value of Hess's law lies in the fact that, as a consequence of this law, thermochemical equations can be added and subtracted like algebraic equations. As a result heats of reaction which cannot be determined by direct experiment can be calculated from other thermochemical data. The heat of formation of hydrogen bromide gas was determined from the measured heats of the following seven reactions; the data are for standard states throughout.

		ΔH^0
(i)	$\mathrm{KBr}(aq) + \frac{1}{2}\mathrm{Cl_2}(g) = \mathrm{KCl}(aq) + \frac{1}{2}\mathrm{Br_2}(aq)$	−11.5 kcal
(ii)	$\frac{1}{2}\mathrm{H_2}(g) + \frac{1}{2}\mathrm{Cl_2}(g) = \mathrm{HCl}(g)$	−22.0
(iii)	$\mathrm{HCl}(g) + aq = \mathrm{HCl}(aq)$	−17.5
(iv)	$\mathrm{KOH}(aq) + \mathrm{HCl}(aq) = \mathrm{KCl}(aq) + \mathrm{H_2O}$	−13.7
(v)	$\mathrm{KOH}(aq) + \mathrm{HBr}(aq) = \mathrm{KBr}(aq) + \mathrm{H_2O}$	−13.7
(vi)	$\frac{1}{2}\mathrm{Br_2}(g) + aq = \frac{1}{2}\mathrm{Br_2}(aq)$	−0.5
(vii)	$\mathrm{HBr}(g) + aq = \mathrm{HBr}(aq)$	−19.9

[It will be noted that processes (iii), (vi) and (vii) represent the addition of large amounts of water to hydrogen chloride, bromine and hydrogen bromide, respectively; the corresponding heat changes are the **heats of solution** of the respective substances (see § 7g).] If the thermochemical equations (ii), (iii), (iv) and (vi) are added together, and from the total the sum of (i), (v) and (vii) is subtracted, the result is

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Br_2(g) = HBr(g) \qquad \Delta Hf^0_{298} = -8.6 \text{ kcal.}$$

The standard heat of formation of hydrogen bromide, from gaseous hydrogen and bromine, is thus −8.6 kcal per mole.

Since all thermochemical calculations are based on the first law of thermodynamics, the law of constant heat summation may be used as an alternative to the procedure described in § 7c and § 7d for calculating heats of formation. For example, to calculate the standard heat of formation of liquid ethanol, use is made of the three thermochemical equations:

$$\begin{array}{llr}
\text{(i)} & C_2H_5OH(l) + 3O_2(g) = 2CO_2(g) + 3H_2O(l) & \Delta H^0 = -326.70 \text{ kcal} \\
\text{(ii)} & C(c) + O_2(g) = CO_2(g) & \Delta H^0 = -94.05 \\
\text{(iii)} & H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(l) & \Delta H^0 = -68.32
\end{array}$$

Equation (ii) is multiplied by 2, and (iii) multiplied by 3 is added; equation (i) is then subtracted, and the result is

$$2C(c) + 3H_2(g) + \tfrac{1}{2}O_2(g) = C_2H_5OH(l) \qquad \Delta Hf^0_{298} = -66.36 \text{ kcal,}$$

as before. This method of calculating the standard heat of formation of ethanol utilizes the same data as that given in the example in § 7d; the difference in procedure is purely formal.

Another application of Hess's law is to determine the heat of a reaction from a knowledge of the heats of combustion of all the reactants and products. Suppose it is required to find the standard heat of the reaction

$$C_2H_4(g) + H_2(g) = C_2H_6(g),$$

at 25°C, utilizing the heats of combustion of ethylene (C_2H_4), hydrogen (H_2) and ethane (C_2H_6). The three thermochemical equations are then written:

$$\begin{array}{llr}
\text{(i)} & C_2H_4(g) + 3O_2(g) = 2CO_2(g) + 2H_2O(l) & \Delta H^0 = -337.2 \text{ kcal} \\
\text{(ii)} & H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(l) & \Delta H^0 = -68.3 \\
\text{(iii)} & C_2H_6(g) + 3\tfrac{1}{2}O_2(g) = 2CO_2(g) + 3H_2O(l) & \Delta H^0 = -372.8
\end{array}$$

If (i) and (ii) are added together and (iii) is subtracted, the result is

$$C_2H_4(g) + H_2(g) = C_2H_6(g) \qquad \Delta H^0_{298} = -32.7 \text{ kcal.}$$

All that is necessary, therefore, is to add the heats of combustion of the reactants and to subtract from this the sum of the heats of combustion of the products; the result will then be equal to the heat change of the reaction under consideration.

7f. Influence of Physical State.—The change in enthalpy in a reaction must depend on the physical state, i.e., crystalline solid, liquid or gaseous, of the substances involved. An illustration of this fact is provided by reactions in which water is concerned; for example, the thermochemical equation for the formation of *liquid* water from its elements at 25°C is

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(l) \qquad \Delta H^0 = -68.32 \text{ kcal.}$$

If, however, water *vapor* is the product, the heat of reaction is obtained by adding the molar heat of vaporization, at 1 atm pressure, at the particular temperature; thus, at 25°,

$$H_2O(l) = H_2O(g) \qquad \Delta H^0 = 10.52 \text{ kcal,}$$

and hence, by addition of the two equations,

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(g) \qquad \Delta H^0_{298} = -57.80 \text{ kcal.}$$

The standard heat of formation of 1 mole of water vapor at 25°C is thus −57.80 kcal.

Different heat changes are generally involved for different allotropic modifications of an element or for different crystalline forms of a compound. If the data are available for a given reaction in which the two separate forms take part, it is possible to evaluate the heat of transition of one form to the other. For example, the heats of combustion of the two allotropic forms of carbon, namely diamond and graphite, are −94.50 and −94.05 kcal, respectively; thus,

$$\text{C(diamond)} + O_2(g) = CO_2(g) \qquad \Delta H^0 = -94.50 \text{ kcal}$$

$$\text{C(graphite)} + O_2(g) = CO_2(g) \qquad \Delta H^0 = -94.05 \text{ kcal;}$$

and hence by subtraction it follows that

$$\text{C(diamond)} = \text{C(graphite)} \qquad \Delta H^0_{298} = -0.45 \text{ kcal.}$$

Consequently, when 12.01 g of diamond are converted into graphite, there is a decrease in enthalpy of 0.45 kcal, that is to say, 0.45 kcal of heat is evolved.

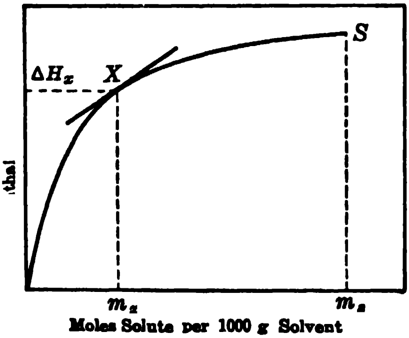

FIG. 7.1. Heat of solution

7g. Heats of Solution and Dilution.—When a solute is dissolved in a solvent to form a solution, there is frequently an evolution or absorption of heat. The heat change per mole of solute dissolved is not constant, however, but usually varies with the concentration of the solution. If the total change of enthalpy ΔH at constant temperature observed when m moles of solute are added to a definite quantity, e.g., 1000 grams, of solvent is plotted against m, for various values of the latter, the type of curve obtained is shown in Fig. 7.1. The curve reaches a limit at the point S when the solution is saturated at the experimental temperature; the solution then contains m_s moles of solute to 1000 grams of solvent. The height of the ordinate ΔH_x at any point, e.g., X, divided by the corresponding number of moles m_x of solute dissolved, i.e., $\Delta H_x/m_x$, represents *the increase of enthalpy per mole of solute when it dissolves to form a solution of a particular concentration;* this quantity is called the **integral heat of solution** at the given concentration. It is evident from Fig. 7.1 that the integral heat of solution is, in general, approximately constant in dilute solution, but becomes smaller with increasing concentration.

When recording integral heats of dilution it is the general practice to state the number of moles of solvent in which 1 mole of solute is dissolved; thus,

$$\mathrm{HCl}(g) + 50\mathrm{H_2O}(l) = \mathrm{HCl}(50\mathrm{H_2O}) \qquad \Delta H_{298} = -17.51 \text{ kcal},$$

indicates that when 1 mole of hydrogen chloride gas is dissolved in 50 moles of water there is an evolution of 17.51 kcal of heat energy. For infinite dilution, that is, when the solution is so dilute that further dilution causes no detectable heat change, the corresponding thermochemical equation for the integral heat of solution would be written

$$\mathrm{HCl}(g) + aq = \mathrm{HCl}(aq) \qquad \Delta H_{298} = -17.96 \text{ kcal}.$$

The integral heats of solution of a number of substances in water, at the specified concentrations, are given in Table 7.3. It will be observed that when the gaseous hydrogen halides and ammonia, and in fact all gases, are dissolved in water there is a decrease in the total enthalpy; in other words, the solution is accompanied by the evolution of heat. For hydrated salts, e.g., $\mathrm{CuSO_4 \cdot 5H_2O}$, and salts which do not form stable hydrates, e.g., $\mathrm{KNO_3}$, the integral heat of solution is positive, so that heat is absorbed when these substances dissolve. When a salt which is capable of existing in a hydrated form dissolves in the anhydrous form, e.g., $\mathrm{CuSO_4}$, there is almost invariably a liberation of heat energy, i.e., the integral ΔH value is negative. The difference in behavior of the hydrated and anhydrous forms of a given salt is due to the change in enthalpy associated with the hydration reaction; there is

TABLE 7.3. INTEGRAL HEATS OF SOLUTION IN KCAL PER MOLE OF SOLUTE IN WATER AT 25°C

Substance	H_2O (moles)	ΔH^0_{298} (kcal)	Substance	H_2O (moles)	ΔH^0_{298} (kcal)
HCl	200	−17.74	KCl	200	+4.20
HBr	200	−20.05	KOH	200	−13.04
NH_3	200	−8.28	KNO_3	400	+8.28
HNO_3	200	−7.85	K_2SO_4	600	+5.93
NH_4NO_3	200	+6.08	$CaCl_2$	400	−19.3
NaCl	200	+1.02	$CaCl_2 \cdot 6H_2O$	394	+3.9
Na_2SO_4	400	−0.36	$CuSO_4$	800	−16.43
$Na_2SO_4 \cdot 10H_2O$	390	+19.02	$CuSO_4 \cdot 5H_2O$	795	+2.42

usually an evolution of heat in these processes, i.e., ΔH of hydration is negative. The value of this heat change can be readily calculated from the integral heats of solution; thus, using the data for copper sulfate in Table 7.3, it is seen that at 25°C

$$CuSO_4(c) + 800H_2O(l) = CuSO_4(800H_2O) \qquad \Delta H^0_{298} = -16.43 \text{ kcal}$$

$$CuSO_4 \cdot 5H_2O(c) + 795H_2O(l) = CuSO_4(800H_2O) \qquad \Delta H^0_{298} = +2.42$$

and hence, by subtraction,

$$CuSO_4(c) + 5H_2O(l) = CuSO_4 \cdot 5H_2O(c) \qquad \Delta H^0_{298} = -18.85 \text{ kcal.}$$

The hydration of 1 mole of solid anhydrous copper sulfate to form solid pentahydrate, by the addition of 5 moles of liquid water, is thus accompanied by the evolution of 18.85 kcal of heat energy at 25°C. The heat of hydration by water vapor at the same temperature would, of course, be different.

Example: Calculate the heat of hydration of 1 mole of $CuSO_4$ by 5 moles of water vapor at 25°C. The heat of vaporization of water at 25° is 10.52 kcal mole^{-1}.

The required thermochemical equations are

$$5H_2O(l) = 5H_2O(g) \qquad \Delta H = 5 \times 10.52 \text{ kcal}$$

$$CuSO_4(c) + 5H_2O(l) = CuSO_4 \cdot 5H_2O(c) \qquad \Delta H = -18.85$$

and hence, by subtraction,

$$CuSO_4(c) + 5H_2O(g) = CuSO_4 \cdot 5H_2O(c) \qquad \Delta H_{298} = -71.45 \text{ kcal.}$$

(It should be noted that this is not a standard state value since the water vapor at 25°C is not at 1 atm pressure.)

The fact that the heat of solution of a solute varies with its concentration implies that there must be a change of enthalpy when a solution is diluted by the addition of solvent. The **integral heat of dilution** is *the change in enthalpy when a solution containing 1 mole of solute is diluted from one concentration to another*. According to Hess's law it is equal to the difference between the integral heats of solution at the two concentrations. The integral heat of dilution of hydrogen chloride from a solution containing 1 mole of solute in 50 moles of water to one at infinite dilution is obtained by subtracting the thermochemical equations given previously for the two heats of solution; the result is

$$HCl(50H_2O) + aq = HCl(aq) \qquad \Delta H^0_{298} = -0.44 \text{ kcal.}$$

7h. Differential Heats of Solution and Dilution: Partial Molal Quantities.—*The increase of enthalpy when 1 mole of solute is dissolved in such a large volume of solution, at a particular composition, that there is no appreciable change in the concentration,* is the **differential heat of solution** at the specified concentration and temperature. This property is given by the slope of the curve in Fig. 7.1 or, expressed mathematically, by $d(\Delta H)/dm$, at the point corresponding to the given concentration. It is seen from the shape of the curve that the differential heat of solution is almost constant in very dilute solutions where the curve is practically a straight line and the slope is consequently constant. In these circumstances the differential and integral heats of solution are essentially equal. At higher concentrations, the differential heat of solution generally decreases as the concentration increases.

The **differential heat of dilution** may be defined as *the heat change when 1 mole of solvent is added to a large volume of the solution at the specified concentration.* This can be obtained by plotting the ΔH of solution at various concentrations against the number of moles of *solvent* associated with a definite quantity of solute, and finding the slope of the curve at the point corresponding to any particular concentration. Because of the approximate constancy of the integral heat of solution at small concentrations, such a curve flattens out at high dilutions, and the differential heat of dilution then approaches zero.

The differential heats of solution and dilution are examples of important thermodynamic quantities, called **partial molal properties,** which must be used whenever systems of variable composition, such as solutions, are involved. Consider, for simplicity, a solution consisting of only two components, namely, n_1 moles of solvent and n_2 moles of solute. Suppose X is any extensive thermodynamic property of the solution; let dX be the change in this property resulting from the addition, *at constant temperature and pressure*, of the infinitesimal amounts dn_1 moles of solvent and dn_2 moles of solute to a large volume of the solution so that the *composition is virtually unchanged.* Since dX is a complete differential, it follows that, under these conditions,

$$dX = \left(\frac{\partial X}{\partial n_1}\right)_{n_2} dn_1 + \left(\frac{\partial X}{\partial n_2}\right)_{n_1} dn_2, \tag{7.3}$$

the subscripts n_1 and n_2 implying that these respective quantities are constant. The partial molal values of X of the solvent and solute, which are represented by the symbols $\bar{X}_1$ and $\bar{X}_2$, respectively, are then defined by

$$\bar{X}_1 = \left(\frac{\partial X}{\partial n_1}\right)_{n_2} \quad \text{and} \quad \bar{X}_2 = \left(\frac{\partial X}{\partial n_2}\right)_{n_1} \tag{7.4}$$

at the given temperature, pressure and composition. Consequently, equation (7.3) may be written as

$$dX = \bar{X}_1 dn_1 + \bar{X}_2 dn_2 \tag{7.5}$$

and upon integration it follows that

$$X = n_1\bar{X}_1 + n_2\bar{X}_2. \tag{7.6}$$

Thus, the partial molal value of the specified property for each constituent of a solution is equivalent to the contribution per mole made by that constituent to the total value for the given solution. In rare cases, the property under consideration may be strictly additive; $\bar{X}_1$ and $\bar{X}_2$ would then be equal to the values for the respective constituents in the pure state. But in the great majority of circumstances this is not so, and then the partial molal quantities are particularly useful.

It can be seen from equation (7.4) that $\bar{X}_2$ is equal to the slope dX/dn_2 of a curve in which the property X is plotted as a function of n_2 for a series of solutions in which n_1 is maintained constant. In other words, it is the change in the value of X accompanying the addition of 1 mole of constituent 2 (solute) to such a large volume of solution at a particular composition that there is essentially no change in the concentration. Comparison of these statements with the definition given at the beginning of this section shows that the differential heat of solution is really the partial molal heat of solution of the solute, i.e., $\overline{\Delta H_2}$. Similarly, the differential heat of dilution is the corresponding partial molal property of the solvent, i.e., $\overline{\Delta H_1}$.* By equation (7.6), therefore, the total increase in enthalpy accompanying the addition of n_2 moles of solute to n_1 moles of solvent, at a specified temperature and pressure, is given by

$$\Delta H = n_1\overline{\Delta H_1} + n_2\overline{\Delta H_2}. \tag{7.7}$$

The integral heat of solution, which is the value of ΔH per mole of solute, is equal to $\Delta H/n_2$, i.e.,

$$\frac{\Delta H}{n_2} = \frac{n_1}{n_2}\overline{\Delta H_1} + \overline{\Delta H_2}. \tag{7.8}$$

The integral heat of solution is thus related to the differential heats of solution and dilution for the given composition.

The integral heat of dilution is equal to the difference in the integral heats of solution at two concentrations, i.e., $(\Delta H/n_2)_f - (\Delta H/n_2)_i$, where the subscripts i and f refer to the initial and final concentrations, respectively. The relationship to the corresponding partial molal (or differential) quantities can be derived from equation (7.8). It should be noted that, due to the change in concentration accompanying the dilution, the values of n_1/n_2, and also of $\overline{\Delta H_1}$ and $\overline{\Delta H_2}$, are different in the initial and final solutions.

7i. Effect of Temperature on Heat of Reaction: Kirchhoff's Equation.—The heat change associated with any process, physical or chemical, usually varies with temperature; the relationship of this variation to other properties of the system can be readily determined by means of the first law of thermodynamics. Consider any process represented by

$$\mathrm{A} \rightarrow \mathrm{B},$$

where A is the initial state, i.e., the reactants, and B is the final state, i.e., the products. The heat of reaction at constant pressure, i.e., ΔH, is equal to the difference between the enthalpies H_B and H_A of the final and initial states, respectively, thus,

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* The differential heat of dilution is consequently sometimes referred to as the partial molal heat of solution of the solvent.

$$\Delta H = H_B - H_A.$$

In order to determine the variation of ΔH with temperature, this expression is differentiated with respect to temperature at constant pressure; the result is simply

$$\left(\frac{\partial(\Delta H)}{\partial T}\right)_P = \left(\frac{\partial H_B}{\partial T}\right)_P - \left(\frac{\partial H_A}{\partial T}\right)_P. \tag{7.9}$$

According to equation (6.22), the quantity $(\partial H/\partial T)_P$ is equal to C_P, the heat capacity at constant pressure; hence, equation (7.9) may be written as

$$\left(\frac{\partial(\Delta H)}{\partial T}\right)_P = C_{P(B)} - C_{P(A)} = \Delta C_P, \tag{7.10}$$

where ΔC_P, equal to $C_{P(B)} - C_{P(A)}$, is the difference in the heat capacities at constant pressure of the final and initial states, e.g., products and reactants in a chemical change. This expression was derived by G. R. Kirchhoff (1858), and is generally referred to as the **Kirchhoff equation.**

It is seen that equation (7.10) gives the rate of change of the heat of reaction ΔH with the temperature in terms of the heat capacities of the substances involved. In order to make practical use of this expression it is integrated between the temperature limits of T_1 and T_2, with the result

$$\int_{\Delta H_1}^{\Delta H_2} d(\Delta H) = \Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_P dT, \tag{7.11}$$

where ΔH_1 and ΔH_2 are the heats of reaction, at constant pressure, at the temperatures T_1 and T_2, respectively. In order to proceed further, it is necessary to know how the heat capacities of A and B, and hence ΔC_P, vary with temperature. In the simplest case the assumption may be made that ΔC_P is constant and independent of temperature, over a limited range; equation (7.11) then becomes

$$\Delta H_2 - \Delta H_1 = \Delta C_P(T_2 - T_1). \tag{7.12}$$

If $T_2 - T_1$ represents an appreciable temperature range, ΔC_P may be taken preferably as equal to $\bar{C}_{P(B)} - \bar{C}_{P(A)}$, where $\bar{C}_P$ is the *mean* heat capacity of the indicated state (or substances) for the particular temperature range concerned.

Example: The standard heat of formation of liquid water is −68.3 kcal at 25°C; calculate the value at 100°C, taking the mean molar heat capacities at constant pressure, in the given temperature range, of $H_2(g)$, $O_2(g)$ and $H_2O(l)$ to be 6.89, 6.97 and 18.0 cal deg^{-1} mole^{-1}, respectively.

Writing the equation for the reaction, with the mean heat capacity $\bar{C}_P$ below each substance,

$$\begin{array}{lcccl} & H_2(g) + & \frac{1}{2}O_2(g) & = H_2O(l) & \\ \bar{C}_P & 6.89 & \frac{1}{2} \times 6.97 & 18.0 & \text{cal deg}^{-1} \end{array}$$

it is seen that

$$\Delta C_P = 18.0 - \{6.89 + (\tfrac{1}{2} \times 6.97)\} = 7.63 \text{ cal deg}^{-1}$$

$$= 7.63 \times 10^{-3} \text{ kcal deg}^{-1}.$$

Let T_1 be 25°C and T_2 be 100°C, so that $T_2 - T_1$ is 75°; the standard heat of reaction ΔH_1^0 at T_1 is thus -68.3 kcal, and hence ΔH_2^0 at 100°C is given by equation (7.12) as

$$\Delta H_2^0 + 68.3 = 7.63 \times 10^{-3} \times 75,$$

$$\Delta H_2^0 = -67.7 \text{ kcal}.$$

For the purpose of more accurate calculations, however, it is necessary to express the heat capacities of products and reactants as functions of the temperature; in this way a complete expression for ΔC_P can be obtained. This can then be inserted in equation (7.11) and the complete integration carried out, as shown in the example below.

It is the common practice to represent the variation with temperature of heat capacities, especially of gases, as a function of successive powers of T; thus,

$$C_P = a + bT + cT^2, \tag{7.13}$$

where a, b and c are constants for the given gas. The values of these constants for a number of common gases are given in Table 7.4.

TABLE 7.4. VARIATION WITH TEMPERATURE OF HEAT CAPACITY AT CONSTANT PRESSURE IN CAL DEG^{-1} MOLE^{-1}

Gas	a	$b \times 10^3$	$c \times 10^7$
H_2	6.947	−0.200	4.808
O_2	6.148	3.102	−9.23
N_2	6.449	1.413	−0.807
Cl_2	7.576	2.424	−9.65
CO	6.420	1.665	−1.96
CO_2	6.214	10.396	−35.45
NH_3	6.189	7.887	−7.28
HCl	6.732	0.433	3.70
H_2O	7.219	2.374	2.67
CH_4	3.381	18.044	−43.00
C_2H_6	2.195	38.282	−110.01
C_2H_4	2.706	29.160	−90.59
C_6H_6	−9.478	119.930	−807.02
CH_3OH	4.398	24.274	−68.55

Example: For the reaction $N_2(g) + 3H_2(g) = 2NH_3(g)$, the value of ΔH^0 is -22.08 kcal at 25°C. The molar heat capacities at constant pressure of nitrogen, hydrogen and ammonia can be expressed as functions of the absolute temperature in the following manner:

$$C_{N_2} = 6.449 + 1.413 \times 10^{-3}T - 0.807 \times 10^{-7}T^2 \text{ cal deg}^{-1}$$

$$C_{H_2} = 6.947 - 0.200 \times 10^{-3}T + 4.808 \times 10^{-7}T^2$$

$$C_{NH_3} = 6.189 + 7.887 \times 10^{-3}T - 7.28 \times 10^{-7}T^2.$$

Calculate the standard heat of reaction at 125°C.

The value of ΔC_P is given by

$$\Delta C_P = 2C_{NH_3} - (C_{N_2} + 3C_{H_2})$$
$$= -14.912 + 14.961 \times 10^{-3}T - 28.18 \times 10^{-7}T^2 \text{ cal deg}^{-1}.$$

Hence,

$$\int_{T_1}^{T_2} \Delta C_P dT = \left[-14.912 + 14.961 \times 10^{-3}\frac{T^2}{2} - 28.18 \times 10^{-7}\frac{T^3}{3}\right]_{T_1}^{T_2}$$

$$= -14.912(T_2 - T_1) + 7.481 \times 10^{-3}(T_2^2 - T_1^2) - 9.39 \times 10^{-7}(T_2^3 - T_1^3)$$

and this is equal to $\Delta H_2^0 - \Delta H_1^0$ by equation (7.11). The temperature T_1 is 25°C, i.e., $273 + 25 = 298°\text{K}$, and T_2 is $273 + 125 = 398°\text{K}$; consequently,

$$\Delta H_2^0 - \Delta H_1^0 = -14.912(398 - 298) + 7.481 \times 10^{-3}\{(398)^2 - (298)^2\} - 9.39 \times 10^{-7}\{(398)^3 - (298)^3\}$$

$$= -1005 \text{ cal} = -1.01 \text{ kcal}.$$

Since ΔH_1^0 (at 25°C) is -22.08 kcal, it follows that

$$\Delta H_2^0 = -22.08 - 1.01 = -23.09 \text{ kcal}.$$

It will be evident from either equation (7.10) or (7.11) that the variation of the heat of reaction with temperature depends on the magnitude and sign of ΔC_P. The larger this difference in the heat capacities of the products and the reactants the greater will be the variation of the heat of reaction with temperature. If ΔC_P is positive, that is to say, if the total heat capacity of the products is greater than that of the reactants, ΔH will increase with increasing temperature. On the other hand, if ΔC_P is negative, so that the reactants have the greater heat capacity, the value of ΔH will diminish as the temperature is raised. If ΔC_P is zero, or very small, the heat of reaction will be independent of temperature.

An alternative integrated form of the Kirchhoff equation is frequently used; thus, the general integration of equation (7.10) gives

$$\Delta H = \Delta H_0 + \int \Delta C_P dT, \tag{7.14}$$

where ΔH_0, equivalent to the hypothetical heat of reaction at the absolute zero, is the integration constant. If the individual values of C_P are expressed as a function of temperature by equation (7.13), then it is possible to write

$$\Delta C_P = \Delta a + \Delta bT + \Delta cT^2, \tag{7.15}$$

where Δa, Δb, Δc, etc., are constants determined by the nature of the reactants and products. Upon inserting this result in equation (7.14), it is seen that

$$\Delta H = \Delta H_0 + \int (\Delta a + \Delta bT + \Delta cT^2)dT$$

$$= \Delta H_0 + \Delta aT + \tfrac{1}{2}\Delta bT^2 + \tfrac{1}{3}\Delta cT^3. \tag{7.16}$$

In this manner, the heat of reaction ΔH at any temperature T is expressed in terms of T, and the constants ΔH_0, Δa, Δb, Δc, etc., which are characteristic of the reaction. The values of Δa, Δb, Δc, etc., are derived from the measured heat capacities, while ΔH_0 is calculated from equation (7.16), utilizing the known heat of reaction ΔH at one particular temperature.

Example: Use the data in the preceding example to express the standard state heat of the reaction $N_2(g) + 3H_2(g) = 2NH_3(g)$ in the form of equation (7.16).

It was found in the preceding example that for this reaction

$$\Delta C_P = -14.912 + 14.961 \times 10^{-3}T - 28.18 \times 10^{-7}T^2 \text{ cal deg}^{-1},$$

and comparison with equation (7.15) shows that

$$\Delta a = -14.912, \qquad \Delta b = +14.961 \times 10^{-3} \qquad \text{and} \qquad \Delta c = -28.18 \times 10^{-7}.$$

Hence, by equation (7.16)

$$\Delta H^0 = \Delta H_0^0 - 14.912T + 7.481 \times 10^{-3}T^2 - 9.39 \times 10^{-7}T^3 \text{ cal.}$$

At 25°C, i.e., 298°K, the value of ΔH^0 is given as −22.08 kcal, i.e., −22,080 cal; hence,

$$-22{,}080 = \Delta H_0^0 - 14.912 \times 298 + 7.481 \times 10^{-3} \times (298)^2 - 9.39 \times 10^{-7} \times (298)^3 \text{ cal}$$

$$\Delta H_0^0 = -18{,}280 \text{ cal},$$

and consequently, converting into kilocalories,

$$\Delta H^0 = -18.28 - 14.912 \times 10^{-3}T + 7.481 \times 10^{-6}T^2 - 9.39 \times 10^{-10}T^3 \text{ kcal.}$$

7j. Calorimetric Measurements.—The heat changes involved in chemical reactions are measured by carrying out the process in a suitable vessel *A* surrounded by a definite amount of water *B*; the apparatus is known as a **calorimeter** (Fig. 7.2). If heat is liberated in the reaction the temperature of the water rises, but if heat is absorbed the temperature falls. The product of the rise or fall of temperature and the heat capacity of the water and other parts of the calorimeter gives the heat change of the reaction. The heat capacity of the calorimeter and its contents may be determined from the weights and specific heats of the various parts. The most accurate method for determining the heat capacity is to place a heating coil in the calorimeter and to generate a definite amount of heat by the passage of an electric current. From the corresponding rise in temperature of the water in the calorimeter the heat capacity can be evaluated.

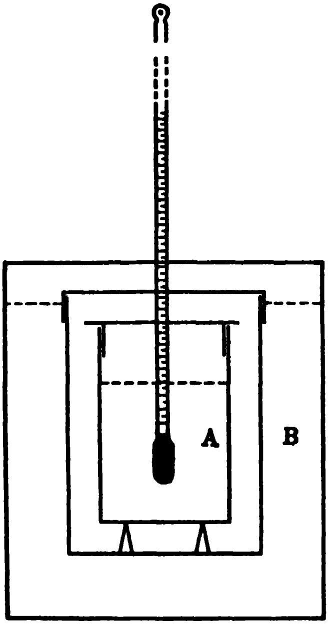

Fig. 7.2. Simple form of calorimeter

One of the great difficulties encountered in carrying out accurate thermochemical measurements is the avoidance of heat losses due to radiation. Two chief procedures have been used to overcome this source of error. In one, the calorimeter vessel containing the water is surrounded by various jackets or, better, it is placed inside a Dewar vacuum vessel, so as to minimize the loss of heat by radiation. In the other method, which employs what is called the **adiabatic calorimeter**, the temperature of an outer jacket, generally containing water, is continuously adjusted during the course of the reaction so as to differ by not more than 0.1° from that of the reaction vessel itself. In this case the amount of heat radiating from or to the latter is quite negligible.

In carrying out a thermochemical measurement it is desirable that the reaction should take place as rapidly and as completely as possible. For this reason, reactions between gases are sometimes accelerated by means of a catalyst placed in a tube contained in the calorimeter reaction vessel. Heats of combustion of organic solids and liquids, including fuels and food materials, are measured by means of an explosion or combustion "bomb." This is a cylindrical vessel, of 400 to 500 ml capacity, made of strong steel or other alloy. A known weight of the material to be studied is placed in the bomb which is then filled with oxygen at a pressure of 25 to 30 atm. The apparatus is inserted in a calorimeter, and the organic compound is ignited by the passage of a small electric current through a fine iron wire sealed into the bomb. Rapid combustion occurs in the oxygen under pressure, and the heat liberated is determined from the rise in temperature of the calorimetric liquid. Various corrections must be applied in order to obtain accurate results.

Example: The combustion of 1.247 gram of benzoic acid at 25°C in a bomb contained in a calorimeter of total heat capacity 2745 cal deg^{-1} was accompanied by a rise of temperature of 2.870°. Neglecting corrections, calculate the molar heat of combustion of benzoic acid at constant volume.

The heat evolved in the combustion is the product of the heat capacity of the calorimeter and the rise of temperature, i.e., 2745×2.870 cal or 2.745×2.870 kcal. This is produced by 1.247 gram of benzoic acid, and since the molecular weight of benzoic acid is 122.12, the molar heat of combustion is

$$\frac{2.745 \times 2.870 \times 122.12}{1.247} = 771.5 \text{ kcal mole}^{-1}.$$

7k. Thermochemical Data.—The best sources of thermochemical (and other thermodynamic) data are the tables, which are supplemented from time to time, issued by the U. S. National Bureau of Standards: "Selected Values of Properties of Hydrocarbons," Circular 461, and "Selected Values of Chemical Thermodynamic Properties," Circular 500. In these tables the standard state temperature is taken as 25°C. In using other sources of information, it should be noted that the temperature is not always 25°C; in some cases it is 18°C and in others 20°C. The corrections to 25°C are usually small and may frequently be ignored, but if they are required they can be calculated by the Kirchhoff equation. When combining thermochemical data from different sources, however, it should be remembered that, although each source may be self-consistent, differences may exist between sources because the values quoted are based on different measurements.

7l. Bond Energies and Heats of Reaction.—When direct experimental data are not available, approximate estimates of heats of reaction can be obtained by the use of **bond energies.** The bond energy is defined as the *average amount of energy (per mole) required to break a particular bond in a molecule, producing free atoms or radicals.* Thus, the C—H bond energy is one fourth the amount required to dissociate 1 mole of methane (CH_4) into gaseous carbon and hydrogen atoms. It is probable that different energies are required to remove the four hydrogen atoms successively from a methane molecule, and so the bond energies generally quoted are mean values. For this reason, they may well vary from one compound to another. The bond energies quoted in Table 7.5 are average values derived from the known heats of reaction involving many compounds. Those involving the carbon atom, e.g., C—C, C═C, C—N, etc., are based on 170 kcal per g atom as the heat of vaporization of solid carbon (graphite). Making the assumption that the energy of a particular bond is always the same, irrespective of the compound in which it is present, heats of reaction can be obtained by adding the contributions of all the bonds broken in the reactants, and subtracting from this the contributions of the bonds formed in the products. In compounds with "resonating" structures (§ 16h), such as carbon dioxide, carboxylic acids and benzene derivatives, allowance must be made for the resonance energy.

TABLE 7.5. MEAN BOND ENERGIES IN KCAL PER MOLE

Bond	Energy (kcal)	Bond	Energy (kcal)
H—H	103	Cl—Cl	57
C—C	80	Br—Br	46
C═C	145	I—I	36
C≡C	198	C—Cl	78
C—H	98	C—Br	54
C—N	59	C—I	46
C—O	80	N—H	92
C═O	173	H—Cl	102
O═O	118	H—Br	87
O—H	110	H—I	71

Example: By using bond energies, calculate the approximate heat of formation of ethane.

The reaction is

$$2C(c) + 3H_2(g) = C_2H_6(g)$$

and the bond energies (and heat of vaporization) are as follows:

Reactants	kcal	Products	kcal
$2C(c) \rightarrow 2C(g)$	$2 \times 170 = 340$	1C—C	80
3H—H	$3 \times 103 = \underline{309}$	6C—H	$6 \times 98 = \underline{588}$
	649		668

Heat of formation per mole of C_2H_6 is thus approximately 649 − 668 ≈ −19 kcal. (The value given in Table 7.1 is −20.2 kcal at 25°C.)

Example: Estimate the heat change of the gas reaction

$$CH_4 + Cl_2 = CH_3Cl + HCl.$$

The bond energies are as follows:

Reactants	kcal	Products	kcal
1C—H	98	1C—Cl	78
1Cl—Cl	57	1H—Cl	102
	155		180

The heat of reaction is thus roughly $155 - 180 \approx -25$ kcal. (It should be noted that, since the CH_3 radical is unchanged in the reaction, its bond energies have been omitted.)

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PROBLEMS

1. A steel cylinder of 10 liters capacity contains 20 moles of oxygen at 27°C. An imperfection in the valve closing the cylinder allows the gas to leak out slowly until the cylinder is "empty." Assuming the atmospheric pressure to have remained constant at 760 mm during this time, calculate the work done by the gas in ergs and calories.

2. (*a*) Derive the equation for the work done in an isothermal, reversible compression of one mole of a gas obeying the van der Waals equation of state. (*b*) Calculate the work when 2 moles of ethylene at 27°C are compressed from 49.4 liters to 5 liters.

3. The relationship $C_P - C_V = \dfrac{\alpha^2 TV}{\beta}$ holds for any substance in the gaseous, liquid or solid state. $\alpha = \dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_P$ is the coefficient of thermal expansion and $\beta = -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial P}\right)_T$ is the isothermal compressibility. Show that for an ideal gas the equation reduces to $C_P - C_V = R$.

4. Determine the work done in an isothermal, reversible expansion of a real gas obeying the virial equation of state, $PV = A + BP + CP^2$.

5. Evaluate $(\partial E/\partial V)_T$ for a van der Waals gas, using the equation

$$P = T(\partial P/\partial T)_V - (\partial E/\partial V)_T.$$

6. Show that $(\partial H/\partial P)_T = 0$ for an ideal gas.

7. A current of 5 amp at 115 volts is passed through a heater immersed in water at 100°C. If the heater is operated for one hour, (*a*) how much water will be evap-

orated, (*b*) how much work will be done and (*c*) what will be the change in internal energy? The heat of vaporization of water at 100° is 539.6 cal g^{-1}; the density of the water vapor is 0.5977 g $liter^{-1}$ and of liquid water 0.9584 g ml^{-1}.

8. For the hydrogenation at 82°C of cyclohexene to form cyclohexane, $C_6H_{10} + H_2 = C_6H_{12}$ all gases, $\Delta H = -28.6$ kcal $mole^{-1}$. Calculate the heat of hydrogenation of benzene to cyclohexane at 82°. The experimental value is -49.8 kcal $mole^{-1}$; explain the discrepancy.

9. Three moles of an ideal, monoatomic gas initially at 27°C and 1 atm pressure are compressed reversibly to one half the initial volume. Calculate q, w, ΔE and ΔH when the process is performed (*a*) isothermally, (*b*) adiabatically.

10. Two hundred grams of carbon dioxide are heated from 27° to 527°C at a constant pressure of 1 atm; it is then compressed isothermally to 100 atm. Calculate the energy absorbed in kcal. Assume carbon dioxide behaves as an ideal gas.

11. A steel cylinder of 4 liters capacity contains 20 moles of helium at 25°C. A leak in the valve allows the gas to escape but so slowly that the temperature remains constant. Calculate how much heat must have been absorbed from the surroundings when the cylinder gauge reads empty.

12. Air at 25°C expands adiabatically and reversibly from 10 atm to 1 atm. How many moles of gas are present if the work done is 3600 cal? Assume air to be an ideal gas.

13. Calculate ΔE and ΔH in calories when 2 moles of mercury are heated from 0° to 100°C at 1 atm pressure. The mean density of mercury is 13.474 g cm^{-3}; the mean heat capacity 6.69 cal $mole^{-1}$ deg^{-1}, the mean cubical coefficient of expansion 0.182×10^{-3} deg^{-1}.

14. Calculate the standard heat of formation of $ZnSO_4(c)$ at 298.15°K from the following data:

$$Zn(c) + H_2SO_4(aq) = ZnSO_4(aq) + H_2(g) \qquad \Delta H^0 = -36.43 \text{ kcal};$$

ΔHf^0 of $H_2SO_4(l) = -193.91$; of $H_2SO_4(aq) = -216.90$; the heat of solution $ZnSO_4(c) = ZnSO_4(aq)$, $\Delta H^0 = -19.45$; all values are in kcal at 25°C.

15. (*a*) Calculate the heat of formation of *n*-butane and *iso*-butane for which the heats of combustion at 25°C are -687.98 and -686.34 kcal $mole^{-1}$ respectively. (*b*) Calculate the heat of isomerization of *n*-butane to *iso*-butane at this temperature.

16. From data available in this chapter calculate the heat of hydrogenation of acetylene to (*a*) ethylene, (*b*) ethane.

17. The heats of combustion of *n*-butane, 1-butene and 1,3-butadiene are -688.0, -649.8 and -607.9 kcal $mole^{-1}$, respectively at 25°C. Calculate the thermal changes in the reactions (*a*) $C_4H_{10} = C_4H_8 + H_2$, and (*b*) $C_4H_{10} = C_4H_6 + 2H_2$.

18. Azobenzene may be isolated in a *cis* and *trans* form; each is reduced to aniline by stannous chloride and hydrochloric acid. On mixing in a calorimeter 400.0 ml of an absolute ethanol solution 0.1995 M in stannous chloride and 1.085 M in HCl with 100.0 ml of 0.2426 M *trans*-azobenzene in absolute ethanol, a temperature rise of 5.405°C was obtained; mixing similar amounts of 0.1988 M stannous chloride and 0.2423 M *cis*-azobenzene gave a rise of 6.380°C. The heat capacities of these solutions were determined by heating the solutions electrically; 0.691 amp at 48.5 volts for 188.2 sec produced a rise of 4.661°. Determine the heat of isomerization of the *cis* to *trans* form of azobenzene.

19. For the reactions *cis*-2-butene → *trans*-2-butene and *cis*-2-butene → 1-butene, $\Delta H^0_{298} = -950$ and $+1771$ cal mole^{-1}, respectively. Determine the heat of combustion of *trans*-2-butene. (Use heat of combustion data from problem 17.)

20. The heats of formation of 1 mole $ZnCl_2(c)$ and of solutions of 1 mole $ZnCl_2$ in various amounts of water at 25°C, in kcal, are as follows:

$ZnCl_2(c)$	-99.40	$ZnCl_2 + 25H_2O$	-110.00	$ZnCl_2 + 200H_2O$	-114.86
$ZnCl_2 + 10H_2O$	-108.98	$ZnCl_2 + 50H_2O$	-112.55	$ZnCl_2 + 800H_2O$	-115.43
$ZnCl_2 + 15H_2O$	-109.88	$ZnCl_2 + 100H_2O$	-114.00	$ZnCl_2 + \infty H_2O$	-116.48

From these data determine the heat change which will occur at 25°C when (*a*) 2 moles of $ZnCl_2$ are dissolved in water to form a 1 *m* solution, i.e., 1 mole per 1000 g of water; (*b*) this solution is diluted to 0.01 *m*.

21. From plots of the preceding data, determine (*a*) the differential heats of solution of solute and solvent for a 10% $ZnCl_2$ solution, (*b*) the thermal effect, when 60 g of $ZnCl_2$ are dissolved in water to form a 10% solution.

22. (*a*) Calculate the heat evolved when 5 liters of methane at 25°C and 1 atm pressure are burned in air. (*b*) If this quantity of methane and sufficient air to give complete combustion were compressed in a bomb of 500 ml capacity and the mixture exploded, how much heat would be produced? The temperature of the products in each case is brought to 25°C.

23. (*a*) Determine the temperature of the flame when methane is burned with the theoretical quantity of air necessary for complete combustion. Assume air to be 20% oxygen and 80% nitrogen, the initial temperature of the gases 25°C and that all the heat produced is used to increase the temperature of the products. (*b*) Repeat the calculation, using pure oxygen instead of air. The temperature is known as the maximum (adiabatic) flame temperature.

24. Steam reacts with coke at 1000°C according to the equation $C(c) + H_2O(g) = CO(g) + H_2(g)$. (*a*) Determine the heat of the reaction at 1000°C. (*b*) What is the heat of combustion of the mixture of CO and H_2 at 25°C? C_P (graphite) $= 2.673 + 2.617 \times 10^{-3}T + 1.169 \times 10^{-7}T^{-2}$.

25. The reaction $C(c) + \frac{1}{2}O_2(g) = CO(g)$ is exothermic and the reaction $C(c) + H_2O(g) = CO(g) + H_2(g)$ is endothermic. It is therefore theoretically possible to pass a mixture of air and steam over coke so that the temperature remains constant. Assuming complete reaction, determine the ratio of steam to air which will keep the coke at 1000°C. The gases are assumed to enter the reaction preheated to 1000° and to leave at 1000°.

26. Titanium is prepared commercially by the reduction of $TiCl_4(g)$ with Mg or Na at high temperature. Assuming other processing factors to be the same, which reaction would require the smaller expenditure for fuel to maintain the same temperature of reaction? The ΔHf^0 values at 25°C in kcal mole^{-1} are as follows: $TiCl_4(g)$, -173.2; $NaCl(c)$, -98.2; $MgCl_2(c)$, -112.0. The heat capacities of the reactants and products may be assumed approximately equal.

27. With the aid of bond energies, estimate (*a*) the heat of formation of gaseous CH_3Cl, (*b*) the heat of the reaction $CH_3COCH_3 + I_2 = CH_3COCH_2I + HI$, (*c*) the heat of the reaction $C_2H_4 + Br_2 = C_2H_4Br_2$.

4

The Second Law of Thermodynamics

ENTROPY

8a. Spontaneous Processes.—The second law of thermodynamics has led to results which are of considerable importance to chemistry, physics and engineering, but to the chemist its greatest value probably lies in the fact that it provides a means of foretelling whether a particular reaction can occur, and if so to what extent. However, thermodynamics can only indicate if the reaction is possible or not; other considerations, which lie outside thermodynamics, are necessary, as will be seen in Chapter 16, to determine whether the process will take place slowly or rapidly. Even with this limitation in mind, it must be admitted that information concerning the fundamental possibility of a reaction, apart from its speed, would be of great interest to the chemist. At one time it was believed that chemical changes always occurred spontaneously in the direction of heat evolution, that is, in the direction leading to a decrease in enthalpy. This conclusion is, however, manifestly incorrect, as is evident from the fact that many reactions which take place spontaneously are known to involve an absorption of heat.

The question being considered resolves itself into the problem of understanding the conditions under which spontaneous processes, in general, take place. It is convenient in this connection to examine some physical processes that are of spontaneous occurrence; the conclusions drawn are found to be applicable to all changes that tend to take place without external influence. Consider, for example, a bar of metal that is hot at one end and cold at the other; heat will be conducted spontaneously along the bar from the hot end to the cold end until the temperature is uniform. It is important to note, however, that *this process is not found to reverse itself spontaneously;* it has not been observed that a metal bar of uniform temperature spontaneously becomes hotter at one end and colder at the other. Nevertheless, the process could be reversed somewhat in the following manner: heat is allowed to pass from one end of the uniform bar to a machine where it is converted into work; by means of friction the work is reconverted into an equivalent amount of heat which is now transferred to the other end of the bar. In this way the bar at uniform temperature might be restored to its original state.

8b. The Second Law of Thermodynamics.—Although there is nothing in the procedure just described, for reversing the spontaneous process of conduction of heat along a bar, that is contrary to the first law of thermodynamics, it is a matter of actual experience that a complete reversal is impossible. The difficulty lies in the fact that *heat cannot be completely converted into an equivalent amount of work without causing other changes in some part of the system or its surroundings.* This conclusion, drawn from actual experience, is one way of stating the **second law of thermodynamics.** In order for a machine to convert heat continuously into work, without producing changes in other parts of the system, it is necessary that the machine take up heat from a "source" at a higher temperature, convert *part* of it into an equivalent amount of work, and then give up the remainder to a "sink" at a lower temperature. The fraction of the heat absorbed at the higher temperature that is converted into work is called the **efficiency** of the machine, and *no machine has yet been made that has an efficiency of unity,* or 100 per cent. This is another way of formulating the second law of thermodynamics.

It will be recalled that in § 6i it was stated that, in the isothermal, reversible expansion of an ideal gas, the work done by the gas was exactly equal to the heat absorbed. In other words, in this process the heat is completely converted into work. However, it is important to note that this result is not contrary to the second law of thermodynamics, for according to this law *it is impossible to carry out this conversion of heat into work continuously without producing changes in some part of the system.* In the case of the isothermal expansion, for example, the volume of the gas is changed, because it is greater at the end of the process than at the beginning. If the gas is restored to its original state by compression, an amount of work exactly equal to that obtained in the expansion will have to be done on the gas, and an equivalent quantity of heat will be evolved. The net result of restoring the system to its original state will be that no heat is absorbed and no work is done. The study of numerous cases of this type has established the reliability of the second law of thermodynamics.

Returning now to the bar of metal which has spontaneously attained a uniform temperature, after being initially hot at one end and cold at the other, it will be apparent that the original state can be restored, without causing changes elsewhere, only if heat can be completely converted into work. Since this is known to be impossible, in accordance with experience, i.e., the second law of thermodynamics, it is evident that the spontaneous process cannot be reversed. A partial reversal is possible, since a portion of the heat could be transformed into the equivalent amount of work, and then back again to heat; the complete reversal would, however, be contrary to experience.

The general conclusions drawn above, in connection with the heated bar, will be found applicable to other spontaneous physical processes, such as expansion of a gas from a region of high pressure to one of low pressure, diffusion of one gas into another, the diffusion of a concentrated solution into water, the conversion of electrical energy into heat, the production of heat by friction, and so on. The conclusions must apply also to spontaneous chemical processes, as may be seen from a consideration of a simple example. A piece of zinc will dissolve spontaneously in an aqueous solution of copper sulfate, according to the reaction

$$Zn + CuSO_4 = ZnSO_4 + Cu,$$

with the evolution of a definite amount of heat. This reaction could be reversed by passing an electric current between the metallic copper and the solution of zinc sulfate in an appropriate manner, thus regenerating the zinc metal and copper sulfate. In order for the reversal to be complete, the heat evolved in the original reaction would need to be completely converted into electrical energy, without leaving changes in any other parts of the system; this again is contrary to experience. It is possible to state, therefore, in the most general terms, that *all natural or spontaneous processes, i.e., processes occurring without external aid, are thermodynamically irreversible in character;* this is still another way of expressing the second law of thermodynamics. The fact that a process is spontaneous means that it is taking place at a finite rate; it is consequently to be expected that it is irreversible, since thermodynamically reversible changes are required to occur infinitesimally slowly.

8c. Entropy.—It having been established that spontaneous processes are thermodynamically irreversible, the next stage in the development is to derive thermodynamic functions to serve as criteria of spontaneity. One of these, of great importance, is known as the **entropy** (Greek: *change*) and is represented by the letter S; like the function E, i.e., the internal energy, it is a property that depends only on the state of a substance or system, and not on its previous history, as will be seen shortly. The actual entropy of a system is not easily defined, and it is more convenient, in the first place, to define the increase of entropy. Thus, *the increase of entropy dS in the course of an infinitesimal change is equal to δq_{rev}, the heat absorbed when the change is carried out in a reversible manner, divided by the absolute temperature T;* thus, by definition,

$$dS = \frac{\delta q_{\text{rev}}}{T}. \tag{8.1}$$

Although δq_{rev} is not an exact differential, it has a definite value for a reversible, isothermal change, and dS as defined by equation (8.1) is an *exact differential.* The entropy S of a system is thus a definite property of the system, depending only on its condition or state.

In order to express the entropy increase ΔS corresponding to a finite change in a system, it is necessary to integrate equation (8.1) between the limits of the initial state 1 and the final state 2; thus,

$$\Delta S = S_2 - S_1 = \int_{T_1}^{T_2} \frac{\delta q_{\text{rev}}}{T}, \tag{8.2}$$

where S_1 is the actual entropy value in the initial state and S_2 is that in the final state of the process. As stated above, the value of ΔS will depend only on the initial and final states of the system, and not on the nature of the connecting path; hence, the entropy change ΔS, which is equal to $S_2 - S_1$, will be the same *irrespective of whether the path from initial to final state is thermodynamically reversible or not.* However, to calculate the actual magnitude of ΔS, equation (8.2) requires the value of the heat absorbed in the *reversible* change, i.e., δq_{rev}. If the process is carried out irreversibly the heat absorbed is an indefinite and uncertain quantity which cannot be used for the determination of the entropy increase.

Since entropy is equal to a quantity of heat divided by the absolute temperature, the dimensions are energy × temperature^{-1}. It is the general practice to express the energy in calories, so that entropy is given in the units of calories per degree, i.e., cal deg^{-1}. This is sometimes referred to as an "entropy unit," and is represented by the symbol e. u. The entropy is an extensive property, in the sense defined in § 6c, and so its value depends upon the quantity of substance concerned; for this reason the amount of substance, usually 1 mole, should be stated.

In a reversible adiabatic process no heat enters or leaves the system (§ 6k) so that δq_{rev} is always zero. It follows, therefore, from equation (8.1) that the corresponding entropy change dS must be zero. The interesting result is thus obtained that *a reversible adiabatic process is associated with no change in entropy;* such processes are referred to as **isentropic.**

8d. Entropy Changes for an Ideal Gas.—For an ideal gas the integral in equation (8.2) can be evaluated and relatively simple expressions for ΔS can be obtained. According to equation (6.25), for a reversible process with an ideal gas in which only pressure-volume work is involved,

$$\delta q_{\text{rev}} = C_V dT + P dV. \tag{8.3}$$

For 1 mole of ideal gas P is equal to RT/V, so that

$$\delta q_{\text{rev}} = C_V dT + RT\frac{dV}{V}. \tag{8.4}$$

It follows, therefore, from equation (8.2), assuming C_V to be independent of temperature for an ideal gas, that for 1 mole of gas

$$\begin{aligned} \Delta S = S_2 - S_1 &= C_V \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V} \\ &= C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}. \end{aligned} \tag{8.5}$$

The entropy change for a process involving an ideal gas thus depends on the initial and final temperatures and volumes.

Since $P_1V_1 = RT_1$ for the initial state and $P_2V_2 = RT_2$ for the final state, it follows that V_2/V_1 is equal to T_2P_1/T_1P_2, and making this substitution in equation (8.5) leads to

$$\Delta S = S_2 - S_1 = C_V \ln \frac{T_2}{T_1} + R \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}. \tag{8.6}$$

According to equation (6.25), $C_V + R$ is equal to C_P, and hence for 1 mole of ideal gas

$$\Delta S = S_2 - S_1 = C_P \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}. \tag{8.7}$$

Three special cases are of particular interest. For an *isothermal process* there is no change of temperature, and hence T_1 is equal to T_2; equations (8.5) and (8.7) are then simplified to give

$$\Delta S_T = R \ln \frac{V_2}{V_1} = -R \ln \frac{P_2}{P_1}, \tag{8.8}$$

the subscript T in ΔS_T being used to indicate constant temperature. If V_2 is greater than V_1, that is, in an expansion process, ΔS_T will be positive, by equation (8.8); the isothermal expansion of an ideal gas is thus accompanied by an increase of entropy of the gas. Similarly, the isothermal compression of an ideal gas is associated with an entropy decrease.

The second case of interest is for an *isobaric* (or *constant pressure*) *process;* in this event, P_1 and P_2, are equal, so that equation (8.7) reduces to

$$\Delta S_P = C_P \ln \frac{T_2}{T_1}. \tag{8.9}$$

Increase of temperature at constant pressure is thus associated with a gain of entropy of the ideal gas.

The third case is for an *isochoric* (or *constant volume*) *process;* equation (8.5) then becomes

$$\Delta S_V = C_V \ln \frac{T_2}{T_1}. \tag{8.10}$$

8e. Entropy Changes at Constant Pressure or Constant Volume.—From equations (6.18) and (6.19), it is seen that

$$\delta q_P = C_P dT \qquad \text{and} \qquad \delta q_V = C_V dT,$$

where δq_P and δq_V have definite values, representing the heat absorbed in infinitesimal processes at constant pressure and constant volume, respectively. The entropy change under these specified conditions is therefore given by

$$dS_P = \frac{\delta q_P}{T} = C_P \frac{dT}{T} \tag{8.11}$$

and

$$dS_V = \frac{\delta q_V}{T} = C_V \frac{dT}{T}. \tag{8.12}$$

For an appreciable change of temperature from T_1 to T_2, *at constant pressure*, the corresponding entropy change is given by integration of equation (8.11) between the temperature limits; thus,

$$\Delta S_P = \int_{T_1}^{T_2} C_P \frac{dT}{T} = \int_{T_1}^{T_2} C_P d \ln T. \tag{8.13}$$

A similar expression, involving C_V, can be obtained for a temperature change occurring at constant volume by integration of equation (8.12). *These equations are of general applicability; they are independent of whether the system under consideration consists of solid, liquid or gas,* for no assumption concerning its nature has been made in deriving equation (8.13) or its analogue for constant volume.

The exact evaluation of the integral in equation (8.13) is possible either if C_P is independent of temperature, or if its variation with temperature is known; in these cases it is a relatively simple matter to determine the entropy increase for a temperature change. The former condition holds for an ideal (monatomic) gas, and then equation (8.13) reduces to the same form as (8.9), viz.,

$$\Delta S_P = C_P \ln \frac{T_2}{T_1}. \tag{8.14}$$

If the heat capacity can be expressed as a function of the absolute temperature (§ 7i), the integration can be carried out in the usual manner. An alternative, approximate, possibility is to take a mean value of C_P in the temperature range T_1 to T_2 and to assume that this remains constant; the entropy change of the gas may then be obtained from equation (8.14).

Example: The molar heat capacity at constant pressure of ammonia gas is expressed by $C_P = 6.189 + 7.887 \times 10^{-3}T - 7.28 \times 10^{-7}T^2$ cal deg^{-1} mole^{-1}. Calculate the increase of entropy when 1 mole of ammonia is heated from 25° to 125°C at constant pressure.

Insertion of the value for C_P in equation (8.13), with T_1 equal to $273 + 25 = 298$°K, and $T_2 = 273 + 125 = 398$°K, gives

$$\begin{aligned}\Delta S_P &= \int_{298}^{398} \left(\frac{6.189}{T} + 7.887 \times 10^{-3} - 7.28 \times 10^{-7}T\right) dT \\ &= 6.189 \ln \tfrac{398}{298} + 7.887 \times 10^{-3}(398 - 298) - 3.64 \times 10^{-7}\{(398)^2 - (298)^2\} \\ &= 2.52 \text{ cal deg}^{-1} \text{ mole}^{-1}.\end{aligned}$$

The change of entropy with temperature at constant pressure can be determined by graphical integration. This method is particularly useful for solids and liquids, because the variation of the heat capacity cannot be expressed as a simple function of the temperature, especially at low temperatures. The experimental values of C_P/T for a number of temperatures are plotted against T, as in Fig. 8.1, or, alternatively, C_P is plotted against $\ln T$. Then, according to equation (8.13), the area under the curve between the temperature ordinates from T_1 to T_2 (or $\ln T_1$ to $\ln T_2$) gives the entropy increase ΔS_P accompanying the temperature change at constant pressure.

8f. Entropy Change Accompanying Change of Phase.—When a substance undergoes a change of phase, e.g., solid to liquid or liquid to vapor, there is an absorption of heat and consequently a change of entropy. Both fusion and vaporization may be carried out reversibly (§ 6f) and the heat taken up, at constant pressure, is equal to the normal heat of fusion or vaporization at the given temperature. The corresponding entropy changes are then obtained by dividing the heat absorbed by the (constant) temperature at which the change of phase occurs. For most purposes the values are required at the melting point and boiling point at atmospheric pressure, and hence the molar entropy of fusion is given by

$$\Delta S_f = \frac{L_f}{T_f}, \tag{8.15}$$

where L_f is the molar heat of fusion, and T_f is the freezing (or melting) point on the absolute scale. Similarly, the molar entropy of vaporization is represented by

$$\Delta S_v = \frac{L_v}{T_b}, \tag{8.16}$$

where L_v is the molar heat of vaporization and T_b is the normal boiling point. Since heat is absorbed in both fusion and vaporization, that is to say, since both L_f and L_v are positive, these processes are accompanied by an increase of entropy. Conversely, the freezing of a liquid and the condensation of a vapor, for which the L values are negative, are accompanied by a decrease of entropy. The entropy of a liquid is therefore greater than that of the solid with which it is in equilibrium at the melting point, and that of the vapor is greater than for the liquid at the boiling point.

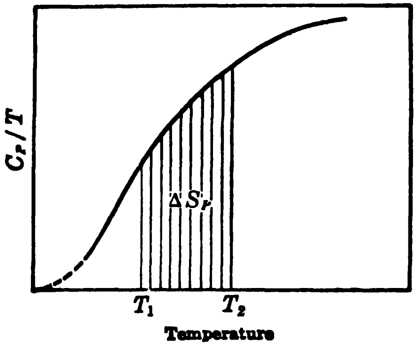

FIG. 8.1. Determination of entropy change

Transition from one crystalline form to another is also associated with a reversible heat change, and hence with a change of entropy. The entropy of transition is equal to the heat of transition L_t divided by the transition temperature T_t on the absolute scale, i.e., $\Delta S_t = L_t/T_t$. If, as a result of changing the temperature, there is an alteration in the phase or crystalline form of the substance whose entropy is being studied, due allowance for this must be made in the calculations for the entropy of fusion, vaporization or transition, as the case may be.

Example: Calculate the increase of entropy when 1 mole of ice at 0°C is heated until it forms steam at 100°C at a constant pressure of 1 atm. The molar heat of fusion of ice at 0° is 1436 cal and the molar heat of vaporization of water at 100° is 9720 cal. The mean specific heat of liquid water may be taken as 1.0 cal deg^{-1} g^{-1}.

The entropy of fusion ΔS_f at 0°C, i.e., 273°K, is 1436/273 = 5.26 cal deg^{-1} mole^{-1}. The increase of entropy accompanying the increase in the temperature of the water from 0° to 100°C, i.e., from 273° to 373°K, is given by equation (8.14); since the specific heat of water is 1.0, the molar heat capacity is 18.0,

$$\Delta S = 18.0 \ln \tfrac{373}{273} = 18.0 \times 2.303 \log \tfrac{373}{273}$$

$$= 5.62 \text{ cal deg}^{-1} \text{ mole}^{-1}.$$

Finally, there must be added the entropy of vaporization at 100°C, i.e., 373°K; this is 9720/373 = 26.06 cal deg^{-1} mole^{-1}. The total entropy increase is thus

$$5.26 + 5.62 + 26.06 = 36.94 \text{ cal deg}^{-1} \text{ mole}^{-1}.$$

8g. Entropy Change in Spontaneous (Irreversible) Processes.—The problem of immediate interest is to determine the nature of the entropy change for a spontaneous, i.e., thermodynamically irreversible, process. For this purpose a simple case will be considered, namely, a system consisting of an ideal gas. This is allowed to expand *spontaneously* into a vacuum at constant temperature; as stated in § 6i, no heat is evolved or absorbed in this process. Consequently no heat is supplied to or removed from the surroundings, and hence the entropy of the latter remains unchanged. However, the entropy of the system, i.e., the gas, increases, because its volume has increased, e.g., from V_1 to V_2, in the expansion. It has been stated previously that the entropy depends only on the temperature and pressure (or volume) of the system, and not on its previous history. The fact that the volume of the ideal gas has increased from V_1 to V_2, at the temperature T, means that the entropy has increased by an amount given by equation (8.8), viz.,

$$\Delta S = R \ln \frac{V_2}{V_1}. \tag{8.17}$$

The total increase of entropy of the *system and its surroundings* is thus equal to ΔS, as represented by equation (8.17), since the entropy change of the surroundings is zero in this case. Since V_2 is greater than V_1, it follows that ΔS is positive, and hence *the spontaneous (thermodynamically irreversible) isothermal expansion of the gas is accompanied by an increase of entropy of the system and its surroundings.*

The isothermal expansion of the gas from V_1 to V_2 could have been carried out infinitesimally slowly and reversibly by allowing it to push back a frictionless piston, the external pressure being adjusted so as to be always less than that of the gas by an extremely small amount (§ 6g). In this case the gas does external work and so a quantity of heat q is absorbed from the surroundings. Since this is taken up reversibly the gain of entropy of the system is equal to q/T. The heat lost by the surroundings, also at the temperature T, is equal to q, and hence the decrease of entropy of the surroundings is q/T. *The total entropy change of the system and surroundings in the reversible process is thus zero.* The results derived above by considering the expansion of an ideal gas are completely general; *a spontaneous (thermodynamically irreversible) process is always accompanied by an increase of entropy of the system and its surroundings, but for a thermodynamically reversible change the entropy remains unaltered.*

Example: One mole of liquid water at 100°C is placed in a thermostat maintained at 25°C. Calculate the net entropy change in the spontaneous (thermodynamically irreversible) process which occurs. The molar heat capacity of liquid water may be taken as having the constant value 18.0 cal deg^{-1}.

The entropy change of the water will be the same as for the process performed reversibly; hence by equation (8.14)

$$\Delta S(\mathrm{H_2O}) = C_P \ln \frac{T_2}{T_1} = 18.0 \times 2.303 \log \frac{298}{373} = -3.29 \text{ e. u.}$$

The entropy change of the thermostat will be given by

$$\Delta S(\text{thermostat}) = \frac{q}{T} = \frac{18.0 \times (100 - 25)}{298} = +4.53 \text{ e. u.}$$

The net entropy change is $-3.29 + 4.53 = +1.24$ e. u. (It is of interest to note that the entropy of the system, i.e., the water, decreases in this particular spontaneous process, but the total entropy of the system and surroundings increases.)

Consider a system subjected to an irreversible process at constant temperature T; let q_{irr} represent the heat absorbed by the system from the surroundings in the course of this process. The increase of entropy of the system, represented by ΔS, is the same, irrespective of whether the process is carried out reversibly or not, for the entropy depends only on the state of the system and not on how that state is attained. The entropy change of the surroundings may be determined by supposing them to be restored reversibly to their original state. This can be achieved by supplying the quantity of heat q_{irr} *in a reversible manner* at the temperature T, i.e., by increasing the entropy by q_{irr}/T. The entropy change of the surroundings in the process under consideration must therefore be the negative of this value, namely $-q_{\text{irr}}/T$. As the process is irreversible, there must be a net increase in the entropy of the system and its surroundings, so that

$$\Delta S - \frac{q_{\text{irr}}}{T} > 0,$$

$$T\Delta S > q_{\text{irr}}. \tag{8.18}$$

For a thermodynamically irreversible process at constant temperature, therefore, *the heat absorbed by the system is less than the product of the temperature and the entropy increase.* For a reversible process the two quantities would, of course, be equal, i.e.,

$$T\Delta S = q_{\text{rev}}. \tag{8.19}$$

When considering an infinitesimal stage of a process, the foregoing results *for the system alone* may be generalized in the expression

$$TdS \geq \delta q, \tag{8.20}$$

where the "greater than" sign refers to an irreversible (spontaneous) process, and the "equal to" sign applies to a thermodynamically reversible (equilibrium) one. This conclusion is of the greatest importance, as will be seen later (§ 9b); by the use of equation (8.20) it is possible to derive relatively simple rules for determining whether a given process can occur spontaneously or not.

8h. The Physical Significance of Entropy.—Although a precise physical interpretation of entropy cannot be given easily, it is nevertheless possible to obtain an indication of its significance in a relatively simple manner. A characteristic of spontaneous processes is that they are accompanied by an increase in the "disorder" or "chaos" of the system. In the metal bar which is hot at one end and cold at the other, there is some sort of order, in so far as most of the high energy (hot) molecules are segregated at one end, while the low energy (colder) molecules are largely at the other end of the bar. As a result of the spontaneous conduction of heat, there is a uniform distribution of energy throughout. The state of partial molecular order has spontaneously become one of greater disorder. The same type of change, from order to disorder, occurs when one gas diffuses into another, when a concentrated solution diffuses into pure water, when a gas expands into a vacuum, and so on for other spontaneous processes. Since all such processes are accompanied by an increase of entropy, it is possible to regard the entropy as a measure of the disorder, chaos or random arrangement of the molecules of a system.

It has been seen, for example, that fusion and evaporation are both associated with an increase of entropy of the substance concerned; in each instance there is a decrease of order. In the solid the atoms, ions or molecules are arranged in a regular manner in the crystal lattice; upon melting most of the order is destroyed, and vaporization results in a further increase of disorder. Increase of temperature of a gas at constant pressure and increase of volume at constant temperature are both processes for which the entropy of the gas is increased; in each case the molecular chaos is increased. Lowering the temperature of a solid results in a decrease of entropy as the molecules or atoms become more and more ordered in their space lattices. In fact, it appears, as will be seen in Chapter 10, that at the absolute zero of temperature, when the order is probably perfect, the entropy of most pure solids is actually zero. The correlation of increase of entropy with increase of disorder is not restricted to physical processes; it is applicable also to chemical changes, although it is not always immediately obvious in such cases.

Since spontaneous processes lead to increasing disorder, it is evident that a disordered state is more probable than one of partial or complete order, for a spontaneous change will obviously occur from a less probable to a more probable state. It is to be expected, therefore, that there might be a connection between entropy, which increases in a spontaneous process, and the probability of the state, which increases at the same time. Considerations of this kind led L. Boltzmann (1896) to put forward the equation

$$S = k \ln W + \text{constant},$$

relating the *actual entropy* S of a system to its **thermodynamic probability** W, where k is the Boltzmann constant, i.e., the gas constant per single molecule. The thermodynamic probability of a system was defined as the ratio of the probability of the actual state to that in which there is complete order, for the same energy and volume. In 1912, M. Planck suggested that the undetermined constant in equation (8.21) should be zero, so that

$$S = k \ln W. \qquad (8.22)$$

In a completely ordered arrangement, as might exist in a solid at the absolute zero, W would be unity and S would be zero; this is apparently the case for most crystalline solids (§ 36a). It may be mentioned that in modern quantum mechanics, equation (8.22) is retained in form, but the symbol W takes on a somewhat modified significance; some aspects of this subject are treated in § 36c.

8i. Efficiency of Reversible Cycle.—Before proceeding to the development of new thermodynamic properties, the idea of entropy will be used to derive an expression for the maximum efficiency of an engine for the conversion of heat into work. In order that such an engine may function continuously, it must operate in **cycles**, *a cycle or cyclic process being a succession of changes as a result of which the system returns to its original state*, all properties of the system, therefore, assuming their original values. The internal energy change ΔE in a complete cycle is evidently equal to zero, and hence the resultant work done in the cycle must be equal to the net heat absorbed. Since maximum work can be obtained from a process only when it is carried out reversibly, it is apparent that the maximum efficiency for the conversion of heat into work is obtainable from a reversible cycle.

A useful cycle consists of several steps involving, as a general rule, both isothermal and adiabatic processes, none of which is retraced during the cycle. Temperature changes are thus a characteristic of useful cycles. It was demonstrated by S. Carnot (1824) that *all engines operating in reversible cycles between the same two temperatures must have identical efficiencies*. Consequently, any convenient thermodynamically reversible cycle can be chosen and its efficiency calculated; the result will then be applicable to all other reversible cycles.

A convenient form of cycle for purposes of calculation is that known as the **Carnot cycle**; the system is an ideal gas, and it is subjected to a series of reversible changes in the following manner:

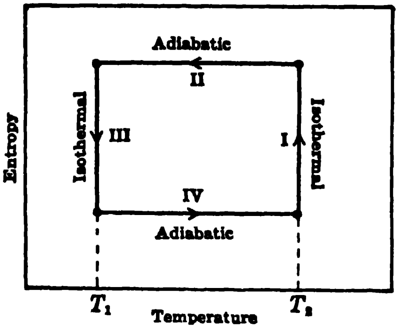

FIG. 8.2. The Carnot cycle

I. The gas is expanded isothermally and reversibly at the higher temperature T_2; this is accompanied by an absorption of heat q_2 from the "source," so that the entropy change of the gas is q_2/T_2.

II. The next stage is a reversible adiabatic expansion which results in a fall of temperature from T_2 to that of the "sink," viz., T_1. Since the change is adiabatic the entropy of the gas remains constant and ΔS is zero.

III. The gas is now compressed isothermally and reversibly at the lower temperature T_1; there is a liberation of heat q_1 to the "sink." The entropy change of the gas in this stage is $-q_1/T_1$.

IV. A final reversible adiabatic compression results in a return of the gas to its original temperature T_2. The entropy change of the gas in this process is again zero.

As a result of these four reversible stages the cycle has been completed, as shown diagrammatically in Fig. 8.2. Since the heat q_2 was taken up by the working substances at the higher temperature, when q_1 was evolved at the lower temperature, the net heat absorbed is $q_2 - q_1$, and this must represent the work w done in the reversible cycle. The efficiency of the engine is the fraction of the heat taken in at the higher temperature that is converted into work; that is,

$$\text{Efficiency} = \frac{w}{q_2} = \frac{q_2 - q_1}{q_2}. \tag{8.23}$$

Since the total entropy change of the gas for the complete cycle is zero, and since the entropy changes in stages II and IV are zero, the sum of the changes in stages I and III must also be zero; thus,

$$\frac{q_2}{T_2} - \frac{q_1}{T_1} = 0 \quad \text{or} \quad \frac{q_2}{T_2} = \frac{q_1}{T_1},$$

and hence from equation (8.23),

$$\text{Efficiency} = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}. \tag{8.24}$$

The efficiency of a reversible engine, which is the maximum possible efficiency, is thus determined by the temperatures of both the "source" and the "sink"; the greater the difference between these temperatures the greater is the efficiency of the cycle. This is one of the reasons why "superheated" steam, at high pressure, is frequently employed in steam turbines. It will be noted, incidentally, from equation (8.24) that, for the complete conversion of heat into work in the cycle, that is, for the efficiency to be unity, it would be necessary for the temperature T_1 of the "sink" to be the absolute zero.

Example: Compare the maximum efficiencies of reversible engines in which the working substances are (i) water, (ii) mercury, the temperatures of the sources being the respective boiling points at 1 atm pressure, viz., 100°C and 357°C. The temperature of the sink is 25°C in each case.

(i) For the engine using water vapor, T_1 is $273 + 100 = 373$°K, and T_2 is $273 + 25 = 298$°K; hence,

$$\text{Efficiency} = \frac{T_2 - T_1}{T_2} = \frac{373 - 298}{373} = 0.201.$$

(ii) For the mercury engine, T_2 is $273 + 357 = 630$°K, and T_1 is 298°K; hence,

$$\text{Efficiency} = \frac{T_2 - T_1}{T_2} = \frac{630 - 298}{630} = 0.527.$$

For a cycle involving an irreversible stage (or stages) the efficiency is less than that given by equation (8.24). In actual practice, of course, no engine can be completely reversible; for one thing, the processes are not carried out infinitesimally slowly, as would be necessary, and for another, irreversible effects, such as friction, cannot be eliminated.

The suggestion was made by W. Thomson (Lord Kelvin) that a thermodynamic temperature scale be defined in such a manner that the actual temperature is proportional to the quantity of heat taken up or given out by the working substance in the isothermal stages of a reversible cycle. Provided the degree is taken as equal to the Celsius degree, the thermodynamic scale is identical with the usual absolute temperature scale based on the volume of an ideal gas (§ 2c). It is for this reason that absolute temperatures are now generally referred to as "degrees Kelvin" and are represented by the symbol °K.

FREE ENERGY

9a. Free Energy and Maximum Work Functions.—Although the entropy is a fundamental thermodynamic property having important significance, it is more convenient for practical purposes to define certain other functions which may be used, in place of entropy, to express the conditions for spontaneous processes. These functions are represented by A and F, and although they have definite physical meanings, as will be seen shortly, they may be expressed, for the present, by the equations

$$A = E - TS \tag{9.1}$$

$$F = H - TS, \tag{9.2}$$

where, as before, E is the internal energy, and H, equal to $E + PV$ (§ 6e), is the enthalpy. Since E, H, T and S are thermodynamic variables, in the sense defined in § 6c, A and F also belong in this category, and changes in these variables, i.e., ΔA and ΔF, are independent of the path of the process.

Let A_1, E_1 and S_1 represent the values of these three functions in a particular state at the temperature T_1; then, from equation (9.1),

$$A_1 = E_1 - T_1S_1. \tag{9.3}$$

Suppose an appreciable change takes place, so that the new values of the functions are A_2, E_2 and S_2, at the temperature T_2; then,

$$A_2 = E_2 - T_2S_2, \tag{9.4}$$

and subtraction of equation (9.3) from (9.4) gives

$$A_2 - A_1 = E_2 - E_1 - (T_2S_2 - T_1S_1)$$

or

$$\Delta A = \Delta E - \Delta(TS).$$

At constant temperature this becomes

$$\Delta A = \Delta E - T\Delta S. \tag{9.5}$$

In exactly the same manner, equation (9.2) leads to

$$\Delta F = \Delta H - \Delta(TS),$$

so that, at constant temperature,

$$\Delta F = \Delta H - T\Delta S. \tag{9.6}$$

It was seen in § 6e that, at constant pressure,

$$\Delta H = \Delta E + P\Delta V, \tag{9.7}$$

and hence, from equations (9.5), (9.6) and (9.7),

$$\Delta F = \Delta A + P\Delta V, \tag{9.8}$$

for a process at constant temperature and pressure.

The equations (9.5) and (9.6) express the changes in A and F in terms of the quantities ΔE, ΔH and ΔS whose significance has been already considered. It will now be shown that ΔA and ΔF have themselves a simple physical interpretation. For a *thermodynamically reversible process* taking place at the *constant temperature* T, the increase of entropy is given by

$$\Delta S = \frac{q_{\text{rev}}}{T},$$

where q_{rev} is the heat absorbed. If this value for ΔS is substituted in equation (9.5), the result is

$$\Delta A = \Delta E - q_{\text{rev}}. \tag{9.9}$$

By the first law of thermodynamics [equation (6.2)],

$$-w_{\text{rev}} = \Delta E - q_{\text{rev}},$$

and comparison with equation (9.9) shows immediately that

$$w_{\text{rev}} = -\Delta A. \tag{9.10}$$

Since a reversible, isothermal process has been postulated, w_{rev} is the maximum work that can be obtained from the system in the given change; hence, $-\Delta A$, i.e., the decrease in the A function, is equal to the maximum work obtainable. For this reason the property A is called the **maximum work function** or, briefly, the **work function.**

The function F, which is much more important from the standpoint of chemistry, is generally known as the **free energy,** although other descriptions have been used. If ΔA in equation (9.8) is replaced by its equivalent, $-w_{\text{rev}}$, it is seen that *at constant temperature and pressure*

$$-\Delta F = w_{\text{rev}} - P\Delta V. \tag{9.11}$$

The quantity $P\Delta V$ is the work of expansion done against the external pressure, and so $-\Delta F$ represents *the maximum work at constant temperature and pressure other than that due to a volume change.* The quantity $w_{\text{rev}} - P\Delta V$ is thus sometimes called the **net work,** and so the decrease $-\Delta F$ in the free energy of a system is equal to the net work obtainable (at constant temperature and pressure) from the system under reversible conditions. An important form of net work, since it does not involve external work due to a volume change, is electrical work. Consequently, a valuable method for determining the free energy change of a process is to carry it out electrically, in a reversible manner, at constant temperature and pressure (§ 47a).

Useful expressions relating to the variation of free energy with temperature or pressure are obtained in the following manner. Since H is equal to $E + PV$, by definition, equation (9.2) may be written

$$F = E + PV - TS, \tag{9.12}$$

and upon differentiation it is seen that

$$dF = dE + PdV + VdP - TdS - SdT. \tag{9.13}$$

By the first law of thermodynamics, $\delta q = dE + \delta w$; if the restriction is applied of assuming that the work δw is due only to a volume change, then

$$\delta q = dE + PdV.$$

If, for the present, it is assumed that the process is reversible, P is the pressure of the system, as in equation (9.13), and, further, $\delta q/T$ is equal to dS, so that δq may be replaced by TdS, giving

$$TdS = dE + PdV. \tag{9.14}$$

Combination of equations (9.13) and (9.14) then yields the result

$$dF = VdP - SdT. \tag{9.15}$$

Two special conditions may be applied to equation (9.15); first, *at constant pressure*, dP is zero, so that

$$dF = -SdT \tag{9.16}$$

or, alternatively,

$$\left(\frac{\partial F}{\partial T}\right)_P = -S. \tag{9.17}$$

Second, *at constant temperature*, dT is zero, and hence from equation (9.15),

$$dF = VdP, \tag{9.18}$$

that is,

$$\left(\frac{\partial F}{\partial P}\right)_T = V. \tag{9.19}$$

For an appreciable process taking place at constant temperature, integration of equation (9.18) or (9.19), between the initial pressure P_1 and the final pressure P_2, gives

$$F_2 - F_1 = \Delta F = \int_{P_1}^{P_2} VdP. \tag{9.20}$$

Since the free energy of a system depends only on its state, the value of ΔF given by equation (9.20) will hold for any change of pressure from P_1 to P_2, irrespective of whether it is reversible or not. The only conditions are that the temperature is constant and that all the work done is due to the volume change accompanying the change of pressure.

In order to evaluate the integral in equation (9.20), the volume may be expressed as a function of the pressure; a particularly simple case is that of an ideal gas, for which V is equal to RT/P per mole. In this instance equation (9.20) becomes

$$\Delta F = RT \int_{P_1}^{P_2} \frac{dP}{P}, \tag{9.21}$$

since R and T are constant. It follows, therefore, that for 1 mole of an ideal gas undergoing a change of pressure at constant temperature,

$$\Delta F = RT \ln \frac{P_2}{P_1}. \tag{9.22}$$

For n moles of ideal gas the free energy change would be n times as great as given by equation (9.22).

9b. Conditions of Spontaneous Change and Equilibrium.—By combining the result of § 8g, as expressed by equation (8.20), i.e., $TdS \geq \delta q$, with the first law relationship $\delta q = dE + PdV$, when the work δw is external work due to a volume change, it follows that, *for the system*,

$$TdS \geq dE + PdV, \tag{9.23}$$

where, as before, the "greater than" sign applies to an irreversible (spontaneous) process and the "equal to" sign refers to a reversible process, i.e., an equilibrium state. If equation (9.23) is now introduced into (9.13), it is seen that

$$dF \leq VdP - SdT. \tag{9.24}$$

Hence, at constant temperature and pressure, i.e., when dT and dP are both zero, it follows from equation (9.24) that

$$(\partial F)_{T,P} \leq 0, \tag{9.25}$$

where the "less than" sign now refers to the spontaneous process. For an appreciable process, equation (9.25) may be written in the form

$$(\Delta F)_{T,P} \leq 0. \tag{9.26}$$

It is seen from equation (9.26) that for any process, physical or chemical, to take place spontaneously, at a definite temperature and pressure, the increase of free energy must be less than zero, that is to say, it must be negative. In other words, *a spontaneous process at constant temperature and pressure is accompanied by a decrease of free energy of the system*, provided the work involved is only work of expansion. For a thermodynamically reversible process taking place under the same conditions there is no change in the free energy. From the aspect of physical chemistry, the foregoing conclusions represent some of the most important results derived from the second law of thermodynamics. They provide the most useful solution to the problem presented at the beginning of this chapter, namely that of foretelling the conditions under which a reaction will occur spontaneously.

Attention should be drawn to the fact that, although the basic thermodynamic criterion of a spontaneous reaction (§ 8g) is that the entropy of the *system and surroundings* should increase, it has been converted into a more practical form involving the change in free energy of the *system alone* at constant temperature and pressure. It is because this quantity can frequently be determined relatively easily that it is usually the more convenient function to employ, e.g., for chemical reactions and phase changes taking place at constant temperature and pressure. It is possible from equation (9.23) to derive an expression analogous to equation (9.26), namely,

$$(\Delta S)_{E,V} \geq 0,$$

for the system alone, but this has little or no practical value in physical chemistry. One reason is that processes of interest are generally not performed under conditions of constant energy and volume.

As long as the physical conditions are not altered, a system in equilibrium is never observed spontaneously to depart from equilibrium; *the free energy of the system must then be a minimum, at the given temperature and pressure*, for it is apparently unable to decrease further. In accordance with the mathematical properties of a minimum, *a small change in the equilibrium system, at constant temperature and pressure, should leave the free energy unaltered*, i.e., for such a change ΔF is zero. This is in agreement with equation (9.26) that for a thermodynamically reversible process, which is actually a succession of equilibrium states, ΔF is zero at constant temperature and pressure.

9c. Phases in Equilibrium: The Clapeyron-Clausius Equation.—The chemical applications of the results given above will be considered more fully in Chapter 10, but it is of interest here to show how they may be utilized to derive an equation, first obtained by B. P. E. Clapeyron (1834) and later developed by R. Clausius (1850), which will be used in the next chapter. Consider any two phases of the same substance, e.g., liquid and vapor, or solid and liquid, in equilibrium with one another at a temperature T and pressure P. By supplying or withdrawing heat very slowly from the system, it is possible to change one phase reversibly into another, e.g., liquid into vapor, the system remaining at equilibrium all the time. In accordance with equation (9.26), since the only work done will be due to a possible change of volume, the free energy change ΔF will be zero, in spite of the change from one phase to another. It follows, therefore, that *equal amounts of a given* *substance must have exactly the same free energy in two phases at equilibrium.*[*] If F_A and F_B are the free energies per mole of the substance in the two phases, indicated by A and B, respectively, at the equilibrium temperature and pressure, then

$$F_A = F_B. \tag{9.27}$$

If the temperature is changed, the pressure must be altered correspondingly if the system is to stay in equilibrium. Suppose the original temperature T is raised to $T + dT$; the equilibrium pressure will then be increased from P to $P + dP$. At the same time the free energy per mole of phase A will become $F_A + dF_A$, while that of phase B will be $F_B + dF_B$. Since the system is in equilibrium at the new temperature and pressure, the free energies per mole of each phase must still be equal; hence,

$$F_A + dF_A = F_B + dF_B. \tag{9.28}$$

It follows, therefore, from equations (9.27) and (9.28) that

$$dF_A = dF_B. \tag{9.29}$$

For an infinitesimal change occurring under such conditions that the only work is due to a volume change, as is true for the type of process under consideration, equation (9.15) is applicable. It is thus possible to write

$$dF_A = V_A dP - S_A dT$$

and

$$dF_B = V_B dP - S_B dT,$$

where V_A and V_B are the molar volumes, and S_A and S_B are the molar entropies of the two phases. Since dF_A is equal to dF_B, by equation (9.29), it follows that

$$V_A dP - S_A dT = V_B dP - S_B dT,$$

and hence,

$$\frac{dP}{dT} = \frac{S_B - S_A}{V_B - V_A}. \tag{9.30}$$

The quantity $S_B - S_A$ is the entropy change accompanying the change of phase; if B is the phase which tends to be formed as the temperature is raised, then,

$$S_B - S_A = \frac{L}{T}, \tag{9.31}$$

where L is the heat absorbed per mole in the phase change, e.g., the molar heat of vaporization, fusion, sublimation or transition. Substitution of equation (9.31) in (9.30) then gives the general form of the **Clapeyron-Clausius equation**

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[*] This important result can be extended to a system of several phases consisting of more than one substance; the partial molar free energy, or chemical potential, of each substance is the same in all the phases at equilibrium (§ 37c).

$$\frac{dP}{dT} = \frac{L}{T(V_B - V_A)}. \tag{9.32}$$

In accordance with its deduction, equation (9.32) is applicable to the equilibrium between two phases of any substance, e.g., liquid and vapor, solid and liquid, solid and vapor, or two crystalline forms of a solid. In each case V_B is the molar volume of the phase which tends to be formed as the temperature is raised, and V_A is the value for the phase that exists at lower temperatures; L is the heat absorbed when 1 mole of the latter is converted into the former at the temperature T. An expression of the form of equation (9.32) can be used to describe the behavior of any univariant system, i.e., a system controlled by one independent variable (§ 37b). If P is specified, T is automatically determined for the given univariant system, and vice versa.

9d. The Gibbs-Helmholtz Equation.—Apart from questions relating to the criteria of equilibria and of spontaneous processes, a number of valuable results can be derived from the second law of thermodynamics. One of these is the Gibbs-Helmholtz equation, which is applicable to any physical or chemical change. Suppose F_1 is the free energy of a system in its initial state at the temperature T, and let $F_1 + dF_1$ be the value at the temperature $T + dT$. Similarly, suppose the free energy of the final state, after the change has occurred, is F_2 at the temperature T, and $F_2 + dF_2$ at the temperature $T + dT$. For a change taking place at constant pressure, equation (9.16) is applicable, so that

$$dF_1 = -S_1dT \quad \text{and} \quad dF_2 = -S_2dT,$$

where S_1 and S_2 are the entropies of the system in the initial and final states of the process. Subtraction of dF_1 and dF_2 then gives

$$d(F_2 - F_1) = -(S_2 - S_1)dT,$$

and writing ΔF for $F_2 - F_1$, the increase of free energy accompanying the process, and ΔS for $S_2 - S_1$, the corresponding entropy increase, it follows that

$$d(\Delta F) = -\Delta S dT.$$

Since constant pressure has been assumed, this result can be written as

$$\left(\frac{\partial(\Delta F)}{\partial T}\right)_P = -\Delta S, \tag{9.33}$$

with the subscript P to indicate constant pressure. If this expression for ΔS is substituted in equation (9.6) the result is

$$\Delta F = \Delta H + T\left(\frac{\partial(\Delta F)}{\partial T}\right)_P, \tag{9.34}$$

which is a form of the important **Gibbs-Helmholtz equation,** deduced by J. Willard Gibbs (1887) and by H. von Helmholtz (1882). The value of this equation lies in the fact that it can be used to calculate the enthalpy change ΔH in a reaction from a knowledge of the free energy change ΔF and its variation with temperature at constant pressure. Some practical applications of the Gibbs-Helmholtz equation will be considered in § 47a.

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PROBLEMS

1. A 500 watt heater is required to maintain the temperature of a thermostat at 70°C when the surrounding temperature is 20°C. After operating for one hour, what is the entropy change in (*a*) the heater, (*b*) the thermostat, (*c*) the surroundings?

2. Three moles of an ideal, monatomic gas, initially at 27°C and 20 atm pressure, expand to a final pressure of 2 atm. Calculate ΔS, ΔA and ΔF if the process is performed (*a*) reversibly and isothermally, (*b*) by expansion into a vacuum.

3. Evaluate $\left(\frac{\partial T}{\partial S}\right)_P$ and $\left(\frac{\partial T}{\partial S}\right)_V$

4. Calculate the change in entropy when 100 g of water at 100°C are mixed under adiabatic conditions and at constant atmospheric pressure with (*a*) 100 g of water at 0°C, (*b*) 100 g of ice at 0°C. The mean specific heat of water may be taken as 1.00 cal g^{-1} and the heat of fusion as 1436 cal mole^{-1}

5. (*a*) Calculate the change in entropy when one mole of oxygen at 25°C and 1 atm pressure expands isothermally to three times its initial volume. (*b*) Determine the change in entropy when two moles of hydrogen and one mole of oxygen, each at 25°C and 1 atm pressure, are mixed. (*c*) The mixture is exploded and the temperature and pressure of the product are adjusted to the original values of the reactants; calculate the enthalpy change of the reaction.

6. Show that $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$. Calculate the change in entropy for the isothermal compression of 50 g of oxygen at 300°K from 5 to 25 atm using (*a*) the ideal gas law, (*b*) the van der Waals equation.

7. Calculate ΔS, ΔA and ΔF for the vaporization of two moles of benzene at its boiling point 80.2°C. The latent heat of vaporization of benzene is 101 cal g^{-1}.

8. Calculate ΔS, ΔA and ΔF for the conversion of one mole of water at 100°C to steam at 100°C and 0.5 atm pressure.

9. A substance melts at -100°C and boils at 0°C. What information is required to enable calculation of the change in entropy in heating the substance from 0°K to 25°C? Express ΔS in the form of an equation.

10. Determine ΔS when 2 moles of $SO_2(g)$ undergo a change of state from 25°C and 1 atm to 325°C and 20 atm pressure. $C_P = 6.077 + 23.54 \times 10^{-3}T - 9.69 \times 10^{-6}T^2$.

11. The difference in entropy of water at 200°C and 0°C is 0.5567 cal deg^{-1} g^{-1}. Determine the energy necessary to heat 2 moles of water from 0° to 200°C.

12. (*a*) Calculate the theoretical efficiency of a mercury vapor engine operating at a boiler pressure of 1 atm and a condenser at 20°C. (*b*) What would be the efficiency of a steam engine operating under the same conditions?

13. For the reaction $Pb(c) + 2AgCl(c) = PbCl_2(c) + 2Ag(c)$ at 25°C and 1 atm pressure, $\Delta F = -22.60$ kcal and this value increases by 8.58 cal deg^{-1}. (*a*) Calculate ΔH for the reaction of 1 kg of lead at 25°. (*b*) Compare this result with the value calculated by applying the first law. $\Delta Hf^0 = -85.85$ kcal for $PbCl_2$.

14. Diphenyl (mp 70°, bp 254°C) and sodium (mp 97.8°, bp 883°C) have been suggested as working substances in a heat engine. Starting at the same maximum operating temperature, which would be more efficient?

15. A refrigerator is essentially a heat engine in reverse, heat being removed at a lower temperature and transferred to a higher temperature by the expenditure of work. How much work must be performed to freeze 1 kg of ice cubes (*a*) on a cool day (room temperature 15°C), (*b*) on a hot day (room temperature 35°C), (*c*) what is the change in entropy of the water, (*d*) of the room?

16. Show that $dH = TdS + VdP$ and $dE = TdS - PdV$.

17. Determine the change in free energy for the conversion of two moles of benzene liquid to vapor at 1 atm pressure (*a*) at the bp 80.1°C, (*b*) at 40°C. The vapor pressure of benzene at 40° is 182.7 mm.

18. Evaluate $\left(\frac{\partial T}{\partial P}\right)_S$ for an ideal gas.

19. Trouton's law states that for many liquids the entropy of vaporization at the boiling point is approximately 21 cal $mole^{-1}$. Estimate the heat of vaporization per gram of chloroform at its bp 61.2°C. The experimental value is 58.8 cal g^{-1}.

20. The vapor pressure of ice at -10°C is 1.950 mm and of supercooled water at the same temperature 2.149 mm. Calculate ΔF for the conversion of two moles of supercooled water to ice at -10°C and constant atmospheric pressure.

21. A gasoline engine operates ideally on an Otto cycle, which consists of the following reversible stages: (1) an adiabatic compression, (2) an isochoric increase in

temperature and pressure, (3) an adiabatic expansion, and (4) an isochoric decrease in temperature and pressure to the initial state. (*a*) Plot these changes on a P-V diagram and a T-S diagram. (*b*) Show that the efficiency $\frac{w}{q} = 1 - \frac{1}{(V_1/V_2)^{\gamma-1}}$ where q is the energy supplied the engine in stage (2) by combustion of the gas-air mixture. Assume ideal behavior of the gases.

5

Liquefaction and the Properties of Liquids

THE LIQUEFACTION OF GASES

10a. The Critical State.—During the early part of the nineteenth century, a number of gases, such as carbon dioxide, sulfur dioxide, hydrogen sulfide, ammonia, etc., were liquefied by the simultaneous use of high pressure and low temperature. Further, by allowing compressed liquid carbon dioxide to evaporate, the temperature was lowered sufficiently for the solid to be obtained. The same principle is used at the present time in the manufacture of "dry ice," as solid carbon dioxide is called. By mixing solid carbon dioxide with ether, M. Thilorier (1835) was able to obtain temperatures as low as −110°C, and this permitted the liquefaction of such gases as ethylene, phosphine and silicon tetrafluoride. In spite of numerous attempts, however, involving the use of pressures up to 3000 atm, the gases hydrogen, oxygen, nitrogen and carbon monoxide could not be liquefied. The general opinion in the middle of the last century was, therefore, that gases such as these were "permanent gases," which could not be converted into liquids under any circumstances; this conclusion was shortly to be proved incorrect.

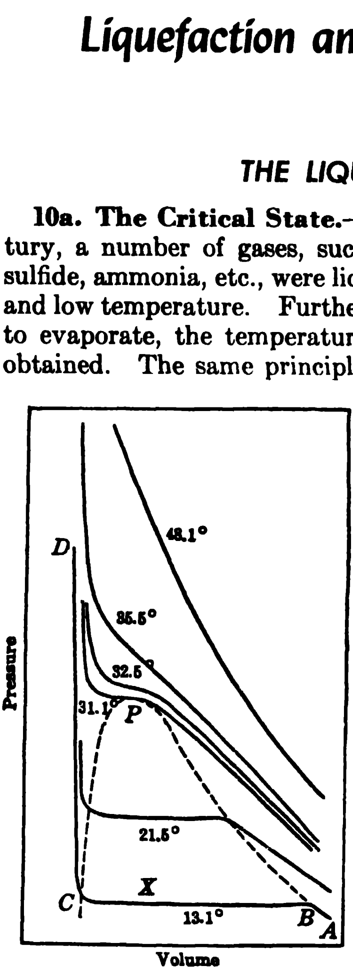

Fig. 10.1. Pressure-volume isothermals of carbon dioxide

The essential conditions for the liquefaction of gases were discovered by T. Andrews (1869) as the result of a study of the pressure-volume-temperature relationships of carbon dioxide. A definite amount of the gas was enclosed in a glass tube kept at a constant temperature, and the volumes at different pressures were measured; the results for a series of temperatures were plotted in the form of isotherms (§ 2b), as shown in Fig. 10.1.

At the lowest temperature employed by Andrews, 13.1°C, the carbon dioxide is entirely gaseous at low pressures, as at A; upon increasing the pressure the volume decreases, as indicated by the curve AB, approximately in accordance with Boyle's law. At the pressure B, however, liquefaction commences, and the volume decreases rapidly as the gas is converted to liquid with a much higher density. At C the carbon dioxide has been completely liquefied, and the steepness of the curve CD is evidence of the fact that the liquid is not easily compressed. It should be noted that the portion AB of the isothermal represents *gas only*, and CD represents *liquid only;* along BC, however, *gas and liquid can coexist* in equilibrium. The proportion of liquid to gas increases as the volume of the system changes from B to C. At a point such as X, the ratio of liquid to gas is equal to BX/CX. Since BC is parallel to the volume axis, it follows that the pressure remains constant while gas and liquid are present together, irrespective of the relative amounts of the two forms. The constant pressure represented by BC is the vapor pressure of the liquid at the temperature of the isotherm; this property of liquids will be considered in § 11a.

The pressure-volume curve at 21.5°C is similar to that for the lower temperature, except that the horizontal portion, over which liquefaction occurs, is shorter. In fact, as the temperature is raised, this section of the isotherm becomes less and less, as indicated in Fig. 10.1 by the dashed boundary curve, sometimes referred to as the **coexistence curve.** Finally, at 31.1°C the isotherm is reduced to a mere point. Above 31.1° there is no indication whatever of liquefaction, and Andrews found that if this temperature was exceeded, carbon dioxide could not be liquefied even at pressures of several hundred atmospheres, whereas below 31.1°C, a pressure of 75 atm was sufficient. It is evident, therefore, that for carbon dioxide there is a limit of temperature above which the gas cannot be liquefied no matter what the pressure. Further investigation, since the time of Andrews, has shown that this property is a general one, although the limiting temperature depends on the nature of the gas. The reason for the failure to liquefy the so-called "permanent gases" is now clear; they had not been cooled sufficiently for liquefaction to be possible.

The maximum temperature at which a gas can be liquefied, that is, *the temperature above which liquid cannot exist*, is referred to as the **critical temperature,** and *the pressure required to cause liquefaction at this temperature* is the **critical pressure.** The pressure-volume curve for the critical temperature is called the **critical isotherm.** The point P in Fig. 10.1 represents carbon dioxide in its **critical state,** *the temperature, pressure and volume being the critical values.* It may be remarked that the term **vapor** is used to describe *a gaseous substance when its temperature is below the critical value;* a vapor can, therefore, be condensed to a liquid by pressure alone.

Just above the critical temperature the P-V isotherms show marked deviations from the rectangular hyperbola to be expected for an ideal gas, e.g., the 32.5° and 35.5°C isotherms in Fig. 10.1. This corresponds to the marked dip in the plot of PV against P for carbon dioxide at 40°C in Fig. 4.1. At higher temperatures, e.g., 48.1°C, the deviation from ideal behavior is evidently very much less, the isotherm in Fig. 10.1 approximating that expected for an ideal gas.

10b. Determination of Critical Constants: The Law of the Rectilinear Diameter.—The obvious and most precise method for the determination of the critical constants of a gas is to use the procedure of Andrews, and to plot the P-V isotherms for a number of temperatures. Other methods, which are much simpler, are, however, available; the essential principle involved is based on the fact that at the critical temperature the densities of liquid and vapor become identical, and the surface of separation—the meniscus—between them disappears. The experimental substance is placed in the bulb A which is attached to a mercury manometer B, as in Fig. 10.2; the bulb is cooled if necessary, so that the surface between the liquid and vapor is apparent. The temperature is raised gradually until the meniscus just disappears; this gives the critical temperature, and the critical pressure can be obtained from the mercury level in the manometer. Modern theoretical and experimental studies indicate that for some liquids there may be a sort of critical region, rather than a definite temperature; the liquid-vapor surface apparently disappears slightly below the temperature at which the liquid ceases to exist.

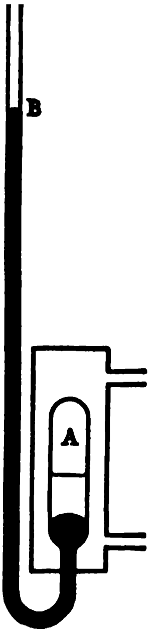

FIG. 10.2. Observation of critical phenomena

The critical volume can be obtained with the aid of the rule of L. Cailletet and E. Mathias (1886), known as the **law of the rectilinear diameter.** According to this law, *the mean value of the densities of any substance in the states of liquid and of saturated vapor at the same temperature,* e.g., as represented by the points B and C in Fig. 10.1, *is a linear function of the temperature.* The densities of the liquid (d_l) and of the saturated vapor (d_v) in equilibrium with it, are known as the **orthobaric densities,** and by the law of Cailletet and Mathias,

$$\tfrac{1}{2}(d_l + d_v) = a + bt, \tag{10.1}$$

where a and b are constants, and t is the temperature. The orthobaric densities of the hydrocarbon n-pentane are plotted in Fig. 10.3; the points on AC give the densities of the saturated vapor and on BC are those of the liquid at various temperatures. The maximum C of the curve occurs at the critical temperature. The mean densities are plotted along CD, and the close approximation to a straight line, as required by equation (10.1), is evident. This line is extrapolated to the critical temperature to give the point C for the critical density; the reciprocal of the latter is the critical volume per gram.

To determine the orthobaric densities, a known mass m of liquid is sealed in a graduated tube and is heated to a particular temperature; the volumes

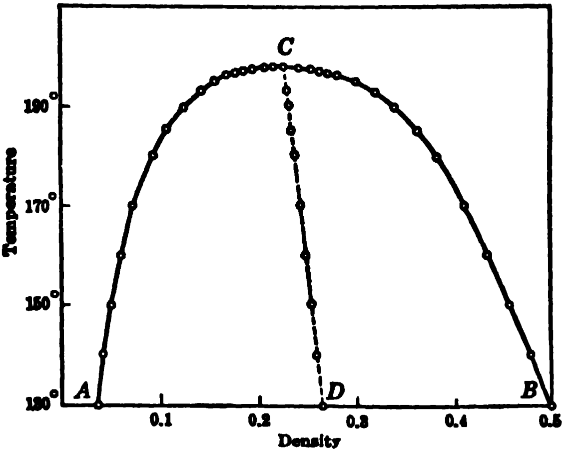

FIG. 10.3. Orthobaric densities and rectilinear diameter of *n*-pentane

v_l and v_v of liquid and vapor, respectively, are then read off from the graduations. Since the densities are d_l and d_v, respectively, it follows that

$$m = v_l d_l + v_v d_v. \tag{10.2}$$

The experiment is repeated at the same temperature with a different mass of substance, and from the two equations, of the form of (10.2), the two unknowns d_l and d_v can be calculated.

The critical constants for a number of common substances are given in Table 10.1. It is seen that the critical temperatures of the "permanent gases" are all below 154°K, i.e., about −120°C. Since the lowest temperature attainable in the middle of the nineteenth century was about −110°C. it can now be readily understood why these gases resisted all attempts at liquefaction.

TABLE 10.1 CRITICAL CONSTANTS

Substance	Temp.	Press.	Molar Vol.	Substance	Temp.	Press.	Molar Vol.
He	5.2°K	2.26 atm	60 ml	H_2S	373.5°K	89.0 atm	127 ml
H_2	33.2°	12.8	68	NH_3	406.0°	112.3	72
N_2	126.0°	33.5	90	Cl_2	417.1°	76.1	124
CO	133.6°	35.5	90	SO_2	430.3°	77.6	125
O_2	154.3°	49.7	74	CCl_4	556.2°	45.0	275
CO_2	304.2°	73.0	95	C_6H_6	561.6°	47.9	256
HCl	324.1°	81.5	89	H_2O	647.3°	217.7	57

10c. Continuity of States.—The transition from gas to liquid (or the reverse) generally occurs suddenly, the two states being sharply distinguished from each other, as indicated by the portions *AB* (gas) and *CD* (liquid) of the 13.1°C isotherm in Fig. 10.1. It is evident, however, that as the critical temperature is approached the volumes, and hence the densities, of liquid and gas become closer together. At the critical point the densities are identical, so that there is then no difference between liquid and gas. This conclusion is in harmony with the fact that the surface of separation between the two phases disappears at (or very close to) the critical point. The possibility arises, therefore, of a gradual transition between gas and liquid, for it is obvious that just below or just above the critical point there can be little difference between the two states.

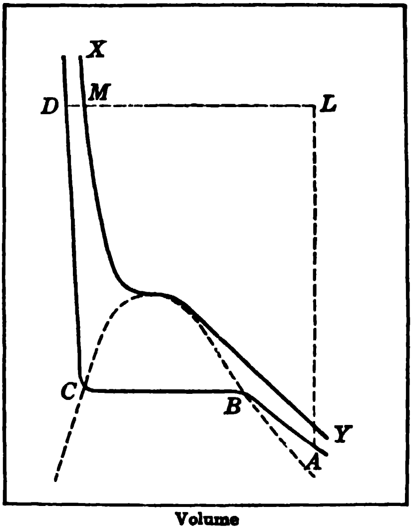

FIG. 10.4. Continuity of states

The idea of the continuity of states can also be brought out in another way. If a gas at A, in Fig. 10.4, is compressed at a constant temperature below the critical point, the behavior is represented by the curve $ABCD$, there being a continuous change from gas to liquid along BC where the two states coexist. Suppose, however, that the volume were maintained constant and the temperature raised, so that the pressure increases from A to L. The pressure is now held constant while the temperature is lowered until the volume is decreased from L to D. The system which was entirely gaseous at A is now completely liquid at D, which is on the same isotherm. The change has been made from gas to liquid at the same temperature without any sharp discontinuity.

The change in state actually occurs in the compression stage LD. To the right of the critical isotherm XY the system is gaseous, to the left it is liquid; consequently, the transition from gas to liquid takes place at the point M. As the temperature is decreased from L to D, the density of the gas increases and at M the molecules are close enough for the forces of attraction to lead to the formation of a definite bounding surface or meniscus. Nevertheless, the change from gas to liquid is gradual, and it may be regarded as a continuous transition from one state to the other.

10d. The van der Waals Equation and the Critical State.—The van der Waals equation (4.1)

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

can be multiplied out and rearranged so as to give the cubic equation

$$V^3 - \left(b + \frac{RT}{P}\right) V^2 + \frac{a}{P} V - \frac{ab}{P} = 0. \qquad (10.3)$$

For a given a and b, such an equation will have three roots, that is, there will be three values of V for given values of P and T; the three roots may be real, or one may be real and the others imaginary. If the values of V are plotted against P, for a constant T, then equation (10.3) should, from purely mathematical considerations, give a curve similar to I in Fig. 10.5. It is evident from this curve that, within a certain range of P values, there will be three real solutions for V, as, for example, the three points B, F and C. As T is increased, the curve is raised along the P axis, e.g., curve II; it will be observed that at the same time the three possible values of V for a given P are much closer together. At a certain value of T, for which the P-V curve is represented by III, the three solutions for V become identical at the point X. If T is raised still further, there is only one real value of V, the other two being imaginary, as is indicated by curve IV.

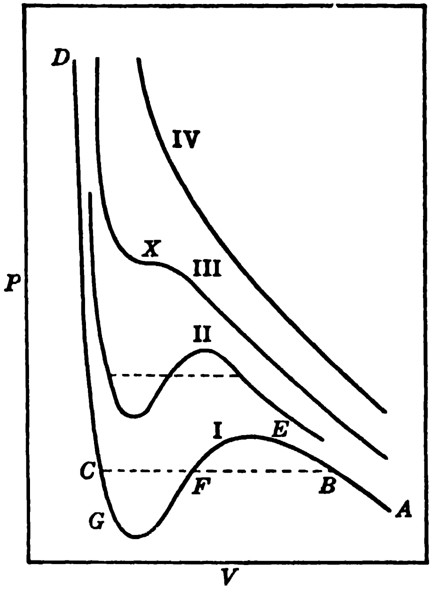

Fig. 10.5. Isothermal curves according to the van der Waals equation

A comparison of Fig. 10.5, which has been derived from purely mathematical consideration of the van der Waals equation in the form of (10.3), with the experimental facts for carbon dioxide represented in Fig. 10.1, shows a striking resemblance. The only essential difference is that the horizontal lines in Fig. 10.1, where liquefaction occurs, are replaced by ~-shaped (sigmoid) curves in Fig. 10.5. It is of interest to mention that portions of the curves corresponding to BE and CG in the latter figure have been realized under the abnormal conditions of "supersaturated vapors" and "superheated liquids," respectively.

The curve III in Fig. 10.5, for which the three real values of V become identical, corresponds to the isothermal in Fig. 10.1 on which the horizontal line representing liquefaction is just a single point, i.e., the critical isotherm; this correspondence can be utilized to express the critical constants of a gas in terms of the van der Waals constants. At the critical point X, the three values of V are all equal to the critical volume V_c, and this condition may be represented by the equation

$$(V - V_c)^3 = 0,$$

which upon multiplying out becomes

$$V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0. \tag{10.4}$$

An alternative expression for the critical isothermal is obtained by substituting P_c and T_c for P and T in equation (10.3); thus,

$$V^3 - \left(b + \frac{RT_c}{P_c}\right)V^2 + \frac{a}{P_c}V - \frac{ab}{P_c} = 0, \qquad (10.5)$$

and according to the arguments presented above, this should be completely identical with equation (10.4). It follows, therefore, that the coefficients of the various terms in the two equations must be identical; thus, comparing the coefficients of V^2, it is seen that

$$3V_c = b + \frac{RT_c}{P_c}, \qquad (10.6)$$

whereas from the coefficients of V, it follows that

$$3V_c^2 = \frac{a}{P_c}. \qquad (10.7)$$

Finally, the constant terms, which do not contain V, must be equal, so that

$$V_c^3 = \frac{ab}{P_c}. \qquad (10.8)$$

If, now, equation (10.8) is divided by (10.7), the result is

$$V_c = 3b,$$

and substitution of this value for V_c in equation (10.7) gives

$$P_c = \frac{a}{27b^2}.$$

Finally, insertion of these results for V_c and P_c in equation (10.6) yields

$$T_c = \frac{8a}{27Rb}.$$

There have thus been obtained, from the van der Waals equation, the expressions

$$\text{(i) } V_c = 3b, \qquad \text{(ii) } P_c = \frac{a}{27b^2}, \qquad \text{and} \qquad \text{(iii) } T_c = \frac{8a}{27Rb} \qquad (10.9)$$

relating the critical constants to a, b and R, for the given gas.

These equations may be tested by determining the van der Waals constants a and b from P-V-T measurements, and seeing how closely the experimental critical data can be reproduced. The results obtained in this manner are, however, not too satisfactory, one reason being that a and b vary with temperature, as mentioned earlier. If the van der Waals constants are derived from P-V-T data obtained not too far from the critical point, then the agreement between calculated and observed critical constants is moderately good, but otherwise there are appreciable differences. As stated in § 4c, it is the general practice to reverse the procedure and to determine the van der Waals constants from the experimental critical data, utilizing the relationships derived above. It is evident, however, that the results can be satisfactory only if the conditions are not too far removed from the critical state.

A further consequence of the van der Waals equation is obtained by combining the three equations (10.9); the result is

$$\frac{RT_c}{P_cV_c} = \frac{8}{3} = 2.67,$$

so that RT_c/P_cV_c should be a constant, irrespective of the nature of the substance, equal to 2.67 for 1 mole. The data in Table 10.2 show, however,

TABLE 10.2. VALUES OF RT_c/P_cV_c

Substance	RT_c/P_cV_c	Substance	RT_c/P_cV_c
Hydrogen	3.28	Chlorine	3.63
Helium	3.18	Sulfur dioxide	3.64
Nitrogen	3.42	Carbon tetrachloride	3.68
Oxygen	3.42	Benzene	3.75
Carbon dioxide	3.68	Ethyl ether	3.81
Hydrogen chloride	3.66	Stannic chloride	3.75

that although RT_c/P_cV_c is approximately constant for a number of elements and compounds, it is appreciably greater than 2.67. This discrepancy indicates that near the critical point allowance for the attraction between molecules requires a function that is more complicated than the a/V^2 term of the van der Waals equation. Some other equations of state lead to somewhat better agreement with experiment than does the van der Waals equation in this connection, but they are more difficult to manipulate and so are used for special purposes only. Substances containing hydroxyl groups, and which are associated in the liquid state, because of hydrogen bonding (§ 16i), give still higher values for RT_c/P_cV_c, e.g., 4.4 for water, 4.0 for ethanol and 5.0 for acetic acid.

For 1 mole of an ideal gas, RT is equal to PV; the fact that RT_c/P_cV_c is about 3.7 for many substances shows, therefore, that the pressure-volume product at the critical point is less than the ideal gas value in the ratio of 1 to 3.7. This is in harmony with the marked dip in the curve showing the variation of PV with P which becomes evident as the critical temperature is approached (see Figs. 4.1 and 4.2).

10e. The Law of Corresponding States.—A plot of the van der Waals equation on a P-V diagram using different values of a and b gives a family of curves similar to those in Fig. 10.5, but displaced with respect to the origin. It is possible mathematically to make such a family of curves coalesce into one set by a suitable transformation in the variables P, V and T, as was shown by van der Waals in 1881. If the pressure, volume and temperature of a gas are expressed in terms of the critical pressure, volume and temperature, respectively, thus,

$$P = \pi P_c, \qquad V = \phi V_c \qquad \text{and} \qquad T = \theta T_c, \tag{10.10}$$

the van der Waals equation becomes

$$\left(\pi P_c + \frac{a}{\phi^2 V_c^2}\right)(\phi V_c - b) = R\theta T_c.$$

If the values for P_c, V_c and T_c, as given by the equation (10.9), are now introduced, the result is

$$\left(\frac{\pi a}{27b^2} + \frac{a}{9\phi^2 b^2}\right)(3\phi b - b) = \frac{8a\theta}{27b}$$

or

$$\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta. \tag{10.11}$$

The quantities π, ϕ (Greek, *phi*) and θ (Greek, *theta*) are called the **reduced pressure, volume** and **temperature,** respectively, and equation (10.11) is the van der Waals **reduced equation of state.** The important point to note about this equation is that it is perfectly general, and does not involve either R or the specific a and b values for any gas; it should thus be applicable to all substances.

According to equation (10.11), *if any two or more substances have the same reduced pressure π, that is to say, their pressures are the same fraction or multiple π of their respective critical pressures, and are at equal reduced temperatures θ, their temperatures being the same fraction or multiple θ of their respective critical temperatures, then their reduced volumes ϕ should be equal, i.e., V/V_c should be the same in each case.* Substances under these conditions are said to be in **corresponding states,** and the foregoing statement may be taken as an expression of the **law of corresponding states.** Although the law has been derived here from the van der Waals equation, it is important to point out that *any* equation of state involving two arbitrary constants, such as a and b, in addition to R can be converted into an equation containing only the reduced quantities π, ϕ and θ. The difference between the various equations of the form of (10.11), as derived from different equations of state, is that they do not give the same numerical relationship between π, ϕ and θ.

A useful application of the law of corresponding states is the development of a single generalized diagram which gives, in principle, the P-V-T relationship for all gases. This is not based on any particular equation of state, but rather on experimental results. The deviation of a gas from ideal behavior at a given temperature and pressure may be expressed by means of a **compressibility factor** K, defined by

$$K = \frac{PV}{RT}. \tag{10.12}$$

It is thus the ratio of the actual volume to that of an ideal gas at the same temperature and pressure. For an ideal gas K is always equal to unity, but for a real gas it may be greater or less than unity according to the conditions.

If P, V and T in equation (10.12) are expressed in terms of the respective reduced values by means of equation (10.10), the result is

$$K = \frac{P_cV_c}{RT_c} \cdot \frac{\pi\phi}{\theta} = c\frac{\pi\phi}{\theta}, \tag{10.13}$$

since the factor P_cV_c/RT_c is known to be approximately constant, i.e., c, for many gases. It follows from equation (10.13) that if the compressibility factor is plotted against the reduced pressure π for a given reduced temperature θ, a single curve will be obtained for all gases. The generalized compressibility curves for several reduced temperatures are shown in Fig. 10.6; they are based upon experimental P-V-T measurements made with a number of different gases. The fact that the values fall on (or close to) the individual curve provides support for the law of corresponding states.

By means of the curves in Fig. 10.6, it is possible to determine, with a fair degree of accuracy, the value of any one of the three variables P, V and T if the other two are known. The procedure is relatively simple when the volume is to be calculated, but evaluation of the pressure or temperature is somewhat more involved.

Example: Determine the volume occupied by 40.0 grams of nitrogen at 0°C and 400 atm pressure.

The critical temperature of nitrogen is 126°K and the critical pressure is 33.5 atm (Table 10.1); hence, the reduced temperature and pressure are

$$\theta = \frac{273}{126} = 2.17 \qquad \text{and} \qquad \pi = \frac{400}{33.5} = 11.9.$$

From Fig. 10.6, these values of θ and π correspond to $K \approx 1.27$ and so, from a rearrangement of equation (10.12), taking R as 0.0820 liter-atm deg^{-1} mole^{-1},

$$V \quad KRT \quad 1.27 \times 0.0820 \times 273 \quad 0.071 \text{ liter mole}^{-1}.$$
$$400$$

Since 40 grams of nitrogen is $40/28 = 1.43$ moles, the required volume is $0.071 \times 1.43 = 0.10$ liter.

Example: Determine the pressure of carbon dioxide gas when 1 mole occupies 0.381 liter at 40°C.

Substituting the values of $V = 0.381$ liter mole^{-1}, $T = 273 + 40 = 313$°K, and $R = 0.0820$ liter-atm deg^{-1} mole^{-1} into equation (10.12), it follows that

$$P = \frac{KRT}{V} = \frac{K \times 0.0820 \times 313}{0.381} = 67.4K.$$

The critical pressure of carbon dioxide is 72.9 atm, so that

$$\pi = \frac{P}{P_c} = \frac{67.4K}{72.9} = 0.925K.$$

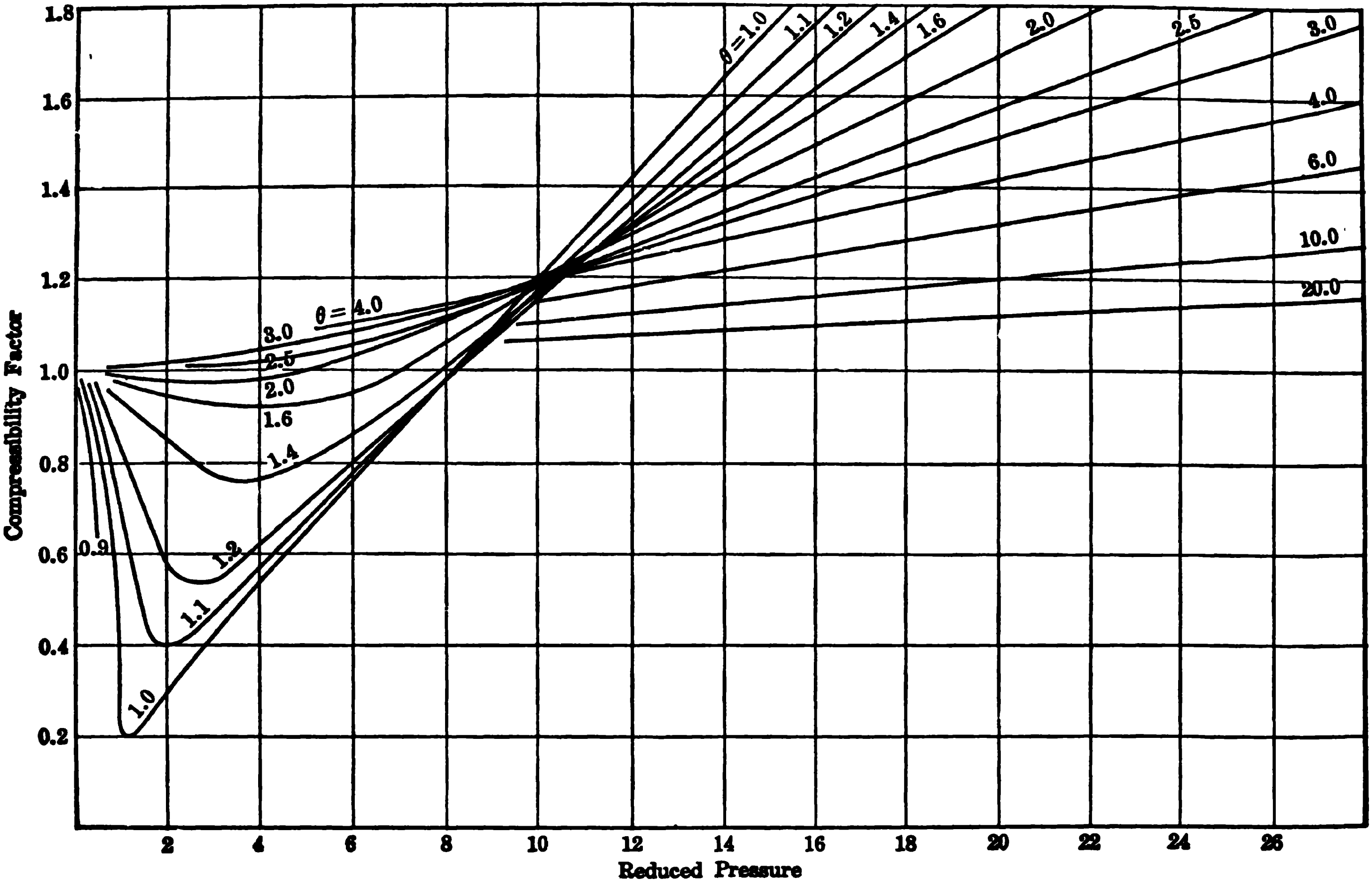

Fig. 10.6. Generalized compressibility curves

The expression $\pi = 0.925K$ is the equation for a straight line through the origin of Fig. 10.6. The intersection of this line with the curve in Fig. 10.6, representing the prescribed reduced temperature, is the required reduced pressure. The critical temperature of carbon dioxide is 304.1°K, and so the reduced temperature $\theta = 313/304.1 = 1.03$. The value of π at which the line $\pi = 0.925K$ intersects the estimated curve for $\theta = 1.03$ is 0.70. Hence $P = 0.70 \times 72.9 = 51$ atm. (The experimental value is 50 atm.)

10f. The Liquefaction of Gases.—As a consequence of the discovery that a gas had to be cooled below a certain temperature before it could be liquefied, attention was concentrated on the problem of obtaining low temperatures. One of the earliest methods, which was used to solidify carbon dioxide and was utilized by R. P. Pictet (1877) for the liquefaction of oxygen, depended on the cooling accompanying vaporization of a readily liquefied gas. For example, by rapid evaporation of liquid sulfur dioxide a temperature of −65°C was obtained. At this low temperature carbon dioxide was readily liquefied, and by vaporization of this liquid under reduced pressure the temperature fell to −130°C. This was sufficient to bring about the liquefaction of compressed oxygen. The cooling associated with evaporation is due to the heat of vaporization which must be supplied to the liquid (§ 11a); if this does not come from an outside source, it will be obtained from the liquid itself, the temperature of which consequently falls. The method of cooling by evaporation is still employed in the production of "dry ice," as already noted, and it is also utilized in commercial and domestic refrigeration. It finds little or no application, however, in the liquefaction of gases at the present day.

Two principles are most widely used to liquefy gases on the large scale. The first, developed by W. Hampson (1895) and by C. von Linde (1895), makes use of the cooling due to the **Joule-Thomson effect** (§4b). The gas, at an initial pressure of about 250 atm, is allowed to stream through a throttle, as a result of which the pressure falls. The gas is thus cooled because of the energy required to overcome the attraction of the molecules during the expansion that accompanies the decrease in pressure. The drop in temperature may not be sufficient to cause liquefaction, but the cooled gas is used to lower the temperature of the incoming gas; after passage through the throttle the gas is now generally cooled to a sufficient extent for liquefaction to occur.

The second principle, known as cooling due to **adiabatic expansion** (see § 6k), was employed by G. Claude (1900) for the commercial liquefaction of air. The gas is compressed to about 200 atm, and is then allowed to expand in an engine where it does mechanical work. As a result, kinetic energy is removed from the gas molecules and the temperature falls. The incoming gas is divided into two streams; one goes to the compression-expansion engine where it is cooled, as just described, while the other, after being cooled by the gas leaving the engine, passes through a throttle and so has its temperature lowered further by the Joule-Thomson effect. The advantage of the Claude method lies in the fact that the Joule-Thomson cooling is greater the lower the temperature, at moderate pressures.

At ordinary temperatures, hydrogen and helium exhibit an unusual Joule-Thomson effect; the temperature increases, instead of falling, when these gases are streamed through a throttle. At low temperatures, however, both hydrogen and helium behave in a normal manner and undergo cooling in the Joule-Thomson expansion. Such behavior is in accord with the change in the shape of the *PV* against *P* curve described in §4a. As may be expected, all gases become warmer in a Joule-Thomson expansion above an appropriate temperature, known as the **inversion temperature.** The point of immediate interest, however, is to note that, starting from ordinary temperatures, hydrogen and helium could not possibly be liquefied by the Joule-Thomson effect alone. If the gases are first cooled below their respective inversion points, either by the method of adiabatic expansion or by utilizing another liquefied gas, subsequent cooling and liquefaction as a result of the Joule-Thomson effect are possible.

The liquefaction of gases is of industrial importance, and the liquids also find application in many laboratory studies requiring the use of low temperatures. Oxygen, argon and neon are obtained in commercial quantities by the fractional distillation of liquid air, while helium is extracted from natural gases by removing the hydrocarbons by liquefaction. Liquid carbon dioxide is employed in the manufacture of "dry ice," and other liquefied gases, such as sulfur dioxide, ammonia, as well as certain patented compounds of the "Freon" type, e.g., difluoro-dichloromethane, are used in refrigeration.

VAPOR PRESSURE AND VAPORIZATION

11a. The Vapor Pressure of Liquids.—In the preceding sections the relationship between gas and liquid has been treated mainly from the standpoint of the gas; it will now be considered with special reference to the liquid. It has been seen that if a gas is compressed when below its critical temperature, liquefaction commences at a certain pressure; this pressure remains constant, at each temperature, as long as liquid and vapor are present together (cf. *BC* in Fig. 10.1). This pressure, under which liquid and vapor can coexist at equilibrium, is the **saturation vapor pressure** or, in brief, the **vapor pressure** of the liquid (§10a). It is seen from Fig. 10.1 that this pressure increases as the temperature is raised, although a limit is set by the critical point. The critical pressure may thus be described as *the highest possible, or limiting, vapor pressure of a liquid.*

In order for molecules to leave the surface of a liquid and become vapor, they have to overcome the forces of attraction of the other molecules in the liquid. Such forces are relatively large because the molecules are much closer together in the liquid than in the vapor state, provided the temperature is well below the critical point. In order to overcome these attractive forces, energy must be supplied to the liquid in the form of heat; this is the (latent) **heat of vaporization** of the liquid. It is the heat absorbed when a definite quantity, e.g., 1 gram or 1 mole, of the liquid is vaporized; if the quantity is 1 mole, then the expression **molar heat of vaporization** is employed.

11b. Vapor Pressure and Boiling Point.—If the pressure above a liquid is adjusted to a definite value, say 1 atm, it is possible to raise the temperature until the vapor pressure is equal to the arbitrary external pressure. At this point bubbles of vapor are seen to form within the liquid and to escape from the surface. This is, of course, the **boiling point** of the liquid, which can consequently be defined as *the temperature at which the vapor pressure is equal to the external pressure.* If the latter is 1 atm, the temperature is the normal boiling point. A lowering of the external pressure will mean that the boiling point is decreased, as in distillation under reduced pressure, but an increase of pressure will result in a rise of the boiling point of a liquid. It is evident from these considerations that a plot of the variation of vapor pressure with temperature will also give the variation of boiling point with the external pressure.

11c. The Determination of Vapor Pressure.—The methods most frequently used for measuring vapor pressure fall into three categories, viz., static, dynamic and gas saturation methods. In the simplest form of the **static method** two barometer tubes are used, one of which is for purposes of comparison. The liquid under investigation is introduced into the other, until the space above the mercury is saturated with vapor, as shown by a small quantity of liquid remaining on the surface of the mercury. The difference in the levels of the mercury in the two tubes gives the vapor pressure of the liquid at the experimental temperature. The measurements can be made at a series of temperatures by surrounding the barometer tubes with a heating jacket.

A useful form of the static method is the **isoteniscope** procedure of A. Smith and A. W. C. Menzies (1910). A bulb A, of approximately 2 cm diameter, is about half-filled with the experimental liquid and the same liquid is contained in the attached U-tube, B (Fig. 11.1). The latter is connected to a mercury manometer C and to a vessel D of large volume to smooth out

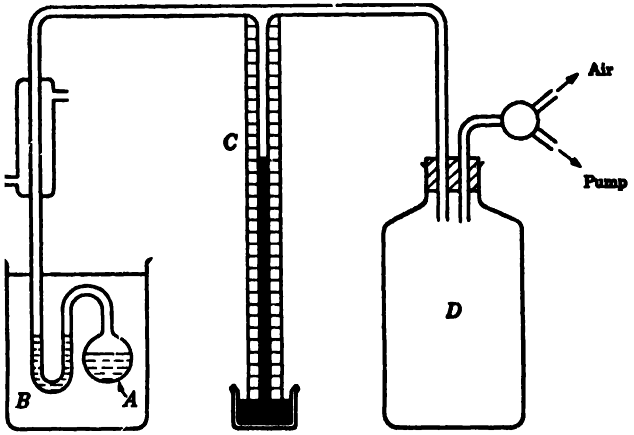

FIG. 11.1. Apparatus for measuring vapor pressure with an isoteniscope

minor pressure fluctuations. The isoteniscope *A*-*B* is placed in a bath at constant temperature, the apparatus is evacuated until the liquid boils and the air in *A* has been removed; the pressure is now adjusted by admitting air to *D*, until the levels are the same in both limbs of the U-tube *B*. The pressure above the liquid in *A*, i.e., the vapor pressure at the bath temperature, is then equal to the pressure in *D*; this is equal to the barometric pressure minus the height of the mercury column in *C*.

In the **dynamic method** the external pressure is fixed, and the temperature at which the liquid boils is then measured. In accordance with the definition of boiling point, given above, this represents the temperature at which the liquid has a vapor pressure equal to the external pressure. Because of the possibility of the liquid becoming superheated, the thermometer is placed in the vapor when the boiling point of a pure substance is being measured. The pressure in the apparatus is then equal to the vapor pressure of the liquid at the temperature recorded on the thermometer.

In the **gas saturation (transpiration) method,** dry air, or other gas, is bubbled through the liquid at constant temperature; the gas becomes saturated with the vapor of the liquid, and the partial pressure of the vapor in the resulting mixture is equal to the vapor pressure of the liquid. Assuming that Dalton's law of partial pressures (§ 2h) holds, then according to the equations (2.24),

$$p = \frac{n_1}{n_1 + n_2} P, \tag{11.1}$$

where p is the vapor (partial) pressure, P is the total pressure of the air and the vapor, i.e., the external atmospheric pressure, n_1 is the number of moles of vapor and n_2 the number of moles of air in the gas leaving the saturator. If the air may be supposed to obey the ideal gas law, then

$$Pv = n_2RT,$$

where v is the volume of the n_2 moles of dry air, before entering the saturator, measured at the atmospheric pressure P. Hence, Pv/RT may be substituted for n_2 in equation (11.1), and n_1 may be replaced by w/M, where w is the weight of the vapor taken up by the volume v of air, and M is the molecular weight of the vapor; equation (11.1) thus becomes, after rearrangement,

$$p = \frac{wPRT}{wRT + MPv} \tag{11.2}$$

The value of w is obtained by determining the loss in weight of the saturator, or the gain in weight of a suitable absorbing agent, resulting from the passage of the volume v of air, measured at the temperature T and pressure P; thus all the information is available for calculating the vapor pressure.

The vapor pressures of a number of familiar liquids at a series of temperatures between 0° and 100°C are collected in Table 11.1.

TABLE 11.1. VAPOR PRESSURES IN MM OF MERCURY

Temp.	Water	Ethanol	Acetic acid	Ethyl acetate	Acetone	Benzene	Anilir
0°C	4.58	12.2	—	24.2	67.3	26.5	—
10°	9.21	23.6	—	42.8	115.6	45.4	—
20°	17.53	43.9	11.7	72.8	184.8	74.7	—
30°	31.82	78.8	20.6	118.7	282.7	119.6	—
40°	55.32	135.3	34.8	186.3	421.5	182.7	—
50°	92.51	222.2	56.6	282.3	612.6	271.3	2.4
60°	149.4	352.7	88.9	415.3	860.6	391.7	5.7
70°	233.7	542.5	136.0	596.3	—	551.0	10.6
80°	355.1	812.6	202.3	832.8	—	757.6	18.0
90°	525.8	—	293.7	—	—	1016.1	29.2
100°	760.0	—	417.1	—	—	—	45.7

11d. Application of the Clapeyron-Clausius Equation.—The vapor pressures of all substances increase with increasing temperature, and the variation is always represented by a curve of the type shown in Fig. 11.2. The highest temperature at which vapor pressure can be measured is, of course, the critical point, since liquid cannot exist above this temperature; provided supercooling does not occur, the lower limit is the triple point, i.e., the freezing point of the liquid under its own vapor pressure. In view of the significance of the boiling point, it is apparent that the same curve represents the influence of pressure on the boiling point, as already mentioned.

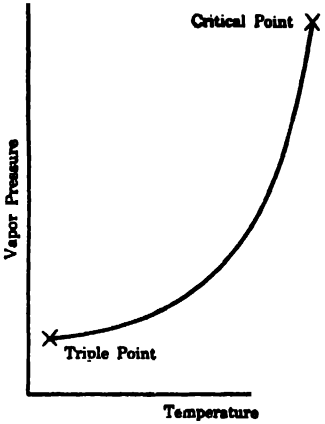

FIG. 11.2. Vapor pressure-temperature curve

The variation of vapor pressure with temperature is best considered in connection with the Clapeyron-Clausius equation (9.32), derived in Chapter 4. For the present purpose, this may be written in the form

$$\frac{dp}{dT} = \frac{L_v}{T(V_v - V_l)}, \tag{11.3}$$

where dp/dT represents the rate of change of vapor pressure with temperature, L_v is the molar heat of vaporization of the liquid, and V_v and V_l are the molar volumes of vapor and liquid, respectively, all at the absolute temperature T. Thus, equation (11.3) gives the slope, at any temperature T, of the plot of vapor pressure against the absolute temperature, as in Fig. 11.2. Since the molar heat of vaporization L_v is equal to $M \times l_v$, where M is the molecular weight and l_v is the heat of vaporization per gram of the liquid, and the molar volumes V_v and V_l are equal to M times the specific volumes, v_v and v_l, i.e., the volumes per gram of vapor and liquid, respectively, equation (11.3) may be written as

$$\frac{dp}{dT} = \frac{l_v}{T(v_v - v_l)}. \tag{11.4}$$

The Clapeyron-Clausius equation is of value in a number of connections; for example, if the rate of change of the vapor pressure with temperature is known, it is possible to calculate the heat of vaporization of the liquid at that temperature. Alternatively, if the latent heat is known, the rate of change of vapor pressure with temperature or, in other words, the change of boiling point with pressure can be determined.

Example: The vapor pressure of water changes by 27.17 mm from 99.5° to 100.5°C; the specific volumes of water vapor and liquid water at 100° are 1674 and 1.04 cc per gram, respectively. Calculate the heat of vaporization of water, in calories per gram, at 100°C.

In the use of the Clapeyron-Clausius equation care must be exercised in the matter of units; the best procedure is to use cgs units, so that the heat is obtained in ergs, which can be converted into calories (see § 6a).

The vapor pressure changes by 27.17 mm of mercury, i.e., 2.717 cm, per degree, and this may be taken as the value of dp/dT at 100°C. To convert to cgs units, i.e., dynes cm^{-2} deg^{-1}, it is necessary to multiply the cm of mercury by the density of the latter (13.595 g cm^{-3}) and by the acceleration due to gravity (980.7 cm sec^{-2}), so that

$$\frac{dp}{dT} = 2.717 \times 13.595 \times 980.7 \text{ dynes cm}^{-2} \text{ deg}^{-1}.$$

Since v_v and v_l are 1674 and 1.04 cc, respectively, $v_v - v_l = 1673 \text{ cm}^3$, the 0.04 being ignored, since the use of more than four significant figures is not justified. Substitution of these figures in equation (11.4), with $T = 273.2 + 100 = 373.2°$, gives l_v in ergs deg^{-1}; to convert ergs into calories it is necessary to divide by 4.184×10^7, so that

$$l_v = T(v_v - v_l)\frac{dp}{dT}$$

$$= \frac{373.2 \times 1673 \times 2.717 \times 13.595 \times 980.7}{4.184 \times 10^7} = 540.5 \text{ cal g}^{-1}.$$

(The directly determined experimental value is 539.9 cal g^{-1}.)

Example: The heat of vaporization of water at 100°C is 539.9 cal per gram. Utilizing the values of v_l and v_v given above, calculate the temperature at which water will boil at a pressure of 770 mm.

This is the reverse of the preceding problem; it is required to calculate dp/dT, or rather dT/dp, to find how the boiling point changes with pressure. Inversion of equation (11.4) gives

$$\frac{dT}{dp} = \frac{T(v_v - v_l)}{l_v} = \frac{373.2 \times 1673}{539.9 \times 4.184 \times 10^7} \text{ deg cm}^3 \text{ dyne}^{-1}.$$

To convert into degree per cm of mercury units, this should be multiplied by 13.595 ×

980.7; the result is found to be 0.368° per cm of mercury. The boiling point of water is thus raised by 0.368° for 1 cm of mercury increase in the pressure. Since the boiling point of water at 760 mm is 100°, the value at 770 mm should thus be 100.37°C.

11e. Vapor Pressure Equations.—If the temperature is not near the critical point, the molar volume V_l of the liquid will be small and can be neglected in comparison with V_v, the molar volume of the vapor; equation (11.3) will then become

$$\frac{dp}{dT} = \frac{L_v}{TV_v}. \tag{11.5}$$

Further, in regions below the critical temperature, the vapor pressure is relatively small and the vapor may be supposed to obey the ideal gas laws, so that pV_v is equal to RT, or $V_v = RT/p$; making this substitution in equation (11.5), the result is

$$\frac{dp}{dT} = \frac{L_v p}{RT^2}. \tag{11.6}$$

Using the mathematical identity,

$$\frac{d \ln p}{dT} = \frac{1}{p} \cdot \frac{dp}{dT},$$

it follows from equation (11.6) that

$$\frac{d \ln p}{dT} = \frac{L_v}{RT^2}. \tag{11.7}$$

This result, first obtained by R. Clausius (1850), is sometimes referred to as the Clapeyron-Clausius equation, although the name is properly applied to the more general form of equation (11.3). This is one form of an important equation which finds wide application in many aspects of physical chemistry (§ 34a). It should be remembered that equations (11.6) and (11.7) are approximate only, because they are based on the ideal gas law; nevertheless, they have many uses.

Example: Given that dp/dT is 2.72 cm of mercury per degree for water at 100°C, calculate the approximate heat of vaporization in cal per gram at this temperature.

The calculation is made very easily by equation (11.6), the question of units being quite simple, as may be seen by writing this equation in the form

$$\frac{1}{p} \cdot \frac{dp}{dT} = \frac{L_v}{RT^2}.$$

Since dp/dT is in cm deg^{-1}, p may be expressed in cm; further, as L_v is required in calories, R may be taken as 1.99 cal deg^{-1} mole^{-1}; hence, since the vapor pressure p of water is 76.0 cm at 100°C, i.e., 373°K,

$$L_v = \frac{RT^2}{p} \cdot \frac{dp}{dT} = \frac{1.99 \times (373)^2}{76.0} \times 2.72 \text{ cal mole}^{-1}.$$

To obtain the heat of vaporization per gram, this is divided by 18, the molecular weight of water; the result is 553 cal g^{-1}, which is just over 2 per cent higher than the experimental value.

If the heat of vaporization can be regarded as constant, equation (11.7) may be readily integrated; thus, after rearrangement,

$$\int d\ln p = \frac{L_v}{R}\int\frac{dT}{T^2}, \tag{11.8}$$

$$\ln p = -\frac{L_v}{RT} + c, \tag{11.9}$$

where c is the integration constant. Upon converting the natural logarithm (i.e., ln) to the base of 10 (i.e., log), equation (11.9) becomes

$$\log p = -\frac{L_v}{2.303RT} + C. \tag{11.10}$$

where C is also a constant. Since the heat of vaporization L_v is assumed to be constant, this equation may be written as

$$\log p = -\frac{A}{T} + C, \tag{11.11}$$

where the constant A is given by

$$A = \frac{1}{2.303R}L_v. \tag{11.12}$$

According to equation (11.11), if the logarithm of the vapor pressure, i.e., $\log p$, is plotted against the reciprocal of the absolute temperature, i.e., $1/T$, the result should be a straight line; the slope of this line, i,e., $-A$, will be related to the molar heat of vaporization by equation (11.12).

That this linear relationship is, at least approximately, true is shown in Fig. 11.3; the full line is drawn straight, and the experimental results are indicated by the points. Exact agreement with equation (11.11) is not to be expected for two reasons; first, the ideal gas laws have been assumed in deriving equation (11.7), upon which (11.11) is based, and second, the heat of vaporization is not constant over an appreciable temperature range.

For many purposes it is more convenient to utilize a different form of the equations given above; thus, if p_1 is the vapor pressure at the temperature T_1, and p_2 is that at T_2, then from equation (11.8),

$$\int_{p_1}^{p_2} d\ln p = \frac{L_v}{R}\int_{T_1}^{T_2}\frac{dT}{T^2},$$

assuming L_v to be independent of temperature. Upon performing the indicated integrations, the result is

$$\ln\frac{p_2}{p_1} = -\frac{L_v}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

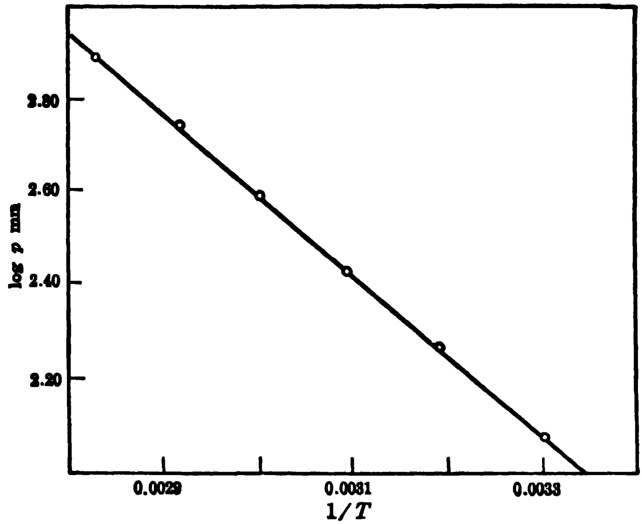

FIG. 11.3. Plot of logarithm of vapor pressure of ethyl acetate against reciprocal of the absolute temperature

and rearrangement and conversion to ordinary logarithms gives

$$\log \frac{p_2}{p_1} = \frac{L_v}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right).$$

If L_v is in calories per mole, then R is 1.987, and this expression becomes

$$\log \frac{p_2}{p_1} = \frac{L_v}{4.576}\left(\frac{T_2 - T_1}{T_1T_2}\right). \tag{11.13}$$

By means of equation (11.13) it is possible to calculate the heat of vaporization if the vapor pressures of the liquid at two temperatures are known; alternatively, the vapor pressure at one temperature can be determined from that at another temperature, together with the heat of vaporization. Since the equation involves a ratio of two pressures, any convenient units may be used.

Example: The vapor pressure of water at 90°C is 526 mm, and the mean heat of vaporization between 90° and 100°C may be taken as 542 cal per gram. Calculate the vapor pressure of water at 100°, according to equation (11.13).

Let T_1 be $273 + 90 = 363$°K, so that $p_1 = 526$ mm; then p_2 is to be found at $T_2 = 273 + 100 = 373$°K. Hence, since L_v is 542×18 cal per mole,

$$\log \frac{p_2}{526} = \frac{542 \times 18}{4.576}\left(\frac{373 - 363}{373 \times 363}\right),$$

$$p_2 = 756 \text{ mm}.$$

(The correct value is, of course, 760 mm.)

11f. Boiling Point Relationships.—A number of interesting properties applicable at the boiling point were discovered empirically, and some of them have been found to have a partial theoretical basis. *The boiling point of a liquid at 1 atm pressure, expressed on the absolute temperature scale, is approximately two-thirds of the critical temperature;* thus,

$$\frac{T_b}{T_c} \approx 0.66, \tag{11.14}$$

where T_b and T_c are the normal boiling point and critical temperature, respectively. The data in Table 11.2 (below), for a variety of liquids, provide support for this relationship; helium is an outstanding exception, but in the liquid state this substance is abnormal in other respects. Since the boiling point is approximately a constant fraction of the critical temperature for most liquids, the former may be regarded as a corresponding temperature, in the sense defined in § 10d.

Another property of liquids at the boiling point is known as **Trouton's rule**; according to this, *the molar heat of vaporization in calories divided by the normal boiling point on the absolute scale has the approximately constant value of 21*, i.e.,

$$\frac{L_v}{T_b} \approx 21 \text{ cal mole}^{-1} \text{ deg}^{-1}, \tag{11.15}$$

as is apparent from the results in Table 11.2. In other words, in view of equation (8.16), Trouton's rule implies that all liquids have the same entropy of vaporization at their respective boiling points. It is evident from Table 11.2 that this is approximate only; it holds more closely for nonassociated substances of molecular weight about 100, and of not too high boiling point. For substances of low boiling point, e.g., hydrogen and helium, the ratio L_v/T_b is much less than 21. On the other hand, for associated liquids, such as water and alcohol, it is greater than the usual value; the reason for this is not difficult to understand. The hydrogen bonds which exist in these liquids are usually absent in the vapor, and so extra energy, over and above the normal heat of vaporization, must be supplied in order to break these bonds. The actual value of the molar heat of vaporization is thus relatively

TABLE 11.2. PROPERTIES OF THE LIQUID AT THE BOILING POINT

Substance	T_b	T_c	T_b/T_c	L_v	L_v/T
Helium	4.2°K	5.2°K	0.81	22 cal mole^{-1}	5.2
Hydrogen	20.3°	33.2°	0.61	216	10.6
Oxygen	90.2°	154.3°	0.58	1610	17.9
Ammonia	239.7°	405.5°	0.59	5560	23.2
Carbon tetrachloride	350°	556°	0.63	7140	20.4
Ethanol	351°	516°	0.68	9450	26.9
Benzene	353°	562°	0.63	7500	21.2
Water	373°	647°	0.58	9700	26.0
Acetic acid	391°	594°	0.66	5810	14.9

larger than for analogous nonassociated liquids. It is true that the boiling points are also raised, but this is not sufficient to compensate for the increase in the heat of vaporization, so that L_v/T_b is greater than 21. It is of interest to mention that the apparent value of the Trouton ratio for acetic acid is 14.9. However, this substance is appreciably associated even in the vapor state (§ 5f), and if allowance is made for the fact that the average molecular weight is about 100, instead of the value for single molecules, L_v/T_b is found to be about 24.

Various attempts have been made to improve the Trouton equation (11.15) so as to make it more widely applicable. One of the most successful of these was proposed by J. H. Hildebrand (1915) who compared the values of L_v/T for different substances under such conditions that the number of moles per unit volume of vapor was the same in every case. For most substances L_v/T obtained in this way is approximately constant, although associated liquids and helium still behave in an exceptional manner.

Boiling points of liquids are usually recorded at 1 atm, i.e., 760 mm, pressure, but this exact pressure is rarely obtained under ordinary experimental conditions. A simple equation for correcting boiling points to the standard pressure would thus be useful; such an expression, which can be derived from a combination of equation (11.6) with Trouton's law, was proposed by J. M. Crafts (1887), viz.,

$$\Delta t = cT_b\Delta p, \tag{11.16}$$

where Δt °C is the change in the normal boiling point T_b due to a difference Δp in the pressure from 760 mm, and c is a constant. The value of c for ordinary liquids can be estimated in the following manner. Since Δt is numerically equal to ΔT, it follows that $\Delta p/\Delta t$ is approximately equal to dp/dT and equation (11.6) can then be written as

$$\frac{\Delta p}{\Delta t} = \frac{L_v}{T_b} \cdot \frac{p}{RT_b}.$$

For ordinary liquids, L_v/T_b at the boiling point is approximately 21 cal mole^{-1} deg^{-1} and taking p as 760 mm and R as 2 cal deg^{-1} mole^{-1}, the result is

$$\frac{\Delta p}{\Delta t} = \frac{21 \times 760}{2T_b} \approx \frac{8 \times 10^3}{T_b} \text{ mm deg}^{-1}$$

or, upon rearrangement,

$$\Delta t \approx 0.00012 T_b \Delta p,$$

where Δp is expressed in mm of mercury. For most ordinary liquids c in equation (11.16) is about 0.00012; for associated liquids 0.00010 should be used and for liquids of very low boiling point the best value of c is 0.00014.

Example: The boiling point of water at 770 mm is 100.37°C; calculate the value at 1 atm by means of Craft's rule.

In this case the liquid is associated, and so c may be taken as 0.00010; T_b is $273 + 100 = 373°$, with sufficient accuracy; and Δp is $770 - 760 = 10$ mm. Hence,

$$\Delta t = 0.00010 \times 373 \times 10 = 0.37.$$

The boiling point at 760 mm is thus $100.37 - 0.37 = 100.00°$C.

PHYSICAL PROPERTIES OF LIQUIDS

12a. Surface Tension.—A molecule in the interior of a liquid is completely surrounded by other molecules, and so, on the average, it is attracted equally in all directions. On a molecule in the surface, however, there is a resultant attraction inwards, because the number of molecules per unit volume is greater in the liquid than in the vapor. As a consequence of this inward pull, the surface of the liquid always tends to contract to the smallest possible area; it is for this reason that drops of liquid and bubbles of gas become spherical, as far as is feasible, for the surface area is then a minimum for the given volume.

In order to extend the area of the surface, it is necessary to do work, to bring molecules from the bulk of the liquid into the surface, against the inward attractive force. The work required to increase the area by 1 sq cm is called the **surface (free) energy.** The tendency for a liquid to contract may thus be regarded as a manifestation of this free energy, since a spontaneous process at constant temperature and pressure must be accompanied by a decrease in free energy (§ 9b).

As a result of the tendency to contract, a surface behaves as if it were in a state of tension. If a cut were made along any line in the surface, a force would have to be applied to hold the separate portions of the surface together. This force is proportional to the length of the cut, and its value per unit length is called the **surface tension.** The latter, represented by the symbol γ, is often defined as *the force in dynes acting along the surface of a liquid at right angles to any line 1 cm in length.* The surface tension is equal, both numerically and dimensionally, to the surface energy. Thus, surface energy is expressed as ergs per sq cm, i.e., in ergs cm^{-2} units; this is equivalent to (dynes $\times$ cm) cm^{-2}, i.e., dynes cm^{-1} or dynes per cm, which is the unit of surface tension. Surface tension is really a measure of surface energy, and it is largely for historical reasons that the former concept has been retained. However, both points of view have their uses in the study of liquid surfaces.

It is frequently stated that, because a surface has a spontaneous tendency to contract, it behaves like a stretched elastic membrane, e.g., a thin sheet of rubber. This analogy must be used with caution for there are fundamental differences between a liquid surface and a stretched membrane. In the first place, the tension in a membrane generally increases as the surface area is increased, but the surface tension of a liquid has a constant value. Further, when the surface area of a liquid decreases, molecules are withdrawn from the surface into the interior of the liquid. In the contraction of a stretched membrane, on the other hand, the number of molecules remains constant, but their distance apart decreases.

One of the consequences of surface tension is that the pressure on the concave side of a surface is greater than that on the convex side. If there were no excess pressure on the concave side, a bubble could not exist, for it would collapse as a result of the force due to surface tension. To illustrate this statement, consider a spherical gas bubble in a liquid; suppose this to be cut by an imaginary plane into two hemispheres (Fig. 12.1). If P dynes per sq cm is the excess pressure inside the sphere, there will be a tendency for the two halves to be driven apart by a force F, equal to the product of the pressure and the area of the circle where the hemispheres meet. The area of this circle, indicated by the dotted line, is πr^2, where r cm is the radius of the sphere; hence,

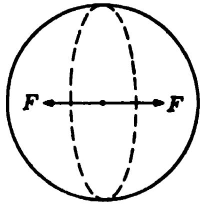

FIG. 12.1. Forces inside spherical bubble

$$F = P \times \pi r^2 \text{ dynes.}$$

The force is counteracted by the surface tension γ dynes per cm, acting along the circumference $2\pi r$ of the same circle, which tends to draw the hemispheres together; the surface tension force F is thus given by

$$F = \gamma \times 2\pi r \text{ dynes.}$$

At equilibrium the two forces must be equal, and by equating the two quantities, it is seen that

$$P = \frac{2\gamma}{r} \text{ dynes per sq cm.} \tag{12.1}$$

The excess pressure inside the spherical bubble, that is, on the concave side, is thus inversely related to the radius of the bubble.

The fact that the pressures inside small bubbles are large accounts for the phenomena of "superheating" and "bumping" that are frequently observed when a pure liquid is heated in a perfectly clean, smooth vessel. In the absence of rough places, excrescences, etc., where bubbles can grow, the bubbles are almost molecular in size, and the pressures required to form them are very high. The temperature thus tends to rise above the normal boiling point of the liquid, so as to increase the pressure of the vapor sufficiently to produce the very small bubbles. As the bubbles grow, however, the pressure is larger than necessary; rapid expansion of the vapor, leading to "bumping," then occurs.

12b. Capillary Action.—Because of the forces acting between the molecules of a liquid themselves, and between these molecules and those of the solid material, e.g., glass, with which it is in contact, the surface of a liquid in a tube, that is, the **meniscus** (Greek: *small moon*), is always curved. The nature of the curvature depends on whether the liquid and the solid attract one another strongly or not; in the former case the liquid "wets" the solid and the meniscus is concave upward, as in Fig. 12.2A, but in the latter case the solid is not wetted, and the meniscus is concave downward as in Fig. 12.2B. In the former case the **contact angle** θ between the liquid and the solid surface is less than 90° and in the latter it is greater than 90°. These two types of behavior are well illustrated by water and mercury, respectively, in contact with glass.

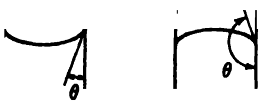

FIG. 12.2. Curvature of liquid surface (meniscus) in a tube

If a liquid is placed in a capillary tube, the radius of curvature of the meniscus will be small; it follows, therefore, from equation (12.1) that there will be a considerable difference of pressure on the two sides of the meniscus, and this has significant consequences. Consider the case of a liquid which wets the surface of glass, and suppose a capillary tube is placed vertically in a large vessel of the liquid, in which the surface is almost flat. Since the liquid wets the glass, the meniscus in the tube will be concave upward, as indicated in Fig. 12.3A. At the point X, just below the surface in the capillary tube, i.e., on the convex side, the pressure will be less than that in the vapor space just above the surface by the amount $2\gamma/a$, where a is the radius of curvature of the surface and γ is the surface tension of the liquid. On the other hand, at the point Y, where the surface is virtually flat and the radius of curvature is very large, there will be little difference of pressure between the two sides of the surface. Since the pressure in the vapor space above X must be the same as that above Y, it follows that the pressure under the surface of the liquid at Y will be greater by the amount $2\gamma/a$ dynes per sq cm than it is under the surface at X.

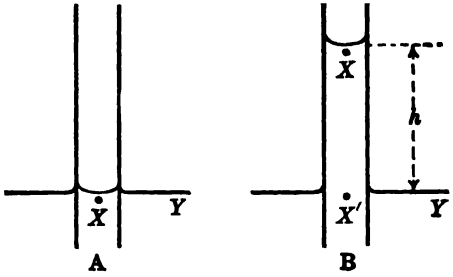

FIG. 12.3. Capillary rise and surface tension

The result of the greater pressure at Y than at X is that the liquid is forced up the capillary tube, and equilibrium is attained only when the surface of the liquid in the tube is h cm above that outside, as in Fig. 12.3B. The pressure at the point X' is now the same as at Y because of the column of liquid above the former. The hydrostatic pressure of the column of h cm of liquid, i.e., hgd dynes per cm, where g is the acceleration due to gravity, and d is the density of the liquid, is then equal to the pressure difference $2\gamma/a$ between X and Y; that is,

$$hgd = \frac{2\gamma}{a},$$

$$\gamma = \tfrac{1}{2}hgda. \qquad (12.2)$$

The radius of curvature a of the meniscus is related to the radius r of the capillary tube by

$$\frac{r}{a} = \cos\theta,$$

where θ is the contact angle (see Fig. 12.2). Hence, equation (12.2) becomes

$$\gamma = \frac{hgdr}{2\cos\theta}. \tag{12.3}$$

This expression relates the surface tension to the height the liquid rises in a capillary tube which it wets. If the meniscus is hemispherical, the angle of contact between the glass and the liquid is zero and thus $\cos\theta = 1$; then equation (12.3) reduces to

$$\gamma = \tfrac{1}{2}hgdr, \tag{12.4}$$

a form applicable, to a good approximation, to water and many other liquids.

A liquid which does not wet glass, e.g., mercury, forms a surface which is convex upward; the pressure just below the meniscus in the capillary tube will thus be *greater* than at a plane surface. The level of the mercury in a glass capillary tube will consequently be forced down below that of the surrounding liquid. Equation (12.4) will be approximately applicable to this case also, where h is the distance of the meniscus in the capillary tube below the flat surface.

The rise or fall of liquid in capillary tubes is seen to be related to the surface tension of the liquid; phenomena associated with surface tension are thus frequently considered under the general headings of **capillarity** or **capillary action.** These terms are sometimes used even though capillary tubes may not actually be involved.

12c. Measurement of Surface Tension.—The best known method for determining surface tension, and one which is capable of considerable accuracy, depends on the measurement of the rise of the liquid surface in a capillary tube. If the height h to which the liquid ascends is ascertained, and the radius r of the tube is known, the surface tension can be calculated by means of equation (12.4). For accurate work, however, a number of corrections must be applied. To avoid the necessity of determining r, it is usual to compare the capillary rise of a liquid with that of a standard liquid, such as water or benzene, of known surface tension. If h is the rise of a liquid of surface tension γ and density d in a given capillary tube, and h_0 is the rise in the same tube of a standard liquid of density d_0 and surface tension γ_0, it follows from equation (12.4) that

$$\frac{\gamma}{\gamma_0} = \frac{hd}{h_0d_0}.$$

Since γ_0 is known, the required surface tension γ can be obtained from measurements of capillary rise and density only.

The weight m of a drop of liquid falling from a narrow vertical tube is approximately proportional to the surface tension γ; this is the basis of the **drop weight method,** used mainly for the comparison of surface tensions. If the values for two liquids are γ_1 and γ_2, respectively, and the mean weights of the drops falling from the same tube are m_1 and m_2, then

$$\frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2}. \tag{12.5}$$

If one of the liquids is water or benzene, whose surface tension is known from capillary rise measurements, the surface tension of the other can be obtained by utilizing equation (12.5).

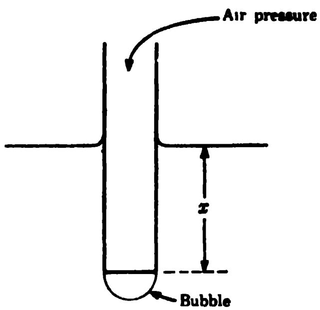

FIG. 12.4. Maximum bubble pressure method for surface tension

A number of other methods for the determination of surface tension have been employed. Among these mention may be made of one which depends on the pressure required to produce gas bubbles at the end of a tube of known radius inserted in the liquid. If the air pressure applied at the top of a moderately wide tube, immersed to a depth x in the liquid, is gradually increased, a bubble will form at the lower end of the tube (Fig. 12.4). When the radius of the bubble is equal to that of the tube r, the air pressure is a maximum and the bubble breaks away. The maximum observed pressure $p_{\max}$ is then given by

$$p_{\max} = xgd + 2\gamma/r,$$

where the first term on the right is the amount required to overcome the hydrostatic pressure of the column x of liquid and the second represents the excess pressure on the concave side of the bubble.

Surface tensions can be determined rapidly with small quantities of liquid using the du Noüy tensiometer, forms of which are available commercially. A horizontal platinum wire ring, about 6 cm in diameter, attached to one arm of a balance, is immersed in the liquid under examination. By means of weights or a torsion wire, force is applied to the other arm of the balance until the ring is detached from the surface of the liquid. Since contact between the liquid and the ring must be broken at both the inner and the outer circumference of the latter, the force required is

$$F = 2 \times 2\pi b\gamma$$

where $2\pi b$ is the circumference of the ring of radius b. Hence, if the force is measured the surface tension of the liquid can be evaluated. As with all the other methods, various corrections must be applied if accurate results are required.

The value of the surface tension is affected to some extent by the nature of the gas above the surface; substances which are able to dissolve in, or to react with, the liquid produce the most marked effects. The results are also dependent on whether the space above the meniscus consists only of the saturated vapor of the liquid or whether it is open to the air. The surface tension values for a number of liquids recorded in Table 12.1 were obtained with the surface in contact with air.

TABLE 12.1. SURFACE TENSIONS OF LIQUIDS AT 20°C

Water	72.8 dynes cm^{-1}	Carbon tetrachloride	26.9 dynes cm^{-1}
Nitrobenzene	41.8	Acetone	23.7
Carbon disulfide	33.5	Methanol	22.6
Benzene	28.9	Ethanol	22.3
Toluene	28.4	Diethyl ether	16.9

12d. Interfacial Tension.—The force, equivalent to surface tension, that is operative at the surface of separation between two insoluble, or sparingly soluble, liquids is called the **interfacial tension.** According to **Antonoff's rule** (G. N. Antonoff, 1907), which holds in many instances, the tension γ_{AB} at the interface between two liquids A and B with surface tensions γ_A and γ_B, respectively, is given by

$$\gamma_{AB} = \gamma_B - \gamma_A.$$

Since surface (and interfacial) tensions are always positive, it follows that the interfacial tension is less than that of the larger of the two surface tensions. This is because the attraction across the interface, between the molecules of one liquid and those of the other, tends to reduce the inward pull of the molecules in the surface by those of the same kind. The greater the molecular attraction between the two liquids the lower is the interfacial tension. For example, the interfacial tensions between the long-chain aliphatic alcohols and acids, on the one hand, and water, on the other hand, are about 10 to 15 dynes per cm; with liquid paraffins and water, however, the values are between 50 and 60 dynes per cm. The polar alcohols and acids, containing OH groups, are attracted by the polar water molecules (see § 54g), but the latter are virtually indifferent to the nonpolar hydrocarbon molecules.

Both capillary rise and drop weight methods have been adapted to the measurement of interfacial tensions, the latter being frequently employed for the purpose. The average weight, or volume, of a drop of one liquid forming in the other is determined. The usual procedure is to fill a pipet with one liquid, e.g., the denser, and to immerse the tip in the other liquid; drops are allowed to fall from the end of the pipet, and by counting their number the average volume v of a drop can be calculated. The effective mass of the drop, equal to $v(d_1 - d_2)$, where d_1 and d_2 are the densities of the two liquids, is proportional to the interfacial tension.

The subject of interfacial tension is of considerable importance in connection with the properties of emulsions (§ 55l), detergents, foams, etc.

12e. Surface Tension and Temperature.—*Surface tensions almost invariably decrease with increasing temperature*, and R. von Eötvös (1886) proposed a relationship between the molar surface energy and the temperature, based on the concept of corresponding states. If v is the specific volume of a liquid, i.e., the reciprocal of the density, and M is the molecular weight, Mv is the molar volume. If this volume is considered to be spherical, which is the stable form, the area of the sphere will be proportional to $(Mv)^{2/3}$; the product of this molar surface area and the surface tension gives the molar surface energy, i.e., $\gamma(Mv)^{2/3}$. According to Eötvös, this quantity varies in a linear manner with the temperature, so that a form of the **Eötvös equation** is

$$\gamma(Mv)^{2/3} = a - kt, \tag{12.6}$$

where a and k are constants, and t is the temperature. The value of a may be derived by utilizing the fact that at the critical temperature t_c, when the surface of separation between a liquid and its saturated vapor disappears (§ 10b), the surface tension should be zero. At this temperature equation (12.6) becomes

$$0 = a - kt_c \qquad \text{or} \qquad a = kt_c,$$

so the Eötvös equation can be written as

$$\gamma(Mv)^{2/3} = k(t_c - t). \tag{12.7}$$

A study of the Eötvös equation was made by W. Ramsay and J. Shields (1893), who found that the experimental results for a number of liquids could be better expressed by the relationship

$$\gamma(Mv)^{2/3} = k(t_c - 6 - t). \tag{12.8}$$

This implies that the surface tension becomes zero at a temperature 6° below the critical point, a fact which may be of significance in connection with the observation, referred to in § 10b, that the meniscus of some liquids disappears at a temperature a few degrees below the point at which the liquid ceases to exist.

The constant k in equations (12.6), (12.7) and (12.8) is the slope of the linear plot of $\gamma(Mv)^{2/3}$ against the temperature t; it is, consequently, the temperature coefficient of the molar surface energy. According to Ramsay and Shields, this coefficient has the same value, namely 2.12, for all normal, non-associated liquids. For certain substances, e.g., water, alcohols and carboxylic acids, all of which contain hydroxyl groups, the temperature coefficient is not only less than 2.12, but it varies with temperature. The abnormal behavior was attributed to the fact that these substances form associated molecules in the liquid state (see § 16i), and attempts were made to calculate the extent of association by determining the value of M which must be used in order to make k in equation (12.6) equal to 2.12. The ratio of this value of M to that for the simple molecules was believed to give a measure of the association factor. More recent work, however, has shown that although associated liquids give temperature coefficients that are lower than 2.1 and that vary with temperature, the so-called factors of association calculated from the results have no exact significance. Further, many substances which are apparently not associated, e.g., succinic nitrile, give very low values of k, viz., 0.56, whereas others, glyceryl tristearate, have very high values, viz., 6.0.

Theoretical considerations suggest that, in addition to association, the temperature coefficient of the molar surface energy will be affected by the shape and orientation of the molecules in the surface of the liquid, and also by their mutual attraction. A *marked* increase of the Eötvös coefficient k with increasing temperature, as observed with hydroxylic compounds, is probably a satisfactory indication that the liquid is associated, but the values certainly have no simple quantitative meaning.

12f. Viscosity and Fluidity.—Liquids, like gases, exhibit the resistance to flow known as viscosity (§ 3h). In general, it is the property which opposes the relative motion of adjacent layers of the liquid, and so it may be regarded as an internal friction. As with gases, the **viscosity** η in poises, i.e., dynes cm^{-2} sec units, is defined as the force per unit area, in dynes per sq cm, required to maintain a difference of velocity of 1 cm per sec between two parallel layers of liquid, 1 cm apart. The relationship between the viscosity and the rate of flow of the liquid through a tube is also given by the Poiseuille equation (3.22) for streamline (nonturbulent) flow,* which may here be written in the form

$$\eta = \frac{\pi r^4 tp}{8vL}, \tag{12.9}$$

where v cc is the volume of liquid flowing in t sec through a *narrow* tube of radius r cm and length L cm, under a driving pressure of p dynes per sq cm. If a liquid has a low viscosity it is said to be "mobile," but if the coefficient is high, the liquid is "viscous" and does not flow easily. The reciprocal of the viscosity is frequently employed; it is called the **fluidity**, and is given the symbol ϕ (Greek, *phi*), that is, ϕ is equal to $1/\eta$. The fluidity is a measure of the ease with which a liquid can flow.

If a solid body is falling through a liquid, the effect of viscosity is to exert a drag on the falling body. Instead of a continued increase in its rate of fall, the body acquires a constant velocity, called the **terminal velocity**, when the gravitational pull downwards just balances the upward drag due to viscosity. For a falling sphere of radius r this steady velocity u is related to the viscosity η by the **Stokes's law** equation

$$u = \frac{2gr^2(d' - d)}{9\eta}, \tag{12.10}$$

where g is the gravitational acceleration, d' is the density of the sphere and d is that of the liquid. If d is small in comparison with d', equation (12.10) reduces to the simple form

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* A liquid of density d g cm^{-3}, flowing through a tube of radius r cm with a velocity v cm sec^{-1} will, as a general rule, exhibit streamline or laminar flow if the **Reynolds number** $2rvd/\eta$ is about 2000 or less.

$$u = \quad 9\eta \qquad (12.11)$$

which is particularly applicable when the medium is a gas instead of a liquid (see § 13b).

12g. Measurement of Viscosity.—The direct measurement of viscosity is based on the Poiseuille equation (12.9), the rate of flow of the liquid, under a definite pressure, through a capillary tube being determined. For general laboratory work, however, a comparative method, using an instrument known as a **viscometer,** is employed. A simple form of viscometer, due to W. Ostwald, is shown in Fig. 12.5. A definite volume of liquid is introduced into the bulb C and is then sucked into A; the time t is observed for the liquid to flow through the capillary tube B, between the marks x and y. The measurement is then repeated with the same volume of another liquid whose viscosity is known. Referring to equation (12.9), it is seen that, since the same viscometer is used for the two liquids, the radius r and length L of the capillary tube, and the volume v of the bulb A, are the same in both cases. The pressure p depends on the head of liquid and its density; the former is constant, but the latter varies for the two liquids. If η_1 and η_2 are the viscosities of two liquids of density d_1 and d_2, respectively, and t_1 and t_2 are the times of flow in the given viscometer, then, by substituting these values in equation (12.9) for each liquid and dividing, the result is

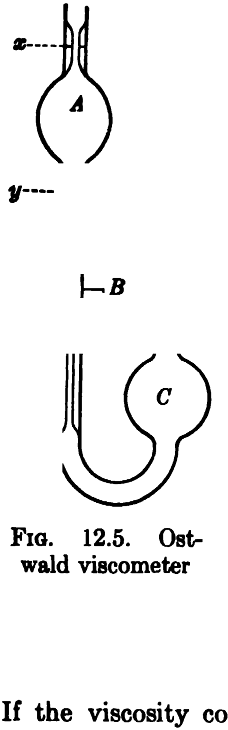

FIG. 12.5. Ostwald viscometer

$$\frac{\eta_1}{\eta_2} \quad \frac{d_1t_1}{d_2t_2}. \qquad (12.12)$$

If the viscosity coefficient η_2 and density d_2 of one liquid are known, the viscosity of the other can be calculated from its density and the times of flow.

For viscous liquids, such as hydrocarbon oils, the **falling sphere method,** which is based on the Stokes equation (12.10), is frequently employed for the determination of viscosity. A small steel sphere is introduced below the surface of the liquid in a tall cylinder, and the time taken for it to fall between two marks is noted. The observation is then repeated with the same sphere and another liquid of known viscosity. The distance fallen is the same in each case, and so the rate of fall u is inversely proportional to the time of fall t; it follows, therefore, from equation (12.10), since g and r are constant, that

$$\frac{\eta_1}{\eta_2} = \frac{t_1(d' - d_1)}{t_2(d' - d_2)},$$

where d' is the density of the steel ball, and d_1 and d_2 are the densities of the two liquids. Since the viscosity of one liquid is known that of the other can be determined from observations on the falling sphere.

The viscosities of a number of liquids at 20°C are given in Table 12.2; the results are expressed in terms of the **millipoise**, equal to 0.001 poise (§ 3h). In general, associated liquids like glycol and glycerol, which have two or more hydroxyl groups, have very high viscosities. The reason is that a network of hydrogen bonds is formed between the molecules; this network extends throughout the liquid, thus making flow difficult. In addition to many applications in industry, viscosity measurements are useful in determining the molecular weights of long-chain polymers (§ 56e).

TABLE 12.2. VISCOSITIES AT 20°C IN MILLIPOISES

Ethyl ether	2.33	Carbon tetrachloride	9.68
Acetone	3.29	Water	10.09
Carbon disulfide	3.68	Ethanol	12.0
Chloroform	5.63	Acetic acid	12.2
Methanol	5.93	Nitrobenzene	20.1
Benzene	6.47	Ethylene glycol	199
Chlorobenzene	8.00	Glycerol	8500

12h. Viscosity and Temperature.—The effect of temperature on the viscosity of a liquid is strikingly different from the behavior with a gas; while in the latter case the viscosity coefficient increases with temperature, *the viscosity of a liquid decreases markedly as the temperature is raised.* The variation of the viscosity of a liquid with temperature is best expressed by means of an exponential or logarithmic equation, viz.,

$$\eta = Ae^{E/RT} \tag{12.13}$$

or

$$\log \eta = \frac{B}{T} + C, \tag{12.14}$$

where A and E, or B and C, are constants for the given liquid. According to equation (12.14), the plot of log η against the reciprocal of the absolute temperature, i.e., $1/T$, should yield a straight line; this has been verified for a large number of liquids.

The entirely different effects of temperature on the viscosities of liquids and gases implies that the fundamental cause of the viscosity is different in the two cases. It has been suggested that before a molecule can take part in liquid flow it must acquire sufficient energy to push aside the molecules which surround it. As the temperature increases the number of such molecules *increases* in proportion to the Boltzmann factor $e^{-E/RT}$ (see § 3g), and hence the resistance to flow, that is, the viscosity, may be expected to *decrease* in a reciprocal manner, i.e., according to the factor $e^{E/RT}$, as in equation (12.13). With associated (hydroxylic) liquids, energy is required, in addition, to break the hydrogen bonds; consequently, E is larger and, at any given temperature, the viscosity is greater than for nonassociated liquids.

An empirical relationship, which may have some theoretical significance, was discovered by A. J. Batschinski (1913); if η is the viscosity and v is the specific volume of a liquid, at the same temperature, then

$$\eta = {}_{\displaystyle v - b}, \qquad (12.15)$$

where b and c are constants for each liquid. Rearrangement of equation (12.15) and introduction of the fluidity ϕ in place of $1/\eta$, gives

$$v = b + \frac{c}{\eta} = b + c\phi, \qquad (12.16)$$

so that over a range of temperature the fluidity should be a linear function of the specific volume. This relationship has been found to hold with an accuracy of better than 1 per cent for over sixty nonassociated liquids. It may be mentioned that the value of b is almost identical with that of the van der Waals constant b for each substance.

12i. The Structure of Liquids.—It was seen earlier that at the critical point the gaseous and liquid forms of a substance become indistinguishable. On the other hand, the small volume change accompanying fusion suggests that there is some similarity between the arrangement of the molecules in the liquid and solid states near the melting point. In a gas the molecules are distributed in a purely random manner, whereas in the solid there is complete regularity of structure (Chapter 7). It appears, therefore, that as the temperature of a liquid is raised the internal structure should change gradually from some sort of order near the melting (or freezing) point to complete disorder at the critical temperature. This conclusion is supported by observations made by means of X-rays. Since these can best be understood after a study of the structure of solids, further data concerning liquid structure will be deferred to § 19h.

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PROBLEMS

1. When 1.480 g of ethanol was heated at 240°C in a sealed tube, it consisted of 2.56 ml liquid and 2.91 ml vapor. In another experiment 2.222 g consisted of 3.50 ml

liquid and 5.13 ml vapor. Calculate the orthobaric densities of ethanol liquid and vapor at this temperature.

2. The orthobaric densities of sulfur dioxide at several temperatures are as follows:

t°C	132.0	145.2	151.7	156.1
d_l g ml^{-1}	0.9567	0.8495	0.7663	0.6718
d_v g ml^{-1}	0.1589	0.2331	0.2998	0.3787

(*a*) Plot the data and determine the critical volume of sulfur dioxide from the graph. The critical temperature is 157.5°C. (*b*) Estimate the critical pressure. (*c*) Determine the equation for the rectilinear diameter (or mean density line).

Use the data given above in conjunction with the Hakala *equation* $d_l + d_v = 2d_c - a(d_l - d_v)^{10/3}$, where a is a constant, to determine the *critical density* d_c *by a graphical* method.

3. The heat of vaporization of cyclohexane (C_6H_{12}) at its boiling point 80.75°C is 85.6 cal g^{-1}. The densities of the liquid and vapor at this temperature are 0.7199 and 0.0029 g cm^{-3}. (*a*) Calculate by exact and approximate methods the value of dp/dT in cm deg^{-1} units. (*b*) Estimate the boiling point at 740 mm pressure. (*c*) If it is to be distilled at 25°C, to what value must the pressure be reduced?

4. The critical temperature and pressure of argon are -122.44°C and 48.00 atm respectively. (*a*) Calculate the van der Waals constants a and b. (*b*) Estimate the critical density. The experimental value is 0.5308 g ml^{-1}. Account for the discrepancy.

5. When 10.5 liters of nitrogen measured at 30°C and 770 mm pressure were bubbled through a saturator containing bromobenzene (C_6H_5Br) at 40°C, the saturator and its contents decreased in weight by 0.8560 g. Calculate the vapor pressure of bromobenzene at 40°.

6. The critical constants of dichlorodifluoromethane are $t_c = 111.5$°C, $P_c = 39.6$ atm and $d_c = 0.555$ g ml^{-1}. Determine the pressure at which 3.0 moles of the gas will occupy 10.0 liters at 25°C using the van der Waals equation.

7. The normal boiling point of hexane is 68.7°C; at what temperature will it boil if the pressure were 1000 mm? The recorded value is 77.8°C.

8. In general, L_v is a function of temperature. Derive the equation for log p as a function of temperature when (*a*) $L_v = a + bT$, (*b*) $L_v = a + bT + cT^2$.

9. A steel container of 3 liters capacity is charged with 1 kg of CO_2. Calculate (*a*) the weights of liquid and vapor, respectively, (*b*) the volumes of liquid and vapor in the cylinder, when the temperature is 20°C. The orthobaric densities in g ml^{-1} at 20°C are: liquid 0.772, vapor 0.190.

10. The Berthelot equation of state (for one mole of gas), $\left(P + \frac{a}{TV^2}\right)(V - b) = RT$, is more useful than the van der Waals equation at pressures below 1 atm. (*a*) Evaluate a, b and R in terms of the critical constants. (*b*) Calculate RT_c/P_cV_c and compare with the values in Table 10.2. (*c*) Derive the reduced equation of state.

11. The vapor pressure of Hg is given by an equation of the Kirchhoff type as

$$\log p\,(\text{mm}) = 10.53 - \frac{}{T}$$

(*a*) Calculate the heat of vaporization at 25°C. (*b*) Express L_v as a function of temperature.

12. The vapor pressure of *n*-butyl alcohol is given by the equation

$$\log p\,(\text{mm}) = -\frac{2443.0}{T} + 9.1362.$$

Calculate l_v at (*a*) the boiling point, 117°C, (*b*) 100°C.

13. The vapor pressure of fluorobenzene at t°C is given by an equation [illegible] Antoine type as

$$\log p\,(\text{mm}) = 6.95208 - \frac{1248.083}{t + 221.827}.$$

Calculate the temperature of the normal boiling point.

14. (*a*) What volume change will occur when 2 moles of Hg are vaporized at its normal boiling point, 356.9°C? The vapor pressure is 723.7 mm at 354°C and 777.9 mm at 358°C, l_v = 70.4 cal g^{-1}. (*b*) Calculate w, ΔE and ΔF for the process.

15. The vapor pressure of *n*-propyl alcohol varies with temperature as follows:

t°C	50	60	70	80
p mm	87.2	147.0	239.0	376

(*a*) Evaluate L_v from a suitable graph of these data. (*b*) At what temperature is the vapor pressure 200 mm?

16. When water at 20°C is added to a capillary U-tube of approximately 0.40 mm diameter, a difference in level of 1.00 mm is observed. What is the difference in the bore of the two arms of the tube?

17. Mercury will not flow out of a porous vessel if the holes are small enough. Calculate the size of the holes which will just prevent leakage of mercury out of a crucible with a porous bottom when the crucible contains a column of mercury 5 cm high. The surface tension of mercury is 476 dynes cm^{-1} at 20°C.

18. A barometer can be read to ±0.1 mm. What is the minimum diameter of a barometer tube such that the capillary effect will produce no error in the pressure reading?

19. Estimate the critical temperature of *n*-hexane (C_6H_{14}) from the following data of its surface tension at several temperatures:

t°C	0	20	40
γ dynes cm^{-1}	20.5	18.4	16.3
d g cm^{-3}	0.6769	0.6594	0.6411

The recorded value is 234.7°C.

Electrons can be produced by several methods, in addition to the one
above. For example, the exposure of various materials, partic-
iolet radiation, i.e., light of short wave length, results
phenomenon is known as the **photoelec-**
tly accompanied by the libera-
alcium and barium
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of

6

Atomic and Molecular Structure

THE FUNDAMENTAL PARTICLES OF MATTER

13a. Cathode Rays: The Electron.—In the discussion of the properties of gases and liquids, it has been sufficient to postulate the existence of molecules as units without consideration of their internal structure. For the study of the solid state as well as for other aspects of physical chemistry, however, it is desirable to go into further detail. In the present chapter, therefore, an account will be given of the information that has been obtained concerning the internal structures of atoms and the factors which determine the combination of atoms to form molecules. Several, apparently independent, lines of investigation have thrown light on these fundamental problems.

When an electrical discharge is passed through a gas at low pressure, e.g., 0.1 mm of mercury or less, a variety of phenomena are observed. Among these is the fact that a stream of rays, known as **cathode rays,** is emitted from the negative electrode or cathode (Fig. 13.1). These rays normally travel in straight lines perpendicular to the cathode, but they can be deflected by the application of an electric or a magnetic field. From various properties of the cathode rays it appears probable that they consist of a stream of negatively charged particles expelled from the cathode with high speed. The particles are called **electrons,** and the magnitude of the charge they carry is equal to the unit charge of electricity. In other words, all electrical charges are integral multiples of the charge carried by a single electron.

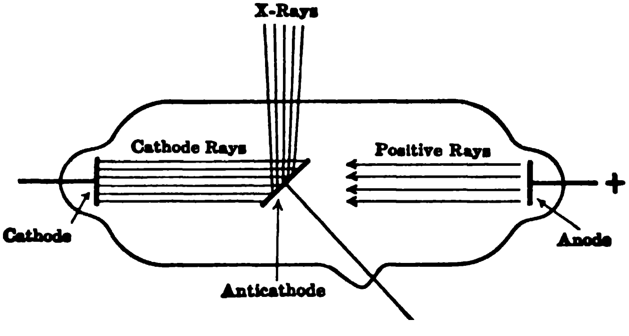

Fig. 13.1. Rays in a discharge tube

Electrons can be produced by several methods, in addition to the one described above. For example, the exposure of various materials, particularly metals, to ultraviolet radiation, i.e., light of short wave length, results in the emission of electrons. This phenomenon is known as the **photoelectric effect.** High temperatures are frequently accompanied by the liberation of electrons, especially from certain oxides, such as calcium and barium oxides containing traces of cerium oxide. This is an illustration of the **thermionic effect** which is utilized in the production of electrons in vacuum (radio) tubes and similar devices.

By studying the deflection in electric and magnetic fields of a stream of electrons accelerated by moving through an electrical potential gradient, it is possible to calculate a quantity ϵ/m, which gives the ratio of the electronic (unit) charge ϵ (Greek, *epsilon*) to the mass m of a single electron. The method used by J. J. Thomson (1897) may be illustrated by Fig. 13.2, which shows an electrical discharge tube with anode A and cathode C. The rays emitted from the cathode pass through a hole in the anode and a narrow beam is selected by the slit S. This beam strikes the extreme right end of the tube at the point F, where it produces a luminous spot. By means of an electromagnet, seen in section at M, outside the tube, a magnetic field is applied to the cathode ray beam, so that it is deflected from its original path. If H is the strength of the magnetic field, ϵ is the charge carried by each cathode ray particle, and v is the velocity, the force exerted on the particle is $H\epsilon v$. Under the influence of this constant force, the beam will describe a circular path of radius r, so that the centrifugal force is mv^2/r. In the actual path shown by the dotted line in Fig. 13.2, the magnetic and centrifugal forces balance, so that

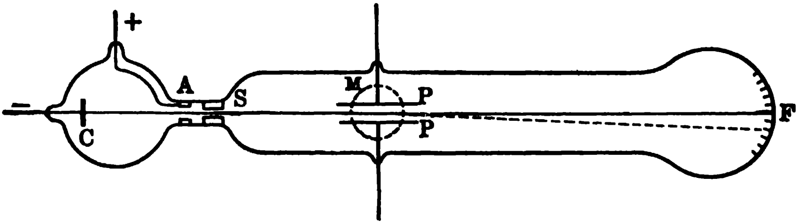

Fig. 13.2. Determination of the velocity of electrons (J. J. Thomson)

$$H\epsilon v = mv^2/r$$

and

$$\epsilon/m = v/Hr. \tag{13.1}$$

An electric field is now applied to the beam by connecting the plates PP, within the discharge tube, to a source of high voltage. The strength E of this field, acting in a direction perpendicular to the magnetic field, is adjusted so as to bring the cathode ray beam back to its original direction, as indicated by the return of the luminous spot to the point F. The force exerted by the electric field is $E\epsilon$, and this just balances that due to the magnetic field; hence,

$$E\epsilon = H\epsilon v$$

and

$$v = E/H.$$

By combining this result with equation (13.1) so as to eliminate v,

$$\epsilon/m = E/H^2r. \tag{13.2}$$

The radius r of the path with the magnetic field alone is determined from the deflection of the luminous spot on the scale at the right end of the tube and, since E and H can be measured, the value of ϵ/m can be obtained from equation (13.2).

As a result of numerous experiments, the best value of ϵ/m has been found to be 1.7589×10^7 electromagnetic units (emu), or 5.2731×10^{17} electrostatic units (esu) per gram.* This result is the same, within the limits of experimental error, for all electrons, no matter what their origin, provided their speed of motion is not too great. This striking constancy of the ratio of charge to mass of electrons, produced under a variety of conditions and from various sources, leads to the important conclusion that *the electron is a definite and universal constituent of matter.*

13b. The Electronic Charge.—Since the charge to mass ratio ϵ/m of the electron is known, the mass can be evaluated if the charge is determined. One type of method employed for the estimation of the charge carried by an electron depends on the fact that if small droplets of liquid, either water or oil, are formed in a space containing charged particles, the latter tend to attach themselves to the drops which thus acquire an electrical charge. The sign of the charge carried by a droplet may be positive or negative, depending on the sign of the attached particle, but the magnitude of the charge must be equal to an integral multiple of the electronic (unit) charge. It appears that, in most cases, each drop of liquid carries one unit charge, but some may carry two or more such charges.

Several procedures have been devised to determine this charge. In some of the earlier experiments, a cloud consisting of small drops of water, which had become electrically charged in the manner just described, was obtained by the sudden expansion of air saturated with water vapor. A cloud of this kind will fall with a constant speed under the influence of gravity. More accurate results can be obtained by following the behavior of a single drop rather than of the entire cloud. Further, to avoid errors due to evaporation, the use of oil instead of water was introduced by R. A. Millikan (1911).

If u_1 is the rate at which a single drop falls in air, w is the mass of the drop, and g the acceleration of gravity, then u_1 will be proportional to wg. Suppose now that an electric field of strength E is applied so as to change the rate at which the drop descends. The force now acting on the drop is $E\epsilon \pm wg$, where ϵ is the magnitude of the unit charge, the plus sign indicating that the

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* To convert emu to esu multiply by the velocity of light, 2.998×10^{10} cm per sec.

field is aiding gravity, and the minus sign that it is opposing gravity. The uniform rate of fall u_2 of the drop under these conditions is thus proportional to $E\epsilon \pm wg$; consequently,

$$\frac{u_1}{u_2} = \frac{wg}{E\epsilon \pm wg}. \tag{13.3}$$

The values of u_1 and u_2 can be determined by observation of the drop, and the field strength E is known, as also is g; hence, the determination of the electronic charge by means of equation (13.3) requires only a knowledge of the mass w of a drop. For this purpose, use is made of Stokes's law (§ 12f), according to which the uniform velocity u of a spherical drop of radius r and density d, falling under the influence of gravity through a gas of viscosity η, is given by equation (12.11), i.e.,

$$u = \frac{2gr^2d}{9\eta}. \tag{13.4}$$

In this case, u of equation (13.4) is the same as u_1 of equation (13.3), that is, the rate of descent of the drop under the influence of gravity alone. If the viscosity of the air and the density of the drop are known, the radius of the latter can thus be calculated, after applying a correction to Stokes's law required by the very small size of the drops observed. Since the drop is supposed to be spherical, the volume is $\frac{4}{3}\pi r^3$, and hence the weight w is equal to the product of this volume and the density; thus,

$$w = \tfrac{4}{3}\pi r^3 d. \tag{13.5}$$

All the information is thus available for the evaluation of the electronic charge.

A diagram of the apparatus used by R. A. Millikan is shown in Fig. 13.3. The vessel A, immersed in a thermostat, contained air at a constant pressure regulated by a pump. Through the atomizer B a fine spray of oil drops could be introduced. Of the two plates C and D, the upper, which had a number of small holes, as at E, was connected to one terminal of a high-voltage battery; the other terminal and the lower plate were grounded. When a drop of oil was observed to enter the space between the plates, by passage through one of the holes, the air was ionized by exposure to X-rays entering at W_1. By attachment to a gaseous ion, the oil drop acquired a charge and could be made to move up or down, according to the sign of the charge and the direction of the electric field, which could be reversed at will. In general, more consistent results were obtained when the drop moved upward. The rate of rise or fall u_2 was measured by observation with a microscope, illumination being provided by a powerful beam of light passing through the window W_2. By switching off the battery, the rate of fall u_1 under the influence of gravity alone was determined.

In the course of the experiments with the oil drop, it was found that although the rate of fall of the drop under the influence of gravity was always constant, the rate of rise, when the electric field was applied, was not neces-

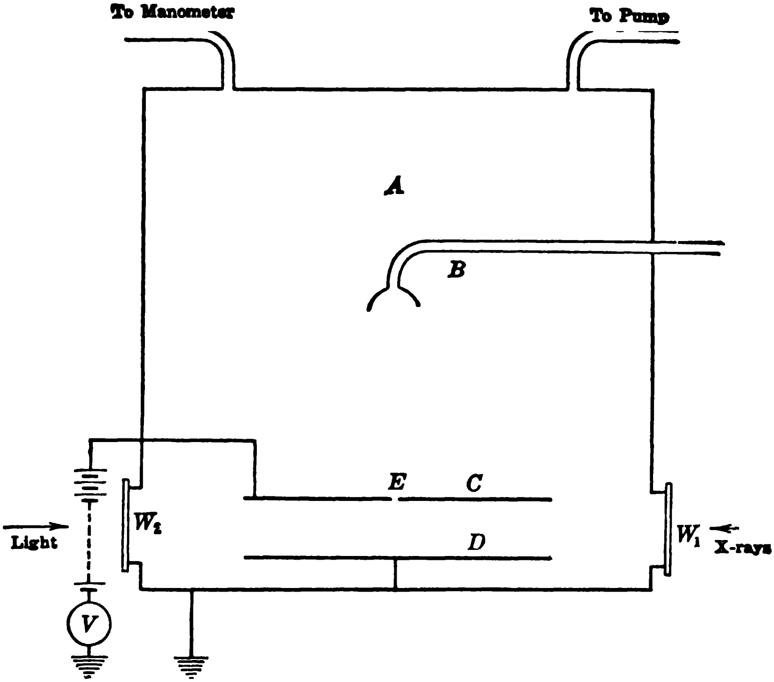

FIG. 13.3. Determination of the electronic charge (Millikan)

sarily the same on successive trips. The explanation of this observation was found to lie in the fact that the oil drop did not always carry the same charge. However, when the values of the charges were calculated, they were always found to be an exact integral multiple of a definite quantity which was taken to be the unit electronic charge. Using the best available value for the viscosity of air in Stokes's equation (13.4), to determine the radius (and mass) of the oil drop, Millikan (1917) concluded that the electron carried a charge of 4.774×10^{-10} esu. Later, the viscosity datum was found to be incorrect, and a recalculation of the results gave 4.805×10^{-10} esu. A more recent repetition of the oil-drop method for the determination of the electronic charge has given a value in very good agreement.

The most accurate procedure for evaluating the charge of the electron depends on an entirely different principle; it involves a knowledge of two important constants, viz., the faraday (§ 43b) and the Avogadro number (§ 3k), both quantities having been determined with great accuracy. For the present, the faraday, which is equal to 2.8929×10^{14} esu,* may be regarded as the total charge on all the molecules in one mole if each carried a unit charge, and the Avogadro number, 6.0232×10^{23}, is the number of indi-

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* The best value of the faraday is 96, 496 abs coulombs; this is converted into esu upon multiplication by 2.998×10^9.

vidual molecules in one mole. It follows, therefore, that the electronic charge is equal to the value of the faraday F divided by the Avogadro number N; thus,

$$\epsilon = \frac{F}{N} = \frac{2.8929 \times 10^{14}}{6.0232 \times 10^{23}} = 4.8029 \times 10^{-10} \text{ esu.}$$

This is the value generally accepted at the present time.

13c. Mass and Radius of the Electron.—The apparent mass of an electron depends on the speed with which it travels; the value of ϵ/m of 5.2731×10^{17} esu, given previously, is for an electron moving with a small velocity, that is, one which is virtually at rest. The electronic mass m derived from this value of ϵ/m is consequently often referred to as the **rest mass.** Since ϵ is equal to 4.8029×10^{-10} esu, it follows that

$$m = \frac{4.8029 \times 10^{-10}}{5.2731 \times 10^{17}} = 9.1083 \times 10^{-28} \text{ gram.}$$

If the mass of the electron were entirely electrical in origin, its rest mass would be approximately equal to rc^2/ϵ^2, where r is the electron radius and c is the velocity of light, 3.0×10^{10} cm per sec. From this the radius of the electron is found to be roughly 2.8×10^{-13} cm.

Utilizing the magnitude of the Avogadro number given above, and taking the gram atom of hydrogen as 1.0079 gram, the mass m_{H} of a single hydrogen atom is given by

$$m_{\text{H}} = \frac{1.0079}{6.0232 \times 10^{23}} = 1.6734 \times 10^{-24} \text{ gram.}$$

It follows, therefore, that the ratio of the mass of a hydrogen atom to that of an electron is

$$\frac{m_{\text{H}}}{m} = \frac{1.6734 \times 10^{-24}}{9.1083 \times 10^{-28}} = 1837.$$

The mass of an electron is consequently only 1/1837th part of the mass of a hydrogen atom, the lightest atom known. On the ordinary atomic weight scale, the mass of an electron, i.e., the weight of a "gram atom" of electrons, is 1.008/1837, i.e., 0.000548 gram.

13d. Positive Particles: The Proton and the Positron.—The discovery of the electron, the unit of negative electricity, naturally led to attempts to find the corresponding unit of positive charge. The discharge tubes, in which cathode rays are observed (Fig. 13.1), also contain **positive rays** consisting of a stream of positively charged particles moving in a direction opposite to that of the cathode rays. A determination of the charge to mass ratio of the particles constituting the positive rays shows, however, that they are very much heavier than electrons. In fact the lightest positively charged particle that has been detected in this manner has about the same mass as the hydrogen atom. This particle is probably *a hydrogen atom that has lost an electron, thus being left with a unit positive charge;* it is known as a **proton** in accordance with the proposal made by E. Rutherford (1922). The proton differs fundamentally from the electron because the latter is to be regarded as merely a charged particle free from matter in the ordinary sense, whereas the former is not; it is a hydrogen atom minus an electron.

Although the existence of positive electrons, as distinct from protons, was predicted theoretically, it was not until 1932 that their discovery was reported by C. D. Anderson. It was observed that positive electrons, now called **positrons,** are produced by the interaction of the cosmic rays, which originate in interstellar space, with matter. Strangely enough, in view of its apparently elusive nature, several other methods of positron production were found soon after the initial discovery of this unit particle of positive electricity free from matter. Experiments with positrons from different sources have shown that their charge and mass are practically identical with the corresponding properties of ordinary (negative) electrons. The two particles are thus to be regarded as the exact electrical opposites of each other. When a positive and a negative electron combine, the result is a neutralization of the charges accompanied by complete annihilation of both particles; in their place there appears an amount of energy, in the form of radiation, equivalent to the masses of the two electrons (§ 65g).

13e. The Neutron.—In 1920, E. Rutherford had suggested that there might exist a particle, which he called a **neutron,** *having no charge but with a mass about the same as that of a proton* (or a hydrogen atom). For several years, however, there was no direct evidence for the occurrence of such a particle, but in 1932, J. Chadwick showed that neutrons are formed when α-rays from radioactive substances (§ 63b) impinge on certain light elements, e.g., beryllium or boron. Neutrons can now be produced in various ways and they always have the same properties; they carry no resultant electrical charge, and their mass is very slightly greater than that of the proton. The mass of the neutron is 1.00871 compared with 1.00732 for the proton, on the chemical atomic weight scale.

13f. Characteristic X-Rays and Atomic Number.—When the cathode rays from a discharge tube fall upon matter, new radiations, known as **X-rays,** are produced (W. C. Röntgen, 1895). These rays differ from cathode rays in many respects; they have a greater penetrating power and are not deflected by electric and magnetic fields. From their properties it is evident that X-rays behave like electromagnetic waves, similar to light but having much shorter wave lengths. The rays constituting visible light have wave lengths of from 4×10^{-5} to 8×10^{-5} cm, but the wave lengths of X-rays are of the order of 10^{-8} cm.

The most convenient method for obtaining X-rays is to place a metal target, called an **anticathode,** in the path of the cathode rays in a discharge tube (Fig. 13.1); the X-rays are then emitted from the anticathode. The wave lengths of the rays so obtained usually cover a fairly wide range, but there are always present certain wave lengths for which the intensity is much greater than that of the general background. The values of these wave lengths depend on the metal used as the anticathode, but they are quite definite for each particular element. The corresponding rays have thus been designated the **characteristic X-rays** of the given element. These characteristic X-rays have been found to fall into a number of groups or series which are represented by the letters K, L, M, N, etc.; the penetrating power, or "hardness," of the rays decreases and the wave length increases in this order. For elements of low atomic weight, members of the K and L series only are generally observed, but with increasing atomic weight the characteristic X-rays of the M, N, and higher series can be detected. There are two or more characteristic radiations in each group, and these are distinguished by the use of Greek letters α, β, etc., as subscripts, e.g., K_α, K_β, L_α, etc.

Just as a ruled grating can be used to determine the wave length of visible light, so a crystal can act as a diffraction grating for evaluating the wave lengths of X-rays (§ 18d). With the object of studying the characteristic X-rays of various elements, H. G. J. Moseley (1913) used a crystal of potassium ferrocyanide as a grating, and allowed the resulting rays to fall on a photographic plate. The position of the line produced on the plate in this manner is then related to the wave length of the characteristic X-radiation of the particular element present in the anticathode.

There is no obvious relationship between the wave length or the frequency, i.e., the velocity of light divided by the wave length, and the atomic weight, but Moseley found a very simple connection between the frequencies of the characteristic X-rays and the **atomic numbers** of the respective elements. For the present, the atomic number may be defined as *the ordinal number of the element in the periodic table*, with due allowance made for vacant spaces. If ν (Greek, *nu*) is the frequency of the characteristic radiation belonging to any particular series, and Z is the atomic number of the element producing that radiation, then

$$\sqrt{\nu} = a(Z - b), \qquad (13.6)$$

where a is a proportionality constant and b has a definite value for all the lines in a given series. For the K_α rays the value of a^2 is $\frac{3}{4}\boldsymbol{R}$, where $\boldsymbol{R}$ is the Rydberg number (§ 15a) in frequency units and b is 1.0.

According to equation (13.6), a straight line should be obtained when the square root of the frequencies of the characteristic X-rays of a given series are plotted against the atomic numbers of the corresponding elements. This is seen to be the case by the results in Fig. 13.4. Although some discrepancies, which actually have an important theoretical interpretation, have been observed for certain elements, the broad relationship between the frequency of the characteristic X-rays and the atomic number, as indicated by equation (13.6), is generally maintained. It may be concluded, therefore, that *the atomic number of an element is a property of fundamental significance*; the exact nature of this significance will be evident shortly.

Since the frequency of the characteristic X-ray in a given series is definitely related to the atomic number of the element, it is clearly possible to determine the latter, by using the appropriate form of equation (13.6), if the former is measured. If this method is applied to the three pairs of elements, viz., argon

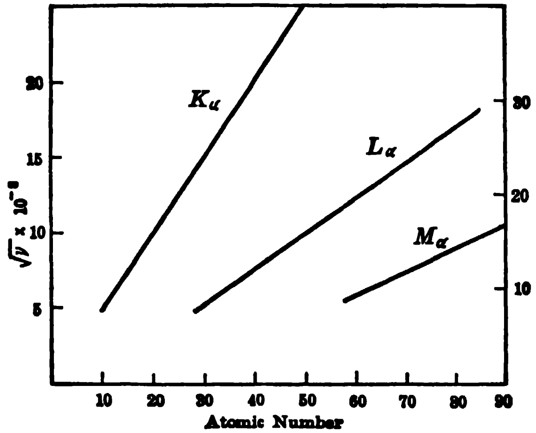

FIG. 13.4. Dependence of frequency of characteristic X-rays on atomic number

and potassium, cobalt and nickel, and tellurium and iodine, which are inverted in the periodic table (Table 13.1), the transposition is found to be justified.

Another use of characteristic X-rays in connection with the periodic table is to indicate the presence of gaps; for example, the atomic numbers of molybdenum and of ruthenium were found to be 42 and 44, respectively, and so there must be an element between them. The missing element of atomic number 43, called technetium, is apparently unstable (radioactive) and does not exist on earth. In this particular instance, it was evident from the chemical properties of molybdenum and ruthenium that they could not occupy immediately successive positions in the table. With the rare-earth elements, however, the characteristic X-rays provided information which could not have been deduced from chemical considerations. Although it can be stated that the rare-earth group lies between barium and hafnium, the properties of the elements in the group are so similar that there would be no way of knowing how many such elements are to be expected. From the frequencies of the characteristic X-rays, it is known that the atomic number of barium is 56, whereas that of hafnium is 72; hence, there must be a total number of fifteen rare-earth elements. Of this total, fourteen are found in nature, but the one with atomic number 61 (promethium) is unstable and has only been obtained artificially. It is of interest to note that the element hafnium was first definitely identified by its characteristic X-rays; its association with zirconium, rather than with the rare-earth minerals, showed that it did not belong to the latter group of elements.

THE STRUCTURE OF THE ATOM

14a. The Nuclear Theory of the Atom.—When α-particles, which are positively charged particles of helium (§ 63b), from a radioactive source pass

TABLE 13.1 THE PERIODIC TABLE

	Groups																	
	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB	IIIB	IVB	VB	VIB	VIIB	0
Period 1	1 H																	2 He
Period 2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
Period 3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
Period 4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
Period 5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 (Tc)	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
Period 6	55 Cs	56 Ba	57–71 Lantha-nides	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
Period 7	87 Fr	88 Ra	89– Acti-nides															

Lanthanide Series	57 La	58 Ce	59 Pr	60 Nd	61 (Pm)	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu

Actinide Series	89 Ac	90 Th	91 Pa	92 U	93 (Np)	94 (Pu)	95 (Am)	96 (Cm)	97 (Bk)	98 (Cf)	99 (Es)	100 (Fm)	101 (Md)	102 (No)	

through matter, such as a thin metallic film, most of them travel in a straight line and suffer no appreciable deflection. A small proportion of the α-particles, however, are deflected through large angles (Fig. 14.1). For example, with a gold foil 0.0004 mm in thickness, one α-particle in 20,000 was found to be deflected through 90° or more. This wide angle **scattering** of α-particles, as the phenomenon is called, must be due to encounters of these particles with the atoms of the metal, and E. Rutherford (1911) showed that the experimental results provided a satisfactory basis for a theory of atomic structure, known as the **nuclear theory.**

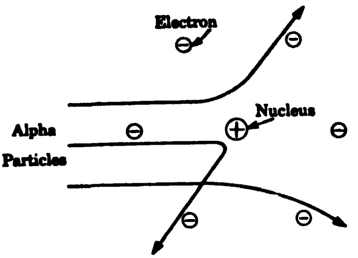

FIG. 14.1. Scattering of alpha particles which approach an atomic nucleus

It was seen in § 13a that the electron is probably a universal constituent of matter, but since matter is normally electrically neutral, there must be positively charged particles to balance exactly the negative charges of the electrons. It was suggested by Rutherford that the whole of the positive charge associated with any atom was concentrated at a very small center or **nucleus.** *This positively charged atomic nucleus would then be surrounded, at relatively large distances, by electrons equal in number to the number of unit positive charges carried by the nucleus*, thus giving an electrically neutral atom. Calculations show that the radius of an atomic nucleus is about 10^{-13} to 10^{-12} cm, which is of the same order as that of an electron. The radii of atoms are, however, in the vicinity of 10^{-8} cm, which is nearly 100,000 times as great, and so it is evident that the atom must have a relatively "empty" structure. It has been estimated, in fact, that the actual volume of the electrons and nuclei constituting matter is no more than about 10^{-12} of the total effective, or observed, volume.

The theory of atomic structure just outlined, which forms the basis of the views accepted at the present day, permits of a ready interpretation of the observations on α-ray scattering. Because of the large amount of "vacant space" in an atom, the great majority of α-particles will pass clear through without any appreciable change of path. It is true that a number of α-particles will encounter electrons, but on account of the small charge and mass of the latter the deflecting effect will be almost negligible. However, an occasional α-particle, which carries two positive charges, as shown below, will enter the powerful electric field in the vicinity of the small positively charged nucleus of the scattering atom; the result will, of course, be a violet deflection of the α-particle from its original path. It is obvious that encounters of this type will be rare, and so a small proportion only of the α-particles will undergo marked scattering.

14b. The Nuclear Charge.—If the atom is to be regarded as consisting of a small positively charged nucleus surrounded, at relatively large distances, by electrons, so as to produce an electrically neutral system, the next point in the development of a theory of atomic structure is to obtain information concerning the number of unit positive charges carried by the nucleus. This will not only give the number of surrounding electrons, which must of course be equal to the number of positive charges, but since the masses of the atom and of an electron are known, the mass of the nucleus can be calculated.

According to the suggestion made by A. van den Broek (1913), *the number of charges on the nucleus of an atom is equal to its atomic number*. In view of the importance of the atomic number, that is, the ordinal number of an element in the periodic table, in determining the physical and chemical properties of an element, and also in view of its direct relationship to the frequencies of the characteristic X-rays, as shown by Moseley, the suggestion appears to be eminently reasonable. Direct experimental proof for it has been obtained in a few cases from quantitative measurements of the scattering of α-particles. By assuming Coulomb's inverse square law of electrical interaction (§ 28a) to apply to the repulsion between the nucleus of an atom and the positively charged α-particle, it is possible to derive an equation relating the charge on the nucleus with the extent of scattering at different angles. The accurate determination of the actual scattering is not easy, but the difficulties were largely overcome by J. Chadwick (1920). From his experimental results he calculated, with the aid of the equation just mentioned, the nuclear charges of copper, silver and platinum; they were found to be 29.3, 46.3 and 77.4 units, respectively, which may be compared with the atomic numbers 29, 47 and 78. Bearing in mind the uncertainties in the measurement of α-particle scattering, the experiments may be regarded as providing confirmation of the idea that the number of unit positive charges carried by the nucleus of any atom is equal to its atomic number.

14c. Constitution of the Nucleus.—Since the positive charges on the nucleus must be balanced by the negative charges of the electrons, the number of the latter that surround the nucleus must also be equal to the atomic number. The highest atomic number for elements that occur in nature is 92, for uranium; hence, the atom correspondingly has 92 electrons. Since the mass of an electron is 0.000548 on the standard atomic weight scale, it is obvious that the electrons do not contribute any appreciable proportion of the mass of the atom, even for elements of high atomic number; the contribution for uranium (atomic weight 238.07) is only 0.05, and for other elements it will be less. It is evident, therefore, that virtually the whole of the mass of an atom is concentrated upon its nucleus. From this fact it follows that the nucleus must be made up of relatively massive positively charged particles.

It is now generally accepted that, with the exception of the hydrogen nucleus which is a single proton, *the nuclei of all atoms are built up of protons and neutrons*. The latter, like protons, have roughly unit mass, but carry no electrical charge; hence, it can be seen, that *the total number of protons and neutrons is equal to the atomic weight of the element, while the number of protons is equal to the atomic number*. Thus, if an element of atomic weight A has an atomic number Z, its nucleus will consist of Z protons, giving a positive charge of Z units, and $A - Z$ neutrons. The mass of the Z protons and of the $A - Z$ neutrons will, of course, add up to the total mass of the nucleus, and hence to that of the atom. To take a specific case, the atomic weight of sodium is 23.0 and its atomic number is 11; the sodium nucleus thus consists of 11 protons and 12 neutrons.

The atomic number of hydrogen is unity, and so the atom possesses just one electron; if this becomes detached, the resulting particle, having a mass of unity and carrying a unit positive charge, thus consists of a nucleus only. Since the proton has a unit positive charge and a mass of unity, it is evidently identical with a bare hydrogen nucleus, and might be represented as H^+. The next element, helium, has an atomic number of two, and if the atom lost two electrons, the resulting nucleus would have a mass of four units, since the atomic weight of helium is 4.00, and a positive charge of two units. These are the characteristic properties of the α-particle as obtained from radioactive sources; hence, the α-particle may be regarded as identical with the bare helium nucleus, He^{++}. For the helium atom, the atomic weight A is 4 and the atomic number Z is 2; consequently, the helium nucleus (or α-particle) should consist of two protons and two neutrons. There are reasons for believing that this system constitutes an exceptionally stable grouping.

THE ELECTRONIC CONFIGURATIONS OF ATOMS

15a. Atomic Spectra.—When a solid is heated or a discharge of electricity is passed through a gas, there is an emission of light; an examination of this light by means of a spectroscope often reveals a series of lines occupying positions in the spectrum corresponding to definite wave lengths or frequencies. These **line spectra** are produced by atoms, and so they are often referred to as **atomic spectra,** as distinct from the so-called band spectra that are characteristic of molecules (§ 29a). From a study of atomic spectra much information has been obtained concerning the arrangements of the electrons surrounding the nuclei of atoms.

In spectoscopic work it is the general practice to express the vibration frequencies of the radiations producing spectral lines in terms of **wave numbers,** that is, in terms of the number of wave lengths per cm. If the frequency of a given line is represented by $\bar{\nu}$ cm^{-1}, in wave numbers, and λ cm is the corresponding wave length, then by definition

$$\bar{\nu} = \frac{1}{\lambda}\ \text{cm}^{-1}. \tag{15.1}$$

The corresponding frequency ν in vibrations per second, i.e., in sec^{-1} units, is given by

$$\nu = \frac{c}{\lambda}\ \text{sec}^{-1}, \tag{15.2}$$

where c is the velocity of light, viz., 3×10^{10} cm per sec. It follows, therefore, from equations (15.1) and (15.2) that

$$\bar{\nu} = \frac{\nu}{c}, \tag{15.3}$$

which relates the frequency in wave numbers (cm^{-1}) to the true frequency (sec^{-1}).

It has been known for some time that *the frequency of any line in a particular spectral series of a given atom can be represented as a difference of two terms*, one of which is constant and the other variable throughout the series. This is the **combination principle** enunciated by W. Ritz (1908) as a generalization of an earlier rule proposed by J. J. Balmer (1885). According to the Ritz principle, the wave number $\bar{\nu}$ of any line in a given series of the spectrum of atomic hydrogen can be represented by

$$\bar{\nu} = R\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right), \tag{15.4}$$

where n_1 and n_2 are integers ($n_1 > n_2$) and R is the **Rydberg constant** for hydrogen. For a particular series, the integer n_2 remains constant throughout but n_1 varies from one line to another. The frequencies of the lines in the Balmer series of atomic hydrogen (Fig. 15.1), first observed in the visible spectrum of the sun, can be expressed with great accuracy by the equation

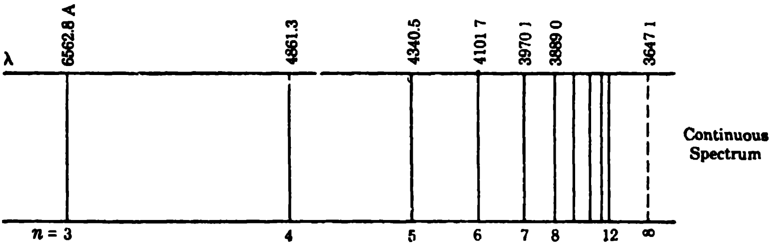

FIG. 15.1. Diagrammatic representation of the Balmer lines of the atomic hydrogen spectrum

$$\bar{\nu} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right), \tag{15.5}$$

where n is 3, 4, 5, 6, etc., for successive lines; the value of R is 109,737.31 cm^{-1}.

Similar expressions in which n_2 is 1, 3, 4 or 5 represent the Lyman (ultraviolet) and the Paschen, Brackett and Pfund (infrared) series, respectively. A diagrammatic representation of the complete atomic hydrogen spectrum is shown in Fig. 15.2. As the value of n_1 in each series increases, $1/n_1^2$ be-

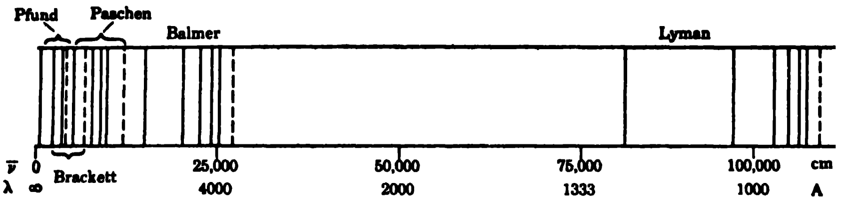

FIG. 15.2. Diagrammatic representation of the atomic hydrogen spectrum (The dotted lines represent the series limits.)

comes smaller and smaller and $\bar{\nu}$ approaches a limit of R/n_2^2; this value, called the **series limit**, corresponds to the wave length beyond which the spectrum is continuous and does not consist of individual lines.

Positive ions of other elements, e.g., He^+, Li^{++}, Be^{+++}, which like atomic hydrogen contain only one electron, give spectral lines similar to those of atomic hydrogen. The wave numbers of these series can be expressed by equation (15.4) multiplied by a factor Z^2, where Z is the nuclear charge (atomic number) of the ion. It should be noted that these hydrogen-like ions, as they are called, do not occur in ordinary chemical reactions; they are generally produced in the high-energy field of an electric spark discharge.

15b. The Quantum Theory.—An interpretation of the significance of the Ritz combination principle was given by N. Bohr (1913), making use of the **quantum theory** of radiation, as postulated by M. Planck (1900) and extended by A. Einstein (1905). According to this theory, a body cannot emit or absorb energy, in the form of radiation, in a continuous manner; *the energy can only be taken up or given out as integral multiples of a definite amount, known as a* **quantum.** If E is the energy of the quantum for a particular radiation of frequency ν sec^{-1}, then by the quantum theory

$$E = h\nu, \tag{15.6}$$

where h is a universal constant, called **Planck's constant.** Since E is an energy quantity and ν is expressed in time^{-1} units, it follows that h has the dimensions of energy × time; this product is sometimes referred to as "action." so that h is the **action constant.** As a result of a variety of measurements the value of h has been found to be 6.6252×10^{-27} erg sec, the energy being in ergs and the time in seconds. Making use of equation (15.3), it is possible to represent the magnitude of the quantum in terms of the frequency $\bar{\nu}$ in wave numbers; thus,

$$E = hc\bar{\nu},$$

and hence

$$\bar{\nu} = \frac{E}{hc}, \tag{15.7}$$

so that the wave number corresponding to the quantum of energy E is obtained upon dividing E by hc, that is, by the product of the Planck constant and the velocity of light.

15c. Energy Levels: Quantum Numbers.—In order to account for the observed frequencies of the lines in the spectra of atoms, Bohr suggested that the electrons belonging to an atom move in definite stable orbits which surround the nucleus, a number of such orbits, corresponding to different energy values, being possible. By assuming the angular momentum of an electron moving in its orbit to be "quantized," that is to say, the angular momentum was supposed to be an exact integral multiple of a definite amount, or quantum, Bohr was able to derive an expression for the frequencies of the spectral lines of hydrogen which was in almost precise agreement with the experimental values. An important weakness of the Bohr theory is that it implies a precise knowledge of the position (orbit) and momentum of an electron; such a knowledge is ruled out, however, by the uncertainty principle (§ 15e).

According to the Bohr postulates the energy of an electron in an atom is not continuously variable, but has one or other of a discrete set of values. In other words, in an atom there are a number of definite **energy levels** and at any instant the energy of the electron can correspond only to one of these levels. It will be seen later that the position of an electron, when it occupies a given level, is not precisely defined, although it can be expressed in terms of a probability by means of the equations of wave mechanics.

As long as the electron remains in a particular energy level, there should be no absorption or emission of radiation. However, if an electron passes from one level to another, there will be a change in the energy of the atom, and a line will be produced in the atomic spectrum. If E' is the energy of the level or state from which the electron starts, and E'' is the energy of the level to which it passes, then according to equation (15.7) of the quantum theory, the wave number of the corresponding spectral line should be given by

$$\bar{\nu} = \frac{E'' - E'}{hc}\ \text{cm}^{-1}, \tag{15.8}$$

since $E'' - E'$ is equal to the energy absorbed or emitted by the atom. Each particular transition from one energy level to another should thus result in the formation of a spectral line with a definite frequency. If the atom acquires energy, so that the electron passes from a lower to a higher level, the line will appear in the **absorption spectrum,** but if the transition is from a higher to a lower level, so that energy is evolved, the line will be part of an **emission spectrum.**

It is evident that equation (15.8) can be written in the form

$$\bar{\nu} = \frac{E''}{hc} - \frac{E'}{hc}, \tag{15.9}$$

and if this is compared with the Ritz equation (15.4), it follows that the energy E of a given level may be represented by

$$E_n = \text{constant} - \frac{Rhc}{n^2}. \tag{15.10}$$

The minus sign has been chosen so as to make the energy increase with increasing values of n, in accordance with a convention to be described below.

Since R, h and c may be regarded as constant, the energy of an electron *in any particular level is apparently determined by the quantity* n^2, where n is an integer for the hydrogen atom, or for hydrogen-like ions with a single electron. By combining the postulates of quantized angular momentum with the methods of classical mechanics, Bohr was able to derive equation (15.10) for the energy in a given level, even to the extent of obtaining the correct value for R, the Rydberg constant, as given by

$$R = \frac{2\pi^2\epsilon^4 m}{h^3 c}, \tag{15.11}$$

where ϵ is the charge and m the mass of an electron. The integer n in equation (15.10) is referred to as a **quantum number**, each value applying to a particular energy level. It will be seen in the next section that the same results can be derived more rigorously by the methods of wave mechanics.

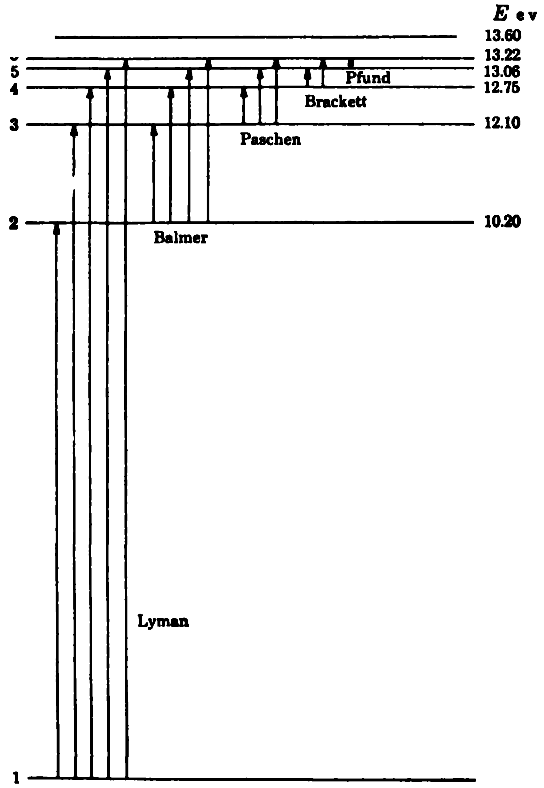

FIG. 15.3. Energy levels of the hydrogen atom and origin of spectra

The concept of energy levels permits of a ready explanation of atomic spectra; thus, the levels of the hydrogen atom for various values of n are indicated in Fig. 15.3. As depicted in the diagram, the Lyman (absorption) *lines result from electronic transitions for which the quantum number n is 1* in the initial state in each case. The energy E' of the initial level is given by equation (15.10) with $n = 1$, and the values of E'' for the various final levels are obtained when $n = 2, 3, 4$, etc. Hence, by equation (15.9), the frequencies of the lines in the Lyman series will be represented by

$$\bar{\nu} = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right),$$

in agreement with observation. For the Balmer series, the initial state for every transition is the level for which n is 2, whereas for the final state n can be 3, 4, 5, etc.; it is evident that the frequencies of the lines are given by an expression equivalent to equation (15.5). The lines of the other spectral series of atomic hydrogen can be accounted for in a similar manner.

In assigning numerical values to the energies of the quantum levels, the convention adopted is to set $E = 0$ for the lowest energy state ($n = 1$), called the **ground state** of the atom. The energy of any level n is then equal to the work required to transfer an electron from the lowest ($n = 1$) level to the nth level. Thus, making use of equation (15.10), the energy E_n of the electron level n of the hydrogen atom would be

$$E_n = Rhc - \frac{Rhc}{n^2} = Rhc\left(1 - \frac{1}{n^2}\right). \qquad (15.12)$$

The energy values can be determined from this equation or they can be calculated from the observed wave numbers or wave lengths of the spectral lines.*

Since R is usually expressed in cm^{-1} units, equation (15.12) gives E_n in ergs. It is a common practice to state atomic (and nuclear) energies in terms of the **electron volt,** represented by ev; this is the energy acquired by a unit (electronic) charge which has been accelerated through a potential of 1 (absolute) volt. Since 1 volt = 1/299.8 esu and the unit charge is 4.803×10^{-10} esu, it follows that

$$1 \text{ ev} = \frac{4.803 \times 10^{-10}}{299.8} = 1.602 \times 10^{-12} \text{ erg}.$$

Hence, energy in ergs is converted into energy in ev upon dividing by 1.602×10^{-12}. The energies of various electronic levels of the hydrogen atom are shown at the right of Fig. 15.3.

The energy required to remove an electron completely from the ground

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* Wave lengths of spectral lines greater than about 2000 A (2×10^{-5} cm) are generally measured in a spectrograph containing air; these must be corrected to the values in vacuo by the relationship $\lambda_{\text{vac}} = n\lambda_{\text{air}}$, where n is the refractive index of air at the particular wave length.

state of an atom, to produce a positively charged ion and a free electron, is called the **ionization energy** or **ionization potential,** usually expressed in electron volts. Its value for atomic hydrogen can be determined experimentally in various ways, e.g., from the wave length (or number) of the series limit,* or it can be calculated by setting $n = \infty$ in equation (15.12), so that

$$\begin{aligned} E_\infty &= Rhc \text{ ergs} \\ &= \frac{109{,}737 \times 6.625 \times 10^{-27} \times 2.998 \times 10^{10}}{1.602 \times 10^{-12}} = 13.60 \text{ ev.} \end{aligned}$$

This is in almost exact agreement with the measured ionization potential of hydrogen.

If an electron acquires more than enough energy to permit its removal from an atom, most of the extra energy is carried off by the free electron as kinetic energy. Because of the very small magnitude of translational energy quanta (§ 3m), this energy is essentially continuously variable. The spectrum beyond the series limit thus appears continuous, although it probably consists of a series of lines so closely spaced that there is little hope of ever resolving them.

15d. Wave-Particle Duality.—The methods of **wave mechanics,** which have proved very successful in the treatment of atomic spectra and atomic structure, are based on the **wave-particle duality** concept of matter. As far back as 1905, A. Einstein suggested that all forms of electromagnetic radiation, including light, which are known to propagate as waves, are not only absorbed and emitted as integral numbers of energy quanta (§ 15b), but are also transmitted through space as "particles," now called **photons.** Each photon carries a single quantum E of energy which is related to the wave number $\bar{\nu}$ of the radiation by equation (15.7). Thus radiation can exhibit both wave and particle properties. In 1923, L. de Broglie suggested that this dual characteristic also applied to matter. By analogy with the quantum theory, de Broglie showed that a particle of mass m moving with velocity v, i.e., with momentum mv, would be associated with a wave length λ given by

$$\lambda = \frac{h}{mv}. \tag{15.13}$$

Thus, the particle property momentum (mv) is related to the wave property (λ) through h, the Planck constant.

The conditions necessary for an experimental test of the de Broglie equation (15.13) with electrons may be derived in the following manner. An electron of charge ϵ accelerated by a potential V acquires kinetic energy $V\epsilon$, which may also be expressed as $\frac{1}{2}mv^2$, so that

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* It is only for the Lyman series, for which the initial electronic level ($n = 1$) is the ground state, that the wave number ($\sim$109,700 cm^{-1}) of the series limit corresponds to the ionization potential. In the other series, less energy is required to remove the electron, and yield a continuous spectrum, since in the initial state $n = 2, 3, 4$ or 5. The respective differences can be calculated by equation (15.10).

$$v = \sqrt{\frac{2V\epsilon}{m}}.$$

Upon substituting this value for v into equation (15.13), the result is

$$\lambda = \quad h$$

and if the known values of h (6.62×10^{-27} erg sec), ϵ (4.80×10^{-10} esu) and m (9.11×10^{-28} g) are introduced, it is found that

$$\lambda = \frac{1}{\sqrt{2V}} \times 10^{-8} \text{ cm},$$

with the potential V in esu. Since 1 esu $\approx$ 1/300 volt, it follows that

$$\lambda = \sqrt{\frac{150}{V}} \times 10^{-8} \text{ cm}, \qquad (15.14)$$

where V is now in volts.

It is evident from equation (15.14) that an electron accelerated through a potential of 100 volts should be associated with a wave length of 1.23×10^{-8} cm, i.e., 1.23 A. It will be seen in Chapter 7 that crystalline solids can act as diffraction gratings for wave lengths, e.g., of X-rays, of this order of magnitude. Hence, the wave nature of electrons would be demonstrated if they could be diffracted by solids in a manner similar to X-rays. In 1927, C. J. Davisson and L. H. Germer, using a metal crystal as a reflection grating, and G. P. Thomson, employing a metal foil as a transmission grating, showed that electrons could be diffracted, and thereby established both their wave nature and the quantitative validity of the de Broglie equation.* A photograph of the diffraction rings obtained by passing accelerated electrons through thin (10^{-6} cm) films of gold is given in Fig. 15.4.

Since 1927 it has been shown that material particles other than electrons have wave properties; thus, diffraction effects have been observed with hydrogen and helium nuclei and also with neutrons. There is little doubt that the wave-particle duality is a property of all forms of matter. However, it can be seen from equation (15.13) that, with increasing mass, the wave lengths become shorter for a given velocity, and so are increasingly difficult to detect. The diffraction of electrons and of neutrons has been utilized in the study of molecular and crystal structure. Further, with the electron microscope, it has been possible to resolve objects as small as 10 A in size, compared with a minimum of about 3000 A in an ordinary microscope.

15e. The Uncertainty Principle.—An examination of the mechanism of the production of the diffraction rings in Fig. 15.4 has important theoretical implications. The complete rings are built up on a photographic plate during the course of several hours by an intense beam of electrons which has passed

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* It is an interesting coincidence that G. P. Thomson is the son of J. J. Thomson who, in 1897, made fundamental studies on the particle aspects of the electron (§ 13a).

FIG. 15.4. Electron diffraction pattern of gold (From *The Wave Mechanics of Free Electrons*, by G. P. Thomson, Cornell University Press.)

through (and been diffracted by) a metal foil. If a single electron is considered, all that can be stated is that it will strike the photographic plate at some point which will later be part of one of the rings; the exact point is, however, quite unpredictable. This means that, although the momentum of the electron is known with precision, from the accelerating potential, its position is uncertain. If the photographic plate were replaced by a scintillation screen, the position of the impinging electron would be sharply defined, but simultaneously its momentum would become uncertain because of the transfer of an unknown amount of energy to the scintillator molecule.

The behavior described above is summarized in the **uncertainty principle** of W. Heisenberg, according to which *it is impossible to determine simultaneously the exact momentum and the exact position of a particle.* Quantitatively, the principle may be expressed as

$$\Delta p \cdot \Delta q \approx h, \tag{15.15}$$

where Δp and Δq are the uncertainties in momentum and position, respectively and h, as before, is the Planck constant. If an experiment is performed in which p is determined very precisely (Δp very small), then q is uncertain (Δq very large); this is a particle experiment. On the other hand, in a wave experiment, q is determined accurately but p is meaningless. Thus, an electron, proton or other form of matter cannot exhibit both particle and wave properties simultaneously.

Since momentum p is mv, equation (15.15) may be written as

$$\Delta v \cdot \Delta q \approx h/m.$$

For heavy particles h/m will be very small and for bodies of macroscopic size it will approach zero. For such bodies the product $\Delta v \cdot \Delta q$ is so small that the uncertainties in velocity (or momentum or energy) and position are virtually nonexistent and far beyond the range of detection. In these circumstances, classical mechanics, which postulates that momentum and position can be simultaneously determined precisely, is applicable. However, for atomic (and similar) particles, classical mechanics is quite inadequate and must be replaced by wave mechanics.

15f. The Wave Equation and Wave Functions.—The wave associated with an electron in an atom must correspond, in some manner, with the orbital motion of the electron. Since the path is a closed one, it is reasonable to suppose that the length (or frequency) of the wave is such that the path is covered in a whole number of wave lengths; waves of other frequencies will destroy themselves by interference. Hence, the electron can have only such energy values as correspond to these permitted frequencies. Thus, the wave theory leads directly to the concept of the existence of discrete energy levels.

Waves of the kind having permitted frequencies, which do not exhibit interference, are stationary (or standing) waves. A one-dimensional example of such a wave motion, as would be observed in a vibrating string fixed at both ends, is shown in Fig. 15.5. It is apparent that the frequencies of the different modes of vibration are integral multiples of the fundamental frequency ν_0, i.e., $\nu_n = n\nu_0$, where $n = 1, 2, 3$, etc., is a quantum number.

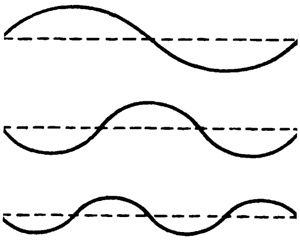


FIG. 15.5. Modes of vibration of a string

Any stationary wave motion may be represented by a sine function of the form

$$A = \psi \sin 2\pi\nu t, \tag{15.16}$$

where A is the displacement of the wave of frequency ν at any point x, y, z at a time t, and ψ is the amplitude of the vibration at the given point; ψ is a function only of the coordinates x, y, z and is independent of time. By combining this expression with the standard wave equation relating the space and time variations of the displacement, and generalizing the result by introducing the de Broglie equation (15.13), E. Schrödinger (1926) derived the expression for particle waves

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0, \tag{15.17}$$

where m is the mass of the particle, E its total energy and V its potential energy; the quantity ψ is here called the **eigenfunction** or **wave function** of the particle.

Just as the function ψ in equation (15.16) has significance only for certain definite values of the frequency, e.g., those given by $\nu_n = n\nu_0$ for a stationary wave on a stretched string, so the wave function ψ is a satisfactory solution of equation (15.17) only for certain values, called the **eigenvalues**, of the total energy E. These energy values are the equivalent of the discrete energy levels postulated by the Bohr theory (§ 15c). The wave mechanical treatment thus leads to the requirement of definite electronic energy states of the atom. Further, solution of the Schrödinger equation (15.17) for the hydrogen atom (or hydrogen-like ions) leads to precisely the same results, e.g., equation (15.11), as does the Bohr theory, avoiding the use of procedures and postulates now believed to be invalid.

15g. Significance of the Wave Function: Orbitals.—The production of diffraction rings by a beam of electrons, as in Fig. 15.4, indicates that there are regions where the electrons in the beam are more likely to be found; between the rings, the electrons are less likely to be present. In other words, for an electron suffering diffraction, there is a high probability of landing in one of the rings, but little (or no) probability between them. The rings, therefore, correspond to regions of high electronic density and, consequently, of high intensity of the associated wave. The intensity of a light (or sound) wave at any point, is proportional to the square of its amplitude at that point, and so, by analogy, the square of the eigenfunction, i.e., ψ^2, can be interpreted as the probability that the electron will appear at any specified point in the diffraction pattern.

The result just obtained may be generalized to apply to the electrons in an atom. The probability of finding the electron at any point x, y, z is proportional to ψ^2 at that point, where ψ is a wave function that corresponds to one of the permitted values of the energy in equation (15.17). Since these energy values are the equivalent of the electronic energy levels represented by the Bohr orbits, the corresponding wave functions are the wave mechanical equivalents of the classical electron orbits. The wave functions are, therefore, frequently referred to as **orbitals.** Whereas the orbit, for a specified momentum, cannot be described with any certainty, the expression for the orbital can be written exactly.

15h. Quantum Numbers and the Pauli Principle.—In the original Bohr theory of spectra, only one quantum number was postulated to describe an electron orbit. However, experimental observations, on the fine structure and the splitting of lines in a magnetic field, showed that, for a complete description of the state of an electron in an atom, four quantum numbers are required. It is of interest to note that three of these, namely, n, l and m, described below, follow naturally from the wave mechanical approach, without any reference to experiment. These three quantum numbers correspond to the three spatial coordinates, e.g., x, y, z (or their polar equivalents), which are the variables in the expression for the wave function for each permitted energy value. The energy is determined primarily by the **principal quantum number** n, referred to earlier; this can have any integral value, but not zero. A secondary effect is exerted by the **orbital quantum num-**

ber l, which, according to classical theory, determines the angular momentum of the electron in its orbital motion around the nucleus. It has been established by wave mechanics that for any particular value of the principal quantum number n, the values of l may be $n - 1, n - 2, \cdots, 0$; that is to say, l may have any integral value from $n - 1$ to zero. For example, if n is 4, then l can be 3, 2, 1 and 0.

When the source of a spectrum is placed in a strong magnetic field, each spectral line is split into several lines (**Zeeman effect**). To account for this effect it is postulated that the electron producing the original line has several possible orientations in the magnetic field for the same angular momentum vector. These orientations are then responsible for the observed splitting of the spectral line. The magnitude of the component in a particular direction is given by the **magnetic quantum number** m, representing the possible orientations of the angular momentum vector in a magnetic field. For a given l, the values of m must be $\pm l, \pm(l - 1), \pm(l - 2), \cdots, 0$, giving a total of $2l + 1$ possible values. If l is 3, for example, then m can be $\pm 3, \pm 2, \pm 1$ and 0, a total of seven possible orientations. Each value of l represents a different type of orbital, and the number of m values, i.e., $2l + 1$, indicates the total number of orbitals of each type.

As stated above, the wave mechanical treatment requires no more than the three quantum numbers n, l and m. These are insufficient, however, to account for the existence of multiplet structure in certain spectral lines; thus, the familiar yellow line of sodium, for example, actually consists of two lines very close together. The existence of such multiplets led to the introduction of a **spin quantum number** s; this can have but two possible values, viz., $+\frac{1}{2}$ or $-\frac{1}{2}$, according as the so-called spin angular momentum is in one direction or in the opposite direction.

The distribution of quantum numbers among the electrons in a given atom is restricted by the **exclusion principle,** enunciated by W. Pauli (1925). This principle has, as yet, no theoretical explanation, but it is in agreement with many known facts; it states that *it is impossible for any two electrons in the same atom to have their four quantum numbers identical.* The principle may be expressed in another form, in which it is often applied. Since a wave function is defined by the values of the three quantum numbers n, l and m, it follows that *no more than two electrons can "occupy" any one orbital, and then only if their spins are in opposite directions, i.e., antiparallel.* By means of this rule the number of electrons that can occur in any quantum group can be derived in a simple manner. If n is 1, for example, l can only be zero, and m must also be zero; s may then be either $+\frac{1}{2}$ or $-\frac{1}{2}$ without infringing the Pauli principle that the four quantum numbers must not be the same for two electrons. The values of n, l, m and s for these two electrons are then as follows:

$$(1)\quad n = 1 \quad l = 0 \quad m = 0 \quad s = +\tfrac{1}{2}$$

$$(2)\quad n = 1 \quad l = 0 \quad m = 0 \quad s = -\tfrac{1}{2}.$$

It is thus seen that in the first ($n = 1$) quantum group, also called the K shell, there may be up to two, and no more, electrons.

For the second ($n = 2$) group (or L shell), l may be 1 or 0; if l is 0, then two electrons are possible, as in the previous case. If l is 1, then there are three possibilities for m, namely -1, 0 and $+1$; in each case the spin s may be $+\frac{1}{2}$ or $-\frac{1}{2}$, so that for $l = 1$ there can be six electrons in the atom. The total number of electrons in the second quantum group is thus $2 + 6$, i.e., 8, and their specifications are given below.

n	2	2	2	2	2	2	2	2
l	0	0	1	1	1	1	1	1
m	0	0	-1	-1	0	0	$+1$	$+1$
s	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$

It is seen that no two electrons have their four quantum numbers identical.

Working in the manner described above the results in Table 15.1 may be derived for the maximum numbers of electrons corresponding to various n and the possible l values.

TABLE 15.1. DISTRIBUTION OF ELECTRONS IN QUANTUM GROUPS

		$l = 0$	1	2	3	4
		s	p	d	f	g
Shell		Maximum Numbers of Electrons				
K	$n = 1$	2	—	—	—	—
L	2	2	6	—	—	—
M	3	2	6	10	—	—
N	4	2	6	10	14	—
O	5	2	6	10	14	18

The symbols customarily used to describe the electrons in an atom are based on the following rules. The letters s, p, d, f, g and h correspond to $l = 0$, 1, 2, 3, 4 and 5, respectively, The n value is a numerical prefix to the letter representing the l value. The number of electrons, if there are more than one having the same n and l values, is added as a superscript to the right of the symbol for the l value. As an example, the six electrons in the carbon atom would be indicated by $1s^2 2s^2 2p^2$.

15i. Electronic Arrangements in Atoms.—In principle, the distribution of electrons around the atomic nucleus could be obtained by means of wave mechanics. So far, the wave equation has been solved completely only for the hydrogen (or hydrogen-like) atom with a single electron. For atoms with many electrons, it would be necessary to write a wave equation for each electron, which is not difficult, and then to solve all the equations simultaneously. This, however, is almost impossible. As an alternative, information concerning the electronic configurations of atoms has been derived from atomic and X-ray spectra together with the data in Table 15.1 based on the Pauli principle.

The complete arguments are somewhat complicated, and so a broad outline only will be given here. The procedure adopted is to imagine the electrons, equal in number to the positive nuclear charge, to be added to the system one at a time until the complete atom is built up. It is then necessary to find in which orbital each successive electron is accommodated. In order to simplify the treatment, the assumption is made that the main inner structure of any atom is the same as that of the preceding one in order of increasing atomic number. All that is required, then, is to determine the position occupied by the additional electron which distinguishes the two atoms. Suppose, for example, the electronic arrangement in the sodium atom has been worked out; in order to find that of the next element, magnesium, it is required merely to discover where the one extra electron must be placed. The structure of the magnesium atom now being known, it is possible to go on to derive that of the aluminum atom, and so on, throughout the periodic table. There are a few cases in which the foregoing assumption requires slight modification, but these do not cause any serious difficulty.

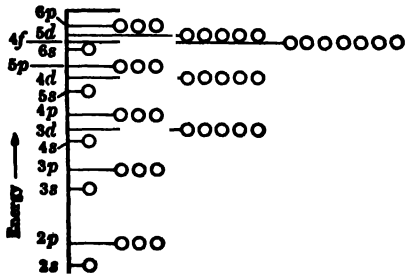


FIG. 15.6. Energies of orbitals

Orbitals are filled in order of increasing energy and an approximate indication of the relative energies for various orbitals is given in Fig. 15.6. The most usual sequence is seen to be 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, etc. It will be shown below that this conclusion is in harmony with the general features of the periodic system of the elements. Where two or more orbitals of a given kind, e.g., *p*, *d*, etc., are available, they are usually first filled singly by electrons with their spins parallel. When a second electron is added to an orbital, its spin is antiparallel to that of the one already there, as required by the exclusion principle. An example of the filling of the three 2*p* orbitals for the elements boron to neon is shown in Fig. 15.7.

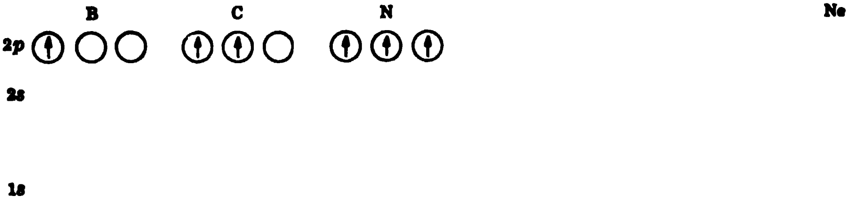


FIG. 15.7. Electron distribution in elements boron to neon

Starting with hydrogen, which has one electron, it is evident that this will be in an $n = 1$, $l = 0$ or 1*s* orbital; similarly, the two electrons of helium, with antiparallel spins, will occupy this orbital. It is seen from Table 15.1

that the $n = 1$, $l = 0$ orbital can contain only two electrons, and so with the helium atom the K shell is completed. In the next atom, lithium, the extra electron must go into the $n = 2$, $l = 0$ or $2s$ orbital; this is completed with the following atom, beryllium. Proceeding in this manner, with increasing atomic number, the electrons in the succeeding atoms enter the $n = 2$, $l = 1$ or $2p$ orbital, which is capable of containing six electrons (Table 15.1). With the element neon, atomic number 10, the first two electron groups, i.e., the K and L shells, $n = 1$ and $n = 2$, are completed. Since the numbers of electrons in the first two shells are 2 and 2 + 6, i.e., 8, respectively, the ten electrons in neon may be represented as $1s^2\ 2s^2\ 2p^6$.

At sodium, which is the next element, the process of filling up the subgroups, starting with the $n = 3$, $l = 0$ or $3s$ orbital, begins to repeat itself; this element has the neon configuration (or core) plus a $3s$ electron. As before, the $l = 0$ orbital is first completed, and then the electrons enter the $l = 1$ orbital, which is just filled when the element argon, atomic number 18, is reached; the electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6$.

At this point, the next electron can either enter the $n = 3$, $l = 2$ or $3d$ orbital, for an orbital with $l = 2$ is now possible for the first time (cf. Table 15.1), or it can enter a $4s$ orbital ($n = 4$, $l = 0$). All the evidence points to the latter alternative for the potassium atom, which thus has the electronic grouping $1s^2 2s^2 2p^6 3s^2 3p^6 4s$. Similarly, for the next atom, calcium, a second $4s$ electron is added. However, with the following element, scandium, a more stable system apparently results when the additional electron enters the still vacant $n = 3$, $l = 2$ or $3d$ orbital rather than the $4p$ orbital. In the succeeding atoms, the $3d$ orbital, which is capable of holding ten electrons, is gradually filled up; it is the introduction of the $l = 2$ orbital which accounts for the fact that the fourth period of the periodic table contains eighteen elements, as compared with eight in the two preceding periods. The $3d$ orbital is completed at zinc, and with the next element, gallium, the $4p$ orbital starts to fill; this is completed with krypton, atomic number 36. These configurations are now somewhat analogous to those of the corresponding elements in the two short periods; it can be understood, therefore, why the elements at the end of the long period begin to resemble the typical elements once more. In the next period, commencing with rubidium, the cycle is repeated, the orbitals filling up in the order $5s$, $4d$, $5p$ (see Fig. 15.6).

The situation now becomes somewhat more complicated, for although the first three (K, L and M) electron shells, with $n = 1$, 2 and 3, are filled, the fourth and fifth shells are still incomplete. An examination of Table 15.1, for example, shows that the $n = 4$ shell is capable of holding a total of 32 electrons, so that there are still 14 orbitals with $l = 3$ to be filled. In addition, there are three vacant orbitals in the $n = 5$ shell. There is no doubt that in the first two elements of the sixth period, cesium and barium, which succeed xenon, a new orbital ($6s$) is started, so that the structures are analogous to those of the first two members of the four preceding series, viz., 2, 8, 18, 18, 8, 1 and 2, 8, 18, 18, 8, 2 respectively. As in the fourth and fifth periods, with the next element, lanthanum, the electron enters an inner orbital, viz., $n = 5$, $l = 2$ (or $5d$). Following this, however, there is an entirely novel development, for the $n = 4$, $l = 3$ or $4f$ orbital, capable of containing 14 electrons, as seen above, begins to be occupied with the element cerium. Apparently, the introduction of an electron in such an inner group has little effect on the chemical properties, so that cerium and lanthanum are similar chemically. These two elements are, in fact, the first of the rare-earth series. With the succeeding thirteen elements the $4f$ orbital is increasingly occupied, and with lutetium is completed. This element, atomic number 71, is the last of the rare-earth or lanthanide group, and hence the occurrence of fifteen elements in this group can be explained.

Following the completion of the rare-earth series of elements, the electrons steadily fill the $5d$ and then the $6d$ orbitals until radon, atomic number 86, is reached. The total number of elements in the sixth period of the periodic table is thus $86 - 54 = 32$; this is 14 more than the number in the two preceding periods, because of the inclusion of the $n = 4$, $l = 3$ or $4f$ orbitals.

Starting with element 87, the sequence of filling the orbitals is two $7s$ electrons followed by one $6d$ electron to give actinium, with an outer configuration $6d7s^2$, comparable to that of lanthanum $5d6s^2$. The elements following actinium have their $5f$ orbitals filled to form an actinide series similar to the lanthanide (rare-earth) series commencing with lanthanum. Only the first four members of the actinide series, atomic numbers 89, 90, 91 and 92, exist in nature, at least to any appreciable extent, but several others have been obtained artificially (see Chapter 18). It is expected that there will be a total of 15 actinide elements, analogous to the 15 lanthanides, so that element 104 will resemble zirconium and hafnium.

The most probable configurations of the electrons in the normal (or ground) states of the atoms are summarized in Table 15.2. The horizontal lines across the table are, in general, at locations where the occupied inner orbitals are filled, and the additional electron, in the elements immediately below, goes into a higher s orbital. These elements are seen to belong to Groups IA and IB of the periodic system (Table 13.1).

THE ELECTRONIC THEORY OF VALENCE

16a. The Electron Octet.—With the information already obtained in connection with the electronic structures of atoms, it is possible to proceed to the consideration of molecular structure. The combination of atoms to form molecules involves what have been called valence forces, and there is no doubt that the "valence bonds" which hold the atoms together in a molecule are related to the electronic configurations of the atoms concerned. This is the fundamental basis of the **electronic theory of valence.**

An examination of the results of § 15i shows that the inert gases, in Group 0 of the periodic table, have the following electronic configurations:

Helium	2
Neon	2, 8
Argon	2, 8, 8
Krypton	2, 8, 18, 8
Xenon	2, 8, 18, 18, 8
Radon	2, 8, 18, 32, 18, 8

TABLE 15.2. ELECTRON CONFIGURATION OF ATOMS IN THE GROUND STATE

Atomic No.	Element	*K*	*L*		*M*			*N*				*O*				*P*				*Q*
		1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	6*s*	6*p*	6*d*	6*f*	7
1	H	1																		
2	He	2																		
3	Li	2	1																	
4	Be	2	2																	
5	B	2	2	1																
6	C	2	2	2																
7	N	2	2	3																
8	O	2	2	4																
9	F	2	2	5																
10	Ne	2	2	6																
11	Na	2	2	6	1															
12	Mg	2	2	6	2															
13	Al	2	2	6	2	1														
14	Si	2	2	6	2	2														
15	P	2	2	6	2	3														
16	S	2	2	6	2	4														
17	Cl	2	2	6	2	5														
18	Ar	2	2	6	2	6														
19	K	2	2	6	2	6		1												
20	Ca	2	2	6	2	6		2												
21	Sc	2	2	6	2	6	1	2												
22	Ti	2	2	6	2	6	2	2												
23	V	2	2	6	2	6	3	2												
24	Cr	2	2	6	2	6	5	1												
25	Mn	2	2	6	2	6	5	2												
26	Fe	2	2	6	2	6	6	2												
27	Co	2	2	6	2	6	7	2												
28	Ni	2	2	6	2	6	8	2												
29	Cu	2	2	6	2	6	10	1												
30	Zn	2	2	6	2	6	10	2												
31	Ga	2	2	6	2	6	10	2	1											
32	Ge	2	2	6	2	6	10	2	2											
33	As	2	2	6	2	6	10	2	3											
34	Se	2	2	6	2	6	10	2	4											
35	Br	2	2	6	2	6	10	2	5											
36	Kr	2	2	6	2	6	10	2	6											
37	Rb	2	2	6	2	6	10	2	6			1								
38	Sr	2	2	6	2	6	10	2	6			2								
39	Y	2	2	6	2	6	10	2	6	1		2								
40	Zr	2	2	6	2	6	10	2	6	2		2								
41	Nb	2	2	6	2	6	10	2	6	4		1								
42	Mo	2	2	6	2	6	10	2	6	5		1								
43	Tc	2	2	6	2	6	10	2	6	6		1								
44	Ru	2	2	6	2	6	10	2	6	7		1								
45	Rh	2	2	6	2	6	10	2	6	8		1								
46	Pd	2	2	6	2	6	10	2	6	10										
47	Ag	2	2	6	2	6	10	2	6	10		1								
48	Cd	2	2	6	2	6	10	2	6	10		2								
49	In	2	2	6	2	6	10	2	6	10		2	1							
50	Sn	2	2	6	2	6	10	2	6	10		2	2							
51	Sb	2	2	6	2	6	10	2	6	10		2	3							

Atomic No.	Element	*K*	*L*		*M*			*N*				*O*				*P*				*Q*
		1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	6*s*	6*p*	6*d*	6*f*	7*s*
52	Te	2	2	6	2	6	10	2	6	10		2	4							
53	I	2	2	6	2	6	10	2	6	10		2	5							
54	Xe	2	2	6	2	6	10	2	6	10		2	6							
55	Cs	2	2	6	2	6	10	2	6	10		2	6			1				
56	Ba	2	2	6	2	6	10	2	6	10		2	6			2				
57	La	2	2	6	2	6	10	2	6	10		2	6	1		2				
58	Ce	2	2	6	2	6	10	2	6	10	2	2	6			2				
59	Pr	2	2	6	2	6	10	2	6	10	3	2	6			2				
60	Nd	2	2	6	2	6	10	2	6	10	4	2	6			2				
61	Pm	2	2	6	2	6	10	2	6	10	5	2	6			2				
62	Sm	2	2	6	2	6	10	2	6	10	6	2	6			2				
63	Eu	2	2	6	2	6	10	2	6	10	7	2	6			2				
64	Gd	2	2	6	2	6	10	2	6	10	7	2	6	1		2				
65	Tb	2	2	6	2	6	10	2	6	10	9	2	6			2				
66	Dy	2	2	6	2	6	10	2	6	10	10	2	6			2				
67	Ho	2	2	6	2	6	10	2	6	10	11	2	6			2				
68	Er	2	2	6	2	6	10	2	6	10	12	2	6			2				
69	Tm	2	2	6	2	6	10	2	6	10	13	2	6			2				
70	Yb	2	2	6	2	6	10	2	6	10	14	2	6			2				
71	Lu	2	2	6	2	6	10	2	6	10	14	2	6	1		2				
72	Hf	2	2	6	2	6	10	2	6	10	14	2	6	2		2				
73	Ta	2	2	6	2	6	10	2	6	10	14	2	6	3		2				
74	W	2	2	6	2	6	10	2	6	10	14	2	6	4		2				
75	Re	2	2	6	2	6	10	2	6	10	14	2	6	5		2				
76	Os	2	2	6	2	6	10	2	6	10	14	2	6	6		2				
77	Ir	2	2	6	2	6	10	2	6	10	14	2	6	7		2				
78	Pt	2	2	6	2	6	10	2	6	10	14	2	6	9		1				
79	Au	2	2	6	2	6	10	2	6	10	14	2	6	10		1				
80	Hg	2	2	6	2	6	10	2	6	10	14	2	6	10		2				
81	Tl	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1			
82	Pb	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2			
83	Bi	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3			
84	Po	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4			
85	At	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5			
86	Rn	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6			
87	Fr	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6			1
88	Ra	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6			2
89	Ac	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1		2
90	Th	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	2		2
91	Pa	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1		2
92	U	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1		2
93	Np	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1		2
94	Pu	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6			2
95	Am	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6			2
96	Cm	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1		2
97	Bk	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1		2
98	Cf	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6			2
99	Es	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6			2
100	Fm	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6			2
101	Md	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6			2
102	No	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6			2

In each of these atoms, with the exception of helium, *the outermost shel contains eight electrons*, irrespective of whether the inner shells have been completely filled or not. Since the inert gases are extremely unreactive, it ma be concluded that an outer group of eight electrons, known as an **electron octet,** is an exceptionally stable arrangement. One of the postulates of the electronic theory of valence is, therefore, that, in general, *when atoms combin they do so in such a manner as to lead to the formation of complete electron octets as far as possible.*

16b. The Ionic Bond.—One way in which complete octet formation ca be achieved is as follows: suppose a particular atom has electrons in exces of the octet while another has a deficit; both atoms could then acquire complete octets if the extra electrons of the former atom were transferred to the latter (W. Kossel, 1916). Each of the alkali metals, namely, lithium, sodium potassium, rubidium and cesium, immediately follows an inert gas in the periodic table; consequently, the atoms of these elements all have one electro in excess of that required for a stable configuration. On the other hand, the halogen atoms, viz., fluorine, chlorine, bromine and iodine, each precede a inert gas, and so these atoms require an additional electron to complete the octet. It follows, therefore, that if the extra electron possessed by an alkali metal atom were transferred to a halogen atom, both would have their octets complete; the resulting system, which would represent an alkali halide, would be a stable one.

Another aspect of the tendency to complete octets becomes apparent by considering a typical alkali halide, such as sodium fluoride. The sodium has eleven positive charges on the nucleus but only ten negative electrons it must consequently have a resultant positive charge. In other words, the sodium is now in the form of a singly charged, or univalent, **positive ion.** Similarly, it is apparent that the fluorine has an excess negative charge, and so it is a univalent **negative ion.** *The two oppositely charged ions will be held together by electrostatic attraction*, and this is the basis of the "valence bond" in sodium fluoride. The same type of union is supposed to exist in all simple salts; such salts are, therefore, said to be **ionic compounds.** In each case, the solid salt consists of positive and negative ions—each with a complete electron octet—held together by electrostatic forces. As a general rule, the positive and negative signs are omitted when writing the formulae, but these must always be understood wherever an ionic bond occurs. It will be noted that *the valence of an atom or group taking part in an ionic bond is equal to the number of electrons gained or lost in the formation of the complete octet.* It may be remarked that support for this interpretation of the bonds in simple salts has been obtained from a study of the internal structures of the crystals (§ 18c) and from the properties of their solutions (§ 45d).

16c. The Covalent Bond.—The theory described above accounts satisfactorily for the formation of salts and salt-like compounds, e.g., oxides and sulfides, by elements which are close to the inert gases in the periodic table, but with others that are farther away difficulties arise. The energy required to remove an electron from an atom increases with the number of electrons removed; it is for this reason that trivalent positive ions are uncommon and quadrivalent ions are very rare. Similarly, simple negative ions carrying three charges are unknown, although complex ions with a valence of three or four can exist. Because of the difficulty in removing three or more electrons from, or adding such numbers to, an atom, the ions B^{+++}, C^{++++}, C^{----} or N^{---} are unlikely to be involved in chemical combination. Atoms like boron, carbon, nitrogen, etc., cannot therefore take direct part in ionic bond formation, and they must combine in another way.

A second manner whereby two atoms with incomplete electron octets can complete these octets is by sharing electrons, as suggested by G. N. Lewis (1916); this leads to another type of valence, known as **covalence.** According to Lewis, the sharing involves pairs of electrons, or **electron duplets,** *each shared duplet being equivalent to one conventional valence bond.* It is of interest to note that Lewis was led to this suggestion by the fact that all stable compounds, with very few exceptions, contain an even number of electrons. In recent years, however, the electron-pair bond has acquired something of a theoretical significance. By means of wave mechanics, W. Heitler and F. London (1927) showed that two hydrogen atoms can come together in two ways, one leading to the formation of a stable hydrogen molecule, whereas the other leads to an unstable system. In order to obtain the stable molecule it is necessary for the two hydrogen atoms to have the spins of their electrons in opposite directions. If the two spins are in the same direction, a stable molecule cannot be formed. From this result it has been inferred that **covalent bond** formation, in general, *involves the pairing of electrons with opposite spins*, not only in hydrogen but in all other molecules. If this is the case, the postulate that electron sharing occurs in pairs can be readily understood.

In most cases, the formation of stable covalent compounds leads to each atom acquiring an octet of electrons. Hydrogen is, however, exceptional since it requires only two electrons (or a duplet) for a stable electronic configuration.

When there are an insufficient number of electrons to complete all the octets (or duplets, in the case of hydrogen) by the sharing of electron pairs, it is possible for two atoms to share two pairs; this is consequently the equivalent of a double bond. Similarly, a triple bond implies the sharing of three duplets between two atoms.

$$\cdot\dot{\mathrm{C}}\cdot + 2\,:\!\ddot{\mathrm{O}} = :\!\ddot{\mathrm{O}}\!:\,:\!\mathrm{C}\!:\,:\!\ddot{\mathrm{O}}\!: \qquad \text{or} \qquad \mathrm{O{=}C{=}O}$$

$$2\,\cdot\underset{\cdot}{\dot{\mathrm{C}}}\cdot + 2\,\mathrm{H}\cdot = \mathrm{H}\!:\!\mathrm{C}\!:\,:\,:\!\mathrm{C}\!:\!\mathrm{H} \qquad \text{or} \qquad \mathrm{H{-}C{\equiv}C{-}H}$$

In each case the octet (or duplet) of every atom is completed by the device of sharing more than one pair of electrons.

It should be mentioned that, although the octet rule is a useful general guide to the problems of bond formation, it is probably not strictly applicable in all cases; it appears that in certain instances groups of more than eight electrons are possible. For example, in SF_6 the six fluorine atoms share electron pairs with the sulfur atom, and so the latter probably has an external group of twelve electrons; similarly, in PCl_5 the phosphorus atom has apparently ten electrons in its outer shell. The explanation of this behavior is that usually only the outermost *s* and *p* orbitals, which can hold a total of eight electrons, are involved in bond formation. This is the basis of the octet rule. Under certain conditions, e.g., in SF_6 and PCl_5, one or more *d* orbitals can be used. On the other hand, there are a few cases, particularly the boron halides, e.g., BF_3 and BCl_3, in which the central atom, i.e., boron, can have only six electrons. In this case, however, there is a strong tendency for the octet to be completed, as is the case in the stable BF_4^- ion and in other compounds.

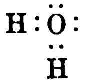
16d. Properties of Ionic and Covalent Compounds.—Although it is not always possible to differentiate strictly between ionic and covalent compounds, there are some generalizations which are useful, even if they are not always exact. According to the electronic theory of valence, ionic compounds, such as simple salts, consist of positive and negative ions held together by electrostatic attraction. These ions presumably exist in the solid, but owing to the restrictive forces in the crystal, they are not free to move under the influence of an applied electric field. However, if the solid is melted, or dissolved in a suitable liquid, the ions acquire mobility and can be directed by an electrical potential. In other words, the molten solid and the solution are capable of conducting an electric current. One characteristic of an ionic compound is, therefore, that *it is an electrical conductor in the liquid state, either when pure or dissolved in a suitable solvent.* A pure covalent compound, on the other hand, does not conduct an electric current. Sometimes a mixture of two covalent substances produces a conducting system, e.g., hydrogen chloride and water; this is the result of a chemical action which leads to the formation of ions (§ 52a).

It will be seen later (§ 18c) that in an ionic solid, the molecule, e.g., sodium chloride, does not exist as a definite entity; instead there are interlocking arrangements of ions, e.g., sodium ions and chlorine ions. Each positive ion is surrounded by a number, often six or eight, of negative ions, while each negative ion is surrounded by positive ions. The result of this type of structure is that very powerful forces hold the crystal together. It is not surprising, therefore, to find that *ionic compounds have high melting points and high boiling points.* Covalent compounds, however, generally exist as single molecules in the solid state. The forces of attraction between the molecules, which are of the type called van der Waals forces (§ 4f), are not large, and so *covalent substances melt and boil at relatively low temperatures.* It is only necessary to make a few comparisons, e.g., sodium chloride and silicon tetrachloride, calcium oxide and carbon dioxide, and sodium sulfide and hydrogen sulfide, to appreciate the approximate truth, at least, of these generalizations. The low boiling point of aluminum chloride (182°C) shows that this substance is a covalent compound. It is true that it forms a conducting solution in water, but this is due to ions formed by chemical reaction.

Ionic compounds are generally soluble in liquids such as water, alcohol and liquid ammonia, which are "polar" compounds (see § 16g), but are insoluble in "nonpolar" solvents, such as hydrocarbons and carbon tetrachloride. With covalent substances the reverse is often true, unless compound formation with the solvent occurs. Many covalent compounds, e.g., alcohol, acetic acid, etc., are soluble in polar liquids, because the former are themselves polar, but there are few cases of ionic compounds being soluble in nonpolar liquids.

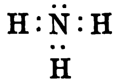
As in many other aspects of science, it is not really possible to make a sharp distinction between ionic and covalent compounds. According to modern ideas, based on wave mechanics, all bonds partake both of ionic and covalent character. Generally one of these predominates greatly over the other; for example, in sodium chloride the ionic character is dominant, whereas in carbon tetrachloride the covalent character is all important. In some cases, however, both are present to a somewhat similar extent; the properties are then intermediate between those of covalent and ionic compounds. It has been found that when the positive ion is small and the negative ion is large, the compound may exhibit some covalent properties. This may be illustrated by lithium iodide, consisting of a small lithium ion and a large iodine ion; this salt has a relatively low melting point, and it is soluble in a number of organic liquids in which most salts are insoluble.

16e. Coordinate Covalence.—In the covalent compounds considered previously, each atom taking part in the formation of a particular bond contributed one electron toward the duplet; in certain circumstances, however, *both electrons are supplied by one of the atoms.* The resultant covalent bond is then called a **coordinate bond** or a **coordinate link.** Certain atoms, particularly those of oxygen, nitrogen, sulfur, phosphorus, and of other bivalent or trivalent elements, in their normal compounds, possess one or two pairs of electrons which are not shared with other atoms. This is seen to be



$$\begin{array}{c}\mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}: \\ \mathrm{H}\end{array}$$

Water



$$\begin{array}{c}\mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{N}}}:\mathrm{H} \\ \mathrm{H}\end{array}$$

Ammonia

the case in the electronic formulae given above for water and ammonia; the oxygen atom has two unshared pairs of electrons, sometimes known as **lone pairs,** while the nitrogen atom has one such pair. Under suitable conditions a lone pair of electrons on one atom may be shared with another atom or ion, thus producing a coordinate covalence. The ammonium and hydrogen (hydronium) ions, for example, are obtained in this manner.

The compounds of ammonia with metallic salts, frequently known as metallic ammines, e.g., cobaltammines, many salt hydrates and complex cyanides, such as those of the transition elements iron, platinum, etc., involve coordinate bond formation between the central metal atom and the molecules of ammonia or water, or the cyanide ion. In each case, a lone pair belonging to the molecule or ion is shared with the metal atom. It is, in fact, because this type of linkage is concerned in the so-called "coordination compounds" of Werner, that it has been referred to as a coordinate bond.

16f. Directed Valence Bonds: Hybridization.—The expression for an electron wave function (or orbital) can be treated as a product of two parts, one of which gives the variation with distance from the atomic nucleus, and the other the angular distribution about the nucleus. The former (radial) portion is much the same for orbitals of different types, but the latter (or directional) portion exhibits interesting differences that have a bearing on the problem of valence. Thus, an *s* orbital is spherically symmetrical, so that it is the same in all directions; a *p* orbital, on the other hand, is much like two spheres in contact (Fig. 16.1). There are three possible *p* orbitals, corresponding to *m* values +1, 0 and −1, and these are identical in shape but differ in orientation. Each lies with its length along one of the three (x, y, z) axes at right angles to one another, so that they are represented by the symbols p_x, p_y and p_z. The physical significance of these results is that the probability of finding an *s* electron is the same in all directions around the atomic nucleus, but *p* electrons tend to concentrate in certain preferred directions.

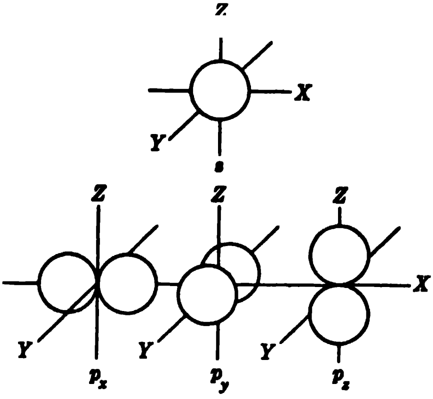


FIG. 16.1. Orientation of *s* and *p* orbitals

It seems reasonable to suppose that, when two atoms join to form a covalent bond, one electron being supplied by each atom, the direction of the bond will correspond to that in which the wave functions of the two electrons overlap as much as possible. If this is the case, *s* electrons will have no directional effect, but *p* electrons will tend to form bonds making an angle of 90° with each other. In the elements of the oxygen and nitrogen groups, bond formation takes place through the outermost *p* electrons, since the *s* electrons have their spins paired. It is to be expected, therefore, that the bond angles should be about 90°. Apart from water and ammonia, in which electrostatic forces of the hydrogen nuclei, due to their close proximity, makes the angle somewhat larger, such is actually the case.

The electronic configuration of the carbon atom in its ground state is $1s^22s^22p^2$, so that there are two $2p$ electrons with unpaired spins. This would imply that carbon has a valence of two, whereas this element is well known to be quadrivalent. Apparently, in chemical combination, an excited state of the carbon atom $1s^22s2p^3$, with one *s* and three *p* unpaired electrons, is first formed. The four orbitals then combine to form four identical **hybrid**

orbitals, *which satisfy the requirement of four equal valence bonds of the* carbon atom. Further, calculations show that these sp^3 hybrid orbitals have maxima in directions making tetrahedral angles (109°28′) with each other. The result provides a theoretical basis for the familiar tetrahedral carbon atom. Similar tetrahedral hybridization occurs in the charged nitrogen atom (N^+) in ammonium compounds; this has the same electronic configuration as carbon.

Another type of hybridization exhibited by the carbon atom can occur between one *s* and two of the *p* orbitals leaving the third *p* orbital unchanged. The three equivalent sp^2 (or trigonal) hybrid orbitals are now found to have their maxima lying in one plane, the directions making angles of 120° with each other. The unaffected *p* orbital is directed at right angles to this plane. In the C═C bond, it is believed that one of the linkages is formed by the overlapping of one of the hybrid trigonal orbitals of each carbon atom and the other by the unchanged *p* orbitals, which are now parallel. The latter bond is much weaker than the former, thus accounting for the fact that a C═C bond is readily converted into a C—C bond by addition of hydrogen, halogen, etc.

For elements having electrons with the principal quantum number equal to 3 or more, *d* orbitals can sometimes take part in bond formation, in addition to *s* and *p* orbitals. In these circumstances other kinds of hybridization are possible. Thus, one *d*, one *s* and two *p* orbitals can combine to give four equivalent dsp^2 orbitals in one plane directed toward the four corners of a square. This is apparently the case in the planar ions $Ni(CN)_4^{-2}$ and $PtCl_6^{-2}$ and in other similar four-coordinated compounds of copper, nickel, palladium, gold and platinum. Bivalent copper can also form from hybrid sp^3 orbitals which, as is to be expected, are tetrahedral. In the six-coordinated compound, for which Werner proposed an octahedral arrangement of bonds about the central atom, the situation is completely accounted for by d^2sp^3 hybridization.

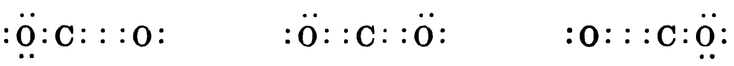
16g. Polar and Nonpolar Molecules.—When two atoms share a pair of electrons, it is generally true, unless the atoms are identical, that the electrons will be drawn more closely to one of the atoms than to the other. The result of this is that the electrical center of the negative charges (electrons) will not correspond with that of the positive charges (nuclei). In other words, the positive and negative charges associated with the covalent bond may be regarded as being displaced relative to one another, so as to form a **dipole.** In general, therefore, every covalent bond between two atoms will be associated with a **dipole moment**; the value of this moment is equal to the product of the electronic charge and the relative displacement of the positive and negative electrical centers. The magnitude of the dipole moment, or the **polarity** of the bond, to use a general term, depends primarily on the relative electron-attracting tendencies of the two atoms concerned. This property, sometimes known as the **electronegativity** of the atoms, varies from one element to another; two examples of series of elements of increasing electronegativity are the following:

$$H < C \ll N < O < F \quad \text{and} \quad I < Br < Cl < F,$$

and similarly for other periods and groups of the periodic table.

Dipole moments of bonds are to be regarded as vectorial in character, that is to say, they have magnitude and direction, the latter being along the direction of the bond. The dipole moment of a molecule as a whole may be regarded as equal to the vector sum of the individual bond moments. Perfectly symmetrical molecules, such as carbon tetrachloride, benzene and other hydrocarbons, have dipole moments of zero; they are consequently called **nonpolar** molecules. Unsymmetrical molecules, however, are almost invariably **polar** in character; such substances possess resultant dipole moments which may be quite large (§ 28b). Compounds containing the groups —OH, —CN, —COOH and —NO_2, which are examples of **polar groups,** are generally highly polar in character, unless they happen to be completely symmetrical. *Nonpolar substances are usually readily volatile and are soluble in other nonpolar compounds.* Polar molecules, having an appreciable electrostatic field because of the resultant dipoles, will attract each other; consequently, *polar liquids have relatively high boiling points.* Further, *such liquids are generally soluble in one another, but do not dissolve so readily in nonpolar solvents.* Although these rules may be regarded as useful generalizations, they are approximate only, for other factors, besides polarity, influence volatility and mutual solubilities.

16h. Resonance.—One of the most interesting consequences of the application of wave mechanics to the problems of valence and molecular structure is the development of the concept of **resonance.** For certain molecules, of which carbon dioxide is a simple example, the conventional chemical formula, e.g., O=C=O, does not account for certain physical (and often chemical) properties. For example, the average energy of the C=O bond in carbon dioxide is 191 kcal per mole, whereas it is 173 kcal per mole for the C=O bond in ketones and aldehydes (see Table 7.5). Further, the bond distance, i.e., the distance between the carbon and oxygen nuclei, is 1.15×10^{-8} cm, i.e., 1.15 A, in carbon dioxide, compared with 1.22 A for the C=O bond in other compounds. The increased bond strength and decreased bond distance suggest that the carbon-oxygen bonds in carbon dioxide are not ordinary double bonds, but have some triple bond character. The actual structure of the molecule is thus somewhere between the three structures



$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:C:::O: \qquad :\overset{\cdot\cdot}{O}::C::\overset{\cdot\cdot}{O}: \qquad :O:::C:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:$$

i.e.,

$$\overset{-}{O}\text{—}C\equiv\overset{+}{O} \qquad O=C=O \qquad \overset{+}{O}\equiv C\text{—}\overset{-}{O}$$

which it is not possible to represent in a conventional manner.

In the language of wave mechanics, it may be stated that the wave function of the carbon dioxide molecule is not adequately represented by that corresponding to the conventional formula. The actual wave function is more complex and a good approximation to it may be obtained by combining, with appropriate coefficients, the wave functions representing the three electronically reasonable structures given above. As a consequence of what is called the variation method in wave mechanics, it is known that the resultant energy corresponding to a combination of wave functions for structures of similar energy, such as the three for carbon dioxide, is less than that corresponding to any of the individual wave functions. In other words, the molecule is more stable and more energy would be required to break the bonds than would be indicated by any single structure. The actual bond energy in excess of that to be expected for the conventional structure is called the **resonance energy.** In carbon dioxide, for example, the average carbon-oxygen bond energy is 18 kcal per mole greater than expected, as seen above; the resonance energy is thus $2 \times 18 = 36$ kcal per mole. As a consequence of the bond energy being greater, the bond distances are less than would be the case for the conventional structure.

A particularly interesting example of the resonance phenomenon is found in the benzene molecule. It has long been known that the simple Kekulé structure, with alternate single and double bonds, is inadequate to account for the chemical and physical properties. The distances between the centers of adjacent carbon atoms in the molecule are all 1.40 A, so that all the bonds are identical. This value may be compared with 1.54 A for the C—C bond and 1.35 A for the C═C bond. It is apparent that all the bonds have considerable double bond character. Further, a comparison of the observed heat of formation with that estimated from bond energies for the Kekulé formula, indicates a resonance energy of 40 kcal with respect to the latter. Thus, benzene is more stable than would be expected for a structure consisting of C—C and C═C bonds alternating in a six-membered ring. Since the actual structure of benzene cannot be represented in a conventional manner, it is said that there is a resonance among five reasonable structures of approximately the same energy, viz.,


I


II


III


IV


V

Of these I and II are alternative Kekulé structures, and the others, III, IV and V, are similar to the Dewar formula for benzene. A good approximation to the actual eigenfunction of benzene is obtained by attributing a coefficient of 0.85 to structures I and II and 0.15 to III, IV and V.

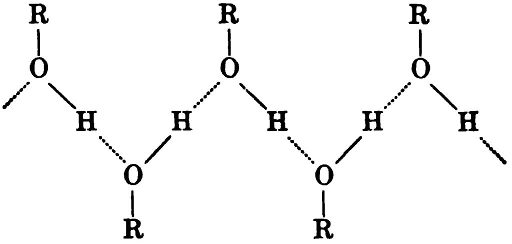
16i. The Hydrogen Bond.—An unusual type of bonding, which is largely electrostatic in nature, is exhibited by hydrogen in certain circumstances.

Although the hydrogen atom possesses but one electron, and is as a consequence normally univalent, it is capable of forming a bond or bridge between two atoms, provided these are small and fairly strongly electronegative in character, e.g., F, O, N (§ 16g). An outstanding example of the formation of such a **hydrogen bond** or **hydrogen bridge,** as it is called, is provided by the familiar acid fluoride ion, HF_2^-, as in the salt KHF_2. There is little doubt that the structure of this ion is to be represented as $(FHF)^-$, with the hydrogen atom acting as a link between the two fluorines. In this instance, because of the very strongly electronegative nature of fluorine, it is probable that the electron of the hydrogen atom has passed completely to the fluorine, so that the HF_2^- ion consists essentially of a proton (H^+) holding two fluoride ions, viz., $F^-H^+F^-$, by electrostatic forces. This is admittedly an extreme case, and in most instances the hydrogen bond formation does not involve complete electron transfer.

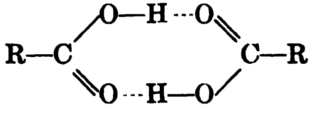
It is well known that the simple hydrogen compounds of nitrogen, oxygen and fluorine, i.e., NH_3, H_2O and HF, differ markedly in physical properties from their homologous compounds in the periodic table. A particular instance is the fact that water is a liquid boiling at 100°C, whereas the analogous compounds of sulfur, selenium and tellurium, viz., H_2S, H_2Se and H_2Te, are gases liquefying at temperatures of about $-62°$, $-42°$ and 0°C, respectively. If water behaved normally in this series, it should be a gas which would condense to a liquid only if cooled below about -80°C at ordinary pressures. Similar discrepancies exist for ammonia and hydrogen fluoride, but the corresponding hydride of carbon, viz., CH_4 (methane), is quite normal in this respect. The explanation of these facts lies in hydrogen bond formation. The hydrogen atom in a molecule of hydrogen fluoride is able to form a bridge between two fluorine atoms, so that chains of the type $\cdots H—F \cdots H—F \cdots H—F \cdots H—F$ are possible. There is evidence that such structures, which are zigzag rather than linear, with the $H—F \cdots H$ angle about 140°, are present in the liquid, and even in the gas. In the homologue, hydrogen chloride, there is little, if any, hydrogen bonding, because of the decreased electronegativity and larger size of the chlorine atom as compared with that of fluorine. It is seen, therefore, that hydrogen fluoride is "associated" (cf. § 5f), and exists as $(HF)_n$ molecules, where n is an indefinite, possibly large, number; hydrogen chloride, on the other hand, exists essentially as single HCl molecules, as do the other homologues, HBr and HI.

Similar hydrogen bond formation accounts for the abnormal properties of water and of liquid ammonia. In the former instance, since there are two hydrogen atoms joined to each oxygen atom, and each of these has two lone pairs of electrons where hydrogen bonds may become attached, it is possible for each molecule of water to be surrounded by four others connected with the central one through hydrogen bonds. This structure actually exists in ice, every crystal of which consists virtually of one large molecule, since each H_2O unit is attached to four others. Upon melting, the same structure persists to a large extent in liquid water in the vicinity of 0°C, but as the temperature is raised there is some breaking of the hydrogen bonds. Nevertheless, at ordinary temperatures there is still considerable complexity in liquid water, for at any instant each H_2O unit is attached by hydrogen bonds to two or three others. Although there is probably a continual interchange of partners in the liquid, it is evident that structures involving large, but indefinite, numbers of molecules will be present in water. Because oxygen is less electronegative than fluorine, water vapor consists of single molecules, with no hydrogen bonding; the same appears to be true for ammonia gas. In methane (CH_4) there is no tendency for hydrogen bonds to occur, since the carbon atom has no lone pairs of electrons and its electronegativity is small. Consequently, there is no association in solid or liquid methane, and its physical properties are not abnormal when compared with those of its homologues.

The alcohols and phenols, which have the general formula ROH, behave like water in respect to hydrogen bond formation. The extent is less marked, however, since the former substances have only one hydrogen atom in the molecule, whereas water has two such atoms. There is evidence that in the crystals of alcohols each ROH unit is attached by hydrogen bonds to two others, in the manner indicated below, and this structure persists to an appreciable extent even in the liquid. As with water, however, the vapors consist essentially of single molecules.



In alcohols, phenols and water there is no obvious limit to the total number of molecules that can be held together by hydrogen bonds (see § 26a), although thermal agitation does set an approximate limit at each temperature. With carboxylic acids, which also possess an —OH group, permitting hydrogen bonding, the union is definitely restricted to a pair of molecules, as represented below. Carboxylic acids, such as formic acid, acetic acid, benzoic acid, etc., would thus be expected to form double molecules very readily. There is ample evidence that such molecules exist in the pure liquid and in solution, and also in the vapor at not too high temperatures (§ 5f).



The formation of hydrogen bridges is not restricted to identical molecules, as in the cases cited above; it is possible for a hydrogen bond to hold together two different molecules, or even to link up two parts of the same molecule. However, there is one essential restriction, namely, that a hydrogen atom can form a bridge only between electronegative atoms, the most important being nitrogen, oxygen and fluorine; the two atoms joined by the bridge may be the same or different. It may be mentioned that hydrogen bonds are very much weaker than ordinary bonds, and so the former are readily broken as the temperature is raised. Finally, there is evidence that in most cases the hydrogen atom forming the bridge is closer to one atom than the other; this fact, together with its weakness, justifies the use of a dotted line, as above, to indicate the presence of a hydrogen bond.

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PROBLEMS

1. An electron emitted by a hot filament is accelerated to an anode by a potential difference of 500 volts. Calculate (*a*) its velocity when it reaches the anode and (*b*) its associated wave length.

2. In order to excite the K_α line in the X-ray spectrum of a particular element, the cathode rays must be accelerated by at least 17.2×10^3 volts. Identify the element.

3. Calculate the wave length associated with a particle of one mg mass moving with a velocity of 5×10^5 cm sec^{-1}.

4. An oil drop of density 0.92 g cm^{-3} and radius 2.76×10^{-4} cm required 11.9 sec to fall 1.02 cm in air of viscosity 1.82×10^{-4} poise. Determine the strength of the electrical field which will keep the drop stationary when it has a single charge.

5. The energy difference between two electronic states is 2.00 ev. What will be the wave length of the light emitted when the electron drops to the lower state?

6. The $K_{\alpha 2}$ line of tungsten has a wave length of 0.2134 A. Calculate the minimum voltage required to excite this X-ray line.

7. (*a*) Calculate the wave length of the fourth line in the Balmer, Lyman and Paschen series of the atomic hydrogen spectrum. (*b*) How much energy will be required to ionize the atom from the respective upper states?

8. The wave numbers of the spectral lines of the hydrogen-like ions are related approximately to those of hydrogen by $\bar{\nu} = \bar{\nu}_H Z^2$, where Z is the nuclear charge. For the He$^+$ ion calculate (*a*) the wave length of the first line in the series with $n_2 = 1$ and (*b*) the ionization potential for the process $He^+ \rightarrow He^{++} + \epsilon$.

7

The Solid State

CRYSTAL STRUCTURE

17a. The Study of Crystals.—The solid state is characterized by a rigidity of form and a tendency to maintain a definite shape; further, the volume of a solid changes only slightly with temperature and pressure. The true solid state is probably always associated with a definite crystalline form; that is to say, there is a complete regularity in the arrangement of the atoms or molecules of which the substance is constituted. Amorphous solids, such as glass and pitch, are really intermediate between solids and liquids; in these substances there may be some regularity of internal structure, but it is only partial, at best (§ 19h). Crystals, or true solids, can be distinguished from amorphous solids in many ways; for example, the former possess a sharp melting point, whereas the latter do not. Another important difference is to be found in the regularity of the external form, as well as in the internal arrangement, of crystals.

Except for those belonging to the cubic or regular system (see below), all crystals have certain properties that vary with the direction. Such substances are said to be **anisotropic,** to distinguish them from cubic crystals and amorphous materials which are **isotropic,** having identical characteristics in all directions. The velocity of light is one property that depends on the direction in which it is measured; the result is that when a ray of light enters an anisotropic crystal, it is split into two separate components which travel with different velocities and follow different paths. This phenomenon, known as **double refraction,** is shown by all solids, except crystals of the cubic system and those, e.g., glass, which are amorphous in nature. The marked double refraction exhibited by Iceland spar (calcium carbonate) is made use of in the Nicol prism for the production and examination of polarized light.

The shape of a crystal of a given compound or element may vary with the conditions under which crystallization occurs, but *the angles between the faces are always constant.* The external shape or **habit** depends on the relative development of the different faces, but the interfacial angles remain unchanged. This is shown in the two-dimensional representations in Fig. 17.1; the angles, such as A, between pairs of corresponding sides are the same in each case, although the shapes are quite different. The measurement of the angles of a crystal is thus an important part of the study of crystals, known as **crystallography**; the instrument used for the purpose is the **goniometer** (Greek: *angle measurer*).

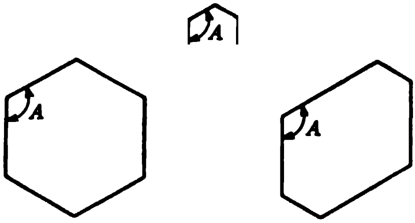

FIG. 17.1. Crystal habit

In addition to the angles, another important property of crystals is their **symmetry**. Several types of symmetry are possible, but only three of the simplest will be described here for purposes of illustration. A crystal is said to have a **plane of symmetry** *when it can be divided by an imaginary plane into two parts, such that one is the exact mirror image of the other.* An **axis of symmetry** is *a line about which the crystal may be rotated so that it presents exactly the same appearance more than once in the course of a complete revolution.* If the original aspect appears again after a rotation through 180°, the axis is said to be one of two-fold (diad) symmetry. Other possibilities are repetition of the original appearance every 120° (three-fold or triad axis), 90° (four-fold or tetrad axis), and 60° (six-fold or hexad axis). In addition, a crystal may have a **center of symmetry**; this is *a point such that any line drawn through it will intersect the surface of the crystal at equal distances in both directions.* A crystal can have one or more planes, and one or more axes of symmetry, but never more than one center of symmetry. In fact, many crystals are not centro-symmetric, for they develop differently at opposite ends. The total number of **elements of symmetry**, as the various possible types of symmetry are called, depends on the nature of the crystal; a cubic crystal, such as one of sodium chloride, possesses twenty-three elements of symmetry, but a crystal of copper sulfate pentahydrate is highly unsymmetric and has no elements of symmetry.

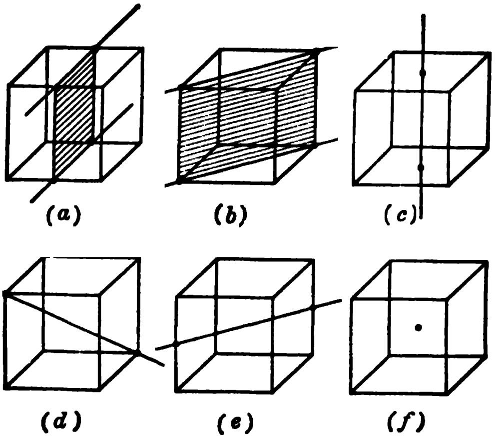

FIG. 17.2. Elements of symmetry of a cube

The significance of the elements of symmetry for a cubic crystal is illustrated in Fig. 17.2. In (*a*) there is a rectangular plane of symmetry, of which there are three, the others being at right angles to the one shown; (*b*) is a diagonal plane of symmetry, there being a total of six such planes passing diagonally through the cube; (*c*) indicates one of the three axes of four-fold symmetry, at right angles to each other; (*d*) shows one of the four axes of three-fold symmetry passing through opposite corners of the cube; (*e*) is one of the six axes of two-fold symmetry, emerging from opposite edges; and finally (*f*) depicts the one center of symmetry at the mass center of the cube. It is seen, therefore, that a perfect cube has a total of twenty-three elements of symmetry.

17b. The Space Lattice.—One of the consequences of the regularity of crystal structure is the development of the idea of the **space lattice;** the concept can be explained most simply by reference to a particular case. Consider, for example, a crystal of sodium chloride; this consists of a perfectly regular arrangement of sodium atoms (or ions) and chlorine atoms (or ions). If the position of each sodium unit in the crystal is represented by a point, the result will be a regular three-dimensional network of points; this is the space lattice of the sodium atoms (or ions) in the crystal of sodium chloride. Similarly, there will be a space lattice for the chlorine units, and the space lattice of sodium chloride is made up of the interpenetration of the sodium and chlorine lattices. The symmetry of the combined lattice determines the symmetry of the crystal as a whole. In some cases, the lattices of the constituent units are identical, as is apparently true for sodium chloride, but in other instances, e.g., calcium fluoride, there are reasons for believing that the space lattices of the constituents, viz., calcium and fluorine, are different.

No matter how complicated the combined space lattice for all the atoms or ions of a crystal, there is always one essential property of the lattice: *each point in the lattice has exactly the same environment as any other point representing the same atom or ion.* For example, in the space lattice of calcium carbonate, every point representing a calcium atom (or ion) will have exactly the same environment of carbon, oxygen, and other calcium atoms. For this reason the three-dimensional space lattice of a crystal has been likened to a patterned wall-paper in two dimensions. Further, just as the pattern on the paper may be regarded as made up of a single pattern which is continuously repeated, so the space lattice of the crystal may be considered as built up of a three-dimensional basic pattern; this is called the **unit cell** and the external appearance of the crystal is determined by the shape and dimensions of the unit cell.

By means of arguments based on geometry, it has been proved that only fourteen different kinds of simple space lattice, called **Bravais lattices** (A. Bravais, 1848), are possible; in other words, there are only fourteen ways in which similar points can be arranged in a regular three-dimensional order. For example, all crystals in the cubic or regular system are made up of one or more of three kinds of lattice; these are (i) the simple cube, (ii) the face-centered cube, and (iii) the body-centered cube. The unit cells corresponding to these space lattices are shown in Fig. 17.3; the actual lattice consists of a repetition of these unit cells in three dimensions. The simple cubic lattice has points only at the corners of each unit cube; in the face-centered lattice there are, in addition, points at the center of each of the six faces, while the body-centered lattice has a point in the center of each cube as well as those at the corners.*

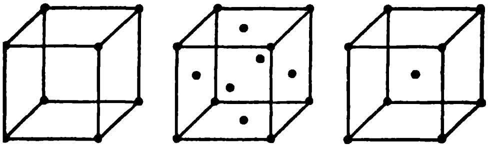
(i) (ii) (iii)

FIG. 17.3. Cubic lattices

From geometrical considerations, it has been found that 32 different combinations of the elements of symmetry of a crystal are theoretically possible. These are referred to as the 32 **point groups.** In conjunction with the Bravais lattices, these point groups lead to 230 different arrangements known as **space groups.** Every crystal, depending upon its symmetry elements, must belong to one or other of these groups.

17c. Crystal Systems.—As a matter of practical convenience, the 14 Bravais lattices and the 32 point groups may be divided into seven **crystal systems.** Basically, these systems are determined by symmetry considerations, but in many cases these correspond to certain characteristics of the angles and relative dimensions of the unit cell. The properties of the seven crystal systems are summarized in Table 17.1. The second column gives the minimum symmetry, that is, the essential requirement for each system; some crystals in a given system may have more symmetry elements than those indicated, but they cannot have less. A line over a number implies an inversion axis of symmetry, i.e., a combination of a symmetry axis with simultaneous inversion through a point. Under the heading of unit cell dimensions are given the angles α, β and γ between three imaginary axes which may best be used to represent the unit cell; a, b and c are the intercepts made by the unit cell along these three axes (see § 17d). It should be pointed out that symmetry considerations determine the particular system to which a crystal belongs; the unit cell dimensions are a secondary consequence of the symmetry. Several cases are known in which, owing to fortuitous circumstances, a crystal which is definitely in one system has the dimensional characteristics of another.

17d. Lattice Planes and Dimensions.—The points in a space lattice can be arranged in a number of ways as a series of parallel and equidistant

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* Attention may be called to the fact that it is the *points* that constitute the space lattice, and not the lines joining them. Such lines are frequently inserted as a convenience to indicate the shape and dimensions of the unit cell, but they are not actually part of the lattice.

TABLE 17.1. PROPERTIES OF THE CRYSTAL SYSTEMS

System	Minimum Symmetry	Unit Cell Dimensions	Examples
Cubic (or Isometric)	More than one 3 (or $\bar{3}$)-fold axis	$\alpha = \beta = \gamma = 90°$ $a = b = c$	NaCl, CaF_2, ZnS, diamond
Tetragonal	One 4 (or $\bar{4}$)-fold axis	$\alpha = \beta = \gamma = 90°$ $a = b \neq c$	SnO_2, TiO_2, $PbWO_4$, Sn (white)
Orthorhombic (or Rhombic)	More than one 2 (or $\bar{2}$)-fold axis; none higher	$\alpha = \beta = \gamma = 90°$ $a \neq b \neq c$	KNO_3, K_2SO_4, $BaSO_4$, S (rhombic)
Monoclinic	One 2 (or $\bar{2}$)-fold axis or both	$\alpha = \gamma = 90°$, $\beta \neq 90°$ $a \neq b \neq c$	$CaSO_4 \cdot 2H_2O$, S (monoclinic)
Triclinic	None (or inversion only)	$\alpha \neq \beta \neq \gamma \neq 90°$ $a \neq b \neq c$	$CuSO_4 \cdot 5H_2O$, $K_2Cr_2O_7$
Hexagonal	One 6 (or $\bar{6}$)-fold axis	$\alpha = \beta = 90°, \gamma = 120°$ $a = b \neq c$	SiO_2, HgS, Mg, Zn
Rhombohedral (or Trigonal)	One 3 (or $\bar{3}$)-fold axis	$\alpha = \beta = \gamma \neq 90°$ $a = b = c$	$CaCO_3$ (calcite), $NaNO_3$

planes; these are known as the **lattice planes.** The external faces of the complete crystal are parallel to these planes; the most frequently occurring types of faces are those corresponding to planes containing the largest number of points. The situation is illustrated, in two dimensions, in Fig. 17.4; e.g., along *AB* the lattice points are closer than along *CD*. Until the introduction of the X-ray method (§ 18a), information on crystal structure and crystal systems was obtained solely from measurements of the angles between external faces of the crystal.

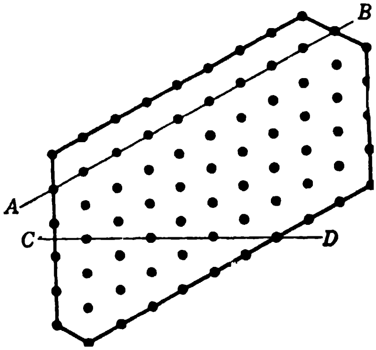


FIG. 17.4. Crystal faces and lattice points

The lattice planes are identified by a method originally used to describe crystal faces (W. H. Miller, 1839). It can be simply explained by considering a crystal lattice, which is conveniently represented in terms of three axes, *OX*, *OY* and *OZ*, at right angles to each other, as shown in Fig. 17.5. Let *a*, *b* and *c* be distances along these axes which characterize the unit cell, then *ABC* is the **unit plane** of the space lattice, and *a*, *b* and *c* are called the **unit intercepts.** In order to define any other lattice plane, such as *LMN* in Fig. 17.5, the intercepts *OL*, *OM* and *ON* are first expressed as multiples (or fractions) of the unit intercepts; in the case illustrated these are seen to be 2, 2 and 3, respectively. The reciprocals of these multiples are $\frac{1}{2}$, $\frac{1}{2}$ and $\frac{1}{3}$, which are in the ratio of 3:3:2. These numbers are the **Miller indices,** or (*hkl*) values, of the plane *LMN* and this is consequently designated a (332) plane. In other words, the Miller indices are inversely proportional to the intercepts of a given lattice plane on the chosen axes.

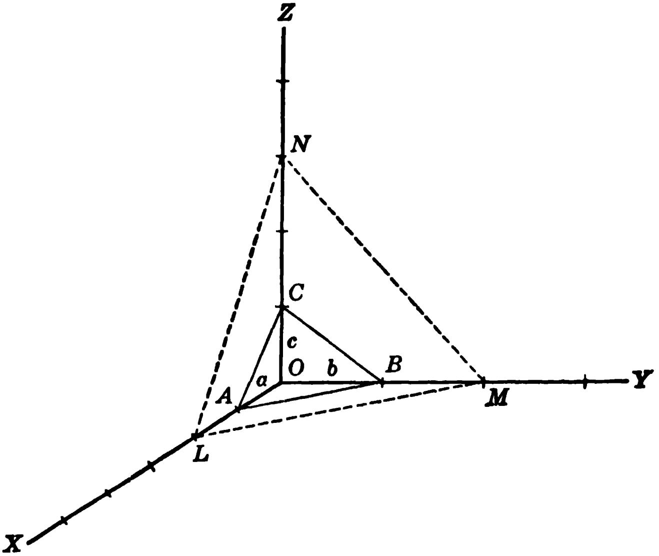
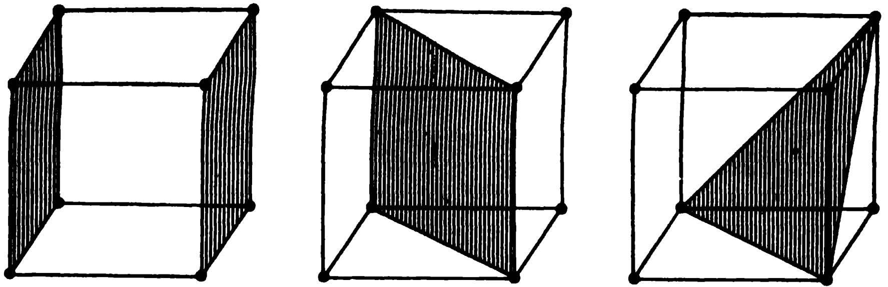


FIG. 17.5. Identification of lattice planes by Miller indices

For the plane *ABC*, the Miller indices are (111), since the multiples of *a*, *b* and *c* are all unity in this case. When a face cuts only two of the axes and is parallel to the third, the intercept on the latter is infinity, and the corresponding index is zero. Thus, a plane passing through *A* and *B* that is parallel to the axis *OZ* would have the indices (110). If the face is parallel to a plane containing two of the axes, so that it has a finite intercept on one plane only, the symbol 00 would be employed. For example, if the face passes through *A* and is parallel to the plane *YOZ*, the Miller indices would be (100).

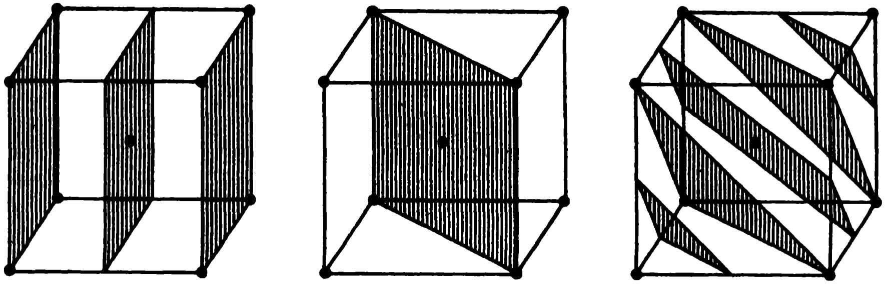
For a simple cubic lattice, of which Fig. 17.3 (i) shows a unit cell, the (100), (110) and (111) planes completely describe the lattice structure. However, for body-centered or face-centered cubes, Figs. 17.3 (ii) and (iii), it is apparent that there are other important lattice planes. For example, in these cases an additional plane, parallel to the (100) plane, can pass through the face-centered or body-centered points. Although, from the external crystallographic viewpoint, this would also be referred to as a (100) plane, it is preferable from the internal unit cell concept to call it a (200) plane, since its



100 planes

110 plane
Simple

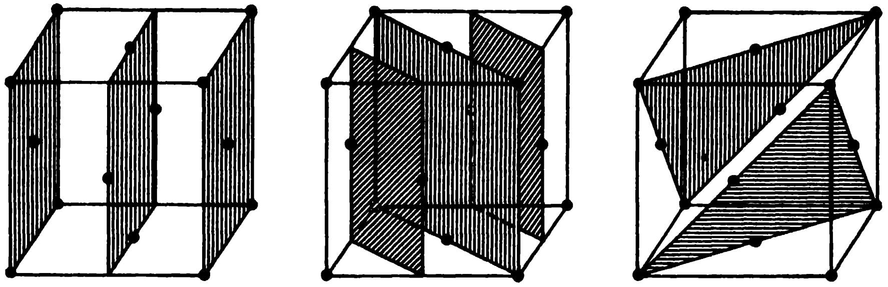
111 plane



200 planes

110 plane
Body-centered

222 planes



200 planes

220 planes
Face-centered

111 planes

FIG. 17.6. Important planes of cubic lattices

intercept (along the X-axis) is one half the unit cell edge. The manner in which some possible lattice planes pass through the three kinds of cubic lattice is shown in Fig. 17.6.

X-RAYS AND CRYSTAL STRUCTURE

18a. Diffraction of X-Rays.—A new and significant field of investigation was opened up by the discovery that X-rays could be used to study the interior structure of crystals. The fact that the wave lengths of X-rays are of the same order, viz., 10^{-8} cm, as the distance between atoms in a crystal, indicated to W. von Laue (1912) the possibility that a crystal might be used as a diffraction grating for X-rays. At his suggestion, W. Friedrich and P. Knipping (1912) passed a beam of inhomogeneous X-rays, that is, a beam consisting of X-rays of many different wave lengths, through a crystal of zinc blende; when the resulting radiation fell on a photographic plate a definite diffraction pattern was obtained. A pattern of this type, given by a crystal of magnesium oxide, is depicted in Fig. 18.1; it is generally referred to as a **Laue photograph** or **Laue pattern.** The important fact that a crystal could behave as a three-dimensional diffraction grating, led W. L. Bragg (1913) to the use of X-rays for the purpose of studying crystal structure. The Laue patterns have been used to a considerable extent for such studies in recent years, but the interpretation of the results is not easy, although special mathematical and geometrical methods have been developed for this purpose.

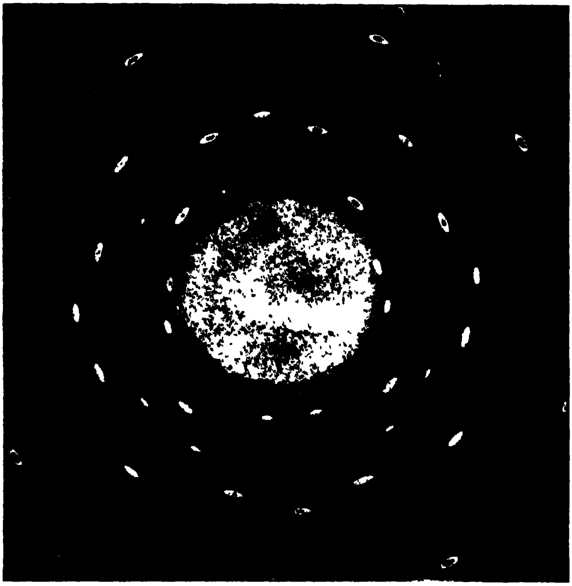


Fig. 18.1. Laue photograph of magnesium oxide

The principle involved in the procedure devised by W. H. Bragg and W. L. Bragg, in which the crystal is used as a reflection grating for homogeneous X-rays, i.e., of uniform wave length, is much simpler to understand. Every atom is able to scatter X-rays to an extent dependent upon the number of its electrons, and every atom-bearing plane in a crystal, that is, every lattice plane, can cause reflection of the rays. Consider, for illustrative purposes, a number of identical lattice planes, represented in section by the lines *AA*, *BB*, etc., in Fig. 18.2; each of these planes really consists of a regular arrangement of points indicating the positions of the atoms in the crystal. A parallel beam of uniform X-rays impinges on the crystal so that the **glancing angle** is θ, as shown. Part of the beam, i.e., LM, will be reflected at M along MN; on the other hand, some of the rays, i.e., PQ, will penetrate the crystal and be reflected along QR by the atoms in the lattice plane BB. If the length of the path LMN differs from that of PQR by a whole number of wave lengths, then the two beams from L and P will reinforce one another after reflection and a strong beam will result.

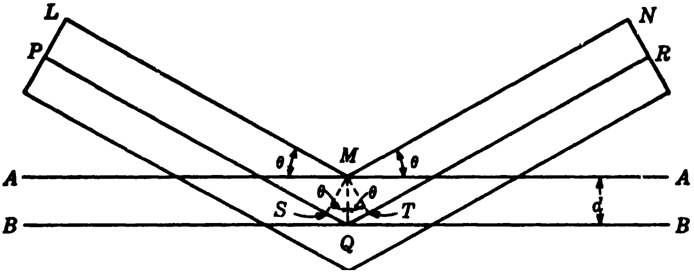


FIG. 18.2. Derivation of Bragg's law

The condition for the reinforcement to occur can be derived in the following manner. The difference in length of the paths LMN and PQR is equal to $SQ + QT$, where MS and MT are drawn perpendicular to PQ and QR, respectively. If d is the distance between successive lattice planes, both SQ and QT are equal to $d \sin \theta$, since the angles SMQ and QMT are each equal to the glancing angle θ. The total path length difference is thus $2d \sin \theta$. For a reflection of maximum intensity this quantity must be a whole number n of wave lengths λ, as stated above; hence, the condition for maximum reflection is

$$n\lambda = 2d \sin \theta. \tag{18.1}$$

This result, known as the **Bragg equation,** is also applicable to reflection from other planes parallel to AA and BB.

For a given set of lattice planes, e.g., (100) planes, d is fixed; further, for homogeneous X-rays the wave length λ has a definite value. The possibility of obtaining maximum reflection will thus depend on θ, the glancing angle. As θ is increased gradually, a series of positions are found, corresponding to n equal to 1, 2, 3, 4, etc., at which the reflection is a maximum. These are separated by regions in which the reflected X-ray beams from successive lattice planes differ in length by a fractional number of wave lengths; the rays are then not "in phase," and so cancel each other to a great extent, thus resulting in a decrease of intensity. By means of a crystal it is thus possible to obtain an X-ray "spectrum," consisting of a number of fairly strong reflections separated by regions of low intensity. The successive maxima are called first, second, third, etc., order reflections, according as the value of n

in equation (18.1) is 1, 2, 3, etc.; their intensity falls off as n increases, and reflections of the fifth or higher order are generally too feeble to be detected.

It is seen from equation (18.1) that for X-rays of a particular wave length, the angle of reflection for a given order increases as the spacing between the lattice planes decreases. Since the maximum value of $\sin\theta$ is unity, it follows that the smallest spacing that will give a reflection of the nth order is $d = n\lambda/2$. Alternatively, it may be stated that the highest order that can be observed is given by $n = 2d/\lambda$. Hence, if $2d$ is smaller than λ, the wave length of the X-rays, so that $2d/\lambda$ is less than one, there will be no reflection maximum.

It has become standard practice in X-ray studies of crystal structure to assume that all reflections are first order ($n = 1$). The Bragg equation shows that a second order ($n = 2$) reflection from (100) planes is mathematically equivalent to a first order reflection from planes with half the spacing, i.e., from (200) planes. Similarly, the second order reflection from (110) and (111) planes may be described as (220) and (222), respectively. The procedure has the merit of avoiding ambiguity where overlapping orders occur. But, more important is the fact that it centers attention on the unit cell, the boundary planes of which are always indicated by the indices (100), (010) and (001).

18b. The Determination of Crystal Structure.—It will be evident from equation (18.1) that if the glancing angles θ are measured for the various orders of maximum reflection, the distance d between successive lattice planes of a given type in the crystal can be calculated, provided the wave length of the X-rays is known. Even if this wave length is not known, it should still be possible to calculate the *ratio* of the separations for planes of different types. In order to determine the positions of maximum reflection intensity, use can be made of the Bragg **X-ray spectrometer**, shown diagrammatically in Fig. 18.3. A beam of X-rays of definite wave length, coming from the anticathode A of an X-ray tube, passes through a slit B and then falls upon a known face of the crystal C mounted on a rotating table, the position of which can be read on the scale D. The rays reflected from the crystal pass through another slit and into a detector E of ionizing radiation, such as an ionization chamber or a Geiger counter. The response of the detector is proportional to the intensity of the entering X-rays.

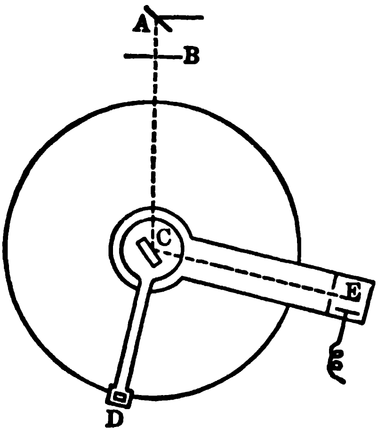


FIG. 18.3. X-ray spectrometer (Bragg)

Starting with a small glancing angle between incident X-rays and the crystal face, the value is increased in stages by rotating the table. The apparatus is so designed that the reflected ray always enters the detector chamber *E*, and the intensities of the reflected X-rays for the various angles are determined. The glancing angles θ for which the strongest reflections are obtained are those which satisfy the Bragg equation (18.1). The procedure just described is repeated for all the important planes of the crystal; if necessary, artificial faces, parallel to some lattice planes, must be cut. For example, the faces of a perfect cube are all (100), and so it would be necessary to cut artificial (110) and (111) faces, to study reflections from the (110) and (111) lattice planes, respectively, which are parallel to these faces.

The X-ray spectrometer method of studying crystal structure requires the use of a relatively large crystal with well defined faces, and since reflections of several orders must be examined for a number of faces, the total labor involved is large. This is compensated for, however, by the comparatively simple interpretation of the results. As already stated, the study of crystals based on the use of the Laue patterns is possible, but the evaluation of the results is complicated. At the present time the Laue method is used mainly to determine the symmetry class of the crystal space lattice.

A widely used alternative technique is the **powder method** of X-ray crystallography, devised independently by P. Debye and P. Scherrer (1916) and A. W. Hull (1917). A narrow beam *AB* of uniform X-rays (Fig. 18.4) is allowed to fall on the finely powdered substance *C* to be examined in the form of a cylinder, e.g., coated on a hair or inside a thin-walled glass tube. The diffracted rays impinge upon a strip of photographic film *FF′* arranged in a circular arc with *C* at its center. In the fine powder the crystals are oriented in all directions, and so a large number will have their lattice planes in the correct positions for maximum X-ray reflection to occur. All crystalline particles whose (100) planes make the proper angle with the incident beam of X-rays will produce first order maxima in directions lying on a circular cone, as shown in Fig. 18.4. Similarly, some crystals will be oriented in such a manner as to produce another circular cone, as the reflection from the (110) planes, and so on for other planes and for higher orders. The strip of film *FF′* cuts each cone in such a way as to produce two arcs; each pair gives the position of a reflection of a definite order from a particular plane. Since the distance *CB* is fixed for a given X-ray camera system, it is only necessary to measure distances such as *BD* and *BE* to evaluate θ for the particular reflection. The structure of the crystalline material can then be determined.

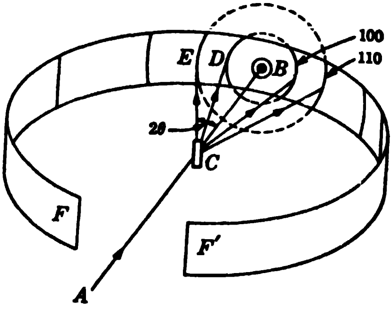


FIG. 18.4. Principle of the powder method

The powder method is most suitable for cubic, hexagonal and tetragonal crystals; the association of the various lines with the possible planes and orders of reflection is then not too difficult. The method has been employed particularly in the study of metals and alloys, for which single crystals are not easily obtained. It has also been used for analytical and identification purposes, as the X-ray powder photograph of a given crystalline substance is characteristic of that substance.

18c. Interpretation of X-Ray Diffraction Results.—The interpretation of X-ray diffraction patterns is often facilitated by the fact that reflections are not necessarily observed from all sets of planes which can pass through lattice points. If one set of planes is uniformly spaced between the planes of another set, then interference of the rays reflected from the two sets will occur at certain grazing angles. As a result, the expected diffraction line will be absent from the X-ray powder pattern. Considering the (100), (110) and (111) planes of the cubic lattice, for example, it is found that, in the simple cube, reflections from all these planes are observed. For the face-centered lattice the reflections from the (100) and (110) planes are absent, since the (200) and (220) planes, respectively, cause interference. Hence, reflections appear from the (111) plane only. Similarly, the diffraction pattern of a body-centered cubic lattice will exhibit only the (110) reflections.

From an examination of the spacings of the various lattice planes in cubic lattices, the conditions for the appearance of reflections in the X-ray diffraction pattern have been found to be as follows:

Simple cubic lattice	h, k, l may have any values
Face-centered cubic lattice	h, k, l are all odd or all even (including zero)
Body-centered cubic lattice	$h + k + l$ must be even

If a is the edge length of the unit cell of a cubic lattice, then the distance between planes is given by

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}, \tag{18.2}$$

and upon combining this with equation (18.1), with $n = 1$, it is found that

$$\sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2). \tag{18.3}$$

Since λ and a are constant in an experiment with a given crystal, the (hkl) values for the various reflections can be determined by finding the simplest relationship between $\sin^2 \theta$ and $h^2 + k^2 + l^2$. Once the Miller indices of a reflection have been identified in this manner, the edge length a of the unit cell can be calculated by either equation (18.2) or (18.3).

The reflections which appear for a particular lattice type are determined by the rules given above, and their spacing, in terms of θ or $\sin \theta$, is defined by equation (18.3). Hence, each lattice type may be identified by the pattern

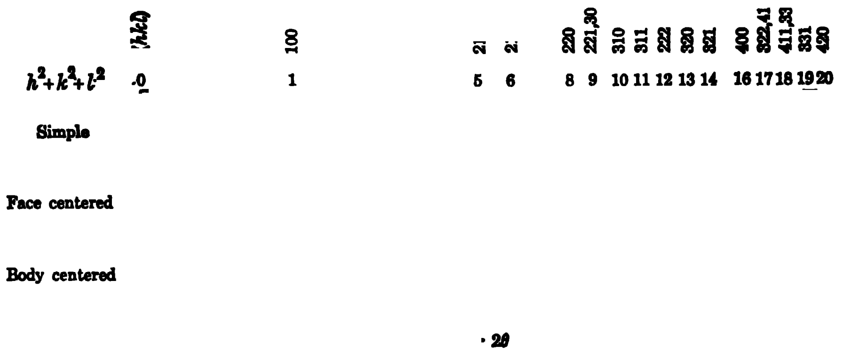


Fig. 18.5. Schematic representation of the location of reflections in X-ray powder patterns of cubic lattices

of reflections observed. The distributions to be expected in the X-ray diffraction for the three types of cubic lattices are shown in Fig. 18.5. The results are quite general and are independent of the particular technique used to study the X-ray diffraction of the crystals. They are particularly useful, however, in connection with the powder method. With experience, it is possible to identify the lattice type merely by comparison of a powder diffraction pattern (Fig. 18.6) with diagrams such as those in Fig. 18.5.

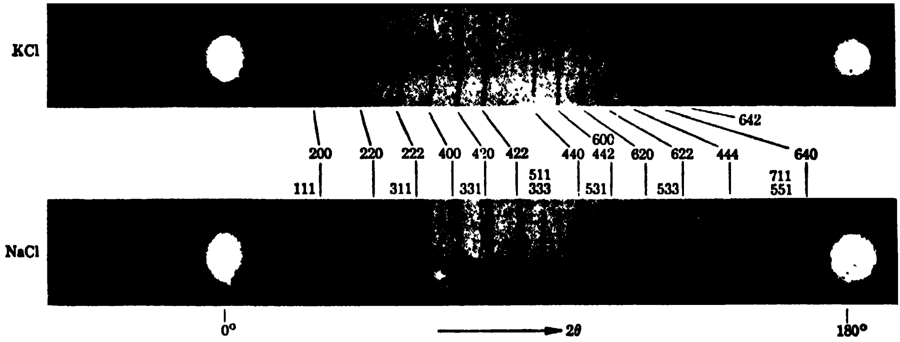


Fig. 18.6. X-ray powder diffraction patterns of sodium chloride and potassium chloride, using copper radiation (*Courtesy of Philips Electronics, Inc.*)

For elements in which all the scattering atoms in a crystal lattice are the same, all the permitted reflections are found in the X-ray diffraction pattern. For compounds, however, the difference in scattering power of the constituent atoms will cause certain reflections to have a diminished intensity, due to interference effects, so that sometimes they disappear completely. This is strikingly illustrated in connection with the powder patterns of sodium and potassium chlorides shown in Fig. 18.6. Although these two salts might be expected to have similar structures, it appears from the Miller indices of the lines that sodium chloride is based on a face-centered cubic lattice and potassium chloride on a simple cubic lattice.

The unit cell of sodium chloride, depicted in Fig. 18.7, is seen to consist of an interpenetrating arrangement of a face-centered sodium (ion) lattice and a similar chlorine (ion) lattice. Each sodium ion is surrounded by six chlorine ions, and each chlorine ion by six sodium ions. The (100) and (110) planes each contain equal numbers of sodium and chlorine ions, and each layer of planes therefore scatters X-rays uniformly to give the expected reflections for a face-centered cubic structure. The (111) planes, on the other hand, are alternating layers containing either sodium ions or chlorine ions only. Consequently, X-rays reflected from the sodium-ion layers will interfere with those from the chlorine-ion layers. Since the scattering power of an atom or ion is largely determined by the number of electrons it contains, only partial interference will occur since the sodium ion has 10 electrons and the chlorine ion 18 electrons. In potassium chloride, however, the potassium and chlorine ions contain equal numbers (18) of electrons, and interference between reflections from alternate (111) planes is complete. The X-ray pattern consequently shows no (111) reflection.

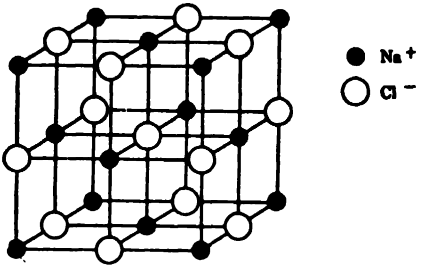


Fig. 18.7. Sodium chloride lattice

The occurrence of the (111) reflection for sodium chloride is strong evidence that the structural units in the crystal are not molecules of NaCl. If the arrangement were molecular, all the (111) planes would contain the same scattering centers and interference would be complete. As is to be expected from the electronic theory of valence (§ 16b), the structural units are ions of sodium and chlorine, and the crystal has what is called an **ionic lattice.** All true ionic compounds possess ionic lattices.

It should be recalled, as noted above, that in depicting a space lattice, the position of an atom or ion is represented by a point, or a small circle. The size of the point or circle provides no information concerning the size of the atom or ion, and this important fact must always be remembered. Actually, there are reasons for believing that *the atoms or ions in a crystal practically touch one another*, with little or no "free space" between them.

18d. Lattice Dimensions: The Avogadro Number.—In Fig. 18.7 the unit cell of the space lattice of sodium chloride is seen to consist of fourteen points representing sodium ions, and thirteen points for chloride ions. Of the former, there is one at each of the eight corners, and one in the middle of each of the six faces. The eight sodium points at the corners are shared equally by eight cubes meeting at each corner, so that there is effectively only one per unit cell; similarly, the sodium points on the six faces are each shared by two cubes, giving an average of three for each unit cell. There are thus an average of four sodium ions associated with the unit cell shown. Of the thirteen chlorine points, the one in the center belongs exclusively to the unit cell, but the other twelve are each shared between four cubes meeting at each of the edges. There are thus four chloride ions that belong to the unit cell. Four "molecules" of sodium chloride, i.e., four sodium ions and four chloride ions, are consequently associated exclusively with the unit cell in Fig. 18.7. If M is the molecular weight of sodium chloride and N is the Avogadro number, the average mass per unit cube must be $4M/N$. Further, if the specific volume, i.e., the volume of unit mass, is v, then the mean volume of the unit cube will be $4Mv/N$. It can be seen from Fig. 18.7 that each edge of the unit cube has a length of $2d_{200}$, and so the volume of this cube must be $(2d_{200})^3$; equating this result to the one just given, it follows that

$$(2d_{200})^3 = \frac{4Mv}{N},$$

$$d_{200} = \sqrt[3]{\frac{Mv}{2N}}. \tag{18.4}$$

For sodium chloride, M is 58.454, v is 0.4621 cm^3 at 20°C and the Avogadro number is 6.023×10^{23}; it follows, therefore, that d_{200} is 2.82×10^{-8} cm, i.e., 2.82 A.

From this result for the distance between successive (200) planes in the sodium chloride crystal, it is possible to calculate the wave length of the X-rays. The first order diffraction maximum of the K_α rays of palladium, reflected from the (200) planes of sodium chloride, occurs at a glancing angle of 5.90°; hence, n is 1 and $\sin\theta$ is 0.103. Making use of equation (18.1), in conjunction with the value of d_{200}, i.e., 2.82×10^{-8} cm, obtained above, it follows that λ is 0.581×10^{-8} cm, i.e., 0.581 A. It is thus seen, as mentioned at the beginning of § 18a, that atomic (or ionic) distances and the wave lengths of X-rays are of the order of 10^{-8} cm.

The wave length of the X-rays can be determined in an absolute manner, not dependent on crystal structure, by using an ordinary line grating and very small glancing angles. Hence, it is possible to reverse the foregoing calculations and thus to determine the Avogadro number. It is of interest to note, in this connection, that a discrepancy between the wave lengths of X-rays as determined by crystal diffraction and line grating methods was traced to an error in the Avogadro number used in equation (18.4). It is generally agreed that one of the most accurate procedures for determining this constant is based on observations of the diffraction of X-rays.

By using the method described above or, better, if the wave length of the X-rays is known, by means of equation (18.3) and the measured scattering angle θ, the dimensions of the unit cell in a crystal can be determined. If the results are combined with the assumption that the atoms (or ions) in the lattice are spheres touching one another, it is possible to obtain the sum of the atomic (or ionic) radii in a compound or actual atomic radii in crystals of elements. For example, in sodium chloride d_{200}, that is 2.82 A, would represent the sum of the radii of the sodium and chlorine ions (see Fig. 18.7). In the case of an element which crystallizes in the cubic system, the atomic radius r can be determined from the dimensions of the unit cell. Thus, in a simple cubic lattice the edge length a is equal to $2r$; in a face-centered lattice the face diagonal ($a\sqrt{2}$) is $4r$; and in a body-centered lattice the cube diagonal ($a\sqrt{3}$) is $4r$.

18e. Other Methods of X-Ray Investigation.—The most modern, and widely applicable, procedure for the X-ray investigation of crystal structure is the **rotating crystal method** or a modification, the **oscillating crystal method.** A moderately small crystal is rotated or oscillated about an axis parallel to one of the crystal axes, and is exposed to a beam of homogeneous X-rays from a direction at right angles. As the crystal rotates, various planes come successively into positions for diffraction to occur, and corresponding spots are produced on a photographic plate. A typical rotation photograph is shown in Fig. 18.8. Three such photographs are taken with crystal rotating about each of the three principal axes, and from the results the lattice spacings and size of the unit cell can be deduced. If, in addition, the intensities of the various spots are measured it is possible to determine the exact positions of the atoms, or ions, in the crystal. For this purpose the detailed information obtained by oscillating the crystal through an angle of about 15° at a time, while the photographic plate (or film) is moved in a synchronized manner, is particularly useful, especially for complex molecules.

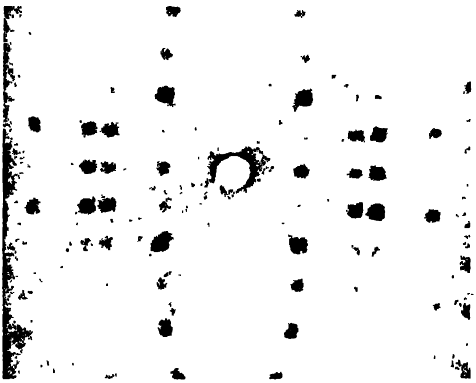


FIG. 18.8. X-ray rotation photograph of benzil

THE STRUCTURE OF SOLIDS

19a. Results of X-Ray Studies of Crystals.—A very large number of crystalline substances have been examined by X-ray methods, and many of the results are of considerable interest and importance to chemistry. A few only of the conclusions will be described here under several headings.

19b. Elements: Nonmetals.—The crystals of nonmetals are characterized by the fact that each atom is joined by definite covalent bonds to one or more adjoining atoms, the actual number being equal to the usual valence of the element. It follows, therefore, that the crystal of a nonmetallic element is constructed in such a manner as to allow every atom to complete its electron octet (§ 16a). The **coordination number** is defined, quite generally, as the number of equidistant nearest neighbors of a given atom or ion. Hence, in the crystals of nonmetallic elements the coordination number is generally equal to the normal valence. This is sometimes expressed by the statement that the coordination number is $8 - N$, where N is the number of the group in which the element occurs in the periodic system or the number of electrons in the outermost shell.

The space lattice of the element carbon in the form of diamond is shown in Fig. 19.1. Although it may not be immediately evident, it consists of two interpenetrating face-centered cubic lattices. For its chemical interest, the diamond lattice is represented in a different form in Fig. 19.2. It is seen that every carbon atom in diamond is surrounded by four others at the corners of a regular tetrahedron. The distance between two adjoining atoms is 1.54 A, which corresponds very closely to the distance between two carbon atoms attached to each other by a single covalent bond, as in aliphatic organic compounds. This agreement, together with the fact that each carbon atom in the diamond has four others situated around it at the corners of a regular tetrahedron, suggests that every atom in the crystal is joined to four others by covalent linkages. A diamond is thus to be regarded as one large carbon molecule, a type of structure for which the term **macromolecule** has been proposed. It is probable that the hardness of diamond is to be attributed to this particular structure.

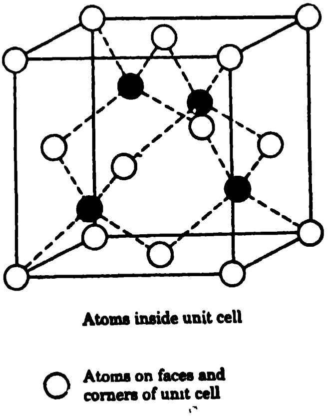


Fig. 19.1. Diamond cubic unit cell

The allotropic form of carbon known as graphite crystallizes in the hexagonal system, and its space lattice is represented in Fig. 19.3. The carbon atoms are seen to be arranged in flat sheets parallel to one another, 3.41 A apart; this distance is too large to correspond to a chemical bond, and so each carbon atom is attached to three others, instead of four as in diamond. In each layer the carbon atoms form flat hexagons, the distance between centers of adjacent atoms being 1.42 A. The arrangement of the atoms in each hexagon corresponds almost exactly to that in the six-membered rings of benzene, naphthalene, etc., and their derivatives.

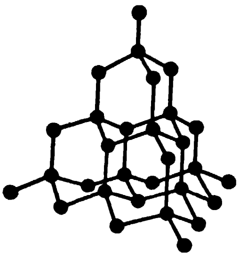


FIG. 19.2. Space lattice of diamond

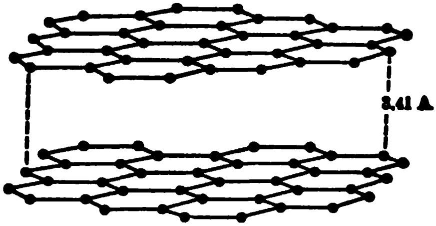


FIG. 19.3. Space lattice of graphite

Crystals consisting of sheets of atoms, not necessarily all in one plane, extending throughout the whole crystal, and separated from one another by a distance too large for chemical bonding, are said to be **layer lattices.** They generally have the property of forming flakes, because cleavage occurs readily between the sheets of atoms. The use of graphite as a lubricant depends upon the ability of one plane of atoms to slide easily over another. Among more complex substances that have layer lattices, and hence form flaky crystals, mention may be made of the minerals mica and talc.

The tendency for every atom to complete its octet, and to exhibit its normal valence in the crystal, results in the other nonmetallic elements of Group IV of the periodic table, viz., silicon, germanium and gray tin, having crystal lattices similar to that of diamond. In Group V, however, the atoms are tervalent, having five electrons in the outermost shell and requiring only three additional electrons to complete their octets; hence, it is found that each atom in the crystal is attached by covalent bonds to three others. This leads to an arrangement of puckered six-membered rings in the rhombohedral crystals of arsenic, antimony and bismuth.

The elements of Group VI have six outer electrons and are bivalent; they thus tend to form chains in which each atom is joined to two others. The crystals of selenium and tellurium are, in fact, made up of a series of such spiral chains held parallel to each other by relatively weak (van der Waals) forces. In rhombic sulfur the inclination to form chains still exists, but instead of being continuous, the ends join to form puckered eight-membered rings. This result, arrived at from X-ray studies of the crystal, is of special interest in view of the fact that the vapor of sulfur just above its boiling point is known to contain S_8 molecules. Plastic sulfur, on the other hand, evidently consists of long chains of atoms.

Iodine is the only halogen atom (Group VII) whose crystal structure has been determined; in the crystal a simple I_2 molecule is situated at each lattice point to form a cubic arrangement. In this case, therefore, the unit of crystal structure is the normal chemical molecule; iodine thus provides an example of a simple **molecular crystal.** Each iodine atom can be attached to only one other iodine atom; since the atoms are univalent, combination in pairs is the sole type of union that is reasonably possible. *The formation of covalent bonds between adjoining atoms in the crystal thus accounts for the transition from macromolecules, through layers and chains (or rings, as in rhombic sulfur), to single diatomic molecules, as the number of electrons in the outermost shell of the atom increases from four in carbon, silicon, etc., to seven in iodine.*

19c. Elements: Metals.—The great majority of metallic elements crystallize in one of three forms, viz., face-centered cubic, close-packed hexagonal, or body-centered cubic lattices. The first two classes are of special interest, as they represent the most efficient packing of spherical units. Suppose a number of spheres are laid close together, as shown by the circles marked ① in Fig. 19.4A and B. It should be understood that the spheres (or circles) are actually in contact, but they are shown separated for purposes of clarity. In the centers of the triangles formed by this first layer of spheres there can be fitted a second layer, shown by the circles marked ②. The addition of a third layer is now possible in two different ways: either the spheres may be placed in the triangles of the second layer so that each sphere of the third layer is directly above one in the first layer (Fig. 19.4A) or they may be placed in the alternative position marked ③, as in Fig. 19.4B. The former type of structure is that of a close-packed hexagonal lattice, while the latter is a face-centered cubic lattice. Since a large proportion of the metallic elements have such crystal lattices, it is apparent that in the solid state most metals consist of approximately spherical atoms packed together as closely as possible. The body-centered cubic lattice structure possessed by some metals, e.g., the alkali metals, is a less compact arrangement; this probably accounts for the unusual softness of the alkali metals. Examples of metallic elements occurring in the three common lattice types are given in Table 19.1.

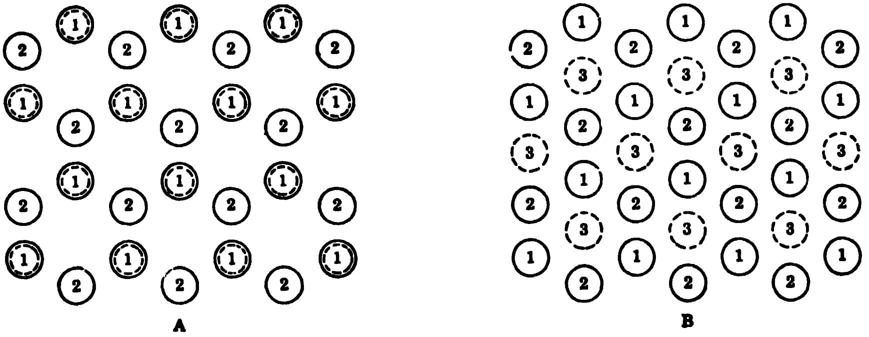


FIG. 19.4. Close packing of spheres: (A) hexagonal, (B) face-centered cubic

TABLE 19.1. LATTICE TYPE OF METALLIC ELEMENTS

Lattice and Type	Elements
Hexagonal close-packed	Be, Mg, Zn, Cd, Ti βCr, αZr, Os, Ru, αCe
Face-centered cubic (Cubic close-packed)	Cu, Ag, Au, Ca, Sr Al, γFe, Ni, Pb, Th
Body-centered cubic	Li, Na, K, Rb, Cs Ba, V, αFe, Mo, Ta

In both the face-centered cubic and close-packed hexagonal lattices, the coordination number is 12, and in the body-centered cubic lattice it is eight. In nonmetallic elements, as seen above, no atom is attached to more than four others; this is the maximum coordination number, observed with elements of Group IV, while for other elements the number is less. It is evident, therefore, that the atoms in a metal cannot be held together by ordinary covalent bonds resulting from the pairings of electrons, since the number of electrons available is quite insufficient for the purpose. It has been suggested, therefore, that the atoms in a metal are held together by a special type of bond, known as a **metallic bond.** It is possible that the metallic atoms lose some of their electrons and so become positive ions; the electrons then form a more or less mobile arrangement which binds the ions together. The high electrical conductance of metals is apparently due to these mobile electrons.

The ductility and malleability of metals are associated with close packing of the atoms. When subjected to stress, a metal distorts along glide planes most densely occupied by atoms. In these planes the atoms are closest and so the cohesive forces are greatest. For a face-centered cubic lattice, these are the (111) planes and for a body-centered cubic lattice the (110) planes. Since there are six possible (111) planes in a cube and only four (110) planes, face-centered cubic metals can yield in more directions and are therefore often less brittle, under comparable conditions, than those having body-centered cubic lattices.

19d. Band Theory of Solids.—The "free electron" theory, which postulates that a solid metal consists of a matrix of positive ions with a number of mobile (or free) electrons capable of moving among them, has been used successfully to explain electrical conductance, heat capacity and other properties of metals. A further development has been the **band theory** which has been extended to include both electrical insulators and semiconductors.

In an isolated atom, the electrons presumably move in a uniform electrical field with its center in the nucleus. The electrons then occupy certain definite energy levels (or orbitals) as explained in Chapter 6, the energy values being the same for all isolated atoms. When the atoms are built up into a solid crystal, however, the electrons are in an electric field that is not uniform, but varies periodically throughout the lattice. As a result, the electronic energy levels are no longer sharply defined, but are replaced by bands of closely spaced levels (or orbitals) which can be occupied by the electrons

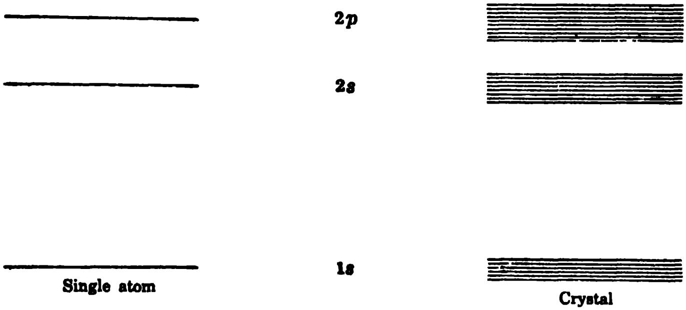


FIG. 19.5. Electronic energy levels in a free single atom and in a crystal lattice atom

(Fig. 19.5). In general, these bands are separated by regions of forbidden energies, although in some cases overlap between bands may occur.

In a metal crystal, the lower bands are filled, that is to say, all the orbitals are occupied, but the uppermost band, called the **conduction band,** is only partly occupied by the "free" electrons (Fig. 19.6A). As seen above, the number of electrons available is insufficient to fill the orbitals required to hold the atoms together by covalent bonds. When an electrical potential (or E.M.F.) is applied to the metal, the electrons in a filled band cannot transfer to other levels, since there are no vacant levels in this band. But those near the top of the partially filled band can transfer into slightly higher unoccupied levels within the same band. They can then move freely from one atom (or ion) to another, so that electrical conduction is possible.

If the electron bands of the solid are completely filled, as in Fig. 19.6B, the substance is an insulator, since there are no unoccupied levels available for the electrons. Such is the case, for example, with many nonmetallic solids, e.g., carbon (diamond), silicon, sulfur, phosphorus, etc., in which each atom has its electron octet completed by forming covalent bonds with all its nearest neighbors. In principle, an insulator could be converted into a conductor if one (or more) of the electrons in the uppermost band could be ex-

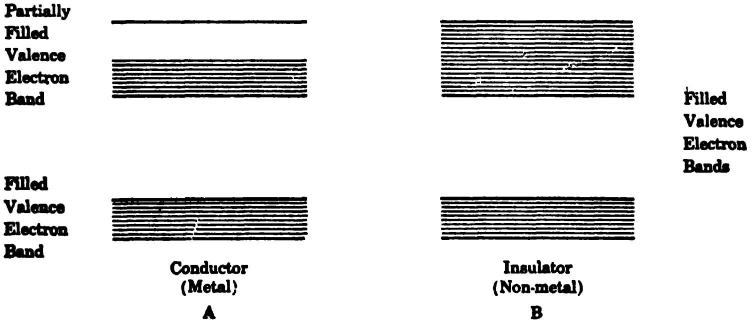


FIG. 19.6. Energy levels in (A) a conductor, (B) an insulator

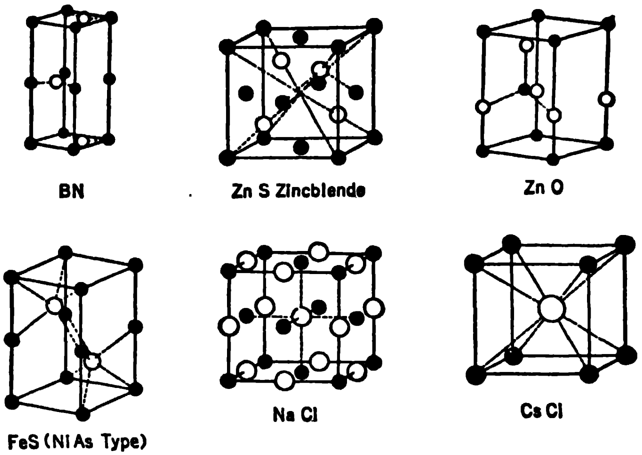
pelled, thus leaving a vacant level in this band. At the same time, the electron is raised to a higher band where many vacant levels are available. As a general rule, a large amount of energy is required to cause this transfer of an electron from one band to another, but in a few instances the energy of a photon of visible light or ultraviolet radiation is adequate. Substances of this kind, e.g., selenium and germanium, are called **photoconductors.**

Photoconductors are actually part of a larger group of substances known as **semiconductors**; these are normally insulators, but can acquire electrical conductance, although much smaller than that of metals, under special circumstances. In recent years, there has been considerable interest in substances for use in transistors, etc., that are conductors due to the presence of traces of impurities. Consider, for example, the element germanium; this is a nonconductor with the same crystal structure as diamond, every atom being bound by covalences to four surrounding atoms. If the germanium is crystallized from a melt containing a small amount of arsenic, a few atoms of the latter will be incorporated into the germanium lattice. Of the five outer (valence) electrons of the arsenic atom, four are required to form covalent bonds with surrounding germanium atoms, but the fifth electron enters an empty "impurity level" where it is free to move and contribute to the electrical conductivity. The material constitutes an *n*-type impurity semiconductor, where *n* refers to the negative (electron) carriers of the current.

If the impurity incorporated into the germanium crystal is a substance with three valence electrons, e.g., gallium, each of these impurity atoms has a vacant electron orbital. An electron from a germanium atom can move into this vacancy, leaving a positive germanium ion. The new vacancy can then be filled with another electron, and so on. The result is equivalent to current being carried by positive ions, so that the substances are called *p*-type impurity semiconductors.

19e. Simple Inorganic Compounds.—A study, by means of X-rays, of the lattice structures of many simple inorganic compounds of the type AX and AX_2 has brought to light some important generalizations. It appears that *the structure of a crystal of a given type of compound*, e.g., AX or AX_2, *is determined essentially by the ratio of the radii of the atoms* (*or ions*), *and also by the tendency of an ionic bond to pass over into a covalent bond* (see § 16d).

Although the majority of alkali halides have face-centered cubic lattices of the sodium chloride (NaCl) type, as in Fig. 18.7, cesium chloride, bromide and iodide crystallize with body-centered cubic lattices. The reason for this will be apparent from the following discussion. Substances of the general formula AX mostly crystallize in one of the six forms shown in Fig. 19.7, each lattice being named according to a familiar compound having that type of structure. Examination of the diagrams shows that the lattice coordination numbers, i.e., the number of equidistant nearest neighbors to any atom or ion, increases from three in boron nitride, to four in zinc sulfide, six in sodium chloride and eight in cesium chloride. The explanation of this variation in behavior of substances having the same general formula lies in the


BN · Zn S Zincblende · Zn O

FeS (NiAs Type) · Na Cl · Cs Cl

Fig. 19.7. Typical AX lattices

The cesium ion is relatively large and so it is possible to pack eight halogen ions around it, thus leading to a body-centered cubic structure, as seen in Fig. 19.7, for cesium chloride, bromide and iodide. With decreasing size of the positive alkali metal ion only six halogen ions can be fitted around it; this leads to the face-centered (NaCl) type of cubic lattice. From geometrical considerations alone it is a simple matter to calculate the ratios of the radii of positive (r_+) to negative (r_-) ions for which various coordination numbers are possible in ionic compounds of the AX type; the results are as follows:

Coordination number	8	6	4
Radius ratio, r_+/r_-	>0.73	0.73-0.41	0.41-0.22

The reason why the ratio r_+/r_- is used as the criterion, rather than the reverse, is because the positive ion is usually smaller than the negative ion, and so it is r_+/r_- which determines the optimum packing in the lattice.

The actual values of the radius ratios for the alkali metal and halogen ions are given in Table 19.2. Although there are certain exceptions it is generally true that when r_+/r_- is greater than 0.73 the CsCl-structure prevails and that when r_+/r_- lies between 0.73 and 0.41 the NaCl-structure is common.

TABLE 19.2. RATIO OF IONIC RADII (r_+/r_-)

	Lithium	Sodium	Potassium	Rubidium	Cesium
Fluoride	0.46	0.70	0.98	1.09	1.24
Chloride	0.35	0.52	0.73	0.81	0.93
Bromide	0.32	0.49	0.68	0.76	0.87
Iodide	0.29	0.44	0.61	0.68	0.78
			NaCl-type		CsCl-type

The occurrence of a coordination number of six among the lithium halides, when four is to be expected from geometrical considerations (r_+/r_- between 0.41 and 0.22), has been explained by the mutual electrostatic repulsion of the negative ions; as a result, there is an effective increase in the size of the lithium ion and in the radius ratio. On the other hand, six-coordination (NaCl-type) exists among the fluorides in particular, of potassium, rubidium and cesium, where eight-coordination (CsCl-type) is theoretically possible. It is probable that deformation of the electron shells, called **polarizability,** of the negative ion in the electric field of the positive ion contributes to the stability of the CsCl-type of lattice. With fluoride ions the polarizability is very small, so that six-coordination is apparently preferred.

When the radius ratio in an AX compound falls below 0.41, a coordination number of four is to be expected. The compound will generally possess either a zinc oxide or a zinc sulfide (zinc blende) type of lattice. In these lattices each ion is surrounded by four others of opposite sign; the zinc blende lattice is, in fact, similar to that of diamond. This type of lattice is favored by substances in which there is a tendency, as in zinc sulfide, for the ionic bond to pass over into a covalent bond. Cuprous bromide, silver iodide, cadmium telluride (CdTe) and the completely covalent silicon carbide (SiC) crystallize in the zinc blende type of lattice.

Similar transitions in lattice type have been observed with changing ionic (or atomic) radii in compounds of formula AX_2; of the eight possible lattice types, three are shown in Fig. 19.8. The coordination number decreases here, too, as the ratio r_+/r_- decreases. For the calcium fluoride (fluorite) lattice-type, this coordination number is eight for A and four for X, for the titanium dioxide (rutile) and cadmium iodide types they are six and three, respectively. It will be noted that the 2 to 1 ratio of the coordination numbers corresponds to the formula AX_2. When the negative ion is small in comparison with the positive ion, the calcium fluoride (fluorite) type of lattice is found, but this passes into the titanium dioxide (rutile) structure with increasing size of the negative ion or decreasing size of the positive ion. According to geometrical considerations, the CaF_2-lattice should occur if r_+/r_- exceeds 0.73, whereas the TiO_2- and CdI_2-lattices require r_+/r_- to lie between 0.73 and 0.41. If, in this latter range, there is a tendency for the formation of covalent bonds, the cadmium iodide type of lattice, which is a layer lattice,

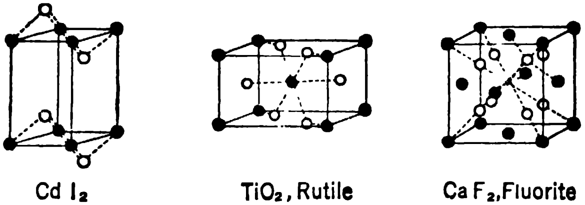


FIG. 19.8. Lattice types of AX_2 compounds

is observed, as in cadmium iodide itself, as well as in the disulfides and diselenides of quadrivalent tin, palladium, titanium, zirconium, etc.

19f. Isomorphism.—The term **isomorphism** (Greek: *same shape*) is used to indicate *the occurrence of different chemical compounds in the same crystalline form;* such substances are said to be **isomorphous** with one another. Isomorphous compounds which have similar chemical properties can usually be represented by similar formulae; however, the reverse of this statement is not necessarily true, for substances with similar formulae and chemical properties are frequently not isomorphous, e.g., sodium and potassium nitrates, and magnesium and strontium carbonates. The explanation of this discrepancy is similar to that given above to account for the change of lattice type in the AX and AX_2 compounds. For example, in passing from the magnesium ion to the strontium ion, the most efficient arrangement of carbonate ions around the central positive ion changes, so that the lattice types and crystal forms are different. It is of interest to record in this connection that calcium carbonate exists in two crystalline forms, one of which, i.e., calcite, is isomorphous with magnesium carbonate, whereas the other, i.e., aragonite, is isomorphous with strontium carbonate. Since the radius of the calcium ion is intermediate between that of the magnesium and strontium ions, both types of packing of the carbonate ions are evidently more or less equally possible.

In order that two salts may be isomorphous, with the same crystal form and approximately equal interfacial angles and axial ratios, four conditions must be satisfied. First, *the two substances must have the same formula type,* although it is not necessary that they should be chemically similar; thus $KMnO_4$ and $BaSO_4$; $KClO_4$ and KBF_4; $NaNO_3$ and $CaCO_3$; and K_2SO_4, K_2BeO_4 and $K_2P(O_3F)$ are isomorphous groups of compounds having the same formula type, but with entirely different chemical properties. Second, *the ionic groups must have the same stereochemical form.* Sodium chlorate ($NaClO_3$), for example, is not isomorphous with $NaNO_3$ or $CaCO_3$; the primary reason is that the ClO_3^- ion has a pyramidal structure while the NO_3^- and CO_3^{-2} ions are flat, as shown by X-ray studies. The third condition for isomorphism is that *the relative sizes of the structural units, atoms or ions, should be approximately equal,* so as to ensure the same type of packing in each case. It should be noted that the actual sizes of the units are not important; it is the relative size which determines the most efficient packing. Fourth, *the ionic and covalent characteristics of the bonds should be similar in the two molecules;* as in the case of the simple AX and AX_2 compounds, the tendency for an ionic bond to pass over into a covalent bond may result in a change of lattice type.

If a mixture containing two isomorphous salts is allowed to crystallize, the solid that separates out is homogeneous in nature, but it contains both substances, the proportions depending on the composition of the solution. Homogeneous solids of this kind, containing two, or more, isomorphous compounds are sometimes called **mixed crystals** or, better, **mix-crystals.** Since the solid is quite homogeneous, it is similar to a solution, and so the term **solid**

solution is frequently employed; this avoids the implication that it is a mere mixture of two or more substances. *The formation of a solid solution upon crystallization is a characteristic property of isomorphous substances. Another criterion of isomorphism is the ability of a crystal of one compound to continue to grow when placed in a saturated solution of another;* this phenomenon is known as the formation of **overgrowths.** The second substance is deposited on the crystal of the first, without change of form.

In some cases where the formation of solid solutions and overgrowths is to be expected, because of isomorphism, these do not actually occur; in other instances solid solutions are formed over a limited range of compositions only. From X-ray diffraction studies of substances having the same crystalline form, it has been concluded that solid solutions and overgrowths can occur only if the dimensions of the unit cells in the crystal lattices do not differ by more than about 10 per cent. If this is exceeded, the entry of one substance into the space lattice of the other, which is what occurs in the formation of solid solutions, would cause so much distortion as to make the crystal unstable.

19g. Organic Compounds.—The crystals of organic compounds have been shown by X-ray analysis to consist of molecular lattices (§ 19b); that is to say, the structural unit in these compounds is the molecule itself. The various atoms are joined by covalent bonds, and it is the arrangement of the complete molecules in a regular pattern that determines the interior structure of the crystals. In aliphatic compounds the carbon atom is found to be tetrahedral in character, as in the diamond; the distance between the centers of two such atoms joined by a single bond is 1.54 A. For double-bonded atoms the corresponding distance is 1.32 A.

In aromatic compounds, such as benzene and its derivatives, the C—C distance in the ring is always 1.40 ± 0.01 A. The benzene ring is itself found to be a regular hexagon with all the adjacent interatomic distances equal. All the carbon-carbon linkages in benzene thus partake of both single bonded and double bonded character. As stated in § 16h this is one of the arguments in favor of the resonance type of electronic structure for the benzene molecule.

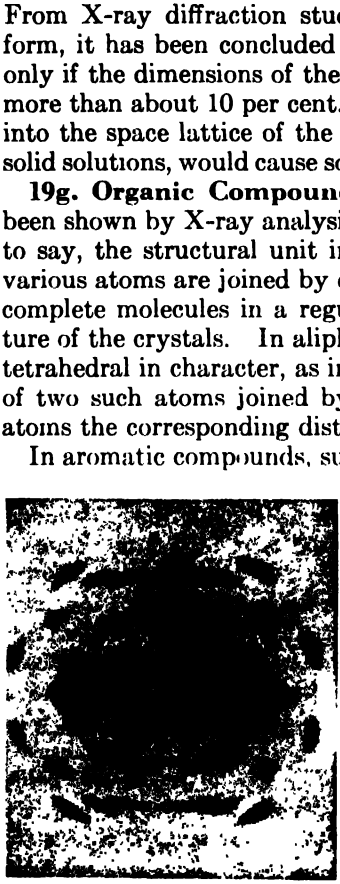


FIG. 19.9. X-ray diffraction pattern of ramie fiber

Although fibrous substances, such as cellulose, silk, wool and hair are not strictly crystalline in nature, they give characteristic X-ray patterns (Fig. 19.9), which are somewhat similar to rotation photographs (see Fig. 18.8). From these patterns it has been shown that natural fibers consist mainly of numbers of long, thin pseudo-crystals, or **crystallites,** arranged with their long axes approximately parallel to the length of the fiber. It is this particular arrangement of the crystallites, which are themselves made up of long molecular chains, which is responsible for the essential properties of a fibrous material. Stretched rubber gives a fiber-like X-ray diffraction pattern, indicating a partial orientation of long hydrocarbon chains. In the unstretched form, however, the chains are apparently distributed in a random manner, for the X-ray pattern consists of diffuse rings like those obtained with a liquid.

19h. The Structure of Liquids and Glasses.—A form of the X-ray method has been used to throw light on the problem of the internal structure of liquids. It appears, in many cases, that provided the temperature is not too far from the melting point, the distances between atoms in the liquid are not greatly different from those in the solid, e.g., for water, 2.90 A between oxygen atoms in the liquid and 2.76 A in the solid; for aluminum, 2.96 A in the liquid and 2.86 A in the solid. Further, the average number of nearest neighbors to any given atom is usually approximately the same as in the solid. This similarity between liquid and solid, especially near the melting point, is not unexpected. As a general rule, the atoms (or molecules) in the solid are packed as efficiently as possible, and since the density of the liquid is not very different from that of the solid, the packing in the former must be similar to that in the latter. However, the resemblance between liquid and solid becomes less marked as the distance from a given atom increases beyond its immediate neighbors. It appears, therefore, that there is some sort of regularity of structure, i.e., "order," in a liquid, but it is of the "short range" variety, extending for a short distance only from any given atom or other unit. A solid possesses both long range and short range order, for the regularity of structure extends throughout the whole crystal; the long range order in a liquid is, however, negligible. Even the short range order in the liquid is not as regular as in the solid, for the order may be regarded as being somewhat "blurred" in the liquid; this is probably due to the larger available volume and hence greater freedom of movement in the liquid state. As the temperature is raised this blurring increases; the distance between nearest neighbors increases, and the number of these neighbors decreases, so that eventually there is a virtually random arrangement of molecules in the liquid, just as in a gas.

When certain liquids are cooled fairly rapidly there is no formation of crystals at a definite temperature, such as occurs on slow cooling. The viscosity of the liquid increases steadily, and eventually a "glass" is obtained. This property of forming glasses is possessed particularly by silica and boron trioxide, and by their mixtures with oxides of the alkali or alkaline-earth metals. It has been shown by means of X-ray diffraction studies that the unit of structure in silica glass, i.e., vitreous silica, is the same as in the crystalline form. Each silicon atom is surrounded by four oxygen atoms, and each of the latter is shared between two silicon atoms, giving the resultant formula $(SiO_2)_n$. In the crystal these units are built up in a completely regular manner, whereas in the glass their arrangement is almost random. The short range order in the glass is virtually perfect, but there is no definite long range order. A glass is thus intermediate in structure between a liquid, as described above, and a solid. Glasses owe their stability to a number of factors; among these may be mentioned their high viscosity which prevents rearrangement of the atoms into the completely regular structure of the crystalline form.

HEAT CAPACITIES OF SOLIDS

20a. Atomic Heat Capacity.—According to the familiar law of Dulong and Petit, the product of the specific heat and atomic weight, i.e., the atomic heat capacity, of solid elements has the almost constant value of 6.2 cal per deg per gram atom at ordinary temperatures. The specific heat of a solid is generally measured at constant (atmospheric) pressure, but, as with gases (§ 31), this includes an allowance for the work done in expansion when the temperature is raised. It would appear, therefore, that atomic heat capacities should be compared at constant volume, rather than at constant pressure. Such a comparison was made by G. N. Lewis (1907), who found that, with the exception of the alkali metals, the atomic heats of seventeen solid elements are close to 5.9 cal per deg per gram atom, as may be seen from Table 20.1. The deviations from constancy are appreciably less than for the atomic heat capacities at constant pressure.

TABLE 20.1. ATOMIC HEATS AT CONSTANT VOLUME AT 25°C IN CAL DEG^{-1} G-ATOM

Al	5.7	Au	5.9	Pt	5.9
Sb	5.9	Fe	5.9	Ag	5.8
Bi	6.2	Pb	5.9	Tl	6.1
Cd	5.9	Ni	5.9	Sn	6.1
Cu	5 6	Pd	5.9	Zn	5.6

The earliest explanation of the constant heat capacity of solid elements was based on the principle of the equipartition of energy (§ 3m). A monatomic solid element, such as a metal, could be regarded as consisting of a space lattice of independent atomic, or ionic, units vibrating about their respective equilibrium positions. Since there will be no preferred direction of vibration, the actual atomic vibrations may be regarded as taking place in three independent directions. As already seen, each mode of vibration makes a contribution of R to the molar heat capacity at constant volume; hence, the three types of vibration in the monatomic solid will give a molar (or atomic) heat capacity of $3R$, i.e., 5.96 cal deg^{-1} g-$atom^{-1}$, in general agreement with experiment.

According to this simple argument the atomic heat capacity of a solid element should be independent of the temperature. However, all heat capacities increase with temperature, the effect being most marked with the light elements, such as beryllium, carbon and boron, whose atomic heats are exceptionally low at ordinary temperatures. Even the heat capacities of those elements which are usually about 6 cal diminish at low temperatures, and so it is partly a matter of chance that they behave in an apparently normal manner. An important advance in the calculation of atomic heat capacities was made by A. Einstein (1907) by application of the quantum theory. In Einstein's treatment it was supposed that all the atoms vibrate with the same frequency, but with different amplitudes, that is, with different amounts (quanta) of vibrational energy. At very low temperatures the great majority of the atoms will have small or zero energy, and the contribution to the heat capacity will be small. As the temperature is raised, the vibrational energy of the atoms increases, and the heat capacity should increase toward the classical value of $3R$.

20b. Debye Theory of Atomic Heat Capacities of Solids.—Although the Einstein theory of the specific heat of elementary solids represented an improvement on the older theory, it predicted a falling off of the atomic heat with temperature that was greater than the observed rate. By introducing the postulate that the vibration frequencies of the atoms are not constant, but vary throughout the solid from zero to a certain maximum value which depends on the nature of the solid, P. Debye (1912) was able to derive an equation for the dependence of atomic heat capacity at constant volume upon the temperature. The essential conclusion drawn from the Debye equation, which is somewhat complicated, is that the heat capacity of an element at any temperature is a definite function of a quantity θ, called the **characteristic temperature,** defined by

$$\frac{h\nu_m}{k}, \tag{20.1}$$

where h is the Planck constant (§ 15b), k is the Boltzmann constant (§ 3d), and ν_m is the maximum vibration frequency of the atoms in the given solid. That this is the case is apparent from Fig. 20.1, in which the atomic heat

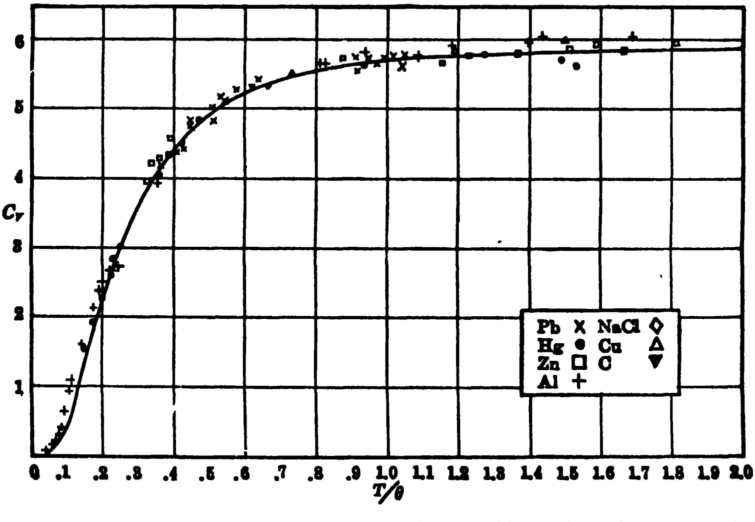


FIG. 20.1. The heat capacity of various solids as functions of T/θ

capacities of various solids, over a range of temperatures, are plotted against the ratio T/θ, where T is the absolute temperature.

If the characteristic temperature θ is small, as it is for all the heavier elements, the heat capacity C_V should rise rapidly, at first, with increasing temperature, and then more slowly toward the limiting (classical) value of $3R$. This is seen to be true for lead, in particular, in Fig. 20.2, which shows the variation of the atomic heat capacity with temperature. On the other hand, if θ is large, as it evidently is for carbon, boron and beryllium, the heat capacity increases slowly, but should attain the same limit of $3R$, as the temperature is raised. By ascribing an appropriate characteristic temperature to each element, it is possible to reproduce closely the actual variation of the heat capacity with temperature, over a considerable range, by means of the Debye equation. At very high temperatures the heat capacities of many metals, especially the alkali metals, exceed $3R$; this is attributed to the absorption of energy by the electrons of these elements, thus increasing the internal energy and heat capacity above that to be expected from the atomic vibrations alone.

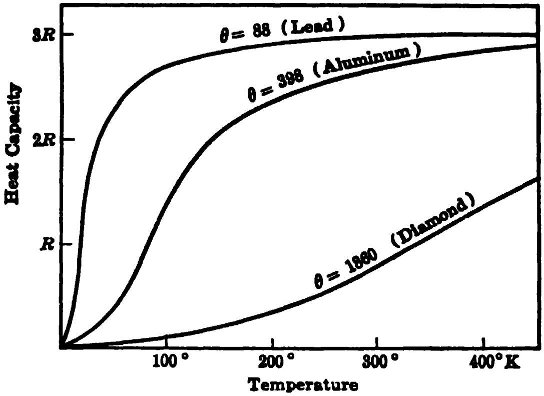


FIG. 20.2. Variation of atomic heat of elements with temperature

An examination of Fig. 20.2 reveals the fortuitous nature of the Dulong and Petit law; it is because most solid elements have values of θ less than 400 that the atomic heat capacity has almost reached its limit of $3R$, i.e., 5.96 cal deg^{-1} g-atom^{-1}, at ordinary temperatures, viz., about 300°K. If it had happened that the characteristic temperatures of most elements had been more than 400, the ordinary form of the Dulong and Petit law would not have held. However, an equivalent law would have been obeyed at higher temperatures when the heat capacities reached their (approximate) limiting values.

For small values of the temperature the Debye equation for the atomic heat capacity reduces to the simple form

$$C_V = 464.5\left(\frac{T}{\theta}\right)^3 \text{ cal deg}^{-1}\text{ g-atom}^{-1}, \qquad (20.2)$$

which has been found to hold, within experimental error, at temperatures below about 25°K. Since the characteristic temperature θ is a constant for each substance, it follows from this result that at low temperatures the atomic heat capacity of a solid should be directly proportional to T^3, that is, to the cube of the absolute temperature. Further, as the temperature approaches the absolute zero, the heat capacity should tend toward zero. Both these expectations have been verified by experiment.

Strictly speaking, the Debye treatment of the specific heats of solids was meant to apply to elements crystallizing in the cubic system. Nevertheless, it has been found to hold for a number of metals belonging to the hexagonal system, and also for some alkali halides. By introducing an empirical correction, G. N. Lewis and G. E. Gibson (1917) showed that the Debye equation could be used to represent the variation with temperature of the heat capacities of a number of nonmetallic elements and even of certain compounds.

SOLID-LIQUID-VAPOR EQUILIBRIA

21a. The Melting Point.—*When a pure crystalline solid is heated it changes sharply into a liquid at a certain temperature*; this is the **melting point** of the solid, which has a definite value depending on the external pressure. If the liquid is cooled solidification will occur at the same temperature, which is the **freezing point**, for the given pressure; hence, for a pure substance the melting and freezing points are identical. The melting or freezing points that are usually quoted in tables are those for a pressure of one atmosphere, that is, 76 cm of mercury.

The variation of the melting point with pressure is represented by an expression analogous to the Clapeyron-Clausius equation (§ 11d); as applied to the phenomenon of melting or **fusion**, as it is frequently called, the equation is written in the inverted form, thus

$$\frac{dT}{dP} = \frac{T(V_l - V_s)}{L_f}, \tag{21.1}^*$$

where the fraction dT/dP represents the rate of variation with the external pressure P of the melting point T on the absolute scale. The quantities V_l and V_s are the molar volumes of liquid and solid, respectively; L_f is the **molar heat of fusion,** that is, the (latent) heat taken up by 1 mole of the solid when it melts. Instead of using the molar volumes and molar heat of fusion, equation (21.1) may be written in the alternative form

$$\frac{dT}{dP} = \frac{T(v_l - v_s)}{l_f}, \tag{21.2}$$

where v_l and v_s are the specific volumes and l_f is the heat of fusion per gram. It is important to note that, since the specific volumes of solid and liquid at

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* A capital P is used here to represent the external pressure, whereas in § 11d the lower case p was employed for vapor pressure; see also, equations (21.4) and (21.5), below.

the melting point are not very different, it is not permissible to neglect one in comparison with the other. The simplification (§ 11e) that was possible with equation (11.3), as applied to vaporization, cannot therefore be made here.

Example: The specific volumes of liquid water and of ice are 1.0001 and 1.0907 cc per gram, respectively, at the normal freezing point, 0°C; the heat of fusion is 79.8 cal per gram. Calculate the change in melting point of ice for an increase of 1 atm in the external pressure.

Since v_l is 1.0001 and v_s is 1.0907, it follows that $v_l - v_s$ is -0.0906 cc g^{-1}; the value of l_f is 79.8 cal g^{-1}, i.e., $79.8 \times 4.184 \times 10^7$ ergs g^{-1}. If these results were inserted in equation (21.2) it would give the change of melting point for an increase of 1 cgs unit, i.e., 1 dyne cm^{-2}, in the pressure. Since the change is required for an increase of 1 atm, i.e., $76.0 \times 13.595 \times 980.7 = 1.013 \times 10^6$ dynes cm^{-2}, it is necessary to multiply by the latter figure. Thus, since the freezing point of water is 0°C, the value of T is 273.2°K, and hence,

$$\frac{dT}{dP} = \frac{273.2 \times (-0.0906) \times 1.013 \times 10^6}{79.8 \times 4.184 \times 10^7} = -0.0075^\circ \text{ per atm.}$$

The negative sign implies that an increase of 1 atm in the pressure, in the vicinity of 0°C, *lowers* the melting point of ice by 0.0075°.

Increase of pressure results in a small decrease in the melting point of ice; the reason why there is a decrease, rather than an increase, is because $v_l - v_s$ in equation (21.2) is negative, that is, because the specific volume of the solid (ice) is greater than that of the liquid (water) at the freezing point. In other words, the melting point decreases with increasing pressure because the density of the solid is less than that of the liquid. Water is one of the few substances exhibiting this unusual behavior of expansion on freezing. *For most substances the solid has a larger density than the liquid, and hence increase of pressure brings about an increase in the melting point.* Because the densities, and hence the specific volumes, of the solid and liquid are never very different at the melting point, $v_l - v_s$ is always small numerically; the effect of pressure on the melting point is consequently also small.

In addition to water, the elements bismuth and antimony expand when they solidify; it is this property which makes the latter an important constituent of "type metal." For both of these elements the melting point decreases as the external pressure is increased, as is to be expected.

21b. Vapor Pressures of Solids: Sublimation.—A solid, like a liquid, has a definite vapor pressure at each temperature; with increasing temperature the vapor pressure increases, and the variation can be represented by a curve similar to that for a liquid (see Fig. 11.2). Such a curve is called a **sublimation curve,** the term **sublimation** being used to indicate direct conversion of solid to vapor without the intervention of liquid. Similarly, under suitable conditions, a vapor may be condensed directly to a solid; this occurs, in general, upon cooling the vapor provided its pressure is less than the vapor pressure of the solid at its melting point. For example, the vapor pressure of ice at 0°C is about 4.6 mm of mercury, and if the partial pressure of water vapor is less than this value, sudden cooling will result in the direct deposition of solid from the vapor. It is in this manner that the formation of frost occurs in nature. If the partial pressure of the water vapor exceeds 4.6 mm, then liquid will first be formed when the temperature is lowered.

The purification of such substances as iodine, sulfur, naphthalene and benzoic acid by sublimation is rendered feasible by the fact that the vapor pressures of these solids have quite high values. If a cold surface is placed in the vapor, the partial pressure of the latter at the surface is maintained below that at the melting point, and condensation occurs directly from the vapor to the solid. Further, because of the high vapor pressure, the rate at which the solid sublimes is sufficiently great to make the sublimation process a practical one.

A particularly interesting case of sublimation is that of carbon dioxide. At the melting point (−56.5°C) the equilibrium vapor pressure of the solid is 5 atm; this means that solid carbon dioxide cannot be converted into liquid unless the pressure exceeds this value. At ordinary atmospheric pressures, therefore, solid carbon dioxide passes directly into gas, at all temperatures, without the intermediate formation of liquid. It is this fact which represents one of the advantages of "dry ice" as a refrigerant, and accounts for the use of the adjective "dry."

The change from solid to vapor, like that from liquid to vapor, or from solid to liquid, is accompanied by an absorption of heat; this is the (latent) **heat of sublimation,** L_s. It is related to the heats of vaporization (L_v) and of fusion (L_f) in the following manner

$$L_s = L_f + L_v, \tag{21.3}$$

where the three values must refer to the same temperature. In other words, the same quantity of heat (L_s) must be supplied to convert 1 mole of solid directly to vapor as would be required first to melt the solid (L_f) and then to vaporize it (L_v) at a given temperature and pressure. This result is in accord with the law of conservation of energy (§ 6b).

The influence of temperature on the vapor pressure of a solid is given by a form of the Clapeyron-Clausius equation which is exactly equivalent to (11.3); thus, the rate of variation of the vapor pressure with temperature, i.e., dp/dT, at the temperature T is expressed by

$$\frac{dp}{dT} = \frac{L_s}{T(V_v - V_s)} = \frac{l_s}{T(v_v - v_s)}, \tag{21.4}$$

where V_v and V_s are the molar volumes, and v_v and v_s are the specific volumes, of vapor and solid, respectively, at the temperature T; l_s is the heat of sublimation per gram. As in § 11c, it is permissible here to neglect V_s in comparison with V_v, since the density of the vapor is very much less than that of the solid; hence, equation (21.4) may be converted into a form analogous to equation (11.7), viz.,

$$d \ln p = \frac{L_s}{RT^2} \qquad (21.5)$$

This expression may be integrated in the manner already described. The chief use of equations (21.4), (21.5), and those obtained by integration, is that they permit the value of the heat of sublimation of the solid to be calculated at any temperature from a knowledge of the sublimation vapor pressures in the vicinity of that temperature.

21c. The Triple Point.—The sublimation curve for the solid form of a substance and the vapor pressure curve for the liquid may be combined in one diagram, as represented in Fig. 21.1. In this figure *OA* indicates the variation of the vapor pressure of the liquid with temperature, while *OB*, the sublimation curve, shows the change in the vapor pressure of the solid form. As seen in § 11a, *OA* extends only as far as the critical temperature; on the other hand, *OB* can continue down to the absolute zero, although it may change in direction if there is a change in the crystalline form of the solid. The vapor pressure curve *OA* indicates the conditions, as given by the temperature and pressure, for a system of liquid and vapor to be in equilibrium (see § 11a). Similarly, the sublimation curve *OB* gives the conditions under which the solid and vapor are in equilibrium with one another. The two curves meet at *O*, and hence at this point, known as the **triple point,** the three physical states of the substance, viz., solid, liquid and vapor, must be able to coexist. The term triple point is used, in general, for *the temperature and pressure at which any three states (phases) of a given substance are in equilibrium.*

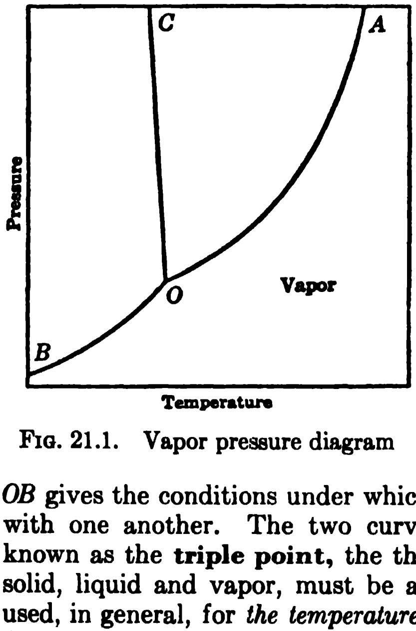

FIG. 21.1. Vapor pressure diagram

The conditions of equilibrium of solid and liquid, which is simply another way of referring to the variation of the melting point with pressure, are represented by the third curve, viz., *OC*, in Fig. 21.1. This must obviously pass through the triple point *O*, where solid, liquid and vapor are in equilibrium. The direction of the slope of the line *OC* depends on whether increase of pressure raises or lowers the melting point. In Fig. 21.1 the curve slopes to the left, implying that the melting point is lowered by an increase of pressure, e.g., water, bismuth or antimony. For other substances, e.g., sulfur, to be considered in Chapter 11, the curve slopes to the right. In any case, because of the small variation of the melting point with pressure, the line *OC* is always almost vertical; its slope has been exaggerated in Fig. 21.1 for the sake of clarity.

Since solid and liquid are in equilibrium at the triple point, this is obviously a melting point. It is not, however, the normal melting point of the solid at 1 atm pressure, but *the melting point at the pressure of the vapor which is in equilibrium with the solid and liquid.* For example, the normal freezing point of water at 1 atm pressure is 0°C, and hence the triple point must be somewhere in this vicinity; the vapor pressure of water, or of ice, is then about 4.6 mm. The triple point of water is thus the melting point of ice, or the freezing point of water, at a pressure of 4.6 mm, rather than at 760 mm, i.e., 1 atm; the pressure is thus 755.4 mm *less* than atmospheric. It was seen above that increase of pressure by 1 atm lowers the melting point of ice by 0.0075°; hence, a decrease of 755.4 mm, which is very nearly 1 atm, must raise the melting point by 0.0075°. The triple point of water, at which solid, liquid and vapor are in equilibrium, should thus be 0.0075° *above* the melting point of pure ice at atmospheric pressure. This result has been confirmed by experiment, the equilibrium vapor pressure being then 4.58 mm of mercury.*

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* The temperature 0.0000°C, defined as the freezing point of water, *saturated with air*, at 1 atm pressure, is 0.0100°C below the triple point. The additional difference of 0.0025°C is due to the effect of the dissolved air in lowering the freezing point (Chapter 8). Since saturation is not easy to maintain at all times, the triple point is used in calibrating instruments for measuring temperatures with the highest precision, since it is independent of external conditions. For ordinary work, the ice point is sufficiently reproducible.

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PROBLEMS

1. (*a*) Show that the volume occupied by equal-sized spheres arranged in a close packed structure is 0.74 the volume of the unit cell. (*b*) What is the corresponding volume for a body-centered cubic structure?

2. The characteristic K_α lines of Cr, Fe and Ni have wave lengths of 2.2909, 1.9373 and 1.6591 A, respectively. (*a*) Which of these can be used to determine a lattice spacing of 1 A? (*b*) What will be the largest value of θ obtained?

3. The X-ray spectrum of a cubic metal using radiation of $\lambda = 1.5418$ A gave lines at the following values of θ:

21.8 25.4 37.2 45.4 47.8 58.8 68.6 72.7°.

(*a*) Index the lines, i.e., determine the *hkl* values of the planes producing the lines. (*b*) Calculate the unit cell edge length. (*c*) Identify the type of unit cell and the element. The density of the metal was 8.93 g ml^{-1}.

4. Aluminum crystallizes in the cubic system with $a = 4.050$ A and density 2.70 g cm^{-3}. (*a*) Determine the unit cell type. (*b*) Calculate the radius of the aluminum atom.

5. At room temperature sodium has a body-centered cubic structure with a cell edge length of 4.2906 A; at -195°C the density is only 4% larger but the cell edge now measures 5.350 A. What type of cubic unit cell does sodium have at -195°?

6. Cesium bromide has the same structure as cesium chloride. Its density is 4.49 g cm^{-3}. Calculate the length of the unit cell edge.

7. Titanium has a hexagonal close-packed structure containing 2 atoms in the unit cell; $a = b = c = 2.953$ A, $d = 4.729$ A. Calculate its density.

8. The 222 planes of cubic tantalum give a reflection at 54.12° with radiation of $\lambda = 1.5418$ A (Cu K_α). (*a*) At what angle would these planes give a reflection with the Mo K_α line $\lambda = 0.7107$ A? (*b*) Determine *a*. (*c*) Determine the spacing of the 100, 110 and 111 planes.

9. White tin crystallizes in the tetragonal system with $a = 5.820$ A and $c = 3.175$ A; its density is 7.29 g cm^{-3}. Determine the numbers of atoms in the unit cell.

10. Silver iodide has the same structure as zinc sulfide; its density is 5.67 g cm^{-3}. Calculate the length of the unit cell edge.

11. The heat of transition of rhombic to monoclinic sulfur at the transition temperature 95.5°C is 88 cal g-atom^{-1}. An increase in pressure of 26.4 atm raises the transition point by 1.00°C. (*a*) Calculate the volume change when 3.2 g of rhombic sulfur changes to the monoclinic form. (*b*) Which form has the larger density?

12. The melting point of mercury is -38.9°C at 1 atm pressure and increases 0.0051°C per atm increase in pressure. The densities of solid and liquid mercury are 14.19 and 13.70 g cm^{-3} respectively. (*a*) Determine the heat of fusion per g-atom. (*b*) Calculate the pressure necessary to raise the melting point to 0°C.

13. The melting point and volume changes on melting of nitrogen vary with pressure as follows:

°K	63.1	82.3	98.6	113.0	137.8
p kg cm^{-2}	1	1000	2000	3000	5000
Δv cm^{3}g^{-1}	—	0.058	0.047	0.040	0.029

Determine the heat of fusion per gram at 4000 kg cm^{-2}.

14. Ordinary white tin is converted into a powdery modification called gray tin at temperatures below 18°C. The respective densities are 6.55 g cm^{-3} (white) and 5.75 g cm^{-3} (gray) and the heat of transition is 0.60 kcal g-atom^{-1}. What will be the transition temperature at a pressure of 100 atm?

15. The vapor pressure of crystalline zirconium chloride follows the equation $\log p\ (\text{mm}) = \frac{-5400}{T} + 11.766$. Calculate (*a*) the heat of sublimation and (*b*) the v.p. at the melting point 437°C.

16. The vapor pressure of solid selenium is given by $\log p\ (\text{mm}) = \frac{-7440}{T} + 12.78$ and of liquid selenium by $\log p\ (\text{mm}) = \frac{-5390}{T} + 8.63$. (*a*) Determine the triple point temperature of selenium. (*b*) What is the vapor pressure at the triple point?

(*c*) What is the melting point? (*d*) Evaluate the heat of fusion per g-atom at the melting point.

17. NH_4Br undergoes a phase transition between two solid forms at 138°C and 1 atm pressure and at 155° at 200 atm. The volume changes are 6.47×10^{-2} and 6.56×10^{-2} cm^3 g^{-1} respectively. Calculate the transition temperature at 100 atm.

18. The vapor pressure of solid violet (red) phosphorus varies with temperature as follows:

t°C	578	581	587.5	588	589.5
p atm	34.35	36.49	41.77	42.10	43.1

Determine the molar heat of sublimation at the triple point 589.5°C. The vapor of phosphorus has the formula P_4.

8

Dilute Solutions

LOWERING OF VAPOR PRESSURE

22a. Raoult's Law.—A solution, which can be gaseous, liquid or solid, may be described as a homogeneous mixture of two or more substances, consisting of a single phase. A solution composed of two substances is called binary, of three substances ternary, and so on. The treatment in the present chapter will refer particularly to liquid binary solutions containing a dissolved solid. It will be seen in Chapter 11 that there is no fundamental difference between the components of a solution, but for certain purposes it is convenient to distinguish between them. The component which constitutes the larger proportion of the solution is called the **solvent,** while the other is referred to as the **solute.** If the concentration of solute, i.e., the amount in a given volume of solution, is small the solution is said to be dilute; the treatment in this and subsequent sections will deal essentially with such solutions.

It has been known for many years that when a nonvolatile solute is dissolved in a liquid the vapor pressure of the latter is lowered. The quantitative connection between the lowering of the vapor pressure and the composition of the solution was discovered by F. M. Raoult (1887) as the result of a large number of experiments with a variety of solutions. If p^0 is the vapor pressure of the pure solvent at a particular temperature, and p is the vapor pressure of the solution at the same temperature, the difference $p^0 - p$ is the lowering of the vapor pressure; if this is divided by p^0 the result, that is $(p^0 - p)/p^0$, is known as the **relative lowering of the vapor pressure** for the given solution. According to one form of **Raoult's law,** *the relative lowering of the vapor pressure is equal to the mole fraction of the solute in the solution.* If n_1 and n_2 are the numbers of moles of solvent and solute,[*] respectively, then in accordance with the definition of mole fraction given in § 2h, the mole fraction x_2 of the solute is

$$x_2 = \frac{n_2}{n_1 + n_2}, \tag{22.1}$$

and hence, by Raoult's law,

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[*] It is a widely used convention for dilute solutions to indicate the solvent by the subscript 1 and the solute by 2.

$$\frac{p^0 - p}{p^0} = x_2 = \frac{n_2}{n_1 + n_2}. \qquad (22.2)$$

The results in Table 22.1, taken from the work of Raoult, show that the law is obeyed, at least approximately, for a number of solutes in ether solution; if the law were exact, the ratio in the last column would have been unity in each case. It is probable that Raoult's law holds only for solutions having a heat of dilution of zero, and for which there is no volume change upon mixing the components in the liquid state. Such solutions, which should obey Raoult's law exactly at all concentrations and all temperatures, are called **ideal solutions.** Actually very few solutions behave ideally (§ 39a) and some deviation from Raoult's law is always to be anticipated; however, for dilute solutions these deviations are small and can usually be ignored.

TABLE 22.1. TEST OF RAOULT'S LAW IN ETHER SOLUTION

Solute	Mole Fraction of Solute	Relative Lowering of Vapor Pressure	Ratio
Nitrobenzene	0.060	0.055	0.92
Methyl salicylate	0.092	0.086	0.93
Ethyl benzoate	0.096	0.091	0.95
Benzaldehyde	0.130	0.132	1.02
Aniline	0.077	0.081	1.05

An alternative form of Raoult's law, which will be used later, is obtained by subtracting unity from both sides of equation (22.2); the result is

$$\frac{p}{p^0} \quad 1 - x_2. \qquad (22.3)$$

The sum of the mole fractions of solvent and solute must always equal unity; hence, if x_1 is the mole fraction of the solvent, and x_2 is that of the single solute, it follows that for a binary solution

$$x_1 + x_2 = 1, \qquad (22.4)$$

and hence equation (22.3) can be reduced to

$$p = x_1 p^0. \qquad (22.5)$$

In words, therefore, *the vapor pressure of the solvent in a solution is directly proportional to the mole fraction of the solvent,* if Raoult's law is obeyed. It will be observed that the proportionality constant is p^0, the vapor pressure of the pure solvent.

22b. Determination of Molecular Weights.—It is possible, by means of Raoult's law, to determine the molecular weight of a dissolved substance. If the solution consists of w_1 grams of solvent of molecular weight M_1, and w_2 grams of nonvolatile solute of molecular weight M_2, the respective numbers of moles are given by

$$n_1 = \frac{w_1}{M_1} \quad \text{and} \quad n_2 = \frac{w_2}{M_2},$$

and, consequently, from equation (22.2),

$$\frac{p^0 - p}{p^0} = \frac{w_2/M_2}{(w_1/M_1) + (w_2/M_2)}. \tag{22.6}$$

For dilute solutions, the small number of moles n_2 of the solute may be neglected in comparison with that of the solvent, i.e., n_1; under these conditions equation (22.2) becomes

$$\frac{p^0 - p}{p^0} \approx \frac{n_2}{n_1} = \frac{w_2}{M_2} \cdot \frac{M_1}{w_1}. \tag{22.7}$$

By making up a solution containing known weights of solvent (w_1) and of solute (w_2), it is possible to determine the molecular weight M_2 of the latter, if the vapor pressure of the solvent (p^0) and solution (p) can be measured. The molecular weight M_1 of the solvent is assumed to be known.

Example: When 18.04 g of the sugar alcohol mannitol were dissolved in 100 g of water, the vapor pressure of the latter at 20°C was lowered from 17.535 mm to 17.226 mm of mercury. Calculate the molecular weight of mannitol.

In this case, w_1 is 100 g and M_1, the molecular weight of water, is 18.02; w_2 is 18.04 g. The values of p^0 and p are 17.535 and 17.226 mm, respectively. The *relative lowering* of the vapor pressure is obviously independent of the units used for the vapor pressures, provided p^0 and p are expressed in the same units. Hence, by equation (22.6),

$$\frac{17.535 - 17.226}{17.535} = \frac{18.04/M_2}{(100/18.02) + (18.04/M_2)},$$

$$M_2 = 181.$$

Although the solution is not particularly dilute, the use of the approximate equation (22.7) gives $M_2 = 184$. The correct value is 182.

22c. Measurement of Vapor Pressure Lowering.—Since the actual lowering of vapor pressure is small, the obvious procedure, of measuring the vapor pressure of the solvent and the solution separately by the methods described in § 11c and subtracting the two values, is not often used. The vapor pressure of the solvent is determined in the usual manner, and then the lowering $p^0 - p$ is measured directly by some type of differential manometer in which one arm is connected to the solution and the other to the pure solvent. By using a nonvolatile liquid of low density as the manometer indicator, the difference in vapor pressures can be determined quite accurately.

The gas saturation (or transpiration) method (§ 11c) has been adapted for the determination of the relative lowering of vapor pressure. The same volume of dry gas, e.g., air, is passed through saturators containing the solvent and solution, respectively, with a suitable absorber in between. From the losses in weight of the saturators, the relative lowering can be calculated, without actually evaluating the separate vapor pressures of solvent and solution.

Another procedure, known as the **isopiestic method,** has attracted attention in recent years. If two vessels containing solutions of different solutes in the same solvent are placed side by side in a closed space at constant temperature, vapor will pass from the solution of higher to that of lower vapor pressure until both solutions have the same vapor pressure. The two solutions are then said to be **isopiestic** (Greek: *equal pressure*), and they are analyzed to determine their concentrations. If one of the solutes is a substance, e.g., potassium chloride, for which the vapor pressures of its solutions at various concentrations are known, the vapor pressure of the isopiestic solution of the other solute, at the measured concentration, is immediately available.

ELEVATION OF THE BOILING POINT

23a. Vapor Pressure and Boiling Point.—A direct consequence of the reduction of the vapor pressure by a *nonvolatile* solute is that the boiling point of the solution, i.e., the temperature at which its vapor pressure becomes equal to 1 atm, must be higher than for the pure solvent. This can be readily seen from the curves in Fig. 23.1, which represent the variation of vapor pressure with temperature of pure solvent and a solution; the latter is, of course, always below the former. The boiling point of the solvent is T_0 and that of the solution is T; the boiling point is thus raised by the amount $T - T_0 = \Delta T$. This quantity is known as the **boiling point elevation,** and it is represented by the distance AB in the diagram. The point A gives the vapor pressure p^0 of the solvent, i.e., 1 atm, while C is that of the solution, both at the temperature T_0; hence, the distance AC is equivalent to $p^0 - p$. Since p^0 is a constant quantity, namely 1 atm, it follows that AC is proportional to the relative lowering of vapor pressure, i.e., $(p^0 - p)/p^0$.

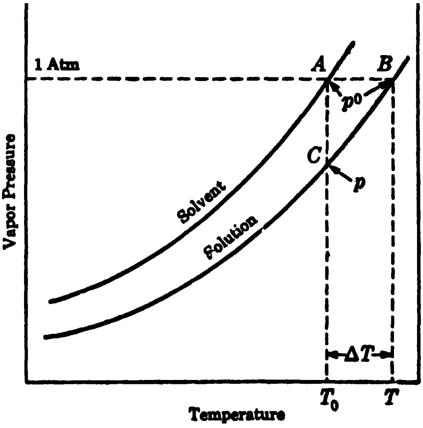

Fig. 23.1. Rise of boiling point of solution

If the vapor pressure curves for a series of solutions are almost parallel in the region of the boiling point, as is probably true for dilute solutions, the ratio of the distances AB to AC will be constant for these solutions. In other words, the boiling point elevation AB will be proportional to the relative lowering of the vapor pressure AC. Further, since the relative lowering is equal to x_2, the mole fraction of the solute, by Raoult's law, it follows that

$$\Delta T = k_b x_2, \tag{23.1}$$

where k_b is the proportionality constant, equal to AB/AC.

The result of equation (23.1) may be derived in a more precise manner which gives the value of the constant k_b in terms of properties of the solvent. In the integrated form of the Clapeyron-Clausius relationship, namely, equation (11.13), T_1 and T_2 may be replaced by T_0 and T, the boiling points of the solvent and of the solution, respectively. It will be seen from Fig. 23.1 that the vapor pressure of the solution at these two temperatures are p and p^0, respectively; hence equation (11.13) becomes

$$\ln \frac{p}{p^0} = -\frac{L_v}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) = -\frac{L_v}{R}\left(\frac{T - T_0}{T_0 T}\right), \tag{23.2}$$

where L_v is the molar heat of vaporization. The temperature difference $T - T_0$ is the rise of boiling point ΔT, and since, for a dilute solution, T and T_0 are not very different, $T_0 T$ may be replaced by T_0^2; further, according to Raoult's law equation (22.3), $p/p^0 = 1 - x_2$. Making these three substitutions, equation (23.2) gives

$$\ln (1 - x_2) = -\frac{L_v}{R} \cdot \frac{\Delta T}{T_0^2}.$$

The term $\ln (1 - x_2)$ may be replaced by the equivalent power series, $-x_2 - \frac{1}{2}x_2^2 - \frac{1}{3}x_2^3 \cdots$; since x_2 is small for a dilute solution, $\ln (1 - x_2)$ $-x_2$, so that

$$x_2 = \frac{L_v}{R} \cdot \frac{\Delta T}{T_0^2}$$

or

$$\Delta T = \frac{RT_0^2}{L_v} x_2, \tag{23.3}$$

which is identical in form with equation (23.1), since R, T_0 and L_v are constants.

The most important application of these equations is for the determination of molecular weights of dissolved substances, and for this purpose an alternative form is more useful. Since the solutions are dilute, the mole fraction x_2 may be replaced by n_2/n_1, that is, by w_2M_1/M_2w_1, as in equation (22.7); hence, (23.3) becomes

$$\Delta T = \frac{RT_0^2}{L_v} \cdot \frac{w_2 M_1}{M_2 w_1}$$

$$\frac{RT_0^2}{l_v} \quad \frac{w_2}{M_2 w_1}, \tag{23.4}$$

where l_v, equal to L_v/M_1, is the heat of vaporization *per gram* of solvent.

In the study of dilute solutions, it has been found convenient to express the concentration of a solution in terms of its **molality**;* this is *the number of moles of solute dissolved in 1000 grams of solvent.* In the solution under consideration w_2/M_2 moles of solute are dissolved in w_1 grams of solvent, and so the molality m is given by

$$m = \frac{w_2}{M_2 w_1} \times 1000. \tag{23.5}$$

Substitution of this result into equation (23.4) leads to

$$\begin{aligned} \Delta T &= \frac{RT_0^2}{1000 l_v} m \\ &= K_b m, \end{aligned} \tag{23.6}$$

where K_b is a constant for each solvent, defined by

$$K_b = \frac{RT_0^2}{1000 l_v} \tag{23.7}$$

and depending only on its boiling point and heat of vaporization. According to equation (23.6), therefore, *the elevation of the boiling point of a solution is proportional to its molality*, provided it is dilute and obeys Raoult's law. This theoretical deduction has been confirmed experimentally for a number of solvents and solutes. Strict proportionality between the molality and boiling point elevation holds only in extremely dilute solutions, but there is an approximate proportionality even in solutions of moderate concentration. Such deviations as are observed are due partly to the solutions not being dilute enough for the approximations made in the derivation of equation (23.6) to be justifiable, and partly because of deviations from Raoult's law due to nonideal behavior.

The constant K_b is called the **molal elevation constant**; it can be seen from equation (23.6) that it is physically equivalent to the rise of boiling point for a solution of unit molality, i.e., $m = 1$. Actually, a solution with a molality of unity would not be sufficiently dilute for equation (23.6) to be valid, and so K_b may be regarded as the boiling point elevation for a unit molal solution, if the value were proportional to that for a dilute solution.

23b. Molecular Weight from Boiling Point Elevation.—Since the molality of a solution is related to the molecular weight M_2 of the solute, according to equation (23.5), measurements of the boiling point elevation can be used to determine molecular weights of dissolved substances. For this purpose, combination of equation (23.5) with (23.6) gives

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* The term "molality" should not be confused with "molarity"; the latter is the number of moles of solute *per liter of solution.* For dilute *aqueous* solutions the molality and molarity are approximately equal.

$$\Delta T = K_b \frac{1000w_2}{M_2 w_1},$$

$$M_2 = K_b \frac{1000w_2}{\Delta T w_1}. \tag{23.8}$$

In order to apply this result it is necessary to know the value of K_b; this may be obtained in two ways. First, from the boiling point and heat of vaporization of the solvent, by means of equation (23.7), and second, by measuring the boiling point elevation ΔT experimentally for a solution containing a solute of known molecular weight M_2 and applying equation (23.8). The results obtained by the two methods are generally in excellent agreement, provided the solutions are dilute, thus supplying confirmation of the theoretical arguments presented above.

Example: Calculate the experimental molal elevation constant of water from the fact that a solution containing 0.450 g of urea (molecular weight 60.06) in 22.5 g of water gave a boiling point elevation of 0.170°C. Compare the result with the value derived from the heat of vaporization of 539.9 cal g^{-1} at the boiling point.

To obtain K_b from the experimental data, equation (23.8) is written in the form

$$K_b = \Delta T \frac{M_2 w_1}{1000w_2} = 0.170 \times \frac{60.06 \times 22.5}{1000 \times 0.450}$$

$$= 0.510.$$

To obtain K_b from the heat of vaporization, use is made of equation (23.7), where l_v is 539.9 cal g^{-1}. The energy units for R must be the same as those for l_v; hence R is 1.987 cal deg^{-1} $mole^{-1}$. The boiling point of water is 100.0°C, and hence T_0 is $273.2 + 100.0 = 373.2$°K; consequently

$$K_b = \frac{1.987 \times (373.2)^2}{1000 \times 539.9} = 0.513.$$

The boiling points and molal elevation constants for a number of common solvents are quoted in Table 23.1, and these may be used for the determination of the molecular weights of a variety of solutes by means of equation (23.8). The principle of the method used is to take a definite weight w_2 of solute, whose molecular weight is to be found, and to dissolve it in a known weight w_1 of solvent; the elevation ΔT of the boiling point is then measured. Since the molal elevation constant is known, the molecular weight M_2 of the solute can be calculated.

TABLE 23.1. BOILING POINTS AND MOLAL ELEVATION CONSTANTS

Solvent	B.Pt.°C	K_b	Solvent	B.Pt.°C	K_b
Water	100.0	0.513	Benzene	80.1	2.63
Methanol	64.7	0.83	Acetic acid	118.1	3.14
Ethanol	75.4	1.20	Chloroform	61.2	3.85
Acetone	56.2	1.72	Carbon tetrachloride	78.8	5.02

23c. Determination of Boiling Point Elevation.—When observing the boiling point of a solution it is necessary that the thermometer be placed in the liquid, and not in the vapor; as a result there is a possibility of serious error due to superheating. Various devices have been described from time to time whose purpose is to overcome this difficulty. A convenient method for obtaining accurate values of the rise of boiling point is that of F. G. Cottrell (1919). A simple form of the apparatus is shown in Fig. 23.2. The thermometer *E* is placed above the surface of the boiling liquid (solvent or solution) in *A*, and bubbles formed at the thick platinum wire *B* force a stream of liquid and vapor to flow through the pump *F* over the thermometer bulb. The latter is thus covered with a thin layer of boiling solution in equilibrium with its vapor; the temperature recorded should then be the true boiling point. The side tube *C* leads to a condenser and the sheath *D* prevents the cold condensate from reaching the thermometer.

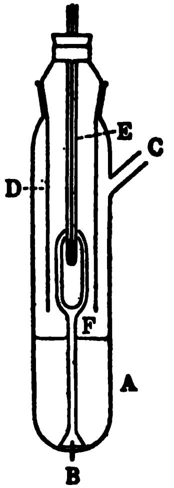

FIG. 23.2. Elevation of boiling point (Cottrell)

In precision work the boiling points of solvent and solution should be determined simultaneously, so as to avoid the error due to possible changes in the atmospheric pressure; the boiling points of many liquids change by 0.01°C for a pressure change of only 0.3 mm of mercury. Since it is only the elevation of the boiling point that is required, and not the actual boiling points themselves, differential methods have been used to measure the difference in temperature between the solvent and solution boiling side by side.

DEPRESSION OF THE FREEZING POINT

24a. Vapor Pressure and Freezing Point.—Another consequence of the lowering of the vapor pressure of the solvent in a solution is that the freezing point of the solution is lower than that of the pure solvent. It has been long known that a dissolved substance depresses the freezing point of water, and the familiar use of common salt to melt snow is based on this fact. The relationship between the freezing point of the pure solvent and that of a solution may be seen with the aid of the vapor pressure curves in Fig. 24.1; these curves show the temperature variation of the vapor pressure of the solvent over the pure solvent (e.g., water), the solution, and the solid solvent (e.g., ice), respectively. Comparison with Fig. 21.1 shows that *A* is the freezing point of the solvent, temperature T_0; similarly, *B*, temperature *T*, is the freezing point of the solution, where the latter is in equilibrium with solid. The freezing point of the solution is obviously lower than that of the solvent, and the **freezing point depression** ΔT is equal to $T_0 - T$. The distance *AC* is equivalent to $p^0 - p$ at the freezing point of the solvent, and since p^0 at this temperature is a constant, it follows, as in § 23a, that *AC* is proportional to the relative lowering of the vapor pressure $(p^0 - p)/p^0$. If, as before, the vapor pressure curves for a number of dilute solutions are almost parallel straight lines in the vicinity of the freezing point, the ratio AC/BC will be constant. For such solutions, therefore, the depression of the freezing point ΔT will be proportional to the relative vapor pressure lowering, and hence to the mole fraction x_2 of the solute. It follows then, as for the boiling point elevation, that

$$\Delta T = k_f x_2. \tag{24.1}$$

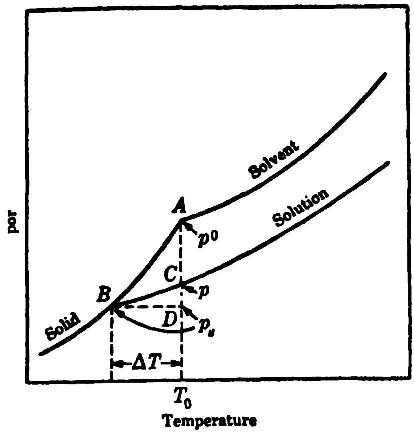

FIG. 24.1. Lowering of freezing point of solution

The more complete derivation of this expression is again based on the Clapeyron-Clausius equation. It is seen from Fig. 24.1 that for the solution, p is the vapor pressure at T_0 and p_s is the value at T; hence, equation (11.3) becomes

$$\ln \frac{p_s}{p} = -\frac{L_v}{R}\left(\frac{T - T_0}{T_0 T}\right). \tag{24.2}$$

For the solid, the vapor pressures are p^0 and p_s at the temperatures T_0 and T, respectively; in this case, equation (21.5) for the vapor pressure of a solid is applicable and the result of integration is

$$\ln \frac{p_s}{p_0} = -\frac{L_s}{R}\left(\frac{T - T_0}{T_0 T}\right), \tag{24.3}$$

where L_s is the molar heat of sublimation. Upon subtracting equation (24.2) from (24.3), replacing $T_0 - T$ by ΔT, the lowering of freezing point, and $T_0 T$ by T_0^2, since T_0 and T are not very different for a dilute solution, and utilizing the fact that the molar heat of fusion $L_f = L_s - L_v$, by equation (21.3), the result is

$$\ln \frac{p}{p^0} = -\frac{L_f}{RT_0^2}\Delta T. \tag{24.4}$$

By the Raoult's law equation (22.3), $\ln (p/p^0) = \ln (1 - x_2)$, and for a dilute solution, $\ln (1 - x_2) \approx -x_2$. Hence upon substituting $-x_2$ for $\ln (p/p^0)$ in equation (24.4) and rearranging, it follows that

$$\Delta T = \frac{RT_0^2}{L_f} x_2. \tag{24.5}$$

This equation is seen to be equivalent to (24.1) and exactly analogous to equation (23.3), except that the molar heat of fusion now replaces the heat of vaporization. By using arguments exactly similar to those employed previously, it is found that for dilute solutions

$$\Delta T = K_f m, \tag{24.6}$$

where the **molal depression constant** K_f is defined by

$$K_f = \frac{RT_0^2}{1000 l_f}, \tag{24.7}$$

l_f being the heat of fusion per gram, and T_0 is the freezing point of the solvent. *The depression of the freezing point is thus proportional to the molality of the solution;* as before, the essential condition is that the solution should be dilute. Experimental determinations of freezing point depressions are in general agreement with this conclusion; with relatively concentrated solutions deviations from equation (24.6) are observed, as is to be expected.

24b. Molecular Weight from Freezing Point Depression.—The molal depression constant must first be determined, and this is obtained either by calculation, from equation (24.7), or by direct measurement of the freezing point depression with a solute of known molecular weight. The results obtained by the two methods are in excellent agreement. The values of the freezing points and the molal depression constants for some familiar solvents are given in Table 24.1. If the depression constant is known, the molecular weight of the dissolved substance can then be derived from the expression

TABLE 24.1. FREEZING POINTS AND MOLAL DEPRESSION CONSTANTS

Solvent	F.Pt.°C	K_f	Solvent	F.Pt.°C	K_f
Water	0.00	1.86	Naphthalene	80.2	7.0
Acetic acid	16.6	3.90	Bromoform	8.3	14.3
Benzene	5.5	5.12	Cyclohexane	6.5	20.2
Nitrobenzene	5.7	6.90	Camphor	179.5	40.0

$$M_2 = K_f \frac{1000 w_2}{\Delta T w_1}, \tag{24.8}$$

which is exactly analogous to equation (23.8).

Example: For a solution of 0.911 gram of carbon tetrachloride dissolved in 50.00 g of benzene, the freezing point depression was found to be 0.603°C. Calculate the molecular weight of the carbon tetrachloride.

According to equation (24.8), using $K_f = 5.12$ from Table 24.1,

$$M_2 = \frac{5.12 \times 1000 \times 0.911}{0.603 \times 50.00} = 155.$$

Attention should be called to the fact that the foregoing treatment will hold only if the solid which separates on freezing the solution is pure solvent, e.g., pure ice from an aqueous solution. Sometimes a solid solution (§ 19f), i.e., a homogeneous solid containing both solute and solvent, will separate; in this event, the equations given above are no longer applicable.

24c. Determination of Freezing Point Depression.—For general purposes, freezing point determinations may be made by placing the solvent in a tube surrounded by an air jacket and a suitable freezing bath. The tube containing the solvent is fitted with a stirrer and a thermometer graduated in hundredths of a degree. By gradually lowering the temperature of the liquid, and stirring at the same time to avoid supercooling, the freezing point, at which the temperature remains stationary, can be observed. A known weight of solute is then dissolved in a definite quantity of solvent, and the freezing point is determined. The difference in the two readings gives the lowering of the freezing point for the solution of known composition. This is the principle used by E. Beckmann (1888) in the first accurate measurements of freezing point depressions.

The method just described has a number of inherent difficulties which have been overcome in what is called the **equilibrium method.** If water is the solvent, the solution is very thoroughly stirred with cracked ice in a vacuum-jacketed vessel until equilibrium is attained. The temperature, which is the true freezing point of the solution, is then recorded; some of the liquid is removed by means of a pipet and analyzed so as to determine its composition. The same procedure, without the necessity for analysis, is carried out with pure water in order to give the freezing point of the solvent. The difference is the required depression of the freezing point. For precision measurements, two similar vessels are used, one containing the solvent (water) and the other the solution, together with crushed ice; when equilibrium is reached the difference in temperature of the two vessels is measured. This gives the freezing point depression directly. Results of a very high order of accuracy have been obtained in this manner.

It will be noted from Table 24.1 that camphor has an exceptionally high molal depression constant; this fact is utilized in a simple, although approximate, method for determining molecular weights of organic compounds that are soluble in camphor. An intimate mixture of the solute with about ten times its weight of camphor is made, and its melting point is determined in a small tube, in the manner commonly used in the organic chemical laboratory. The depression of the freezing point from that of pure camphor, measured in the same manner, is of the order of 10° or more, and so may be read with sufficient accuracy on a thermometer graduated in degrees.

OSMOSIS AND OSMOTIC PRESSURE

25a. Semipermeable Membranes.—An important property of solutions, related to those already considered in this chapter, is that of **osmosis** (Greek: *push*); this term is used to describe *the spontaneous flow of solvent into a solution, or from a more dilute to a more concentrated solution, when the two liquids are separated from each other by a suitable membrane.* Osmosis strictly refers to the flow of *solvent only;* if there is a movement of solute, in the opposite direction, the behavior is then called diffusion. The essential property of a membrane which permits osmosis to occur is that it allows free passage of the solvent, e.g., water, but not of the dissolved substance, e.g., sugar. Membranes possessing this property are said to be **semipermeable.**

The phenomenon of osmosis may be illustrated in a simple manner by tying an animal membrane, e.g., bladder, over the end of an inverted thistle tube (Fig. 25.1), which is then partly filled with a concentrated solution of sucrose (cane sugar) and dipped into a beaker of water, as shown in the figure. The level of the liquid will rise in the tube until the hydrostatic pressure so produced is sufficient to stop the flow of water. It is seen, therefore, that as a result of osmosis a pressure is developed which opposes the tendency for the solvent to pass through the semipermeable membrane into the solution. This pressure is called the **osmotic pressure** of the solution; it is best defined as *the excess pressure which must be applied to a solution to prevent the passage into it of solvent when the two liquids are separated by a perfectly semipermeable membrane.* There has been some tendency to think of osmotic pressure as a pressure produced by the solution, but this point of view is misleading. The osmotic pressure is brought into existence *only* when the solution is separated from the solvent by a semipermeable membrane. The resulting osmosis, or tendency for osmosis to occur, then produces an excess pressure in the solution. When this excess pressure attains the value of the osmotic pressure, the tendency for solvent to enter the solution is exactly counterbalanced by the reverse tendency, and a condition of equilibrium results.

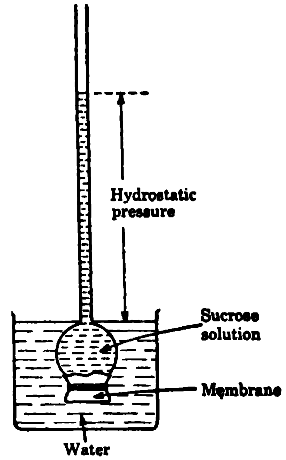

FIG. 25.1. Osmosis through animal membrane

The arrangement shown in Fig. 25.1 is not satisfactory for making quantitative measurements of osmotic pressure. In the first place, the entry of solvent into the solution dilutes the latter, so that its concentration is indefinite. This problem can be largely overcome by measuring the hydrostatic pressure in a capillary tube or better, by using a sealed manometer. A more serious problem arises from the fact that the animal membrane is not completely semipermeable. The sugar from inside the thistle tube thus tends to diffuse out into the water, and as a result the level of the liquid in the tube falls slowly.

For the accurate measurement of osmotic pressure it is necessary to have a membrane that is as near as possible to being perfectly semipermeable. In 1864, M. Traube suggested the use of artificial membranes made of copper ferrocyanide, $Cu_2Fe(CN)_6$, and this is still regarded as the best material for the purpose. Many improvements have since been made in the method of supporting the membrane but no better substance has yet been found for aqueous solutions.

25b. Osmotic Pressure and Its Measurement.—Following upon Traube's discovery of the semipermeable property of a copper ferrocyanide membrane, quantitative measurements of osmosis were made by W. F. P. Pfeffer (1877). He produced the membrane by allowing copper sulfate solution to diffuse from one side and potassium ferrocyanide solution from the other side of the walls of a porous pot. The two solutes meeting in the wall interacted to form a precipitate of copper ferrocyanide which filled the pores. Improvements in the deposition of the semipermeable membrane were made by H. N. Morse and J. C. W. Frazer and their collaborators (1901-23), who used an electric current to drive the copper and ferrocyanide ions into the walls of the porous vessel. Membranes made in this manner were capable of withstanding pressures up to 270 atm without leakage.

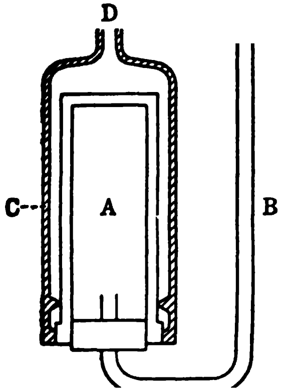

FIG. 25.2. Measurement of osmotic pressure (Frazer)

The method used by Frazer to measure osmotic pressures may be illustrated by reference to Fig. 25.2. The cell A, in the walls of which the semipermeable membrane has been deposited, and the tube B are filled with water. The cell is surrounded by solution contained in the bronze cylinder C. The solvent tends to pass from A into C and the resulting hydrostatic pressure in the vessel C, equal to the osmotic pressure, is measured by a manometer attached to D.

Another accurate procedure for osmotic pressure measurement is that employed by the Earl of Berkeley and E. G. J. Hartley (1906-09). The solvent is placed in the horizontal cell A (Fig. 25.3), which has been impregnated

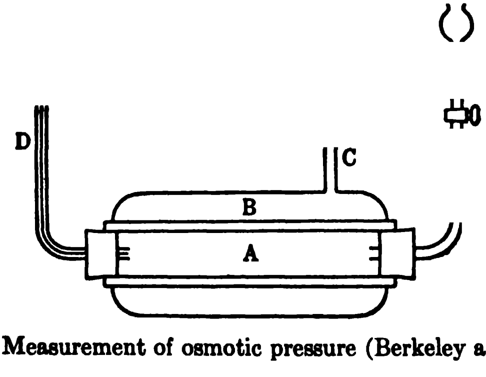

FIG. 25.3. Measurement of osmotic pressure (Berkeley and Hartley)

with copper ferrocyanide, and this is placed within the vessel B containing the solution. A gradually increasing pressure is applied to the solution, through C, by means of a pump. The pressure which just prevents the flow of solvent from *A* into *B*, as indicated by the liquid level in the manometer *D*, is the osmotic pressure of the solution.

25c. Comparison of Osmotic Pressures: Isotonic Solutions.—Plant and animal cells usually contain solutions of salts, sugars, etc., enclosed in membranes that are largely, although not completely, semipermeable in character. In a normal, healthy plant cell water has entered through the membrane and has set up an excess pressure in the interior; this causes the cell material to be pressed against the walls, producing the phenomenon known as "turgidity." If such a cell is placed in water or in a solution of osmotic pressure less than that of the solution in the cell, there will be a tendency for water to enter, but owing to the rigidity of the outer cellulose walls little change is observed. On the other hand, if the cell is immersed in a solution having a higher osmotic pressure, water will pass out from the interior of the cell through the membrane. The material of the cell will thus shrink and will detach itself from the walls; this effect is referred to as **plasmolysis.**

By taking a number of solutions of a given substance at different concentrations and observing the change in the plant cells, it is possible to find the solution which just fails to bring about plasmolysis. *This solution has then the same osmotic pressure as the cell solution*, and is said to be **isotonic** (Greek: *same tension*) with it.* Working in the same manner with a variety of solutes, and a given type of cell, it is possible to prepare a series of isotonic solutions of different substances; such solutions have approximately the same osmotic pressure. If the osmotic pressure of one of these solutions is known by direct measurement, the value gives the approximate osmotic pressure of all the other solutions. The results are not exact, however, because the cell membranes are not perfectly semipermeable.

25d. Results of Osmotic Pressure Measurements.—Although Pfeffer made measurements on solutions of sucrose, dextrose, potassium nitrate and other substances, his results with sucrose have become of historical importance. Some of the data on the influence of concentration on osmotic pressure are recorded in Table 25.1; they were obtained at a temperature of about 15°C. The approximate constancy of the ratio of the osmotic pressure to the concentration, i.e., Π/c, as shown by the figures in the last column, indicates that at constant temperature the osmotic pressure of a solution is almost directly proportional to its concentration.

TABLE 25.1. OSMOTIC PRESSURES OF SUCROSE SOLUTIONS

Concentration (c)	Osmotic Pressure (Π)	Ratio (Π/c)
1 per cent	535 mm Hg	535
2	1016	508
4	2082	521
6	3075	513

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* Isotonic solutions are also isopiestic (§ 22c), for they have the same vapor pressure (cf. § 25e).

The effect of temperature is demonstrated by the results in Table 25.2, which Pfeffer obtained with a 1 per cent sucrose solution. It is evident that

TABLE 25.2. INFLUENCE OF TEMPERATURE ON OSMOTIC PRESSURE

Temperature (T)	Osmotic Pressure (Π)	Ratio (I
280.0°K	505 mm Hg	1.80
286.9°	525	1.83
295.2°	548	1.85
305.2°	544	1.79
309.2°	567	1.83

the osmotic pressure increases with temperature, and the approximate constancy of the ratio of the osmotic pressure to the absolute temperature i.e., Π/T, shows the close proportionality between these quantities.

It was shown by J. H. van't Hoff (1887) that Pfeffer's measurements o osmotic pressure indicated a parallelism between the properties of solution and of gases. If c is the concentration of a solution, expressed in moles pe unit volume of solution, and V is the volume of the solution, in the same units containing 1 mole, then c is equal to $1/V$. As seen above, the osmotic pressur divided by the concentration is constant at a given temperature; even thoug the concentration units in Table 25.1 are not the same as defined here, th values are roughly proportional. Hence, it is possible to write

$$\frac{\Pi}{c} = \text{constant},$$

where Π is the osmotic pressure, and replacing c by $1/V$, it follows that

$$\Pi V = \text{constant}, \tag{25.1}$$

at constant temperature. This result is seen to be the analogue of Boyle' law, with the osmotic pressure of the solution substituted for the pressure o the gas.

Further, the proportionality between osmotic pressure and the absolut temperature, at a given concentration (Table 25.2), shows that a law equivalent to Gay-Lussac's law for gases applies to solutions; thus,

$$\frac{\Pi}{T} = \text{constant}, \tag{25.2}$$

for a solution of a definite concentration. Combination of equations (25.1) and (25.2), as is the case with gases, leads to the result

$$\Pi V = RT, \tag{25.3}$$

where R is a constant. By inserting actual values of the osmotic pressur for a solution of known concentration at a definite temperature, the interesting fact has emerged that the constant R in equation (25.3) is almost identica with the familiar gas constant. The equation (25.3), frequently referred t as the **van't Hoff equation** for dilute solutions, is thus seen to be exactly analogous to the ideal gas equation.

For convenience in evaluating R from osmotic pressure data, equation (25.3) may be written as

$$\Pi = RTc, \tag{25.4}$$

since the concentration c is equal to $1/V$. According to Pfeffer's results in Table 25.2, a solution of 1 gram of sucrose in 100 grams of water gave an osmotic pressure of 505 mm of mercury at 280.0°K. Suppose R is to be expressed in liter-atm per degree per mole, the dimensions generally used in osmotic pressure calculations, Π must be in atm, and c in moles per liter. The volume of the solution containing 1 gram of sucrose was 100.6 ml, and since the molecular weight of sucrose is 342, it follows that

$$c = \frac{1.00}{342} \times \frac{1000}{100.6} = 0.0291 \text{ mole per liter.}$$

The osmotic pressure Π is 505/760 atm, and the absolute temperature is 280°K; hence, from equation (25.4),

$$R = \frac{\Pi}{Tc} = \frac{505}{760} \times \frac{1}{280 \times 0.0291} = 0.0816 \text{ liter-atm deg}^{-1} \text{ mole}^{-1}.$$

This may be compared with the value of 0.0820 in the same units for the ideal gas constant.

The constant R in equations (25.3) and (25.4) may thus be taken as being equal to the gas constant, and these equations may consequently be used for the purpose of calculating approximate osmotic pressures. Alternatively, if the osmotic pressure is known the molar concentration of the solution can be evaluated. This result can be utilized to determine the molecular weight of the solute, provided the weight concentration is known.

The measurement of osmotic pressure is actually used to obtain the molecular weights of complex molecules, such as proteins, carbohydrates and various polymers (§ 56a). Because of the large molecular weights and low solubility of such substances, the mole fraction of solute in the solution is inevitably very small. Consequently, vapor pressure, boiling point and freezing points changes are too small to be measurable with any degree of accuracy. The osmotic pressures are, however, large enough to be measured with good precision, especially if the hydrostatic pressure is determined with a liquid (solvent) of low density.

Example: A solution containing 4.0 g of a polyvinyl chloride polymer in 1 liter of dioxane was found to have an osmotic pressure of 6.4×10^{-4} atm at 27°C. Calculate the approximate molecular weight of the polymer.

The concentration of the solution is $4.0/M$ mole liter^{-1}, where M is the required molecular weight; since the osmotic pressure is given in atm, R is expressed in liter-atm deg^{-1} mole^{-1}, i.e., 0.082, and hence, by equation (25.4),

$$6.4 \times 10^{-4} = 0.082 \times 300 \times 4.0/M$$

$$M = 1.5 \times 10^{5}.$$

The more accurate measurements of osmotic pressure made in recent years have shown that the van't Hoff equation (25.3) or (25.4) is applicable only in very dilute solution. As the concentration increases the deviations become more and more marked, the observed osmotic pressures being greater than the calculated values. Better agreement with experiment is obtained by using the modified equation proposed by H. N. Morse (1905) in which V, the volume of the solution, in equation (25.3), is replaced by V', *the volume of the solvent* associated with 1 mole of solute; thus,

$$\Pi V' = RT. \tag{25.5}$$

In dilute solutions, the difference between the volumes of solvent (V') and of solution (V) is negligible, and so equation (25.3) may be used. However, as the concentration is increased, V' becomes increasingly less than V, and hence the osmotic pressures calculated from equation (25.5) become increasingly greater than those given by (25.3), in agreement with the experimental results.

To some extent the deviations from equation (25.3) exhibited by solutions, with increasing concentration, are comparable with the deviations from ideal behavior shown by real gases as the pressure is increased (§ 4a), but the situations are not quite similar. It will be shown in § 25f that even if a solution behaved ideally, it would not be expected to obey the van't Hoff equation except at very high dilutions. At appreciable concentrations deviations are to be anticipated for ideal, as well as nonideal, solutions. This fact is very important, for it calls attention to the danger of carrying too far the apparent analogy between gases and solutions.

25e. Mechanism of the Semipermeable Membrane and of Osmotic Pressure.—It can be shown theoretically that the magnitude of the osmotic pressure developed when a solution and solvent are separated by a semipermeable membrane should be independent of the actual nature of the membrane. Differences have sometimes been observed with different membranes, but this is due to the fact that certain membranes are not completely semipermeable. Such membranes, which allow the passage of solute molecules, even to a small extent, will give low values for the osmotic pressure. These are, however, not true osmotic pressures, for the latter are developed only if the membrane is perfectly semipermeable.

Numerous attempts have been made to explain the property of semipermeability possessed by certain materials, but the problem cannot yet be regarded as solved. Some indication of the action of semipermeable membranes may be obtained from the following experiment, using an apparatus similar to that shown in Fig. 25.1. The animal membrane is first thoroughly soaked in water, and then the thistle tube is filled with a mixture of ether and benzene. If the thistle tube is now immersed in a beaker containing moist ether, the level of the liquid in the tube will be seen to rise, just as in the experiment described in § 25a to illustrate osmosis. The animal membrane saturated with water behaves just like a semipermeable membrane, permitting the passage of ether molecules through it from the outside, while not allowing benzene molecules to pass in the opposite direction. The explanation of this result is to be found in the solubility of ether in the water with which the membrane is saturated; ether molecules can thus move through the membrane with ease. On the other hand, benzene is insoluble in water and its passage is consequently prevented.

It appears from this and similar experiments that semipermeability, in connection with osmosis, might be explained by supposing the solvent to be soluble in the membrane whereas the solute is insoluble. It is not easy to see exactly what is meant by "soluble" and "insoluble" in a semipermeable material like copper ferrocyanide. One view, which has found wide acceptance, is that the solvent, e.g., water, molecules are attracted by the membrane surface, that is to say, they are "adsorbed" (§ 54a). As a result, there is a continuous connection between the solvent molecules on both sides of the membrane; these molecules can therefore pass through without difficulty. The molecules of solute, however, are unable to penetrate the complex network of pores that constitutes the semipermeable membrane, since there is no direct connection from one side to the other.

Another suggestion which has received some support is that the semipermeable material consists of a large number of fine capillaries that are not wetted by the liquid; direct passage of liquid through the capillaries is thus not possible. Molecules of the vapor are nevertheless able to diffuse into the pores, so that when pure solvent is placed on one side of the membrane and solution on the other side, distillation occurs through the capillaries from the region of higher vapor pressure, i.e., the solvent, to that of lower vapor pressure, i.e., the solution, and hence osmosis results. This mechanism does not account so well as the one given above for the behavior of different membranes toward different solvents. For example, copper ferrocyanide acts as a semipermeable membrane when water is the solvent, but for certain nonaqueous solvents other membranes must be used, e.g., vulcanized rubber for pyridine and acetone. If the function of the semipermeable membrane is merely to act as a structure of nonwettable capillaries, this result would not have been expected, for pyridine is likely to wet rubber whereas water is not. The adsorption theory, however, is in better agreement with the facts, for rubber would adsorb the molecules of the organic solvent, but copper ferrocyanide would adsorb water molecules.

Various mechanisms have also been proposed to account for osmotic pressure. As a result of the apparent analogy between solutions and gases, attempts were made to explain osmotic pressure as being due to bombardment by the molecules of solute. As mentioned earlier, the so-called analogy may be misleading, and in any case the bombardment theory encounters many difficulties. Another view of osmotic pressure is based on the bombardment of the semipermeable membrane by the molecules of solvent, rather than of solute. Since there are relatively more solvent molecules in the pure solvent than in the solution, there should be a resultant pressure tending to drive solvent molecules into the solution, as is actually the case. The theory that a semipermeable membrane consists of dry capillaries through which the molecules of vapor distil from solvent to solution, as mentioned in the preceding paragraph, provides another interpretation of osmosis. As the external (osmotic) pressure on the solution increases so its vapor pressure increases (§ 25f); when the latter becomes equal to that of the solvent, the distillation, i.e., the flow of solvent, ceases. The external pressure at which this occurs would be the osmotic pressure of the solution.

In recent years there has been a growing opinion, first voiced by van't Hoff himself in 1892, that the actual mechanism of osmotic pressure is not important. Both solvent and solute molecules will undoubtedly bombard the semipermeable membrane, and distillation may also occur at the same time through the pores. All this is, however, immaterial; in the study of osmotic pressure the essential point is that, for some reason connected with the presence of solute molecules, the "escaping tendency" or "activity" of the solvent molecules is less in a solution than it is in the pure liquid. This decrease of escaping tendency or activity is immediately evident in the fact that the vapor pressure of the solution is less than that of the solvent. One result of this difference in escaping tendency is that molecules of solvent will always tend to pass from the solvent to the solution. Expressed in more precise thermodynamic terms, it may be said that the free energy of 1 mole of solvent molecules in the solution is less than in the pure solvent. The transfer of these molecules from pure solvent to solution will thus be accompanied by a decrease of free energy; consequently such a transfer will tend to occur spontaneously, in accordance with the conclusions reached in § 9b.

If solvent and solution are placed in two vessels side by side, in an enclosed space, the difference in free energy, escaping tendency or activity of the solvent molecules will manifest itself by distillation from the solvent to the solution. If two solutions of different concentrations are used the process will continue until they have the same vapor pressure; this principle has been employed in the isopiestic method for studying vapor pressures of solutions (§ 22c). Similarly, when solvent and solution are separated by a semipermeable membrane, the difference in free energy, etc., must result in the passage of solvent molecules into the solution until equilibrium is attained by the building up of an excess pressure, the osmotic pressure. It follows, therefore, that the setting up of an osmotic pressure is the inevitable result of the introduction of a semipermeable membrane between the solvent and solution, since the escaping tendencies of the solvent molecules are different on the two sides of the membrane. When a state of equilibrium is reached under the influence of the external (osmotic) pressure acting on the solution, the escaping tendency (vapor pressure) of the solvent molecules in the solution must, of necessity, become equal to the value in the pure solvent.

25f. Osmotic Pressure Relationships.—From the foregoing statements it is clear that there should be a relationship between the osmotic pressure of a solution and its vapor pressure as compared with that of the pure solvent. Such a connection can be derived from thermodynamics, and is quite independent of the mechanism of osmotic pressure. Suppose that, under the influence of an external pressure P_0, e.g., 1 atm, the vapor pressure of a pure solvent is p^0, while that of a solution at the same temperature is p. J. H. Poynting (1881) showed theoretically that increasing the external pressure on a liquid in equilibrium with its vapor must cause an increase in the vapor pressure. Let P be the external pressure at which the vapor pressure of the solution increases to p^0, the value for the pure solvent at the pressure P_0. It follows, therefore, that the excess pressure $P - P_0$, which must be applied to the solution in order to bring it into equilibrium with the solvent, is equal to the osmotic pressure Π. The problem now is to derive a relationship between P_0 and P, on the one hand, and p^0 and p, on the other hand.

Consider a solution under an external pressure P, in equilibrium with vapor of the solvent at pressure p; in accordance with the results in § 9c, the free energy per mole of solvent will be the same in both liquid and vapor phases. If the external pressure on the solution is altered, the vapor pressure will change, so as to maintain the equality of the molar free energy. Since the behavior of a solution is being considered, it is really the corresponding partial molal property, i.e., the partial molal free energy, of the solvent constituent which is being considered (§ 7h). In this case, equation (9.18), which gives the relationship between the change in free energy and the corresponding pressure change at constant temperature, should be written as

$$d\bar{F} = \bar{V}dP, \tag{25.6}$$

where $\bar{F}$ and $\bar{V}$ are the partial molal free energy and volume, respectively, of the solvent constituent. It is the common practice, following its early use by J. Willard Gibbs, to use the term **chemical potential** for the partial molal free energy and to represent it by the symbol μ; thus, equation (25.6) may be written as

$$d\mu = \bar{V}dP. \tag{25.7}$$

Suppose the external pressure on the solution is increased by a small amount from P to $P + dP$, and the equilibrium vapor pressure is consequently changed by dp to $p + dp$, the corresponding chemical potential changes at constant temperature are given by equation (25.7) as

$$d\mu_l = \bar{V}_l dp \qquad \text{and} \qquad d\mu_v = \bar{V}_v dp,$$

where the subscript l refers to the liquid (solution) phase and v to the vapor. The quantity $\bar{V}_l$ is the partial molal volume of the solvent constituent in the solution, i.e., the change in volume resulting from the addition (or removal) of 1 mole of solvent from a very large quantity of the solution at the given concentration, at the pressure P. Similarly, $\bar{V}_v$ is the partial molal volume of the solvent in the vapor, but since the latter does not contain any solute, this is the same as the actual molar volume, V_v. For the system to remain in equilibrium after the pressure changes, the partial molal free energy (or chemical potential) changes must be the same for solution and vapor; hence, at a given temperature,

$$\bar{V}_l dP = V_v dp.$$

At low vapor pressures the vapor may be supposed to obey the ideal gas laws, so that V_v may be replaced by RT/p; hence,

$$\bar{V}_l dP = RT\frac{dp}{p}. \tag{25.8}$$

As seen above, when the external pressure is changed from P_0 to P, where $P - P_0$ is equal to the osmotic pressure of the solution, the vapor pressure is increased from p to p^0; consequently, the left-hand side of equation (25.8) must be integrated between the limits of P_0 to P, and the right-hand side from p to p^0, viz.,

$$\int_{P_0}^{P} \bar{V}_l dP = RT\int_{p}^{p^0}\frac{dp}{p}. \tag{25.9}$$

Following the usual convention (§ 22a, footnote), $\bar{V}_l$ may be replaced by $\bar{V}_1$, the partial molal volume of the solvent in the solution; assuming this to remain constant, integration of the equation (25.9) then gives

$$\bar{V}_1(P - P_0) = RT\ln\frac{p^0}{p}.$$

Since $P - P_0$ is equal to Π, the osmotic pressure of the solution, it follows that

$$\Pi\bar{V}_1 = RT\ln\frac{p^0}{p}. \tag{25.10}$$

This relationship between osmotic pressure and vapor pressure can be obtained thermodynamically in several different ways; it is independent of any theory or mechanism of osmotic pressure. It is exact, provided the vapor behaves as an ideal gas and the solution is incompressible; these are the only approximations made in the treatment so far. The agreement between equation (25.10) and actual experiment will be shown below.

If the solution under consideration behaves ideally, in the sense that Raoult's law is obeyed, then by equation (22.3),

$$\frac{p}{p^0} = 1 - x_2$$

and so, for an ideal solution, equation (25.10) becomes

$$\Pi\bar{V}_1 = -RT\ln(1 - x_2).$$

If the ideal solution is also dilute, the mole fraction x_2 of solute is small, and hence

$$\ln(1 - x_2) \approx -x_2,$$

so that

$$\Pi\bar{V}_1 = RTx_2. \tag{25.11}$$

For a dilute solution x_2 may be replaced by n_2/n_1, where n_1 and n_2 are the numbers of moles of solvent and solute, respectively, in the solution; equation (25.11) may therefore be written as

$$\Pi \bar{V}_1 \frac{n_1}{n_2} = RT. \tag{25.12}$$

In a dilute solution, $\bar{V}_1$ is generally identical with V_1, the ordinary molar volume of the solvent. The product $V_1 n_1$ is then the total volume of solvent in the solution, and $V_1 n_1/n_2$ is the volume of solvent per mole of solute. This quantity has previously (§ 25d) been represented by the symbol V'; hence, equation (25.12) becomes

$$\Pi V' = RT, \tag{25.13}$$

which is identical with the empirical Morse equation (25.5). It is obvious, from the foregoing deduction, that this expression can be expected to hold only for a moderately dilute solution, provided Raoult's law is obeyed.

For an extremely dilute solution the volume V' of the solvent may be replaced by the volume V of the solution containing 1 mole of solute; under these conditions

$$\Pi V = RT, \tag{25.14}$$

which is the van't Hoff equation. Since the solvent in a dilute solution almost invariably satisfies Raoult's law, it follows that the necessary condition for equation (25.14) is a very low molar concentration of solute.

It is of interest to compare the osmotic pressures calculated from the various equations derived above and those obtained by experiment. A number of results of measurements on sucrose solutions at 30°C are given in Table 25.3, together with the osmotic pressure values calculated from equation (25.10), the Morse equation (25.13) and the van't Hoff equation (25.14). It is seen that the theoretical equation (25.10), which involves measured vapor pressures, is in good agreement with experiment at all the concentrations; the van't Hoff equation fails in all but the most dilute solutions, but the Morse equation is somewhat of an improvement.

TABLE 25.3. OSMOTIC PRESSURES OF SUCROSE SOLUTIONS AT 30°C

Molality of Solution	Observed Osmotic Pressure	Calculated Osmotic Pressure Eq. (25.10)	Eq. (25.13)	Eq. (25.14)
0.1	2.47 atm	2.47	2.47	2.40 atm
1.0	27.22	27.0	24.7	20.4
2.0	58.37	58.5	49.4	35.1
3.0	95.16	96.2	74.2	45.5
4.0	138.96	138.5	98.9	55.7
5.0	187.3	183.0	123.6	64.5

The relationship between the osmotic pressure and vapor pressure of a solution is given by equation (25.10), but since the vapor pressure is also related to the lowering of the freezing point and the elevation of the boiling point, a quantitative connection between these properties of a solution and its osmotic pressure is also to be expected. The simplest way of deriving this connection for dilute solutions is to combine equation (23.3), or the exactly analogous (24.5), with equation (25.11) after replacing $\bar{V}_1$ by V_1. The result, for both cases, may be put in the form

$$\Pi = \frac{LT}{V_1 T_0^2} \Delta T, \tag{25.15}$$

where L, T_0 and ΔT represent the molar heat of vaporization, boiling point of the solvent and rise of the boiling point, respectively, or the molar heat of fusion, freezing point of the solvent and depression of the freezing point, respectively; T is the temperature at which the osmotic pressure is measured, and V_1 is the molar volume of the solvent at this temperature. The quantities L, T_0 and V_1 are virtually constant for a given solvent, and hence it is seen from equation (25.15) that, at constant temperature, *the osmotic pressure of a dilute solution is directly proportional to the elevation of the boiling point or the depression of the freezing point.*

Example: The osmotic pressure of a 0.100 molal aqueous solution of sucrose at 30°C is 2.47 atm; the molar volume of water at this temperature is 18.10 cc. Calculate the elevation of boiling point of this solution, and compare it with the value to be expected from the known molal elevation constant of water.

In this problem particular care must be exercised in the matter of units; the best plan is to express Π, L and V_1 in cgs units; thus, Π is converted into dynes cm^{-2}, L into ergs mole^{-1} and V_1 into cc. Hence,

$$\Pi = 2.47 \text{ atm} = 2.47 \times 1.013 \times 10^6 \text{ dynes cm}^{-2}$$

$$L = 539.9 \times 18.02 \text{ cal mole}^{-1} = 539.9 \times 18.02 \times 4.184 \times 10^7 \text{ ergs mole}^{-1}$$

$$V_1 = 18.10 \text{ cc}$$

The temperature T at which the osmotic pressure was measured is $273.2 + 30.0 = 303.2$°K, and T_0, the boiling point of water, is 373.2°K; consequently, by equation (25.15),

$$\Delta T = \frac{V_1 T_0^2}{LT} \Pi = \frac{18.10 \times (373.2)^2 \times 2.47 \times 1.013 \times 10^6}{539.9 \times 18.02 \times 4.184 \times 10^7 \times 303.2}$$

$$= 0.0511\text{°K (or °C)}$$

From Table 23.1 the molal elevation of the boiling point of water is 0.513°, and hence for a 0.1 molal solution the rise of boiling point should be 0.0513°C.

The lowering of vapor pressure, the rise of boiling point, the depression of the freezing point and the osmotic pressure of a solution are all properties which depend, as a first approximation, on the *molecular concentration of the solute in the solution, and not on the nature of the solute.* Thus a 0.1 molal solution of any substance in a given solvent should produce the same lowering of vapor pressure, rise of boiling point, and so on.

IDEAL AND NONIDEAL SOLUTIONS

26a. Molecular Weights and Ideal Behavior.—In view of the direct connection with the molar concentration, any of the four properties of solutions referred to above could be used for the determination of molecular weights of dissolved substances. Except for the special case of compounds of high molecular weight, mentioned earlier, the lowering of vapor pressure, the elevation of boiling point and depression of freezing point methods are most generally employed for this purpose. As a rule, the molecular weights obtained are in good agreement with the values to be expected, so that the broad accuracy of the equations derived in the preceding sections may be accepted. In certain cases, however, marked deviations have been observed, even in moderately dilute solutions; these may be attributed, in general terms, to departure of the solutions from ideal behavior.

The essential postulate made in the deduction of the various equations for the elevation of boiling point, depression of the freezing point and osmotic pressure is that Raoult's law is applicable to the solvent. For solutions obeying this law, therefore, the equations should be satisfactory. Strictly speaking, an ideal solution is defined as one obeying Raoult's law *at all concentrations*, but it is frequently observed that the law applies to the solvent, to a good approximation, for dilute solutions, although derivations occur at higher concentrations (§ 39b). These solutions are not completely ideal, but they may be treated as ideal, for present purposes, in the dilute range in which Raoult's law is approximately obeyed by the solvent. The equations derived in this chapter will then apply to these dilute solutions in the same region as they behave as ideal. Theoretical considerations (§ 39a) have shown that the condition for Raoult's law to hold is that the solute should not affect the forces acting between the molecules of solvent. This will be the case if the solvent and solute have similar characteristics, e.g., both are nonpolar or both are related polar substances. As a very rough generalization, it may be stated, therefore, that Raoult's law, and hence such equations as (22.6), (23.6), (24.6) and (25.11), will hold moderately well for solutions of appreciable concentration, e.g., up to about 0.1 molal, if these conditions are satisfied. On the other hand, the presence of a polar solute in a nonpolar solvent, or vice versa, will so affect the forces between the molecules of solvent that Raoult's law would not be expected to hold with any degree of accuracy in solutions of appreciable concentrations; under these conditions the equations will fail, except for very dilute solutions.

This conclusion may be illustrated by reference to the determination of the molecular weight of nitrobenzene in benzene as solvent; the molecules of the former are highly polar (see Table 28.2) while those of the latter are nonpolar. Deviations from ideal behavior are thus to be anticipated in all solutions except the most dilute. The molecular weight of nitrobenzene, $C_6H_5NO_2$, is 123, and the observed value, derived from the depression of the freezing point of benzene, was found to be 126.7 in a 0.12 molar solution; at 0.5 molar the apparent molecular weight was 137, and at 1.0 molar it was about 150. With solutions of nitrobenzene in cyclohexane even greater discrepancies, mainly due to departure from the ideal Raoult's law, have been noted.

Apart from deviations due to changes in the intermolecular forces, there is another important type due, mainly, to the fact that the solute does not exist in solution in a simple molecular form; that is to say, the solute forms associated molecules (§ 5f). The number of moles, or the mole fraction, of the solute is then not equal to that derived from the ordinary molecular weight; hence, Raoult's law *appears* to fail for such solutions. For example, the molecular weights of acetic acid, benzoic acid and other carboxylic acids, as determined from measurements on benzene solutions, are almost exactly twice the expected values in all but the most dilute solutions. This result is attributed to the actual formation of double molecules, in agreement with the conclusions reached from molecular weight determinations made with the vapors of carboxylic acids (§ 5f). If proper allowance were made for the fact that these substances have molecular weights which are double the values calculated for the simple molecular formulae, the solutions of carboxylic acids in benzene, etc., would exhibit relatively little departure from ideal behavior.

Other hydroxylic compounds, such as alcohols and phenols, have molecular weights in benzene and other nonhydroxylic solvents that increase steadily with increasing concentration. This result, as in the case of nitrobenzene in benzene, is partly due to the difference in polarity of solute and solvent, but there is probably also some association of the molecules of the hydroxylic solute. Whereas the association of carboxylic acids leads to the formation of definite double molecules, with alcohols and phenols the character of the association is much less well defined. For this reason the apparent molecular weight does not have a value which is a definite multiple of that of the simple molecules, but increases steadily with concentration, as the general extent of the association increases.

In studying the effect of the solvent on the molecular weight of associated substances, it has been found that in hydroxylic solvents, such as water and alcohols, the results are almost what might be expected for simple molecules. Such solvents have been described as **dissociating solvents,** for they tend to split up or dissociate the double molecules into single molecules. In contrast to the behavior of these hydroxylic solvents, the nonpolar solvents, such as benzene, have been referred to as "associating solvents." It is doubtful, however, if this description can be justified, for the solutes are already associated, both in the vapor and liquid states, and the solvent does not increase the extent of association as the name would imply.

26b. Dissociation in Electrolytic Solutions.—An entirely different type of departure from ideal behavior, which is of great chemical significance, has been observed with aqueous solutions of strong acids and bases, of salts, and, in general, with solutions capable of conducting an electric current. For these solutes, particularly in water as solvent, the molecular weights are found to be considerably less than those anticipated; the values become smaller, approaching a limiting value, with decreasing concentration, that is, with increasing dilution, of the solution. To obtain agreement between calculated and experimental values, equation (25.14) must be written in the form

$$\Pi V = iRT,$$

where i, called the **van't Hoff factor,** is the ratio of the effective molecular weight M_0 to the apparent experimental value M in the solution, i.e., M_0/M. This factor is sometimes defined in an alternative, but exactly equivalent, manner, as the ratio of the observed lowering of the vapor pressure, elevation of boiling point, depression of the freezing point or osmotic pressure to the corresponding value calculated from the theoretical molecular weight of the solute. Thus, if Δ represents the experimental value of one of these colligative properties, and Δ_0 is the expected value if the solution behaved ideally, then by definition

$$i = \frac{\Delta}{\Delta_0} = \frac{M_0}{M}.$$

For salts such as NaCl, KNO_3, $MgSO_4$, etc., consisting of two radicals, the van't Hoff factor i tends towards a limiting value of 2.0 in dilute solution; for salts made up of three radicals, of which two may be the same or all three different, e.g., K_2SO_4, $CaCl_2$, $NaHSO_4$, etc., the value of i approaches 3.0 as the concentration decreases. In general, the van't Hoff factor has an integral value at infinite dilution equal to the total number of radicals constituting the salt.

The fundamental significance of the results just described was realized by S. Arrhenius (1887); he was able to correlate the apparently abnormal behavior with the fact that the corresponding solutions were good conductors of electricity. The suggestion was made that *when an acid, base or salt is dissolved in water it splits up, or dissociates, spontaneously into positively and negatively charged ions*; this is the basis of the **theory of electrolytic dissociation.** A salt such as sodium chloride will dissociate into two ions, thus

$$NaCl = Na^+ + Cl^-,$$

whereas potassium sulfate will yield three ions upon dissociation,

$$K_2SO_4 = 2K^+ + SO_4^{-2}.$$

The number of charges carried by an ion is equal to its normal valence (§ 16b).

The presence of free ions would account for the ability of the solutions to conduct an electric current, for electricity is always carried by charged particles, either ions or electrons. Further, the formation of the free ions explains the apparently abnormal properties of these solutions. As already seen, the properties considered in this chapter depend on the number of molecules present in the solution; if each ion behaves in this respect as a molecule, and there is no apparent reason why it should not, then a molecule of sodium chloride, for example, will produce twice the lowering of vapor pressure, elevation of boiling point, etc., to be expected for the single molecule. This will account for the limiting value of 2.0 for the van't Hoff factor for sodium chloride and analogous salts. Similarly, because potassium sulfate, calcium chloride, etc., dissociate into three ions, the van't Hoff factor should approach a value of 3.0. The experimental facts can thus be explained in a satisfactory manner by the theory of electrolytic dissociation.

Although the van't Hoff factor for sodium chloride, for example. tends towards a limiting value of 2.0 at infinite, i.e., very high, dilution, at appreciable concentrations it is less than 2.0, e.g., 1.90 in a 0.05 molal solution, and 1.87 in a 0.10 molal solution. For potassium sulfate, with a limiting value of 3.0, the corresponding values of i at the indicated concentrations are 2.45 and 2.32. In general, the deviations from the ideal limiting value increase with concentration, and are more marked the higher the valence of the ions of the solute.

If each molecule in solution were completely dissociated into ions, the value of the van't Hoff factor for the solution would be the limiting value. Consequently, incomplete dissociation would be one way of accounting for values of i smaller than the limiting value. At one time this was thought to be the main reason for the discrepancy, but it has been realized in recent years that for simple salts, e.g., sodium and potassium chlorides, nitrates, etc., and for the strong mineral acids, e.g., nitric and hydrochloric acids, such is not the case. These substances, called "strong electrolytes," are split up into free ions to a very large extent at all reasonable concentrations, and the fact that i is less than the limiting value, is ascribed to electrostatic attractions between the oppositely charged ions. This aspect of the subject of solutions and the relationship of ions to the conductance of solutions will be considered more fully in later chapters.

26c. The Activity Concept.—The departure of a solution from ideal behavior is commonly represented in terms of a property known as the **activity.** The activity concept was introduced by G. N. Lewis (1907), and although it has been widely applied in the study of solutions of electrolytes, e.g., salts, acids and bases, it is equally applicable to nonelectrolytes and even to gases.* Various methods have been used for developing the idea of activity; the following is simple and is adequate for present purposes.

Consider a system of two large vessels, one containing a solution in equilibrium with its vapor at the pressure p', and the other containing another solution, of the same solvent and solute at a different concentration, whose vapor pressure is p''. The external pressure, e.g., 1 atm, and the temperature T are the same for both vessels. One mole of solvent is then vaporized isothermally and reversibly from the first solution at constant pressure p', by the method described in § 6f; the quantity of solution is supposed to be so large that the removal of 1 mole of solvent does not appreciably affect the concentration or vapor pressure. The vaporization has been carried out reversibly, and so every stage represents a state of equilibrium. Further, the temperature and pressure have remained constant, and hence by equation (9.26) there is no change of free energy.

The mole of vapor at pressure p' is now removed and compressed or expanded reversibly at constant temperature until its pressure is changed to p'', the vapor pressure of the second solution. If the pressures are sufficiently low for the vapor to be treated as an ideal gas without incurring serious error,

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* The activity of gases is customarily called the **fugacity** and represented by the symbol f; wherever a appears in the following equations, f is substituted if the system under consideration is gaseous.

as is generally the case, the increase of free energy is given by equation (9.22) as

$$\Delta F = RT \ln \frac{p''}{p'}. \tag{26.1}$$

Finally, the mole of vapor at the constant pressure p'' is condensed isothermally and reversibly into the second solution. The change of free energy for this stage, like that for the first stage, is again zero; the total free energy change for the transfer of 1 mole of solvent from the first solution to the second is thus given by equation (26.1).

Let μ_1' represent the partial molal free energy of solvent in the first solution and μ_1'' the value in the second solution, then since the latter solution gains 1 mole while the former loses 1 mole, the free energy increase ΔF is equal to $\mu_1'' - \mu_1'$; it is thus possible to write, from equation (26.1),

$$\Delta F = \mu_1'' - \mu_1' = RT \ln \frac{p''}{p'}. \tag{26.2}$$

If both solutions behave ideally, so that Raoult's law is applicable, the vapor pressure is proportional to the mole fraction of the solvent in the particular solution [equation (22.5)]; hence, for ideal solutions, equation (26.2) becomes

$$\mu_1'' - \mu_1' = RT \ln \frac{x_1''}{x_1'}, \tag{26.3}$$

where x_1' and x_1'' are the mole fractions of the solvent in the two solutions.

For *nonideal solutions* this result is not applicable, but the **activity** of the solvent, represented by a, is defined in such a way that the free energy change accompanying the transfer of 1 mole of solvent from one solution to the other is given *exactly* by

$$\mu_1'' - \mu_1' = RT \ln \frac{a_1''}{a_1'}, \tag{26.4}$$

where a_1' and a_1'' are the respective activities of the solvent in the two solutions. This means, in a sense, that the activity is the property for a real solution that takes the place of the mole fraction for an ideal solution, in the free energy equation.

Although the definition of activity as represented by equation (26.4) has been derived with particular reference to the solvent, an exactly similar result is applicable to the solute. If μ_2' is the partial molal free energy of the solute in one solution, and μ_2'' is the value in another solution, the increase of free energy accompanying the transfer of 1 mole of *solute* from the first solution to the second is then given by

$$\mu_2'' - \mu_2' = RT \ln \frac{a_2''}{a_2'}, \tag{26.5}$$

where a_2' and a_2'' are, by definition, the activities of the *solute* in the two solutions.

It should be noted that equations (26.4) and (26.5) do not define the actual or absolute activity, but rather the *ratio* of the activities of the particular substance in two solutions. In order to be able to express activities numerically, it is convenient to choose for each constituent of the solution a reference state, or **standard state,** *in which the activity is arbitrarily taken as unity.* The activity of a component, solvent or solute, in any solution is thus really *the ratio of its value in the given solution to that in the chosen standard state.* The actual standard state chosen for each component is the most convenient for the purpose, and varies from one to the other, as will be seen shortly. If the solution indicated by the single prime is taken as representing the standard state, then a' will be unity, and equation (26.4) or (26.5) may be written in the general form

$$\mu = \mu^0 + RT \ln a, \tag{26.6}$$

the double primes being omitted, and a superscript zero is used, in accordance with the widely accepted convention, to identify the standard state of unit activity. This equation defines the activity or, more correctly, the activity relative to the chosen standard state, of either solvent or solute in a given solution.

26d. The Activity Coefficient.—The deviation of a solution from ideal behavior can be represented by means of the quantity called the **activity coefficient,** which may be expressed in terms of various standard states. In this discussion the solute and solvent may be considered separately; the treatment of the activity coefficient of the *solute* in dilute solution will be given first. If the molar concentration, or molarity, of the solute is c_2 moles (or g ions) per liter, it is possible to express the activity a_2 by the relationship

$$a_2 = f_2 c_2 \qquad \text{or} \qquad f_2 = \frac{a_2}{c_2}, \tag{26.7}$$

where f_2 is the activity coefficient of the solute. Upon inserting this into equation (26.6) there is obtained the expression

$$\mu = \mu_c^0 + RT \ln f_2 c_2, \tag{26.8}$$

applicable to ideal and nonideal solutions. An ideal (dilute) solution is defined as one for which f_2 is unity, but for a nonideal solution it differs from unity. Since solutions tend to a limiting behavior as they become more dilute, it is postulated that at the same time f_2 approaches unity; hence,

$$f_2 \rightarrow 1 \qquad \text{as} \qquad c_2 \rightarrow 0$$

and, therefore, by equation (26.7)

$$a_2 \rightarrow c_2 \qquad \text{as} \qquad c_2 \rightarrow 0. \tag{26.9}$$

That is, the activity of the solute approaches its molar concentration as the dilution increases. The standard state of unit activity may thus be defined as *a hypothetical solution of unit molar concentration possessing the properties of a very dilute solution.*[*]

Another standard state for solutes that is employed especially in the study of galvanic cells (Chapter 13) is that based on the relationships

$$a_2 = \gamma_2 m_2 \qquad \text{or} \qquad \gamma_2 = \frac{a_2}{m_2}, \tag{26.10}$$

where m_2 is the molality of the solute, i.e., moles (or g ions) per 1000 g solvent, and γ_2 is the appropriate activity coefficient. Once again it is postulated that γ_2 approaches unity as the solution becomes more and more dilute, thus,

$$\gamma_2 \rightarrow 1 \qquad \text{as} \qquad m_2 \rightarrow 0$$

and, hence,

$$a_2 \rightarrow m_2 \qquad \text{as} \qquad m_2 \rightarrow 0, \tag{26.11}$$

so that the activity becomes equal to the molality at high dilutions. The standard state of unit activity is consequently defined as *a hypothetical solution of unit molality possessing the properties of a very dilute solution.* The difference between the actual value of the activity coefficient and unity is a measure of the departure of the actual solution from an ideal solution, regarded as one having the same properties as at high dilution.

In view of equations (26.9) and (26.11), it is evident that in the defined *ideal dilute solutions* the activity is equal to the molarity or to the molality, respectively. It follows, therefore, that the activity may be thought of as an idealized molarity (or molality) which may be substituted for the actual molarity (or molality) to allow for departure from ideal dilute solution behavior. The activity coefficient is then the ratio of the ideal molarity (or molality) to the actual molarity (or molality). At infinite dilution both f and γ must, by definition, be equal to unity, but at appreciable concentrations the activity coefficients differ from unity and from one another. However, it is possible to derive an equation relating f and γ, and this shows that the difference between them is quite small in dilute solutions.

When treating the *solvent*, the standard state of unit activity is almost invariably chosen so that the activity coefficient of the solvent, like that of the solute, becomes unity in a very dilute solution. The activity coefficient γ_1 of the solvent in any solution is defined by

$$a_1 = \gamma_1 x_1 \qquad \text{or} \qquad \gamma_1 = \frac{a_1}{x_1}, \tag{26.12}$$

where x_1 is the mole fraction of the solvent. As the solution becomes more dilute, $x_1 \rightarrow 1$, and according to the chosen standard state for the solvent

$$\gamma_1 \rightarrow 1 \qquad \text{as} \qquad x_1 \rightarrow 1.$$

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[*] The word "hypothetical" is employed in this definition because a real solution at a concentration of 1 mole (or g ion) per liter will generally not behave ideally in the sense of having the properties of a very dilute solution.

Thus in very dilute solution or, in other words, as the pure solvent is approached, $a_1 \rightarrow x_1$. It follows, therefore, that in the pure liquid state of the solvent a_1 and x_1 are both equal to unity, and the activity coefficient is then also unity on the basis of the chosen standard state.

26e. Determination of Activities and Activity Coefficients.—Several methods have been devised for the determination of activities; two only will be mentioned here, but others will be referred to in Chapters 13 and 14. Without going into details, it can be seen in a general way that measurements of vapor pressure, freezing point depression, etc., might be used to determine departure from ideal behavior, and hence to evaluate activities. The vapor pressure method has been used particularly to obtain the activity of the solvent, in the following manner. The equation (26.2) is applicable to any solution, ideal or nonideal, provided only that the vapor behaves as an ideal gas; comparison of this with equation (26.4) shows that the activity of the solvent in a solution must be proportional to the vapor pressure of the solvent over the given solution. If a_1 represents the activity of the solvent in the solution, and p_1 is its vapor pressure, then $a_1 = kp_1$, where k is a proportionality constant. The value of this constant can be determined by making use of the standard state postulated above, namely that $a_1 = 1$ for the pure solvent; the vapor pressure is then p_1^0. It follows, therefore, that

$$1 = kp_1^0 \qquad \text{or} \qquad k = 1/p_1^0;$$

hence, in general,

$$a_1 = \frac{p_1}{p_1^0}. \tag{26.13}$$

The activity of the solvent in a solution can thus be determined from measurements of the vapor pressure of the solvent in the solution (p_1) and of the pure solvent (p_1^0) at a given temperature. It is obvious that for an ideal solution obeying Raoult's law p_1/p_1^0 will be equal to x_1, the mole fraction of solvent. The activity coefficient as given by equation (26.12) will then be unity. For a nonideal solution the activity coefficient of the solvent will, of course, differ from unity, and its value can be determined by dividing the activity as derived from equation (26.13) by the mole fraction of the solvent.

The determination of activities and activity coefficients from vapor pressure measurements may be illustrated by the data in Table 26.1; the first column gives the mole fraction of acetone in acetone-chloroform mixtures, while in the second column are quoted the corresponding vapor pressures of

TABLE 26.1. ACTIVITY OF ACETONE IN ACETONE-CHLOROFORM MIXTURES AT 35.2°

Mole Fraction	Vapor Pressure	Activity	Activity Coefficient
1.000	344.5 mm	1.000	1.000
0.9405	322.9	0.937	0.997
0.8783	299.7	0.870	0.991
0.8165	275.8	0.801	0.981
0.7103	230.7	0.670	0.943

acetone over these solutions at 35.2°C. The activities and activity coefficients of the acetone, regarded as the solvent, are derived by means of equations (26.13) and (26.12), respectively.

The freezing point method for evaluating activity coefficients is based on the following equation obtained by combining equations (24.4) and (26.13), namely,

$$\ln a_1 = -\frac{L_f}{RT_0^2}\Delta T_f, \tag{26.14}$$

where a_1 is the activity of the solvent in a solution giving a freezing point depression of ΔT_f. As usual, L_f is the molar heat of fusion of the solvent, and T_0 is its freezing point.

For many purposes it is of more interest to know the activity, or activity coefficient, of the solute rather than that of the solvent. Fortunately, there is a simple equation, which can be derived from thermodynamics, that relates the activity a_1 of solvent to that of the solute, a_2; thus,

$$n_2 d \ln a_2 = -n_1 d \ln a_1, \tag{26.15}$$

where n_1 and n_2 are the numbers of moles of solvent and solute, respectively, in the solution. If the values of a_1 for the solvent are known, from vapor pressure or freezing point measurements, at a series of concentrations, the activity a_2 of the solute can be determined by graphical integration of equation (26.15).

The foregoing descriptions of methods for the evaluation of activities and activity coefficients refer particularly to solutes that are nonelectrolytes. The procedures have been adapted to electrolytes, but the calculations are somewhat involved. Special methods have also been devised for solutes of this type and these will be described in later sections.

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PROBLEMS

1. A solution containing 6.31 g of a nonvolatile solute in 50.0 g of water at 20°C has a vapor pressure of 17.319 mm. The vapor pressure of water at the same temperature is 17.535 mm. Calculate the molecular weight of the solute.

2. A solution is prepared by dissolving 24.4 g of biphenyl ($C_{12}H_{10}$) in 100 g of benzene. Calculate (*a*) the vapor pressure of the solution at 80.1°C, (*b*) its boiling point and (*c*) its freezing point. The boiling point of pure benzene is 80.1°.

3. The vapor pressure of water at its boiling point changes 27.6 mm per degree Celsius. Calculate the molal elevation constant.

4. If a solution containing 6.06 g of triphenylmethane, $(C_6H_5)_3CH$, in 1000 g of benzene is cooled to 0.221°C below the freezing point of pure benzene, (*a*) how much solvent will crystallize out and (*b*) what will be the molality of the residual solution?

5. Estimate the heat of fusion of naphthalene from its molal depression constant and its freezing point.

6. It is desired to determine the molecular weight of a nonvolatile solute with a precision of 1%. If a 0.100 *m* solution in carbon tetrachloride is used, what error is permissible in measuring the boiling point of the solution?

7. A sample of naphthalene has a melting point of 79.6°C. Estimate the purity of the sample.

8. Methanol and ethylene glycol are common antifreezing agents. (*a*) What are the relative weights of each which must be added to water to prevent deposition of ice down to $-10°C$? (*b*) What is the composition of each solution?

9. When 10.0 g of thallium are dissolved in 49.8 g of mercury, the vapor pressure of the resulting amalgam at 26°C is 1.52×10^{-3} mm compared to 2.00×10^{-3} mm for pure mercury. Determine the activity and activity coefficient of mercury in the amalgam.

10. The boiling point of a solution of 5.00 g of sulfur in 100 g of carbon bisulfide is 0.476° above that of the pure solvent. Determine the molecular formula for sulfur in this solvent. The boiling point of pure carbon bisulfide is 46.30°C and its heat of vaporization 84.1 cal g^{-1}.

11. When a current of dry air was passed through a saturator containing 6.832 g of a nonvolatile solute in 110 g of water, the loss in weight was 1.0073 g. The same volume of air passing through pure water vaporized 1.0592 g. Determine the molecular weight of the solute.

12. The osmotic pressure of a solution of 1.80 g of serum albumin in 100 g of water at 25°C is 76.7 mm of water. Calculate (*a*) the molecular weight of the solute and (*b*) the freezing point of the solution.

13. Calculate the osmotic pressure of a 2.00 *m* solution of sucrose in water at 30°C. The experimental value is 58.37 atm.

14. A 0.1197 *m* solution of mannitol in water gives a freezing point depression of 0.2225°C. Show that the solution may be considered ideal.

15. Calculate the free energy change accompanying the transfer by osmosis at 27°C of one mole of water from a 2.0 *m* sucrose solution to a 6.0 *m* solution.

9

Physical Properties and Molecular Structure

ADDITIVE PROPERTIES

27a. Additive, Constitutive and Colligative Properties.—Many physical properties of a system can be classified broadly in three categories. An **additive property** is one which is the sum of the corresponding properties of the individual constituents of a system. Mass is, of course, a strictly additive property, but there are other molecular properties, such as molar volume, which are largely additive in character, as will be seen below. A property is said to be **constitutive** when it depends primarily on the arrangement of the atoms in the molecule, and to a lesser extent on their nature and number. Many properties are partly additive and partly constitutive; in some the former aspect is predominant and in others the latter is more important. A **colligative property** is one depending primarily on the number of molecules and not on their nature. The lowering of vapor pressure and related properties of solutions considered in the preceding chapter are in this category.

27b. Molar Volumes at the Boiling Point.—Strictly speaking, molecular weight is the only exactly additive property of a molecule, but certain other properties of liquids are at least approximately additive in nature. One of these, as was discovered by H. Kopp (1855), is the molar volume at the boiling point. Although Kopp's choice of the boiling points of liquids as the temperatures for comparison of molar volumes was empirical, it evidently has some theoretical basis, for the boiling points are corresponding temperatures, as seen in § 11f. The molar volume is equal to the product of the molecular weight M and the specific volume v, i.e., the volume per gram; the latter is equal to the reciprocal of the density d, and so it follows that

$$\text{Molar volume} = Mv = \frac{M}{d}.$$

If the molar volumes of isomeric compounds of similar constitution, e.g., propyl formate, ethyl acetate and methyl propionate, are compared at their respective boiling points, the values are found to be almost identical. Further, in any particular homologous series of organic compounds, a constant difference of about 22.2 cc is found in the molar volume at the boiling points for each CH_2 group. These facts suggest that the molar volume might be largely an additive property, and this has been confirmed by evaluating the volume equivalents of various elements in the following manner. Paraffins have the general formula C_nH_{2n+2}, and if from the molar volume of a particular paraffin is subtracted the contribution of the nCH_2 groups, i.e., $n \times 22.2$ cc, the result may be taken as the volume equivalent of the two remaining hydrogen atoms. From an examination of a number of liquid paraffins, this mean difference was found by G. Le Bas (1912) to be 7.4, i.e., 3.7 cc per hydrogen atom. Since a CH_2 group contributes 22.2 cc to the molar volume at the boiling point, the volume equivalent of a carbon atom is $22.2 - 7.4$, i.e., 14.8 cc. Now that the equivalents for carbon and hydrogen atoms are known, it is a relatively simple matter to derive those for other elements, e.g., oxygen from the molar volume of an alcohol, ether, aldehyde, ketone, etc., and halogen from the molar volume of an alkyl halide.

From such determinations it has become evident that the molar volume at the boiling point is not entirely additive in character; for example, the oxygen atom in alcohols and ethers, represented by —O—, contributes 7.4 cc, while in a carbonyl group, indicated by =O, the contribution is 12.0 cc. Further, in benzene derivatives there is apparently a *contraction* of 15.0 cc. It follows, therefore, that the molar volume is partly a **constitutive property**, for it depends to some extent upon the arrangement of the atoms within the molecule.

The volume equivalents of a number of atoms and for the benzene ring are given in Table 27.1; their application may be illustrated by calculating the molar volume of a liquid at its boiling point and comparing it with the experimental value. Consider, for example, ethyl benzoate, $C_6H_5COOC_2H_5$; this contains nine carbon atoms, ten hydrogen atoms, two oxygen atoms (one —O— and one =O), and a benzene ring. The contributions are as follows:

TABLE 27.1. VOLUME EQUIVALENTS AT THE BOILING POINT

Hydrogen	3.7 cc	Iodine	37.0 cc
Carbon	14.8	Oxygen (—O—)	7.4
Chlorine	22.1	Oxygen (=O)	12.0
Bromine	27.0	Benzene ring	−15.0

$$\begin{aligned} 9C &= 9 \times 14.8 = 133.2 \\ 10H &= 10 \times 3.7 = 37.0 \\ \text{—O—} &= 1 \times 7.4 = 7.4 \\ =O &= 1 \times 12.0 = 12.0 \\ \text{Benzene ring} &= -15.0 \\ \hline & \quad 174.6 \text{ cc} \end{aligned}$$

This result, 174.6 cc, agrees exactly with the observed molar volume of ethyl benzoate at its boiling point. The molar volume is thus seen to be mainly an additive, and partly a constitutive, property. By utilizing the known volume equivalents, it is possible to calculate the molar volume, and hence the density, of a liquid at its boiling point.

27c. The Parachor.—It was observed by D. B. Macleod (1923) that the surface tension γ of a liquid was related to the orthobaric densities d_l and d_v, of liquid and saturated vapor (§ 10b), at the same temperature, by the expression

$$\frac{\gamma^{1/4}}{d_l - d_v} = C, \tag{27.1}$$

where C is a constant over a considerable range of temperature; the value of C depends on the nature of the liquid. If both sides of the Macleod equation (27.1) are multiplied by M, the molecular weight of the substance, the result is

$$\frac{M\gamma^{1/4}}{d_l - d_v} = MC = \text{constant, } [P]. \tag{27.2}$$

The constant $[P]$ has been called the **parachor** (S. Sugden, 1924), a name which implies that it is a comparative or relative volume.

If the density d_v of the saturated vapor is neglected in comparison with that of the liquid, as is justifiable provided the temperature is not too near the critical point, equation (27.2) may be written as

$$\frac{M}{d_l}\gamma^{1/4} = [P]. \tag{27.3}$$

The quantity M/d_l is the molar volume of the liquid, as already defined; hence, if the temperature is such that the surface tension γ is unity, the molar volume is equal to the parachor, according to equation (27.3). It follows, therefore, that the parachor may be regarded as the molar volume of a liquid when its surface tension is unity. A comparison of the parachors of different substances is thus equivalent to a comparison of molar volumes under conditions of equal (unit) surface tension. Since the molecular attractions would then be approximately equal, it is to be expected that the parachor may provide a better basis for the comparison of molar volumes than the measurements at the boiling point (§ 27b).

From an examination of the data for isomeric substances and of members of homologous series, the parachor has been found to be primarily an additive, and partly a constitutive, property. By the procedure described in § 27b for molar volumes, the parachor equivalents have been determined for a number of elements and also for certain structural factors; some of the results are recorded in Table 27.2.

TABLE 27.2. PARACHOR EQUIVALENTS

Carbon	7.2	Sulfur	48.5	Nitrogen	12.5
Hydrogen	16.2	Chlorine	53.8	Double bond	23.2
Oxygen	20.0	Bromine	68.0	Triple bond	46.6
O_2 in esters	60.0	Iodine	90.0	6-membered ring	6.1

Example: The density of acetone is 0.7910 g cm^{-3} at 20°C; utilize the additivity of the parachor to calculate the surface tension of acetone.

Acetone, CH_3COCH_3, contains three carbon atoms, six hydrogen atoms, one oxygen atom, and one double bond; the parachor calculated from the equivalents in Table 27.2 is thus:

$$(3 \times 7.2) + (6 \times 16.2) + 20.0 + 23.2 = 162.0.$$

The molecular weight of acetone is 58.08 and the density at 20° is 0.7910; hence, by equation (27.3)

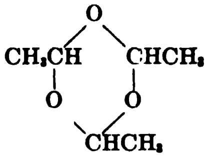
$$\frac{58.08}{0.7910} \times \gamma^{1/4} = 162.0$$

$$\gamma = 23.7 \text{ dynes cm}^{-1}.$$

(The experimental value is also 23.7 dynes cm^{-1}.)

In view of the appreciable contributions made by structural factors, such as double and triple bonds, and by ring formation, it is evident that the parachor might be used in certain cases to decide between alternative possible configurations. One example of this type will be cited here. Acetaldehyde forms a liquid polymer, known as *paraldehyde*, having the formula $(C_2H_4O)_3$; its parachor, determined from surface tension and density measurements, is 298.7. Two reasonable formulae for paraldehyde have been favored, one involving a ring (I) and the other a straight chain (II); these, together with the corresponding calculated parachors are represented below. The observed parachor of 298.7 thus favors formula I. Unfortunately parachor equivalents are not strictly additive, and so the method described does not always lead to unequivocal conclusions.

I



$6C = 6 \times 7.2 = 43.2$
$12H = 12 \times 16.2 = 194.4$
$3O = 3 \times 20.0 = 60.0$
6-membered ring = 6.1

303.7

II

$CH_3CH(OH)CH_2CH(OH)CH_2CHO$

$6C = 6 \times 7.2 = 43.2$
$12H = 12 \times 16.2 = 194.4$
$3O = 3 \times 20.0 = 60.0$
Double bond = 23.2

320.8

27d. Molar Refraction.—The property of molar refraction is characteristic of both gaseous and liquid states, but as it is usually measured on the liquid, it is convenient to consider it in the present chapter. It is well known that when light passes from one medium to another, it almost invariably suffers **refraction**, that is, *a change of direction*. If a beam of light travels, as shown in Fig. 27.1, from air (or vacuum) into a more dense medium, e.g., a liquid, then i is called the angle of incidence and r is the angle of refraction; the **refractive index** n of the medium is then defined by

$$n = \frac{\sin i}{\sin r}. \tag{27.4}$$

By measuring the angles of incidence and refraction in a suitable manner, the refractive index n can be determined. The value of this quantity depends on the wave length of the light, and for most purposes either the familiar D-line of sodium or the α-, β- or γ-lines of the hydrogen (Balmer) spectrum are employed. A subscript to the letter n, e.g., n_D, n_α, etc., indicates the particular type of light used for the measurement of the refractive index.

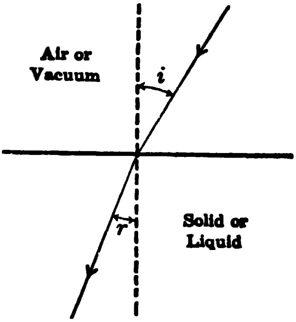


FIG. 27.1. Refraction of light

The theoretical work of H. A. Lorentz (1880) and L. V. Lorenz (1880) indicated that the **molar refraction** of a compound, defined by the expression

$$R_M = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}, \qquad (27.5)$$

where M is the molecular weight and d the density, was a characteristic property of a substance independent of the temperature. The value is almost the same in both gaseous and liquid states. Since n is dimensionless, the presence of the factor M/d shows that the molar refraction is proportional to the molar volume. If the refractive index were the value for light of very long wave length, the molar refraction should, according to theory, be equal to the actual volume of the molecules present in 1 mole of the substance.

Like other forms of molar volume considered earlier, the molar refraction is an additive and constitutive property. The refraction equivalents, based on refractive indices measured with the D-line of sodium, and which have been derived in the usual manner, are recorded in Table 27.3.

TABLE 27.3. REFRACTION EQUIVALENTS FOR THE D-LINE

Carbon	2.42 cc	Chlorine	5.97 cc
Hydrogen	1.10	Bromine	8.87
Oxygen (in CO group)	2.21	Iodine	13 90
Oxygen (in ethers)	1.64	Double bond	1.73
Oxygen (in OH group)	1.53	Triple bond	2.40

Example: The refractive index n_D of acetone is 1.3591 and the density is 0.7910 g cm^{-3} at 20°C. Calculate the molar refraction of this substance, and compare it with the value obtained from the refraction equivalents in Table 27.3.

The molecular weight of acetone, CH_3COCH_3, is 58.08; hence, by equation (27.5)

$$R_M = \frac{(1.3591)^2 - 1}{(1.3591)^2 + 2} \cdot \frac{58.08}{0.7910} = 16.17 \text{ cc.}$$

The calculated value is 3×2.42 (for 3 C atoms) $+ 6 \times 1.10$ (for 6 H atoms) $+ 2.21$ (for O in CO) $= 16.07$ cc.

It is evident from the data in Table 27.3 that the molar refraction is decidedly a constitutive property; for example, the refraction equivalent of the oxygen atom depends on whether it is present in a hydroxyl, carbonyl or ether grouping. Similar variations have been found for the nitrogen atom. In addition to the normal contribution of the double bond, the presence of conjugated double bonds in a straight chain molecule, e.g., $CH_3—CH═CH—CH═CH—CH_3$, results in a further increase of the molar refraction. Because of these marked constitutive influences, molar refractions have been used to decide between alternative structures of some organic compounds; the particular formula is accepted as the correct one which gives a calculated molar refraction in best agreement with the experimental value.

CONSTITUTIVE PROPERTIES

28a. Dielectric Constant: Molar Polarization.—The magnitude of the force acting between two given electric charges placed at a definite distance apart in a uniform medium is determined by a property of the latter known as the **dielectric constant.** All forms of matter, gaseous, liquid and solid, possess definite dielectric constants; the dielectric properties of solids are important, but the subject will not be treated here. It may be mentioned that the dielectric constants of gases are very close to that for a vacuum, which is taken as unity. If e_1 and e_2 are the values of two electric charges placed at a distance r apart in a uniform medium, then the force F acting between them is given by Coulomb's law as

$$F = \frac{e_1 e_2}{Dr^2}, \tag{28.1}$$

where D is the dielectric constant of the medium. If the two charges have opposite signs, the force is one of attraction, and it is seen that the higher the dielectric constant the smaller is the force of attraction between the charges; this fact is of importance in connection with the electrical properties of salts in solvents of different dielectric constants.

The dielectric constant of a substance is usually measured by determining the electrostatic capacitance C of a capacitor containing the given material between the plates; if C_0 is the value for the same capacitor when completely evacuated, then

$$D = \frac{C}{C_0}. \tag{28.2}$$

In actual practice dielectric constants are usually obtained by comparing the capacitance of the capacitor when filled with a given liquid with that for the same capacitor containing a standard liquid, e.g., benzene, whose dielectric constant is known from precise measurements based on equation (28.2). If D_1 and D_2 are the dielectric constants of the experimental and standard liquids, respectively, and C_1 and C_2 are the capacitances of a capacitor when filled alternately with these liquids, then

$$\frac{D_1}{D_2} = \frac{C_1}{C_2}.$$

Since C_1 and C_2 can be measured, and D_2 is known, the value of D_1 can be calculated. The results for a number of liquids at 25° are given in Table 28.1;

TABLE 28.1. DIELECTRIC CONSTANTS OF LIQUIDS AT 25°C

Hexane	1.90	Chloroform	4.80
Cyclohexane	2.03	Acetone	21.2
Carbon tetrachloride	2.24	Ethanol	24.3
Benzene	2.28	Nitrobenzene	34.8
Diethyl ether	4.30	Water	78.5

it will be noted that nonpolar substances, e.g., benzene and other hydrocarbons, and carbon tetrachloride, have low dielectric constants, but polar liquids, e.g., water, nitrobenzene and ethanol, have higher dielectric constants.

When molecules are subjected to the action of an electric field, two effects can be produced in them: first, there is a distortion of the electric charges, referred to as **polarization,** of the molecule and second, if the molecule is polar (§ 16g), there is an orienting effect in addition. For a nonpolar substance, e.g., carbon tetrachloride, hydrocarbons and carbon dioxide, the centers of positive and negative charge coincide in the absence of an electric field. In such a field, however, a dipole (§ 16g) is induced in the molecule by a distortion of the normally symmetrical distribution of nuclei and electrons (Fig. 28.1). When the field is removed the polarization disappears and the symmetrical charge distribution is restored. The extent of this temporary, induced polarization, as determined by the magnitude of the induced dipole, depends only on the field strength and the structure of the molecule. It is independent of temperature, i.e., of the thermal motion of the molecules, because the distortion of the charge distribution is independent of the orientation of the molecule with respect to the field.

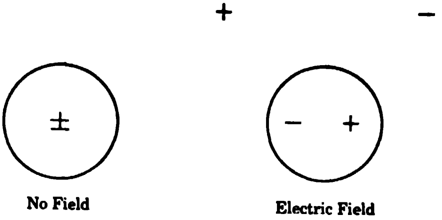


FIG. 28.1. Induced polarization

In polar molecules there is a normal displacement of the center of positive and negative charge, so that such molecules have a permanent dipole moment, in addition to the temporary moment induced by a field. When subjected to an electric field, the polar molecules will tend to become oriented parallel to one another so that the positive ends of the permanent dipole point toward the negative plate of the field and the negative ends toward the positive plate. However, thermal agitation of the molecules opposes this tendency to perfect alignment. It is to be expected therefore, that the orienting effect of this electric field on molecules with permanent dipoles will decrease with increase in temperature. A criterion for distinguishing between polar and nonpolar substances can thus be based on the different effects of temperature on the behavior of these substances in an electric field.

The molar polarization, derived by O. F. Mosotti (1850) and R. Clausius (1879), is a convenient property for this purpose; it is defined by

$$P_M = \frac{D-1}{D+2} \cdot \frac{M}{d}, \tag{28.3}$$

where D, M and d are the dielectric constant, molecular weight and density, respectively, of the substance. For nonpolar molecules the molar polarization does not vary with temperature, but for polar molecules it decreases as the temperature is raised. This is apparent from Fig. 28.2 where the molar polarization of a few substances, in the gaseous state, is plotted against the reciprocal of the absolute temperature. For the nonpolar compound, carbon tetrachloride, the value of P_M is seen to be independent of the temperature, but for the polar compounds P_M increases as $1/T$ increases; i.e., P_M decreases with increasing temperature.

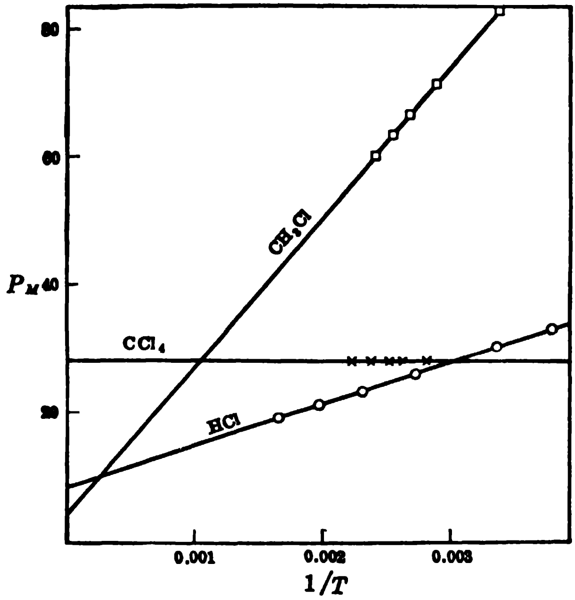


FIG. 28.2. Variation of molar polarization with temperature [a]

28b. Dipole Moments.—Dielectric constant measurements are usually made with an alternating electric field of frequency 10^6 to 10^7 cycles (or 10^3 to 10^4 kilocycles) per sec. At these frequencies the reversal in polarity of the field is sufficiently slow to permit the orientation of the permanent dipoles and the displacement of both positive (nuclei) or negative (electron) charges to adjust to the alternations of the field. The molar polarization defined by equation (28.3) thus gives the sum of the induced polarization P_I and the orientation polarization P_O due to permanent dipoles. According to the theoretical treatment of P. Debye (1912), based on the supposition that there is no restriction to the rotation of molecules in an electric field, the orientation polarization is given by

$$P_O = \frac{4\pi N}{9kT}\mu^2, \tag{28.4}$$

where μ (Greek, *mu*) is the magnitude of the dipole moment of the substance, N is the Avogadro number, T is the absolute temperature and k is the Boltzmann constant (§ 3d), i.e., the gas constant per single molecule. It follows therefore, that

$$P_M = \frac{D-1}{D+2}\cdot\frac{M}{d} = P_I + P_O = P_I + \frac{4\pi N}{9kT}\mu^2. \tag{28.5}$$

According to the electromagnetic theory of light, the passage of a beam of light through a substance subjects the molecules to an alternating field of high frequency. If the wave length of the light is sufficiently great, e.g., beyond the infrared region, the alternations of the field are slow enough to permit both electrons and nuclei to respond. However, the oscillations are still too fast to permit the permanent dipoles to orient themselves. The dielectric constant measured with such a field would then give, when inserted in the Mosotti-Clausius equation (28.3), only the induced polarization. According to electromagnetic theory, this hypothetical dielectric constant is equal to the square of the refractive index at very long wave lengths, i.e., n_∞^2, so that

$$P_I = \frac{n_\infty^2 - 1}{n_\infty^2 + 2}\cdot\frac{M}{d}. \tag{28.6}$$

If visible light, with a frequency of about 10^{12} kilocycles per sec, were used, only the electrons would respond to the alternations, but not the nuclei. The substitution of the ordinary refractive index, e.g., for the sodium D-line, in equation (28.6) then gives that part of the induced polarization due to the distortion of the electron field; this is called the electron polarization, represented by P_E, so that

$$P_E = \frac{n^2 - 1}{n^2 + 2}\cdot\frac{M}{d} = R_M, \tag{28.7}$$

and comparison with equation (27.5) shows this to be identical with the molar refraction. The total induced polarization includes the atom polarization P_A, due to the distortion of the nuclear charge field, as well as the electron polarization, i.e., $P_I = P_E + P_A$, but since the P_A term is usually a small fraction of P_I it can be ignored. In these circumstances, equation (28.5) may be written as

$$P_M = \frac{D-1}{D+2}\cdot\frac{M}{d} \approx R_M + \frac{4\pi N}{9kT}\mu^2. \tag{28.8}$$

This result is quite general, applying equally to nonpolar and polar molecules;

for the former, however, the permanent dipole moment is zero, and so the last term in equation (28.8) vanishes.

Example: The dielectric constant of cyclohexane is 2.033, the refractive index (D-line) is 1.427 and the density is 0.7784 g cm^{-3} at 20°C. Determine the molar, electron and atom polarizations.

The formula of cyclohexane is C_6H_{12} and so the molecular weight is 84.16; hence, by equation (28.3)

$$P_M = \frac{2.033 - 1}{2.033 + 2} \cdot \frac{84.16}{0.7784} = 27.69 \text{ cc.}$$

By equation (28.7),

$$P_E = \frac{(1.427)^2 - 1}{(1.427)^2 + 2} \cdot \frac{84.16}{0.7784} = 27.75 \text{ cc.}$$

The difference between P_M and P_E is so small, within the limits of experimental error, that the molecule is obviously nonpolar and P_A is negligible.

By using equations (28.5) or (28.8), two methods are possible for the experimental determination of dipole moments. One is to plot P_M, measured at various temperatures, against $1/T$ as in Fig. 28.2. Since R_M, which is equivalent to the induced polarization, is independent of temperature, it follows from equation (28.8) that this plot should be a straight line with a slope of $4\pi N\mu^2/9k$. Hence, if the slope is determined, the dipole moment μ can be readily evaluated. An alternative application of the same principle is to obtain P_M at two temperatures and then to solve equation (28.5) for μ. As mentioned above, the Debye equation (28.4) is applicable only if the dipolar molecules are free to rotate in an electric field. This condition does not hold in liquids because of the interaction of adjacent molecules. The procedure just described, which is capable of giving accurate values for the dipole moment, is thus applied to gases and vapors where the molecules are relatively far apart.

The second method of determining dipole moments is to obtain P_M at a single temperature; then, since R_M can be derived from refractive index measurements, it is a simple matter to evaluate μ from equation (28.8). Some improvement in accuracy is possible if an allowance is made for the atom polarization. But since the value of P_A is not known, the results are inevitably somewhat uncertain. This procedure, which has the great advantage of simplicity, is generally used for measurements on dilute solutions of a polar substance in a nonpolar solvent, e.g., benzene or cyclohexane. Determinations of dielectric constant are made at several concentrations and the molar polarization of the solute is calculated in the following manner. If x_1 and x_2 are the mole fraction of solvent (nonpolar) and solute (polar), respectively, in the solution and M_1 and M_2 are their molecular weights, the polarization $P_{1,2}$ is given by

$$P_{1,2} = \frac{D - 1}{D + 2} \cdot \frac{x_1M_1 + x_2M_2}{d},$$

where D and d now apply to the solution. If the polarizations are additive

$$P_{1,2} = x_1P_1 + x_2P_2,$$

and since P_1 for the nonpolar solvent may be regarded as known, P_2 for the solute can be calculated. The results so obtained are extrapolated graphically or by the use of equations to infinite dilution of the solute to give the P_M value for the latter. The underlying assumption is that at extreme dilutions the polar molecules will not interfere with one another, and the extrapolated molar polarization will satisfy equation (28.4). However, this is not strictly true, because of the presence of the solvent molecules, and the dipole moment obtained from solution measurements are not of a high order of accuracy. Nevertheless, the method is so simple and convenient that it has been widely used.

For the calculation of dipole moments the Boltzmann constant k is expressed in ergs per molecule per degree, i.e., 1.38×10^{-16}; the value of μ is then obtained in terms of esu-cm. The observed moments of polar substances are of the order of 10^{-18} in these units, as is to be anticipated theoretically. Let A and B in Fig. 28.3 represent the normal electrical centers of the positive ($+q$) and negative ($-q$) charges in a polar molecule. The charges are equal in magnitude but opposite in sign since the molecule as a whole is electrically neutral. If r is the distance between A and B, then the dipole moment $\mu = qr$. As a general rule, q is of the order of magnitude of the electronic charge, i.e., about 10^{-10} esu, and r is roughly the distance between atomic centers, i.e., about 10^{-8} cm. Hence, dipole moments may be expected to have values around $10^{-10} \times 10^{-8} = 10^{-18}$ esu-cm.

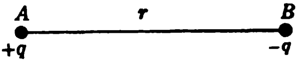


FIG. 28.3. Dipole and dipole moment

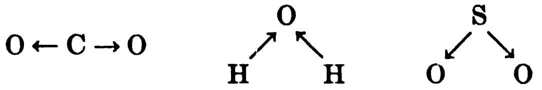
It is the general practice to express dipole moments in **Debye units**, where one such unit is equal to 10^{-18} esu-cm. The dipole moments of a number of polar compounds are recorded in Table 28.2. In addition to the data in the table, it may be noted that hydrogen, nitrogen, carbon dioxide, carbon disulfide, carbon tetrachloride, stannic chloride, boron trichloride, paraffins, cyclohexane and benzene have zero moments. In fact all molecules possessing a center of symmetry are nonpolar; the explanation of this fact is important. It was seen in § 16g that the dipole moment is really a property of every bond between two different atoms; *the observed dipole moment of a molecule is the vector sum of all the individual bond moments,* the term "vector sum" implying

TABLE 28.2. DIPOLE MOMENTS IN THE GASEOUS STATE IN DEBYE UNITS (D)

Water	1.84	Chloroform	1.02	Chlorobenzene	1.70
Ammonia	1.46	Diethyl ether	1.15	Aniline	1.53
Sulfur dioxide	1.63	Ethanol	1.70	Diphenyl ether	1.23
Hydrogen chloride	1.03	Methyl chloride	1.87	Benzonitrile	4.42
Hydrogen bromide	0.80	Acetone	2.88	Nitrobenzene	4.22

that the *direction and magnitude* are taken into account in the summation. In carbon tetrachloride, for example, each C—Cl bond possesses a dipole moment, but since the molecule is symmetrical the four bond moments cancel each other exactly to give a resultant dipole moment of zero. The same is true for stannic chloride and for the hydrocarbons.

The zero dipole moment of carbon dioxide indicates that the molecule is symmetrical and linear, but the association of a definite moment with the water molecule and with sulfur dioxide suggests that these latter substances have angular structures, as indicated in Fig. 28.4. The arrows, which point from the positive to the negative end of the dipoles, indicate the directions of the various bond moments. In carbon dioxide the two C—O bond moments cancel each other exactly, but the vector sums of the O—H moments in water, and of the S—O moments in sulfur dioxide, are not zero, since the molecules are not linear.

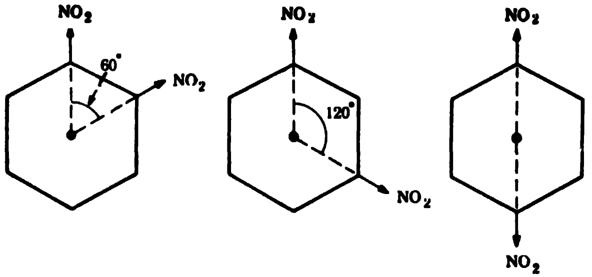


Carbon Dioxide Water Sulfur Dioxide

FIG. 28.4. Bond dipoles

Numerous applications, similar to those just described, have been made of dipole moments in the elucidation of the structures of inorganic and organic molecules; a few illustrations only will be given here. The fact that boron trichloride has a zero moment whereas phosphorus trichloride, and analogous compounds of other elements of Group V, have appreciable moments, suggests that the BCl_3 molecule is flat and symmetrical, but the molecules of PCl_3, $AsCl_3$, NH_3, etc., are not. The latter are probably in the form of triangular pyramids with the phosphorus or similar atom at the apex.

Measurements of dipole moments of benzene derivatives have confirmed that the benzene ring is a planar, regular hexagon, for only upon this basis is it possible to explain quantitatively the observed moments of ortho-, meta- and para-compounds. In ortho-compounds, the bond moments of the two substituent will be coplanar and inclined at an angle of 60° and in the meta-compounds the angle will be 120°. If the two substituents are the same, the para-component should have zero dipole moment. In the example in Fig. 28.5, the observed and calculated values of the dipole moments of the three dinitrobenzenes are given. The calculated values are based on 3.90D for the moment of the $—NO_2$ group. The discrepancy in the case of the ortho-compound which occurs with many of the ortho-substituted substances is attributed to the repulsion between the two groups. This makes the angle between the bond dipoles larger than 60° and the resultant dipole moment is consequently less than expected. It should be mentioned that para-compounds in which the substituent in both positions is —OR or $—NR_2$, do not have zero moments. The reason is that, like H_2O and NH_3 respectively,



μ (obs.)	6.00 D	3.89 D	0 D
μ (calc.)	6.90 D	3.98 D	0 D

FIG. 28.5. Dipole moments of dinitrobenzenes

these groups have an angular structure and the group moment is not directed toward the center of the benzene ring as it is with groups such as —NO$_2$ (see Fig. 28.5), —Cl, —CH$_3$ and —CN.

MOLECULAR SPECTRA

29a. Band Spectra.—The spectra of molecules are often called **band spectra** to distinguish them from the characteristic line spectra of atoms (Chapter 6). It was thought at one time, that the spectra of gaseous molecules were actually in the form of bands, but further more detailed analysis has shown these bands to consist of a large number of closely spaced individual lines. The structure of band spectra has been interpreted by postulating that the electronic, rotational and vibrational energies of molecules are quantized; that is to say, for a given molecular species, these energies can have certain definite values only and do not vary continuously.

A molecule, like an atom, can exist in a number of electronic energy states (or levels) and the change from one particular state to another results from the absorption or emission of a definite amount of energy. As a result, a line of definite frequency should appear in the spectrum. Because of the simultaneous changes which occur in rotational or vibrational energies of the molecule, a number of closely spaced lines actually appear in the form of a band, as will be seen shortly. This system of bands constitutes the **electronic spectrum** of the molecule. Such spectra appear in regions of fairly short wave length, because the energy involved in an electronic transition is relatively large. For colorless substances, the electronic spectra are in the ultraviolet but for colored materials the bands are in the visible region.

In each electronic state, the molecule has a number of possible vibrational energy levels. Further, in each of these vibrational states, a number of values of the rotational energy are possible. The various levels may be represented diagrammatically, as in Fig. 29.1. The two electronic energy levels A and B each have a number of vibrational sublevels, indicated by v = 0, 1, 2, etc., and every one of these has several possible rotational sublevels for which J = 0, 1, 2, etc. The separation of successive vibrational energy states is much less than for the electronic levels, and for the rotational states the energy difference is smaller still.

It is because of the vibrational and rotational energy changes that occur at the same time, that the transition from one electronic state to another produces a spectrum consisting of a number of closely spaced lines, rather than a single line. The set of lines due to rotational energy changes occurring simultaneously with a particular vibrational transition constitutes a band in the spectrum, and each vibrational transition yields a band of this type. The whole set of bands for a given electronic change is called a **band group** or **band system.** Such a band system can be very complex, especially for nonlinear polyatomic molecules which have three modes of rotation and $3n - 6$ modes of vibration, where n is the number of atoms in the molecule (§ 3m).

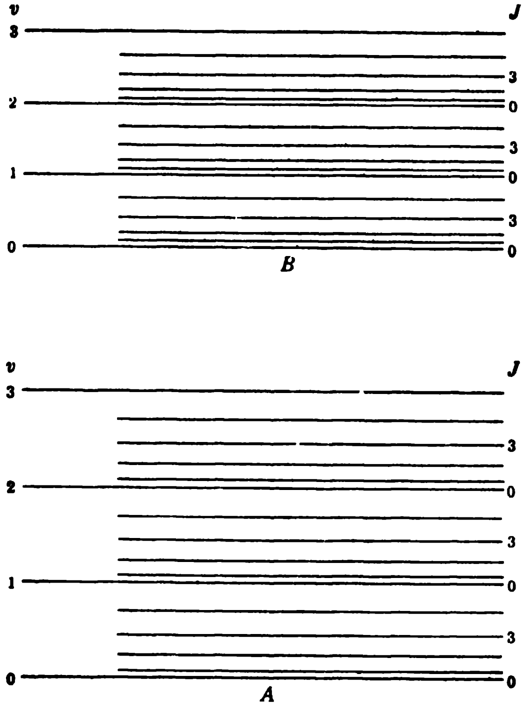


Fig. 29.1. Energy levels in a molecule

29b. Rotational Spectra.—If the energy absorbed by a molecule is sufficient to produce changes in the rotational energy only, without any accompanying vibrational or electronic transition, the resulting spectrum consists of a series of lines called the **rotational spectrum.** Spectra of this type are found in the far infrared, with wave lengths of the order of 10^6 A, i.e.,

10^{-2} cm, or more. According to wave mechanics, the rotational energy E_J of a diatomic molecule is given by

$$E_J = \frac{h^2}{8\pi^2 I} J(J + 1), \tag{29.1}$$

where h is Planck's constant (§ 15b), I is the moment of inertia of the molecule about the axis of rotation and J is the rotational quantum number which may be 0, 1, 2, 3, etc. In the transition from any level J to another level J', the energy change is

$$E_J - E_{J'} = \frac{h^2}{8\pi^2 I}[J(J + 1) - J'(J' + 1)], \tag{29.2}$$

assuming the moment of inertia to be the same in both levels. As a general rule, rotational transitions are restricted to those in which $J - J' = 1$; hence, in this case,

$$E_J - E_{J'} = \frac{h^2}{4\pi^2 I} J. \tag{29.3}$$

By equation (15.8), this is equal to $hc\bar{\nu}$, where $\bar{\nu}$ is the frequency, expressed in wave numbers, of the corresponding line in the rotational spectrum; consequently

$$\bar{\nu} = \frac{h}{4\pi^2 Ic} J, \tag{29.4}$$

where c is the velocity of light.

Since J can take on the values 0, 1, 2, etc., it is evident that the frequency separation of successive lines in the rotational spectrum of a diatomic molecule is $h/4\pi^2 Ic$ cm^{-1}. It is thus possible to determine the moment of inertia of the molecule if the frequency separation can be measured. Actually, because of small changes in the moment of inertia, the separation of successive lines is not constant, but the experimental values can be corrected to give the value for the lowest rotational state. The moment of inertia is related to the masses m_1 and m_2 of the atoms in the diatomic molecule and the distance r between their centers (or nuclei) by

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2. \tag{29.5}$$

Hence, if I is known the value of r can be calculated. Thus, rotational spectra provide a method for determining interatomic distances in molecules. Because of the difficulties of measurement of pure rotational spectra in the far infrared, other spectra, involving rotational transitions, are often used to to provide this information.

Example: The frequency separation of successive line in the rotational spectrum of hydrogen chloride gas has been found to be 20.83 cm^{-1}. Determine the distance between the nuclei of the two atoms in this molecule.

Since the frequency separation is equal to $h/4\pi^2 Ic$, it follows that

$$I \quad \frac{m_1m_2}{m_1 + m_2}r^2 = \frac{h}{4\pi^2c \times 20.83}$$

The mass of an atom is equal to its atomic weight divided by the Avogadro number, $N = 6.023 \times 10^{23}$, so that $m_1 = 1.008/N$ and $m_2 = 35.46/N$; h is 6.625×10^{-27} erg sec and c is 2.998×10^{10} cm sec^{-1}. Upon inserting these values, r^2 is found to be 1.68×10^{-16} cm^2, so that r is 1.28×10^{-8} cm. (The diameter of the hydrogen chloride molecule is thus 2.56 A, which may be compared with the collision diameter of 2.86 A derived from viscosity measurements (§ 3j)).

It should be noted that symmetrical diatomic molecules, such as H_2, O_2, N_2, Cl_2, etc., do not exhibit rotational spectra. In order to do so, the molecule must be polar and possess a permanent dipole movement. However, in an electronic transition, even a nonpolar molecule can undergo changes in rotational energy. Consequently, for such molecules, it is necessary to determine the separation of the rotational lines in a band of the electronic spectrum in order to determine the moment of inertia.

The foregoing discussion has referred specifically to diatomic molecules; these have one mode of rotation in which appreciable changes can occur (§ 3m) and one moment of inertia. More complex molecules can have two or three modes of rotation and an equal number of moments of inertia. The rotational spectra are thus more complex than for a diatomic molecule, but their interpretation and use for the determination of interatomic distances are basically similar to those given above.

29c. Microwave Spectra.—Developments of recent years in microwave techniques, such as are used in radar, have resulted in important contributions to the study of rotational spectra. These microwaves are electromagnetic radiations with wave lengths in the region of 0.1 to 100 cm, and many rotational spectra fall in this range. The method of studying the microwave spectra of gaseous molecules is identical in principle to that employed in other spectroscopic work. The microwaves, produced by a suitable (klystron) oscillator, pass through an absorption cell, consisting of a metal tube containing the experimental gas, and then on to a detector.

In order that transmission through the absorption cell can occur, the diameter of the tube must exceed the microwave length. The frequency (or length) of the microwave is gradually altered and at the same time the extent of absorption is indicated by an oscilloscope attached to the detecting system. The frequencies at which absorption of energy occurs, due to rotational transitions in the molecule, can thus be readily determined. With suitable electronic amplification, absorption of one part in 100,000 can be detected in an absorption path length of 1 meter. The microwave method is thus far more sensitive and much simpler than the infrared grating spectrometer technique formerly used to study rotational spectra.

By determining the separation of the "resonant" frequencies, as they are called, at which absorption occurs, it is possible to determine the moment of inertia and interatomic distances for polar gaseous molecules. The methods used are identical with those described above.

29d. Vibration-Rotation Spectra.—If a molecule absorbs energy sufficient to produce a change from one vibrational state to another, within the same electronic level, the corresponding spectrum appears in the near infrared region. Each vibrational transition is usually accompanied by a number of different changes in the rotational energy, and as a result the spectrum consists of a band made up of a series of closely spaced lines (Fig. 29.2). This is

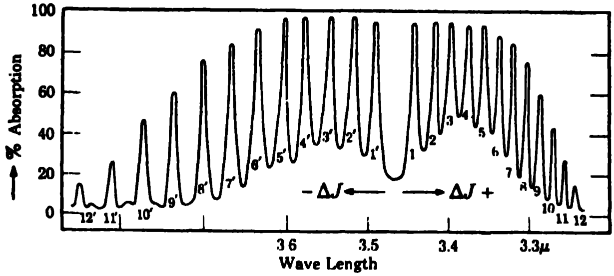


FIG. 29.2. Rotational lines in the 3.46μ vibrational band of gaseous HCl

called a **rotation-vibration spectrum.** For most molecules spectra of this type appear in the region of the infrared with wave lengths from about 10,000 to 30,000 A. As is the case with pure rotation described above, only molecules possessing permanent dipole moments produce rotation-vibration spectra.

Suppose, for simplicity, that the two atoms in a (polar) *diatomic molecule* undergo harmonic oscillations with respect to one another; that is to say, the force tending to restore an atom to its equilibrium position is proportional to the displacement from that position (Hooke's law). Then, according to wave mechanics, the vibrational energy E_v is

$$E_v = (v + \tfrac{1}{2})hc\omega, \tag{29.6}$$

where v is the vibrational quantum number which may be 0, 1, 2, 3, etc., and ω is the vibration frequency (in wave numbers) of the harmonic oscillator; h and c have their usual significance. As a general rule, the vibration of the atoms in a molecule is not strictly harmonic and an additional term of small magnitude should appear in equation (29.6). But this is not important for the present purpose and so it will be ignored.

Attention may be called, in passing, to an interesting aspect of equation (29.6). When $v = 0$ a molecule still possesses vibrational energy, namely,

$$E_0 = \tfrac{1}{2}hc\omega.$$

This is called the **zero-point energy** of the (diatomic) molecule. Thus, even at the absolute zero of temperature, when other forms of motion (rotation and translation) cease, vibration still persists. The energy of the molecule, apart from electronic energy, is then equal to the zero-point energy. This result is in harmony with the uncertainty principle described in § 15e. For, at the absolute zero when the momentum is zero, so that it is known precisely, the position of the atoms is uncertain since they are still oscillating.

In a transition from the vibrational state v to the state v', the energy change is

$$E_v - E_{v'} = [(v + \tfrac{1}{2}) - (v' + \tfrac{1}{2})]hc\omega = (v - v')hc\omega. \tag{29.7}$$

If there is no interaction between the vibrational and rotational motions of the molecule, the change in rotational energy, given by equation (29.3), may be added to, or subtracted from, the value of $E_v - E_{v'}$ to yield the total energy change ΔE in a combined vibration-rotation transition; thus

$$\Delta E = (v - v')hc\omega \pm \frac{h^2}{4\pi^2 I} J,$$

the rotational transition being restricted to cases in which $J - J' = \Delta J = \pm 1$ (see Fig. 29.2).

By equation (15.8), the frequencies of the lines in the spectrum are then given by

$$\bar{\nu} = (v - v')\omega \pm \frac{h}{4\pi^2 Ic} J. \tag{29.8}$$

If the vibrations were harmonic, the only transitions permitted would be those with $v - v' = 1$, so then equation (29.8) would reduce to

$$\bar{\nu} = \omega \pm \frac{h}{4\pi^2 Ic} J. \tag{29.9}$$

For various values of J, namely 0, 1, 2, etc., this expression gives the frequencies of the lines in the **fundamental band** of the vibration-rotation spectrum.* Since the motion is not strictly harmonic, transitions with $v - v' = 2, 3$, etc., occur to some extent, but the probability is less than for $v - v' = 1$. Hence, the spectrum contains a number of bands which are much fainter than the fundamental; these are called **harmonic** or **overtone** bands. As a first approximation the frequencies of the lines in any band can be expressed by replacing ω in equation (29.9) by $n\omega$, where n is 1 for the fundamental, and 2, 3, etc., for the harmonics.

It is seen from equation (29.9) that the frequency separation, in wave numbers, of the rotational lines in a vibration-rotation band is equal to $h/4\pi^2 Ic$. Hence, as is the case for pure rotational spectra, the results may be used to determine the moment of inertia of the molecule and the equilibrium distance between the atomic nuclei.

Further, when $J = 0$, the corresponding spectral frequency $\bar{\nu}$ is equal to the equilibrium vibration frequency ω of the molecule, expressed in cm^{-1} units. Frequently, the $J = 0$ line is missing, but the value of ω can, nevertheless, be readily determined from the frequencies of the lines present in the spectrum. For a harmonic oscillator, the restoring force per unit dis-

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* Strictly speaking the fundamental band is the one for which the vibrational transition is from $v = 0$ to $v' = 1$ in absorption and the reverse in emission.

placement k, generally referred to as the **force constant,** is related to the vibration frequency by

$$k = 4\pi^2\omega^2c^2 \frac{m_1m_2}{m_1 + m_2},$$

where m_1 and m_2 are the masses of the oscillating atoms. Hence, the force constant of a molecule can be determined if ω is known. If cgs units are used for ω, c and m, the result will be expressed in dynes per cm.

The results obtained from the vibration-rotation spectra of the hydrogen halides are collected in Table 29.1. It will be observed that the binding force between the hydrogen and halogen atoms decreases with increasing atomic weight of the latter. This is in agreement with the observed readiness of the molecules to dissociate upon heating.

TABLE 29.1. MOLECULAR CONSTANTS OF HYDROGEN HALIDES FROM VIBRATION-ROTATION SPECTRA

Molecule	ω (cm^{-1})	I (g cm^2)	r (10^{-8} cm)	k (dynes cm^{-1})
Hydrogen fluoride	4141	1.35×10^{-40}	0.92	9.2×10^5
Hydrogen chloride	2989	2.65	1.28	4.8
Hydrogen bromide	2650	3.31	1.42	3.9
Hydrogen iodide	2309	4.22	1.60	3.0

29e. Vibration of Polyatomic Molecules.—It was seen in § 3m that a linear polyatomic molecule has $3n - 5$ modes of vibration and a nonlinear (or bent) molecule has $3n - 6$ modes. Of these $n - 1$ are stretching vibrations and the remainder are bending vibrations. The vibrations of any particular type are, however, not always different, for as a result of symmetry factors two or more vibrational modes may be identical. Such vibrations are said to be **degenerate modes.** For purposes of illustration, the four modes of vibration of a linear triatomic molecule and the three modes of a nonlinear molecule are shown in Fig. 29.3. For the linear molecule, ν_1 and ν_2 are the stretching vibrations and ν_3 and ν_4 the bending vibrations. Actually, ν_3 and ν_4 are identical, one being in a plane at right angles to the other; they are consequently degenerate. There are thus only three different characteristic vibration frequencies of the molecule. For the nonlinear molecule, ν_3 is the stretching vibration; the other two are bending vibrations.

In principle, every mode of vibration of a polyatomic molecule might give rise to a set of vibration-rotation bands. In addition, bands based on combination frequencies often occur, so that the spectra of polyatomic molecules can be quite complex. Actually, some of the vibrational modes of a polyatomic molecule may be inactive. This is the case when the particular vibration is not accompanied by a change in dipole moment. For example, in the symmetrical linear molecule, carbon dioxide, the ν_1 mode is inactive, since the dipole moment remains zero during the vibration; the ν_2 and ν_3 (and ν_4) modes are, however, active. In an unsymmetrical linear molecule, such as

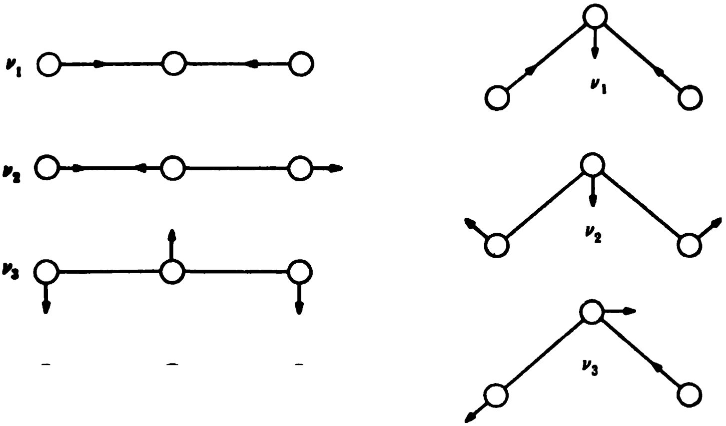

FIG. 29.3. Modes of vibration of triatomic molecules

carbon oxysulfide, on the other hand, the ν_1 mode is also active. It should be mentioned that even if a particular vibrational mode is inactive, it is generally apparent as a combination frequency with one of the active vibrations. Thus, analysis of the spectra of polyatomic molecules, although frequently a difficult undertaking, can be used to evaluate the frequencies of both active and inactive vibrational modes.

29f. The Raman Effect.—A technique for studying vibrational and rotational energy changes in a molecule which does not involve the difficult measurements in the infrared region of the spectrum is based on the **Raman effect.** This was predicted theoretically by A. Smekal (1923) and confirmed experimentally by C. V. Raman (1928). If any substance, gaseous, liquid or even solid, is exposed to light of a certain frequency, then the light scattered at right angles contains frequencies differing from that of the incident light and characteristic of the exposed substance. The series of lines in the scattered light is called the Raman spectrum. If $\bar{\nu}_i$ is the frequency of the incident light and $\bar{\nu}_s$ that of a particular line in the scattered spectrum, the difference $\bar{\nu}_i - \bar{\nu}_s$ is referred to as the Raman frequency. This frequency difference is determined only by the nature of the scattering material and is independent of the frequency of the initial radiation.

The accepted mechanism of the Raman effect is that a molecule absorbs the incident radiation and is thereby raised to a higher energy state; it then emits the Raman scattered radiation and falls to another level, usually somewhat above the initial level. The energy $hc(\bar{\nu}_i - \bar{\nu}_s)$ is then the difference between the initial and final states. In some instances the final level has less energy than the initial value, but such transitions are not common.

An examination of the Raman spectra of many compounds has shown that $hc(\bar{\nu}_i - \bar{\nu}_s)$ almost invariably corresponds to the energy change in a rotational or vibrational transition of the molecule (Fig. 29.1). The latter type of spectra are more common and the Raman frequencies have provided information concerning the vibration frequencies of molecules whose vibration-rotation spectra are very complex. A simple illustration is provided by the Raman spectrum of hydrogen chloride in Fig. 29.4. The incident light is the mercury line of wave length 4046.0 A, so that $\bar{\nu}_i$ is $1/(4046.0 \times 10^{-8}) =$ 24,716 cm^{-1}; the scattered line is at 4581.8 A, i.e., $\bar{\nu}_s$ is $1/(4581.8 \times 10^{-8}) =$ 21,824 cm^{-1}. The difference is 2892 cm^{-1} which is close to the equilibrium vibration frequency (2989 cm^{-1}) given in Table 29.1.

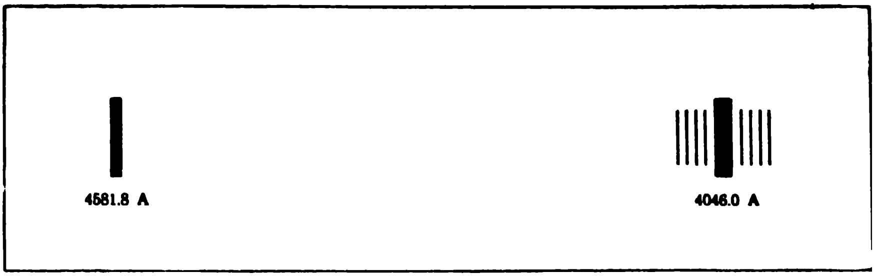

FIG. 29.4. Raman spectrum of gaseous HCl, showing a vibrational and several rotational Raman lines (schematic)

The Raman method of studying spectra has many advantages. It can be used for liquids and solids where ordinary rotational or vibration-rotation spectra are so diffuse as to be of no quantitative value. By appropriate choice of the incident radiation, the scattered lines are brought into a convenient region of the spectrum where they are easily observed. Vibrational modes which are inactive in normal spectra are frequently active in Raman spectra, e.g., vibrations of symmetrical diatomic molecules such as the ν_1 mode (Fig. 29.3) of carbon dioxide. Because of the ease with which the Raman effect can be studied, a large amount of work has been done in this field. References to some results of interest will be made shortly.

29g. Electronic Spectra.—As stated earlier, the electronic spectra of gases, generally appearing in the near ultraviolet region, consist of a number of bands representing different vibrational transitions, the initial state being in one electronic level and the final state in the other level. Each band is made up of a number of fine lines due to changes in rotational energy which occur simultaneously with the electronic and vibrational transitions (Fig. 29.1). Provided the spectra are not too complicated, as they frequently are, and analysis is possible, information concerning vibration frequencies and moments of inertia can be obtained for both upper and lower electronic states. Electronic spectra have advantages over those in the infrared because they can be studied photographically and the line frequencies can be determined with great precision. Further, all vibrational modes, including those of non-polar diatomic molecules, are active and although this makes the spectra complex, they can provide much information.

It is often observed that the bands belonging to a particular group in an electronic spectrum crowd closer and closer together toward the shorter wave length, i.e., higher energy, region of the spectrum. Beyond a certain point the bands merge and the fine structure disappears in a region of continuous absorption. This phenomenon has some features in common with that observed in the spectra of atoms, where the individual lines crowd together and merge into a continuous spectrum beyond the series limits (§ 15a). In atomic spectra, the continuous region is ascribed to the ionization of the atom into an electron and a positive ion. The analogous behavior in molecular spectra is attributed similarly to dissociation of the molecule into separate atoms, so that there are no longer any quantized vibrational levels.

Physically, the occurrence of dissociation in an electronic transition may be described as follows. Since the energy involved in an electronic transition is very much larger than the vibrational energy quantum, i.e., the energy difference between successive vibrational levels, a molecule can acquire a considerable number of such quanta in the transition. As the vibrational energy increases, due to higher and higher vibrational transitions, the vibrations of the molecule become more and more vigorous, the maximum displacement becoming larger and larger. Ultimately, a point is reached when the vibrational energy increase is so great that the molecule flies apart into individual atoms. In other words, the vibrational energy is sufficient to bring about dissociation of the molecule. As there is now no definite vibration of the molecule, there are no vibrational lines (or bands) in the spectrum and so the latter is continuous. Any energy absorbed in excess of that required for dissociation appears as kinetic energy of the separated atoms. The importance of these phenomena to photochemistry will be described in Chapter 17.

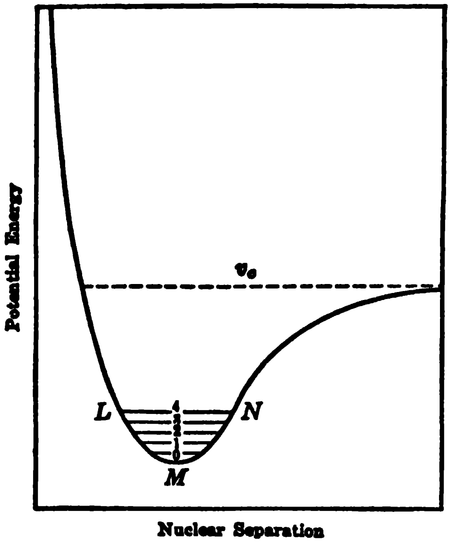

FIG. 29.5. Potential energy curve for diatomic molecule

29h. Potential Energy Curves.—The vibrational behavior of a molecule in a particular electronic state can be conveniently represented by means of a potential energy curve which has some features in common with the curves described in § 4b for the interaction of molecules. The general nature of the variation in potential energy, e.g., for a diatomic molecule, as a function of the nuclear separation is shown in Fig. 29.5. As the atoms are brought together from a distance, the attractive force causes the potential energy to decrease. The minimum at *M* represents the equilibrium distance between the nuclei in the molecule. Any attempt to bring the atoms closer together is opposed by strong repulsive forces and so the potential energy increases sharply.

Since the atoms are always vibrating, the potential energy of the stable molecule will oscillate about the minimum (or equilibrium) position *M*. The vibrational energy levels may thus be indicated by the horizontal lines marked with appropriate quantum numbers. Consider the line *LN*, for example; as the molecule vibrates, the potential energy changes as the nuclei recede and approach, from *L* through *M* to *N*, and back again, and so on. If the motion were simple harmonic, the curve *LMN* would be symmetrical about *M*; this is approximately true for small values of the vibrational quantum number, i.e., for small vibrations. But as the vibrational energy increases, the departure from harmonic behavior becomes increasingly marked. As a consequence, when the vibrational quantum number attains the value indicated by v_c in Fig. 29.5, the nuclear separation will become extremely large during the course of a vibration. In other words, the molecule will then fly apart into separate atoms. It should thus be possible to cause a molecule to dissociate into its constituent atoms by supplying sufficient vibrational energy. This type of dissociation is rare in the normal state of the molecule but, as seen above, it can occur as the result of an electronic transition.

29i. Force Constants and Characteristic Frequencies of Bands.—The force constant for a diatomic molecule can be determined directly from the vibration frequency, as seen in § 29d. For polyatomic molecules, however, there are more unknowns, the force constants, than there are knowns, the frequencies. Certain assumptions, therefore, must be made if the force constants are to be determined, and the most successful of these is to associate a force constant with every valence bond, representing its resistance to stretching, and with every bond angle, which measures the resistance to bending.

The force constant for a given bond type is found to be almost, although not entirely, independent of the nature of the molecule in which it occurs. Some mean values of the force constants of single, double and triple bonds are given in Table 29.2. It is seen that the force constant increases approximately in proportion to the multiplicity of the bond. Thus a determination of the force constant from spectroscopic measurements can often provide information concerning the bond type. In carbon dioxide, for example, the force constant for the carbon-oxygen bonds is 15.2×10^5 dynes cm^{-1}. Comparison with the data in Table 29.2 shows that these bonds are somewhere between double and triple in character. This is in harmony with the resonance structure considered in § 16g.

TABLE 29.2. FORCE CONSTANTS OF VARIOUS BOND TYPES IN DYNES PER CM

Bond	Force Constant	Bond	Force Constant	Bond	Force Constant
C—C	4.6×10^5	C—O	4.9×10^5	C—N	4.8×10^5
C=C	9.5	C=O	12.3	C=N	12.1
C≡C	15.8	C≡O	18.6	C≡N	17.5

Although the vibration frequencies determined from spectra are those of the molecule as a whole, it is often the force constants of particular bonds that have a determining influence on certain frequencies. It has, therefore, become the practice to associate a characteristic frequency with each type of bond. This is an admitted approximation, but it has some useful applications. For the identification of these frequencies, the Raman spectra have been generally employed because of their simplicity. As seen above, the characteristic Raman frequency is often equal to the molecular vibration frequency. The results recorded in Table 29.3 were generally obtained in this manner. Since the force constants and bond frequencies are related, there is a definite parallelism between the data in Tables 29.2 and 29.3.

TABLE 29.3. CHARACTERISTIC FREQUENCIES OF BOND TYPES

Bond	Frequency	Bond	Frequency	Bond	Frequency
C—C	800-860 cm^{-1}	C—O	820-880 cm^{-1}	C—N	880-930 cm^{-1}
C=C	1600-1650	C=O	1710-1750	C=N	1650
C≡C	2100-2250	C≡O	2160	C≡N	2150

The bond frequencies can be employed in the elucidation of molecular structure. For example, the characteristic frequency of the isocyanide group is about 2150 cm^{-1}. This shows that the linkage between carbon and nitrogen must be essentially a triple bond, indicating the structure $—\overset{+}{N}\equiv\overset{-}{C}$ and not —N=C. The carbon-carbon frequency in an aromatic ring is roughly 1600 cm^{-1}, so that all the bonds are essentially double in character. There is no evidence of a single bond, with a frequency in the region of 800 to 850 cm^{-1}. Hence, all the carbon-carbon bonds are equivalent, approximating to double bonds, as is to be expected from the resonance structure (§ 16g).

29j. Ortho- and Para-Hydrogen.—One of the most remarkable discoveries, which had its origin in the study of electronic spectra, is concerned with the ortho- and para-forms of hydrogen molecules. In 1924, R. Mecke observed a marked alternation in the intensities of successive rotational lines in the band spectrum of hydrogen gas. W. Heisenberg (1927) and F. Hund (1928) showed that this result was to be expected, for two molecular forms of hydrogen should exist, depending on the orientation of the nuclear spins. In one form the two hydrogen nuclei have their spins in the same direction; this has subsequently become known as **orthohydrogen.** In the other, the spins are opposed and this form is called **parahydrogen.** Since nuclear spins are difficult to reverse, each kind of hydrogen molecule can retain its spin character even when interacting with radiation.

Theoretical considerations, which are in agreement with observations from band spectra, show that in its normal or low-energy state orthohydrogen can have odd ($J = 1, 3, 5,$ etc.) rotational levels only. On the other hand, parahydrogen is restricted to the zero or even ($J = 0, 2, 4,$ etc.) levels. The alternate rotational lines in the spectrum are thus due to the ortho- and para-molecules, respectively. From the intensities of the lines it is deduced that ordinary hydrogen at normal temperature consists of three parts of orthohydrogen to one of parahydrogen.

As the temperature of the gas is lowered, and the energy content of the molecule decreases, more and more of the molecules are in their lowest rotational energy levels. Near the absolute zero, therefore, the majority of the hydrogen molecules will be in the $J = 0$ state. Since this value of J is possible only for parahydrogen, it is to be expected that as the temperature of hydrogen gas is lowered, the composition will change steadily from the normal ortho- to para-ratio of 3 to 1 to essentially pure parahydrogen. This expectation has been confirmed experimentally, the change in ortho-para ratio being accompanied by changes in the vapor pressure of the liquid hydrogen, in the heat capacity of the gas and in the relative intensities of the rotational lines in the electronic spectrum. Because of the difficulty of reversing nuclear spins the change from ortho- to parahydrogen is relatively slow, but it can be accelerated by various catalysts, especially substances like oxygen, sesquioxides of chromium and the rare earth elements, which are paramagnetic in character.

All diatomic molecules having *identical* atoms with nuclei possessing spin should exist in ortho- and para-forms and exhibit alternation of intensity in the rotational lines. This has been confirmed in a number of cases, e.g., D_2, N_2, Cl_2 and Br_2. Only in the case of hydrogen and deuterium, however, has an appreciable change in the ortho-para ratio been achieved. The deuterium nucleus has a spin of one unit and so the even rotational levels ($J = 0, 2, 4$, etc.) occur in the ortho-state. Consequently, at very low temperatures the deuterium molecules are converted into this form. The oxygen (O^{16}) nucleus has no spin and so ordinary oxygen gas consists of a single form. Actually, the molecules are all in what is equivalent to the ortho-state with $J = 1, 3, 5$, etc., in the lowest electronic (ground) state. The even rotational lines are thus missing from the spectrum.

Certain symmetrical polyatomic molecules, e.g., H_2O and C_2H_2, behave in a similar manner to hydrogen, since the oxygen and carbon nuclei have no spin. The electronic spectra of both water vapor and acetylene show an alternation in intensity of the rotational lines, so that the molecules evidently exist in ortho- and para-states.

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PROBLEMS

1. The dielectric constant of gaseous NH_3 at 1 atm pressure was found to vary with temperature as follows:

°K	241.7	274.4	296.7	371.4	456.9
D	1.009280	1.007132	1.006117	1.004018	1.002734

Determine the dipole moment of ammonia assuming the gas to behave ideally.

2. The dielectric constant and density of solutions of chloroform in the nonpolar solvent n-hexane at 20°C are

Mole fraction $CHCl_3$	0.0517	0.1277	0.2862	0.4953
Dielectric constant	1.976	2.086	2.348	2.800
Density, g cm^{-3}	0.7116	0.7522	0.8462	0.9914

The refractive index, n_D, and density of pure n-hexane at 20° are 1.3754 and 0.6595 g cm^{-3}, respectively, and for pure chloroform, 1.4467 and 1.4895 g cm^{-3}. Determine the dipole moment of chloroform.

3. Calculate the dipole moments of ortho-, meta-, and para-chlorotoluene. The dipole moment of toluene is 0.37D and of chlorobenzene 1.58D.

4. The refractive index of gaseous N_2O at 0°C and 760 mm is 1.000516, and its dielectric constant 1.00100. (*a*) Calculate the dipole moment. (*b*) How are the atoms arranged in the molecule?

5. The density of ether at 20°C is 0.715 g cm^{-3}. Determine its refractive index, n_D.

6. The dielectric constant of the nonpolar liquid carbon disulfide is 2.641 and its density 1.263 g cm^{-3} at 20°C. Determine (*a*) the molar refraction of carbon disulfide and (*b*) the refraction equivalent of sulfur.

7. In the far infrared absorption spectrum of HCl(g), a band appears at 120.4 μ. (*a*) Determine the J value of the band. (*b*) Calculate the frequency of the band for $J = 10$. (*c*) Calculate the moment of inertia.

8. When the Raman spectrum of HCl gas is excited with Hg radiation of 2537 A, a line appears at 2737 A. Determine (*a*) the vibration frequency and (*b*) the force constant of HCl.

9. Calculate the wave lengths of the rotational bands for $J = 1$ in the fundamental vibrational band of HF, using the data of Table 29.1.

10

Free Energy and Chemical Equilibrium

EQUILIBRIUM CONSTANTS

30a. Reversible Reactions.—It is probable that all chemical reactions can take place in both directions, but in many cases the extent of the reverse reaction is so small as to be negligible. Such chemical reactions may thus be regarded as proceeding to completion in one direction. Consider, for example, the reaction between two parts of hydrogen and one part of oxygen; explosion of a mixture of these gases at ordinary temperatures, by means of an electric spark, results in complete conversion into water. There is no detectable residue of the reacting gases, provided they were present in the correct proportion. Nevertheless, at temperatures above about 1500°C, water vapor is decomposed to an appreciable extent into hydrogen and oxygen. The reverse reaction thus definitely occurs at high temperatures, and it undoubtedly takes place to some extent under ordinary conditions. Because this is so small as to be virtually undetectable, the combination of hydrogen and oxygen is regarded as a reaction which proceeds to completion at normal temperatures and pressures.

When the conditions are such that *forward and reverse reactions can both occur to a noticeable extent*, the process is described as a **reversible reaction.*** If such a process takes place in a closed vessel, so that the products of the forward reaction do not escape, the reactants cannot combine completely. As the products accumulate they tend to react so as to reverse the process and regenerate the reacting substances; hence the reaction does not go to completion in either direction. If hydrogen and oxygen were heated together in a closed space at a temperature of 2000°C, for example, some of the reacting gases would remain unchanged, no matter how long the process was allowed to continue. Similarly, to take the case of a reaction which is appreciably reversible at much lower temperatures, a mixture of hydrogen gas and iodine vapor will not unite completely to form hydrogen iodide if heated in a closed vessel at 450°C. In the vicinity of this temperature hydrogen and

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* It should be noted that the term "reversible" is not used here in the thermodynamic sense. A reversible chemical reaction, like other chemical reactions, takes place spontaneously and so the actual process is thermodynamically irreversible. The thermodynamic changes, e.g., ΔF, etc., can be calculated by assuming the reaction to occur in a thermodynamically reversible manner and the results would, of course, be the same for the spontaneous reaction.

iodine react to yield hydrogen iodide, but the latter decomposes to an appreciable extent into its constituent elements; the reversible nature of the reaction is indicated by writing

$$H_2 + I_2 \rightleftharpoons 2HI.$$

Finally, reference may be made to a reversible process occurring in a liquid phase at ordinary temperatures; this is the esterification reaction between ethanol and acetic acid leading to the formation of ethyl acetate and water. If equal molecular amounts of the reactants are taken, the action apparently ceases when only two-thirds of the initial amounts of alcohol and acetic acid have been used up.

It has been found that after the lapse of a sufficient interval of time all reversible reactions reach a state of **chemical equilibrium,** that is, *a state in which no further change in the composition with time can be detected,* provided the temperature and pressure are not altered. If the conditions are properly chosen, *exactly the same state of equilibrium may be attained from either direction for a given reversible reaction.* For example, at a temperature of 425°C, the equilibrium mixture consists of 12 molecular per cent of hydrogen, 12 per cent of iodine vapor and 76 per cent of hydrogen iodide, irrespective of whether the starting point is hydrogen iodide or an equivalent mixture of hydrogen and iodine.

Since the composition of the system at equilibrium undergoes no further change if the temperature and pressure are not altered, there are evidently two possibilities. Either all chemical reaction has ceased entirely so that the system is stationary, or the forward and reverse reactions are taking place simultaneously at exactly the same rate. It is now universally accepted that the latter condition is actually operative and that the system is in a state of **dynamic equilibrium.**

30b. The Law of Mass Action.—The concept of dynamic equilibrium provides a simple means for determining the relationship between the quantities of reacting substances and products that are present at equilibrium. Such a relationship was actually first derived from the second law of thermodynamics (A. Horstmann, 1873; J. H. van't Hoff, 1877), and this, as will be seen below, is independent of any mechanism. Nevertheless, the method based on the so-called **law of mass action** of C. M. Guldberg and P. Waage (1864-1879) is of interest and will be given here. According to this law, in its final form, *the driving force of a chemical reaction is proportional to the active masses of the reacting substances.* If it is assumed that it is the "driving force" which determines the rate of the reaction and that the "active mass" is equivalent to the concentration, then the law is in agreement with present concepts (§ 57a). In the language of modern physical chemistry, therefore, it will be postulated that *the rate of a chemical reaction is proportional to the molar concentration of the reacting substances.*

Consider a perfectly general reversible reaction in which the reactants are the atoms or molecules A and B, and the products are C and D; thus,

$$\mathrm{A + B \rightleftharpoons C + D.}$$

According to the law given above, the rate of the forward reaction will be proportional to the molar concentrations of A and B; if the proportionality constant is taken as k, then

$$\text{Rate of forward reaction} = kc_{\mathrm{A}}c_{\mathrm{B}},$$

where c is used to represent the molar concentration of the species indicated by the subscript. Similarly, the rate of the reverse reaction will be proportional to the molar concentrations of C and D; hence, if k' is the proportionality constant for the reverse reaction,

$$\text{Rate of reverse reaction} = k'c_{\mathrm{C}}c_{\mathrm{D}}.$$

When the state of chemical equilibrium is attained, the rates of forward and reverse reactions must be equal, so that

$$kc_{\mathrm{A}}c_{\mathrm{B}} = k'c_{\mathrm{C}}c_{\mathrm{D}}, \tag{30.1}$$

where the various concentration terms now refer to the values *at equilibrium.* By rearrangement of equation (30.1), it is seen that

$$\frac{c_{\mathrm{C}} \times c_{\mathrm{D}}}{c_{\mathrm{A}} \times c_{\mathrm{B}}} = \frac{k}{k'} = K_c, \tag{30.2}$$

the constant K_c being called the **equilibrium constant** of the reaction, the subscript c indicating that the equilibrium condition is expressed in terms of the concentrations, e.g., moles per liter, of the various species.

In this derivation it has been tacitly assumed that the reactions occur by the direct interaction of A and B on the one hand and C and D on the other hand. It will be seen in Chapter 16 that many apparently simple reactions, e.g., combination of hydrogen and chloride (or bromine), are actually quite complex and take place in stages. The observed reaction rate is then not merely proportional to the product of the concentrations of the reactants. However, any additional terms appearing in the expression for the rate of the forward reaction must also occur in that for the reverse reaction and the net result is the same as in equation (30.2). The situation may be regarded in another way: the state of equilibrium cannot be dependent on the mechanism whereby it is attained. Consequently any reasonable and convenient mechanism may be postulated, as above, to obtain the desired result.

In the foregoing treatment, the process considered has involved only a single molecule of each of the reactants and products. For the general reaction

$$a\mathrm{A} + b\mathrm{B} + \cdots \rightleftharpoons l\mathrm{L} + m\mathrm{M} + \cdots,$$

the expression for the equilibrium constant, in terms of concentration, is

$$\frac{c_{\mathrm{L}}^{l} \times c_{\mathrm{M}}^{m} \times \cdots}{c_{\mathrm{A}}^{a} \times c_{\mathrm{B}}^{b} \times \cdots} = \frac{k}{k'} = K_c. \tag{30.3}$$

It should be noted that the reciprocal of K_c as defined by equation (30.3) would also be a constant; however, the convention adopted by physical chemists when expressing the equilibrium constant of a reaction is to place in the numerator the concentrations of the reaction products, i.e., of the substances on the right-hand side of the reaction as written. If the reaction were written in the opposite direction, viz.,

$$lL + mM + \cdots \rightleftharpoons aA + bB + \cdots,$$

as it might very well be, the equilibrium constant would be inverted, in accordance with convention; thus,

$$K_c \quad \frac{c_A^a \times c_B^b \times \cdots}{c_L^l \times c_M^m \times}$$

As a rule the equilibrium constant varies with the temperature of the reaction; at each temperature the constant K_c will have a definite value, depending on the nature of the reaction. If the reversible process is one whose equilibrium lies well to the side of the products, at the given temperature, e.g., the hydrogen-oxygen reaction below about 2000°C, the equilibrium constant will be large. On the other hand, if the equilibrium constant is small, it follows that in the equilibrium condition the extent of the reverse reaction predominates over that of the forward reaction.

The importance of the foregoing deductions lies in the fact that they have led to a definite connection between the concentrations of the reactants and products of a reversible process when the state of equilibrium is attained. No matter what are the initial amounts of the reacting species, A, B, etc., and whether any or all of the products L, M, etc., are present at the commencement or not, the concentrations at equilibrium must be related to one another in such a way that equation (30.3) holds. Once the value of the equilibrium constant is determined, from a single measurement at a given temperature, it is possible to calculate the composition of the system at equilibrium for any specified initial state at the same temperature. Some examples of this type of calculation will be given later.

30c. Thermodynamic Derivation.—The thermodynamic method for deriving the expression for the equilibrium constant has the great merit of not requiring any postulated reaction mechanism, so that the difficulty mentioned above concerning the expressions for the reaction rates does not arise. Consider the general reaction

$$aA + bB + \cdots \rightleftharpoons lL + mM + \cdots,$$

and suppose that the reactants A, B, etc., and the products L, M, etc., are not necessarily present in their equilibrium amounts, but *in any arbitrarily chosen state.*[*] Since the system under consideration is a mixture whose composition may vary, its thermodynamic properties must be expressed in terms

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[*] The word "state" here refers essentially to the partial pressure or concentration of any substance present in the system; the temperature is regarded as constant.

of the partial molal quantities, as explained in § 7h. If, in the given arbitrary states, the partial molal free energies of the various substances taking part in the reaction are $\mu_A, \mu_B, \cdots, \mu_L, \mu_M, \cdots$, where the μ's are the partial molal free energies or chemical potentials (§ 25f) of the indicated species, then, by equation (7.6),

$$\text{Free energy of products} = l\mu_L + m\mu_M + \cdots$$

$$\text{Free energy of reactants} = a\mu_A + b\mu_B + \cdots$$

The increase of free energy ΔF accompanying the reaction with the reactants and products in the specified states is the difference between these two quantities; hence, at constant temperature and pressure,

$$\Delta F = (l\mu_L + m\mu_M + \cdots) - (a\mu_A + b\mu_B + \cdots). \tag{30.4}$$

The chemical potential of a substance in any state can be expressed in terms of its activity a in that state by means of equation (26.6), i.e.,

$$\mu = \mu^0 + RT \ln a, \tag{30.5}$$

where μ^0 is the chemical potential in the standard state of unit activity. If the values of $\mu_A, \mu_B, \cdots, \mu_L, \mu_M, \cdots$, in equation (30.4) are replaced by the corresponding expressions as derived from equation (30.5), it is seen that

$$\begin{aligned}\Delta F = {} & [l(\mu_L^0 + RT \ln a_L) + m(\mu_M^0 + RT \ln a_M) + \cdots] \\ & - [a(\mu_A^0 + RT \ln a_A) + b(\mu_B^0 + RT \ln a_B) + \cdots],\end{aligned} \tag{30.6}$$

where $a_A, a_B, \cdots, a_L, a_M, \cdots$, are the activities of the various substances involved in the reaction *in their arbitrary states.* Upon rearranging equation (30.6), the result is

$$\Delta F = \Delta F^0 + RT \ln \frac{a_L^l \times a_M^m \times \cdots}{a_A^a \times a_B^b \times \cdots}, \tag{30.7}$$

where ΔF^0, the increase in free energy accompanying the reaction when all the reactants and products are *in their respective standard states,* is given by an equation analogous to (30.4), viz.,

$$\Delta F^0 = (l\mu_L^0 + m\mu_M^0 + \cdots) - (a\mu_A^0 + b\mu_B^0 + \cdots). \tag{30.8}$$

It was seen in § 9b that for a system in equilibrium the free energy change ΔF is zero, provided the temperature and pressure at equilibrium are not allowed to alter. Consequently, when the arbitrarily chosen conditions represent those for equilibrium, ΔF in equation (30.7) may be put equal to zero, so that

$$\Delta F^0 = -RT \ln \left(\frac{a_L^l \times a_M^m \times \cdots}{a_A^a \times a_B^b \times \cdots}\right)_e, \tag{30.9}$$

where the subscript e indicates that *the activities are those for the system at equilibrium.* Since the standard free energy change ΔF^0 refers to the reactants and products in the definite states of unit activity, it is apparent that ΔF^0 must be constant; consequently, the right-hand side of equation (30.9) must also be constant. The gas constant R has, of course, a definite value, and so it follows that if the temperature T is constant,

$$\left(\frac{a_{\mathrm{L}}^{l} \times a_{\mathrm{M}}^{m} \times \cdots}{a_{\mathrm{A}}^{a} \times a_{\mathrm{B}}^{b} \times \cdots}\right)_{e} = \text{constant} = K, \tag{30.10}$$

where K is the equilibrium constant for the reaction. This result is applicable to reversible reactions of all types, irrespective of whether gases, liquids or solids are involved.

30d. Forms of the Equilibrium Constant: Gas Reactions.—If the reactants A, B, etc., and the products L, M, etc., of the reaction are *ideal gases or approximate closely to ideal behavior*, the activity of each substance is proportional to its partial pressure and also to its molar concentration. For an ideal system it is thus possible to write equation (30.10) for the equilibrium constant in the alternative forms, viz.,

$$K_p = \frac{p_{\mathrm{L}}^{l} \times p_{\mathrm{M}}^{m} \times}{p_{\mathrm{A}}^{a} \times p_{\mathrm{B}}^{b} \times \cdots} \tag{30.11}$$

and

$$K_c = \frac{c_{\mathrm{L}}^{l} \times c_{\mathrm{M}}^{m} \times \cdots}{c_{\mathrm{A}}^{a} \times c_{\mathrm{B}}^{b} \times \cdots}, \tag{30.12}$$

where the p and c terms are the partial pressures and concentrations, respectively, at equilibrium. The two equilibrium constants are represented by K_p and K_c; they are frequently referred to as "classical" constants in contrast to the thermodynamic constant K, defined by equation (30.10). In the expression for K_p the various activity terms are replaced by the corresponding partial pressures, while in that for K_c concentrations, in moles per unit volume, are used. It should be mentioned that equations (30.11) and (30.12) are applicable only to a system involving ideal gases. For real gases, the actual concentration (or partial pressure) must be replaced by the activity, or fugacity, which may be regarded as an ideal concentration (or ideal partial pressure).

If the reaction takes place at moderate pressures and relatively high temperatures, the deviations from ideal behavior are not great, and equations (30.11) and (30.12) may be employed with a fair degree of accuracy. Under these conditions the values of K_p and K_c are found to be almost independent of the pressure, as they should be. At high pressures, however, when the departure from ideal behavior is appreciable, the substitution of concentration or partial pressure for activity is no longer justifiable; in these circumstances K_p and K_c derived from equations (30.11) and (30.12) vary with the pressure. The true or thermodynamic equilibrium constant, as given by equation (30.10), is an exact constant, and does not depend in any way on the pressure.

In the subsequent treatment it will be assumed, as a first approximation, that the gases concerned do not deviate markedly from ideal behavior under the experimental conditions existing at equilibrium. It will then be possible to utilize equations (30.11) and (30.12) to express the equilibrium constants with respect to partial pressures and concentrations, respectively. A simple relationship between K_p and K_c can be readily obtained, as follows. By equation (2.21) the partial pressure p_i of any gas in a mixture of ideal gases occupying a total volume v at the temperature T is related to the number of moles n_i of the given gas by the expression

$$p_iv = n_iRT,$$

$$p_i = \frac{n_i}{v}RT. \qquad (30.13)$$

The quantity n_i/v is equal to the number of moles in unit volume, and this is the same as the molar concentration c_i; it follows, therefore, that

$$p_i = c_iRT. \qquad (30.14)$$

If the equilibrium partial pressures in equation (30.11) are replaced by the corresponding values of cRT, according to equation (30.14), it is seen that

$$K_p = \frac{c_{\text{L}}^l \times c_{\text{M}}^m \times \cdots}{c_{\text{A}}^a \times c_{\text{B}}^b \times \cdots} \times \frac{(RT)^{l+m+\cdots}}{(RT)^{a+b+\cdots}} = K_c(RT)^{[(l+m+\cdots)-(a+b+\cdots)]}$$

$$= K_c(RT)^{\Delta n}, \qquad (30.15)$$

where $\Delta n = (l + m + \cdots) - (a + b + \cdots)$ is equal to the increase in the number of molecules in the chemical reaction as written. If the reaction is one in which the number of molecules of reactant is equal to the number of molecules of products, Δn is zero; for such a reaction K_p and K_c are identical.

Example: For the reversible reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at 500°C, the value of K_p, with partial pressures in atm, is 1.44×10^{-5} at low pressures, where the gases behave almost ideally. Calculate the corresponding value of K_c with concentrations in moles per liter.

Since the pressures in K_p are in atm, while K_c is required in terms of moles per liter, it can be seen from equations (30.13) or (30.14) that R must be in liter-atm deg^{-1} mole^{-1}, i.e., 0.0820. Further, Δn is here equal to $2 - 4$, i.e., -2; T is $273 + 500 = 773$°K; hence, by equation (30.15),

$$K_p = K_c \times (0.0820 \times 773)^{-2},$$

$$K_c = 1.44 \times 10^{-5}/(0.0820 \times 773)^{-2} = 5.79 \times 10^{-2}.$$

30e. Experimental Determination of Equilibrium Constants.—The experimental method used for the determination of the equilibrium constant of a gas reaction depends on the nature of the reaction and the temperature. Two types of procedure have been most generally employed. In the first of these the reacting substances are sealed into glass or silica bulbs, and are heated at the required temperature for sufficient time for equilibrium to be established. The bulbs are then cooled very rapidly so as to fix or "freeze" the equilibrium, and the contents are analyzed in some convenient manner. The second procedure is the "flow method," in which the gases are passed through a tube, frequently containing a catalyst, heated to the appropriate temperature. The catalyst facilitates the attainment of equilibrium without affecting its position (§ 60a). The exit gases are cooled rapidly by passing through a capillary tube, and they are then collected and analyzed.

In the experiments just described it is, of course, essential that a state of equilibrium should be reached before the composition of the system is determined by analysis. The chief criterion of chemical equilibrium is that the same condition is approached from either side of the reaction (§ 30a) and that it does not change further with time, in the case of the observations made with sealed bulbs, or with decreasing rate of passage of the gases in the flow method. From the analytically determined concentrations of the reactants and products in the system when equilibrium is attained, the equilibrium constant can be calculated by means of equation (30.12).

If the reaction being studied is accompanied by a change in the number of molecules, the equilibrium constant can sometimes be determined by measurements of the volume occupied by a known mass at a given pressure and temperature. In other words, vapor density measurements, such as those described in § 5d, may be employed. When a substance dissociates in the vapor state, the fraction of dissociation can be determined from the experimental pressure, volume and temperature data. It will be shown below that provided equilibrium is attained in the vapor, the dissociation fraction can be used to calculate the equilibrium constant.

30f. The Le Chatelier Principle.—It will be seen subsequently that the effect of temperature and pressure on the position of equilibrium of a reversible reaction can be calculated quantitatively. In the meantime it is of interest to consider a convenient rule, known as the **Le Chatelier principle,** whereby the same general conclusions may be reached in a qualitative manner. The principle, which is based fundamentally on the second law of thermodynamics, may be stated in the following form. *If a change occurs in one of the factors, such as temperature or pressure, under which a system is in equilibrium, the system will tend to adjust itself so as to annul, as far as possible, the effect of that change.* Consider, first, the effect of pressure on the position of equilibrium: an increase in pressure will cause the composition of the equilibrium system to change in such a manner as to decrease the number of molecules, since this implies a tendency for the pressure to decrease. Similarly, an increase of temperature will change the composition at equilibrium in the direction leading to an absorption of heat. Specific examples of the application of the Le Chatelier principle will be given later in this chapter.

HOMOGENEOUS GASEOUS EQUILIBRIA

31a. Reactions without Change in the Number of Molecules.—It is convenient to consider homogeneous reversible reactions, involving gases only, under two main headings; first, reactions in which the number of molecules of reactants is the same as the number of molecules of products and, second, those in which there is a change in the number of molecules. Instances of the former type of equilibria will be discussed in this section. One of the most completely studied reversible reactions between gases is that involving gaseous hydrogen and iodine, on the one hand, and hydrogen iodide, on the other hand, viz.,

$$H_2 + I_2 \rightleftharpoons 2HI.$$

In this case a total of two gaseous molecules of reactants produce two gaseous molecules of product, so that there is no net change in the number of molecules, i.e., Δn is zero. As seen in § 30d, for reversible reactions of this type the equilibrium constants K_p and K_c will be identical; it is thus immaterial which is considered, since the results will be the same in each case, and in any event the subscript p or c may be omitted.

The equilibrium constant for the reaction under consideration is determined by heating mixtures of hydrogen and iodine at a constant temperature, and analyzing the system when equilibrium is reached. The results are confirmed by approaching the equilibrium from the opposite direction, by starting with hydrogen iodide alone and determining the amounts of hydrogen and iodine formed. If n_{H_2}, n_{I_2} and n_{HI} are the numbers of moles of hydrogen, iodine and hydrogen iodide, respectively, present at equilibrium, and v is the volume of the system, the respective molar concentrations are then

$$c_{H_2} = \frac{n_{H_2}}{v}, \qquad c_{I_2} = \frac{n_{I_2}}{v} \qquad \text{and} \qquad c_{HI} = \frac{n_{HI}}{v}.$$

The equilibrium constant for the reaction, omitting the subscript, is thus

$$K = \frac{c_{HI}^2}{c_{H_2} \times c_{I_2}} = \frac{(n_{HI}/v)^2}{(n_{H_2}/v)(n_{I_2}/v)}$$

$$= \frac{n_{HI}^2}{n_{H_2} \times n_{I_2}}. \tag{31.1}$$

It will be noted that the volume v has disappeared from the final result, and hence need not be known. This is characteristic of all reactions in which the number of molecules remains unchanged; the volume factor appears an equal number of times in the numerator and denominator of the expression for the equilibrium constant, and hence the values cancel each other.

The accuracy of equation (31.1) was first confirmed by the classical work of M. Bodenstein (1897), but the results of the more recent experiments of A. H. Taylor and R. H. Crist (1941) at 457.6°C are quoted in Table 31.1. The approximate constancy of the figures in the last column, in spite of the variations in the amounts of the substances present at equilibrium, is a satisfactory verification of equation (31.1). The equilibrium constant for the reaction as written above is thus 48.7 at 457.6°C.

Once the equilibrium constant for the reaction is known, it is possible to calculate the composition of the equilibrium system for any given initial

TABLE 31.1. THE HYDROGEN-IODINE-HYDROGEN IODIDE REACTION AT 457.6°C

$c_{H_2} \times 10^2$ mole liter^{-1}	$c_{I_2} \times 10^2$ mole liter^{-1}	$c_{HI} \times 10^2$ mole liter^{-1}	K
0.5617	0.05936	1.270	48.38*
0.3841	0.1524	1.687	48.61*
0.4580	0.09733	1.486	49.54*
0.1696	0.1696	1.181	48.48†
0.1433	0.1433	1.000	48.71†
0.4213	0.4213	2.943	48.81†

* Equilibrium approached from hydrogen and iodine.

† Equilibrium approached from hydrogen iodide.

conditions, at the same temperature. Suppose a mixture of a moles of hydrogen and b moles of iodine vapor are heated together until equilibrium is attained; at this point it is found that y moles of each have disappeared, thus producing $2y$ moles of hydrogen iodide. At equilibrium, therefore, the system contains $a - y$ moles of hydrogen, $b - y$ moles of iodine vapor and $2y$ moles of hydrogen iodide. Insertion of these values for n_{H_2}, n_{I_2} and n_{HI}, respectively, in equation (31.1) then gives

$$K = \frac{4y^2}{(a - y)(b - y)}. \tag{31.2}$$

If the initial amounts a and b of hydrogen and iodine are known, in addition to the equilibrium constant, it is obviously possible to evaluate y by means of equation (31.2); the number of moles of hydrogen iodide present at equilibrium is then $2y$.

Example: A mixture of 1.24×10^{-2} mole of H_2 and 2.46×10^{-2} mole of I_2 was heated at 457.6°C until equilibrium was attained; how many moles of HI were then present?

Let $2y$ represent the number of moles of HI formed at equilibrium; the number of moles of H_2 remaining will then be $0.0124 - y$, while the number of moles of I_2 will be $0.0246 - y$. Since the equilibrium constant K, from Table 31.1, is 48.7 at 457.6°C, it follows, by equation (31.2) that

$$K = 48.7 = \frac{4y^2}{(0.0124 - y)(0.0246 - y)}.$$

The two solutions of this quadratic equation are

$$2y = 5.75 \times 10^{-2} \quad \text{and} \quad 2y = 2.31 \times 10^{-2} \text{ mole.}$$

The former of these has obviously no physical significance as it is larger than twice the initial amount of either H_2 or I_2; it follows, therefore, that 2.31×10^{-2} mole of HI is present at equilibrium.

According to the principle of Le Chatelier, pressure should have no effect on the equilibrium composition at a given temperature. Since there is no variation in the number of molecules accompanying the reaction, it is evident that the system is not able to adjust itself so as to counteract an increase or decrease of external pressure. It is to be expected, therefore, that change of pressure should not alter the position of equilibrium; this has been confirmed experimentally. The same conclusion may be drawn from an examination of the equilibrium constant expressed in terms of partial pressures, viz.,

$$K = \frac{p_{\mathrm{HI}}^2}{p_{\mathrm{H}_2} \times p_{\mathrm{I}_2}} \tag{31.3}$$

The partial pressure of any gas in a mixture, as given by equation (2.24) or (2.25), is equal to the product of the total pressure P and the mole fraction of that gas, where the mole fraction is equal to the number of moles of the gas divided by the total number in the mixture. It follows, therefore, that the equilibrium partial pressures of hydrogen, iodine and hydrogen iodide, respectively, are

$$p_{\mathrm{H}_2} = \frac{n_{\mathrm{H}_2}}{N} P, \qquad p_{\mathrm{I}_2} = \frac{n_{\mathrm{I}_2}}{N} P \qquad \text{and} \qquad p_{\mathrm{HI}} = \frac{n_{\mathrm{HI}}}{N} P,$$

where N is equal to the total number of molecules, i.e., $n_{\mathrm{H}_2} + n_{\mathrm{I}_2} + n_{\mathrm{HI}}$. If these partial pressures are inserted into equation (31.3) the result is

$$K = \frac{\left(\frac{n_{\mathrm{HI}}}{N} P\right)^2}{\frac{n_{\mathrm{H}_2}}{N} P \times \frac{n_{\mathrm{I}_2}}{N} P} = \frac{n_{\mathrm{HI}}^2}{n_{\mathrm{H}_2} \times n_{\mathrm{I}_2}}. \tag{31.4}$$

This quantity is, as it should be, indentical with equation (31.1), but the point to which attention must be called is that the P, i.e., the total (or external) pressure, factors have cancelled one another. In other words, the composition of the system at equilibrium, as represented by n_{H_2}, n_{I_2} and n_{HI}, is independent of the external pressure. Exactly the same result holds for any reaction in which there are equal numbers of molecules on both sides of the chemical equation. The expression for the partial pressure equilibrium constant will have an equal number of P factors in the numerator and denominator, and the equilibrium composition of the system will thus be unaffected by the total pressure.

The reversible reaction

$$\mathrm{CO}_2 + \mathrm{H}_2 \rightleftharpoons \mathrm{CO} + \mathrm{H}_2\mathrm{O},$$

in which the water is present in the gaseous state, is one of considerable importance; it is generally known as the "water gas" reaction. The equilibrium constant is given by

$$K = \frac{n_{\mathrm{CO}} \times n_{\mathrm{H}_2\mathrm{O}}}{n_{\mathrm{CO}_2} \times n_{\mathrm{H}_2}}, \tag{31.5}$$

where, as before, the n's are the numbers of moles of the indicated species present at equilibrium.

Example: Starting with equimolar amounts of carbon monoxide and steam, calculate the molar percentage composition of the water gas system at equilibrium at 1000°K; the equilibrium constant at this temperature is 0.719.

Since the numbers of moles of CO and H_2O are equal at the commencement, they must obviously remain equal throughout the reaction; let these values be n_1 at equilibrium. Similarly, the numbers of moles of CO_2 and H_2 must be equal; let these be n_2 at equilibrium. It follows then from the expression for the equilibrium constant, i.e., equation (31.5),

$$K = 0.719 = \frac{n_1^2}{n_2^2},$$

$$\frac{n_1}{n_2} = \sqrt{0.719} = 0.848.$$

The amounts of CO, H_2O, CO_2 and H_2 at equilibrium are therefore present in the molar ratio of 0.848:0.848:1.00:1.00; the molar percentages of CO and H_2O are consequently each

$$\frac{0.848}{(2 \times 0.848) + (2 \times 1.00)} \times 100 = 22.9\%.$$

The molar percentages of CO_2 and H_2 are then each 27.1%. The composition of the water gas at equilibrium at 1000°K is thus CO, 22.9; H_2O, 22.9; CO_2, 27.1; H_2, 27.1 moles per cent.

31b. Reactions with Change in the Number of Molecules.—For gaseous reactions in which the numbers of molecules of reactants and of products are different, the composition of the system at equilibrium depends on the total pressure. This is in harmony with the principle of Le Chatelier, which requires an increase of external pressure to be accompanied by such a shift of the equilibrium composition as will decrease the total number of molecules present. It is important to understand that *the pressure merely changes the position of equilibrium, i.e., the composition of the system at equilibrium; the equilibrium constant is, however, unaffected by the external (total) pressure.* The concentrations or partial pressures of the various constituents must adjust themselves when the total pressure is changed so as to leave the equilibrium constant unaffected.

The dissociation of nitrogen tetroxide to form nitrogen dioxide, viz.,

$$N_2O_4 \rightleftharpoons 2NO_2,$$

is a simple instance of a reversible reaction in which there is a change in the number of molecules. The equilibrium constant K_p in terms of partial pressures is given by

$$K_p = \frac{p_{NO_2}^2}{p_{N_2O_4}}. \qquad (31.6)$$

In this case, of course, K_p and K_c must be distinguished; the increase Δn in the number of molecules in the reaction is equal to 2 − 1, i.e., 1, and hence by equation (32.9), K_p is equal to $K_c \times RT$. Since it is the common practice to use K_p for equilibria involving gases, this form of the equilibrium constant will be employed in the subsequent discussion.

If $n_{N_2O_4}$ and n_{NO_2} are the numbers of moles of gaseous tetroxide and dioxide present in the system at equilibrium, and N, equal to $n_{N_2O_4} + n_{NO_2}$, is the total number of moles, the respective partial pressures are defined by

$$p_{N_2O_4} = \frac{n_{N_2O_4}}{N} P \quad \text{and} \quad p_{NO_2} = \frac{n_{NO_2}}{N} P,$$

where P is the total pressure. Insertion of these values into equation (31.6) then gives

$$K_p = \frac{\left(\dfrac{n_{NO_2}}{N} P\right)^2}{\dfrac{n_{N_2O_4}}{N} P} = \frac{n^2_{NO_2}}{n_{N_2O_4} \times N} P. \tag{31.7}$$

It will be observed that the expression for K_p now contains the value of the total pressure P. Since K_p is a constant, it follows that the numbers of moles n_{NO_2} and $n_{N_2O_4}$ at equilibrium must adjust themselves as the pressure is altered. It is apparent from equation (31.7) that if P is increased, n_{NO_2} might be expected to decrease while $n_{N_2O_4}$ increases in order to maintain K_p constant. That is to say, increase of pressure should displace the equilibrium in the direction of the nitrogen tetroxide, i.e., to the left of the reaction as written above. This is in the direction of a decrease in the number of molecules, as required by the Le Chatelier principle. However, while this principle merely indicates the direction in which the equilibrium is shifted, equation (31.7) permits the actual equilibrium composition at any pressure to be calculated, provided the value of K_p is known, at the same temperature.

For this purpose, the equilibrium constant K_p may be expressed in a somewhat different form. Suppose the system contains initially 1 mole of N_2O_4, and let α be the fraction that has dissociated into NO_2 when equilibrium is attained; there are then $1 - \alpha$ moles of undissociated N_2O_4 and 2α moles of NO_2 in the given volume. The total number of moles is $1 - \alpha + 2\alpha$, i.e., $1 + \alpha$, at equilibrium; hence, the partial pressures of N_2O_4 and NO_2 are

$$p_{N_2O_4} = \frac{1 - \alpha}{1 + \alpha} P \quad \text{and} \quad p_{NO_2} = \frac{2\alpha}{1 + \alpha} P,$$

respectively, where P is the total pressure. Introducing these values into equation (31.6) the expression for the equilibrium constant becomes

$$K_p = \frac{\left(\dfrac{2\alpha}{1 + \alpha}\right)^2 P^2}{\left(\dfrac{1 - \alpha}{1 + \alpha}\right) P} = \frac{4\alpha^2 P}{1 - \alpha^2}. \tag{31.8}$$

It is evident from this result that if K_p is known the fraction of the N_2O_4 dissociated at equilibrium, and hence the composition of the system, can be readily calculated at any pressure. Such calculations are, of course, based on the fundamental assumption that the gases behave ideally over the whole range of pressure concerned. Provided the reaction is accompanied by a change in the number of molecules, as it is in the dissociation of N_2O_4, the degree of dissociation can be determined from pressure-volume (or vapor density) measurements in the following manner. Consider a perfectly general case in which one molecule of the substance under examination dissociates into m molecules of product when completely dissociated. If α is the fraction of the material that has dissociated, at the experimental temperature and pressure, then for every molecule of original substance, $1 - \alpha$ will remain undissociated while $m\alpha$ molecules of products are formed; the total number of moles in the vapor will thus be $1 - \alpha + m\alpha$ for every 1 mole expected theoretically if there were no dissociation. If w grams of a substance of molecular weight M_0 occupy a volume v_0, at a temperature T and pressure P, when no dissociation occurs, then by equation (5.2), assuming ideal behavior,

$$Pv_0 = \frac{w}{M_0} RT.$$

As a result of dissociation, however, the number of moles, i.e., w/M_0, is increased by a factor of $1 - \alpha + m\alpha$, as shown above; the volume v occupied by the dissociated vapor is then determined by

$$Pv = \frac{w}{M_0}(1 - \alpha + m\alpha)RT. \tag{31.9}$$

From this equation it is possible to calculate the fraction of dissociation α at any temperature and pressure from a knowledge of the volume v occupied by a known weight w of the substance as vapor; M_0 is the theoretical molecular weight.

Example: In a vapor density experiment, 1.35 gram of nitrogen tetroxide (N_2O_4) was found to occupy a volume of 0.501 liter at 45°C and a pressure of 795 mm. Calculate the value of K_p at this temperature.

The dissociation reaction is $N_2O_4 = 2NO_2$, and since 1 molecule of N_2O_4 dissociates into 2 molecules of NO_2, the value of m is 2; equation (31.9) therefore becomes

$$Pv = \frac{w}{M_0}(1 + \alpha)RT.$$

The simplest units to employ are P in atm and v in liters, so that R is 0.0820 liter-atm deg^{-1} mole^{-1}; P is then 795/760 atm, v is 0.501 liter, T is $273 + 45 = 318$°K, w is 1.35 g and M_0, for N_2O_4, is 92.0. Substitution in the above equation gives

$$\frac{795}{760} \times 0.501 = \frac{1.35}{92.0}(1 + \alpha) \times 0.0820 \times 318$$

$$\alpha = 0.370.$$

Upon inserting this value for α into equation (31.8) and setting $P = 795/760$ atm, the result is

$$K_p \quad \frac{4 \times (0.370)^2 \times (795/760)}{1 - (0.370)^2} \quad 0.664$$

Example: Calculate the fraction of dissociation of N_2O_4 at 45°C and a total pressure of 10 atm, assuming ideal behavior. Show that the result is in agreement with the Le Chatelier principle.

From equation (31.8) it is seen that

$$\alpha = \sqrt{\frac{K_p}{4P + K_p}},$$

and since K_p at 45°C is 0.664, as obtained from the preceding example, it follows that at a pressure of 10 atm,

$$\alpha = \sqrt{\frac{0.664}{(4 \times 10) + 0.664}} = 0.128.$$

Comparison of this result with the value of α at a pressure of 1 atm, viz., 0.378, shows that increase of pressure is accompanied by a decrease in the extent to which N_2O_4 is dissociated into NO_2; higher pressures thus favor the formation of N_2O_4, as required by the Le Chatelier principle.

Another familiar reversible gas reaction in which there is a change in the number of molecules is the dissociation of phosphorus pentachloride, viz.,

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2.$$

In this case, as in the previous one, increase of pressure moves the position of equilibrium in the direction of the smaller number of molecules, i.e., to the left in the reaction as written, and hence causes a decrease in the extent of dissociation. An expression for the dissociation constant may be obtained in the same manner. If α is the fraction of PCl_5 dissociated, the equilibrium constant K_p for the reaction is,

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PC}} = \frac{\alpha^2 P}{1 - \alpha^2}. \tag{31.10}$$

It is thus possible to calculate the equilibrium constant from the experimentally determined fraction of dissociation at a known total pressure.

The variation of α with pressure may be derived by solving equation (31.10); thus,

$$\alpha = \sqrt{\frac{K_p}{K_p + P}}. \tag{31.11}$$

If the pressure P is high it is often possible to neglect K_p in comparison with P in the denominator of this expression; it then reduces to the simple form $\alpha = \sqrt{K_p/P}$. It is obvious from these results that the extent to which phosphorus pentachloride dissociates must decrease with increasing pressure, as deduced above from the Le Chatelier principle.

A reversible reaction of great industrial importance is the combination of nitrogen and hydrogen to yield ammonia; thus

$$N_2 + 3H_2 \rightleftharpoons 2NH_3.$$

It is evident from the principle of Le Chatelier that the formation of ammonia at equilibrium should be favored by an increase of pressure, and high pressures, 200 atm or more, are used in practice.

Example: In a mixture of 1 part of N_2 to 3 parts of H_2, the mole per cent of NH_3 at equilibrium was found to be 1.20 at 500°C and a total pressure of 10 atm. Calculate the value of K_p and the pressure at which the equilibrium mixture at this temperature contains 10.4 mole per cent of NH_3.

Let x be the mole fraction of NH_3 at equilibrium, so that $100x$ is the mole per cent. The sum of the mole fractions of N_2 and H_2 must then be $1 - x$, and since these gases are in the ratio of 1 to 3, it follows that

$$x_{N_2} = \tfrac{1}{4}(1 - x) \qquad \text{and} \qquad x_{H_2} = \tfrac{3}{4}(1 - x)$$

and so, if P is the total pressure,

$$K_p = \frac{p^2_{NH_3}}{p_{N_2} \times p^3_{H_2}} = \frac{(xP)^2}{\tfrac{1}{4}(1 - x)P \times [\tfrac{3}{4}(1 - x)P]^3}.$$

In the present example, P is 10 atm; $100x$ is 1.20 so that $x = 0.0120$ and $1 - x = 0.988$. Consequently

$$K_p = \frac{(0.0120 \times 10)^2}{(\tfrac{1}{4} \times 0.988 \times 10) \times (\tfrac{3}{4} \times 0.988 \times 10)^3} = 1.43 \times 10^{-5}$$

with the pressure in atm. It is now required to calculate P corresponding to $100x$ 10.4, i.e., $x = 0.104$ and $1 - x = 0.896$; thus,

$$K_p = 1.43 \times 10^{-5} = \frac{(0.104 \times P)^2}{(\tfrac{1}{4} \times 0.896 \times P) \times (\tfrac{3}{4} \times 0.896 \times P)^3}$$

$$P = 105 \text{ atm}.$$

(It may be noted that experimentally $100x$ is found to be 10.4 at 100 atm. The difference between this pressure and the calculated value of 105 atm is to be ascribed to departure of the gases, particularly the ammonia, from ideal behavior at these high pressures.)

31c. Influence of Products and Inert Gases on Dissociation.—As a consequence of the fact that the composition of a system at equilibrium is always determined by the equilibrium constant, it follows that the presence of one or other of the products of a particular dissociation will repress that dissociation. For example, if phosphorus pentachloride is vaporized into a space containing chlorine gas, the extent to which the pentachloride dissociates will be less than if the chlorine were not initially present. The reason for this may be readily seen by considering the general dissociation reaction

$$A \rightleftharpoons B + C,$$

for which the expression for the equilibrium constant is

$$K_p \qquad (31.13)$$

If an excess of one of the dissociation products, e.g., B, is added, the value of p_B is increased, and in order to maintain the constancy of the fraction in equation (31.13) it is necessary for p_C to decrease while p_A increases to some extent. If B is present before dissociation, p_B will always remain larger than p_C as the reaction proceeds to equilibrium. Since C arises from the dissociation of A, it is evident that this reaction will occur to a lesser extent than it would if the excess of B were not present. Similarly, an excess of C, instead of B, would have the same effect of decreasing the extent of dissociation of A. If the equilibrium constant of the reaction is known, the new position of equilibrium can be readily calculated.

Example: The value of K_p for the dissociation of PCl_5 at 250°C is 1.78, with pressures in atm. Calculate the fraction of dissociation at equilibrium when 0.040 mole PCl_5 is vaporized in a vessel containing 0.20 mole Cl_2 gas, (i) when a constant pressure of 2 atm is maintained, (ii) when the volume is kept constant at 4.0 liters. Compare the results with those for the same final pressures in the absence of excess chlorine.

(i) Let y be the number of moles PCl_5 dissociated at equilibrium; the fraction of dissociation α is then $y/0.04$. At equilibrium the vessel will contain $0.04 - y$ mole PCl_5, y mole PCl_3 and $0.2 + y$ mole Cl_2; the total number of moles is thus $0.24 + y$. Since the total pressure is constant at 2 atm, it follows that

$$K_p = 1.78 = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \frac{\dfrac{y}{0.24 + y}2 \times \dfrac{0.2 + y}{0.24 + y}2}{\dfrac{0.04 - y}{0.24 + y}2}$$

$$y = 0.0205, \qquad \alpha = 0.0205/0.04 = 0.51.$$

The value of α in the absence of excess chlorine may be obtained by replacing 0.2 moles Cl_2 by zero in the foregoing calculations; in this case it is found that α is 0.69.

(ii) In this case the pressure is not given, and so a somewhat different method of calculation must be employed; use is made of the relationship $p_i = n_i RT/v$ [equation (30.13)] to obtain the partial pressures. As before, y is taken as the number of moles of PCl_5 dissociated at equilibrium; then

$$p_{PCl_5} = (0.04 - y)\frac{RT}{v}, \qquad p_{PCl_3} = y\frac{RT}{v} \qquad \text{and} \qquad p_{Cl_2} = (0.2 + y)\frac{RT}{v}$$

$$K_p = 1.78 = \frac{y\dfrac{RT}{v} \times (0.2 + y)\dfrac{RT}{v}}{(0.04 - y)\dfrac{RT}{v}} = \frac{y(0.2 + y)}{0.04 - y} \cdot \frac{RT}{v}.$$

The temperature T is 250°C, i.e., 523°K, and v is given as 4.0 liters; since the pressures in K_p are in atm, R must be in liter-atm deg^{-1} $mole^{-1}$, i.e., 0.0820; hence,

$$1.78 = \frac{y(0.2 + y)}{0.04 - y} \times \frac{0.082 \times 523}{4.0},$$

$$y = 0.0173, \qquad \alpha = 0.43.$$

The total pressure is equal to the sum of the three partial pressures, i.e., to $(0.24 + y)RT/v$; now that y is known, this can be evaluated as 2.8 atm. At this pressure the fraction of PCl_5 dissociated in the absence of added chlorine is found from equation (31.11) to be 0.63. The results show that in both cases (i) and (ii), the presence of an excess of chlorine produces an appreciable decrease in the extent of dissociation of the PCl_5.

The presence of an inert (or nonreacting) gas may affect the degree of dissociation at equilibrium by its effect in decreasing the partial pressures of the reacting gases. For reactions in which there is no change in the number of molecules, the pressure has no effect on the equilibrium, as seen above. Since the pressure of the system would include that of any inert gas that might be present, it follows that in this instance the dissociation will be unaffected. On the other hand, whenever there is a change in the number of molecules, the position of equilibrium and the dissociation, at a given total pressure, will be influenced by the inert gas.

Example: Calculate the degree of dissociation of N_2O_4 in the presence of 0.25 atm of N_2 at 45°C and a total pressure of 1.00 atm; K_p is 0.664 with pressures in atm.

The sum of the partial pressures of N_2O_4 and NO_2 must be 0.75 atm, and this is the value of P in equation (31.8); from this equation,

$$0.664 = \frac{4\alpha^2 \times 0.75}{1 - \alpha^2}$$

$$\alpha = 0.43$$

This may be compared with $\alpha = 0.37$ at a total pressure of 1 atm in the absence of inert gas. The increased dissociation is to be expected from the Le Chatelier principle as a result of the decrease in pressure of the reacting substances.

31d. Combination of Equilibria.—In some equilibria two or more different reversible reactions, which have some reactants or products in common, are taking place simultaneously. If this is the case, the equilibrium constants of these simultaneous reactions are related to one another. Consider, for example, the water gas reaction

$$CO_2 + H_2 = CO + H_2O,$$

for which the partial pressure equilibrium constant is

$$K_p = \frac{p_{CO} \times p_{H_2O}}{p_{CO_2} \times p_{H_2}}. \tag{31.14}$$

In addition to this reaction there will be at least two other reversible processes involving some of the same substances; these are

$$(1)\quad 2H_2O \rightleftharpoons 2H_2 + O_2 \qquad \text{and} \qquad (2)\quad 2CO_2 \rightleftharpoons 2CO + O_2,$$

for which the equilibrium constants in terms of partial pressures are

$$K_1 = \frac{p_{H_2}^2 \times p_{O_2}}{p_{H_2O}^2} \qquad \text{and} \qquad K_2 = \frac{p_{CO}^2 \times p_{O_2}}{p_{CO_2}^2}, \tag{31.15}$$

respectively. When the system as a whole is in equilibrium, the three reversible reactions are all simultaneously in a state of equilibrium. It follows then that the partial pressures in equations (31.14) and (31.15) refer to the same system, and hence it is seen that

$$\frac{K_2}{K_1} = \frac{p^2_{\mathrm{CO}} \times p^2_{\mathrm{H_2O}}}{p^2_{\mathrm{CO_2}} \times p^2_{\mathrm{H}}} = K^2_p$$

and so

$$K_p = \sqrt{\frac{K_2}{K_1}}. \tag{31.16}$$

This gives the relationship between the various equilibrium constants. Similar results can be obtained in other cases.

The importance of equations of the type of (31.16) is that they can often be used to determine the equilibrium constant for a reaction which cannot be obtained by direct measurement with any degree of accuracy. For example, in the reaction considered above, K_p for the water gas reaction and K_1 for the dissociation of water vapor are readily determined by experiment, so that the equilibrium constant K_2 for the dissociation of carbon dioxide, at the same temperature, can be calculated.

HOMOGENEOUS EQUILIBRIA IN LIQUID SYSTEMS

32a. The Esterification Reaction.—For reactions occurring in the liquid phase, the exact expression for the equilibrium constant is still given by equation (30.10); if the various components behave ideally, the activities may be replaced by their respective mole fractions (§ 26c). For the general reversible reaction

$$a\mathrm{A} + b\mathrm{B} + \cdots \rightleftharpoons l\mathrm{L} + m\mathrm{M} + \cdots$$

occurring in an ideal liquid system, the equilibrium constant may be written as

$$K_x = \frac{x^l_{\mathrm{L}} \times x^m_{\mathrm{M}} \times \cdots}{x^a_{\mathrm{A}} \times x^b_{\mathrm{B}} \times \cdots}, \tag{32.1}$$

where the x's are the mole fractions of the indicated substances. *If the various components are all present in dilute solution, the mole fractions may be replaced by the respective molar concentrations,* to which they are then proportional.* Under these conditions, the equilibrium constant, now represented by K_c, is given by

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* In dilute solution, the mole fraction x_i of any reaction component i is approximately equal to n_i/n_0, where n_0 is the number of moles of solvent; hence, $x_i \approx n_i/(w_0/M_0)$, where w_0 is the weight of solvent and M_0 is its molecular weight. Furthermore, in a dilute solution, the volume V_0 of the solvent is not greatly different from the volume V of the solution. The molar concentration c_i is equal to n_i/V and because this is approximately equal to n_i/V_0, it is proportional to n_i/w_0, and hence to x_i, since M_0 is a constant.

$$K_c = \frac{c_L^l \times c_M^m \times \cdots}{c_A^a \times c_B^b \times \cdots}. \qquad (32.2)$$

One of the most familiar instances of a reversible reaction in a homogeneous liquid system is that between acetic acid and ethanol to form the ester, ethyl acetate, and water; thus,

$$\underset{\text{acid}}{CH_3COOH} + \underset{\text{alcohol}}{C_2H_5OH} \rightleftharpoons \underset{\text{ester}}{CH_3COOC_2H_5} + \underset{\text{water}}{H_2O}.$$

If the mixture is assumed to behave ideally, the equilibrium constant is

$$K_x = \frac{x_{\text{ester}} \times x_{\text{water}}}{x_{\text{acid}} \times x_{\text{alcohol}}}. \qquad (32.3)$$

The mole fraction of a given substance is equal to the number of moles n of that substance divided by the total number of moles N; since there are the same number of factors in the numerator and denominator in equation (32.3) the N's cancel, so that

$$K_x = \frac{n_{\text{ester}} \times n_{\text{water}}}{n_{\text{acid}} \times n_{\text{alcohol}}}. \qquad (32.4)$$

By taking known amounts of alcohol and acetic acid in a sealed tube, heating them at 100°C to permit equilibrium to be reached, and then analyzing the resulting mixture, the equilibrium constant was found to be 4.0.

Once the equilibrium constant is known, it is possible to calculate the composition of the equilibrium system for any given initial amounts of the two reactants, in the presence or absence of the products. If a and b are the numbers of moles of acetic acid and alcohol present at the beginning, and y is the number of moles of ester, and also of water, produced at equilibrium, there will then remain $a - y$ moles of acid and $b - y$ moles of alcohol; it is assumed here that neither of the products is present in the initial system. Substituting these values in equation (32.4), the result is

$$K_x = \frac{y \times y}{(a - y)(b - y)}. \qquad (32.5)$$

Since K_x has been determined experimentally, it is a simple matter to solve the quadratic equation (32.5) so as to give the value of y for any particular initial amounts of acid and alcohol. The data in Table 32.1 are quoted from

TABLE 32.1. THE ACETIC ACID-ETHANOL-ESTER-WATER EQUILIBRIU

Acid	Alcohol	Ester Formed	
a	b	y (calc.)	y (obs.)
1.00 mole	0.18 mole	0.171 mole	0.171 mole
1.00	0.33	0.301	0.293
1.00	0.50	0.423	0.414
1.00	1.00	0.667	0.667
1.00	2.00	0.850	0.858
1.00	8.00	0.970	0.966

the classical work of M. Berthelot and P. St. Gilles (1862) at 100°C; the number of moles of ethyl acetate y, as calculated from equation (32.5), with K_x taken as 4.0, are compared with the observed values. The agreement is seen to be very satisfactory; such deviations as do occur are due partly to experimental errors and partly to deviations from ideal behavior.

It will be apparent from the results in Table 32.1 that as the proportion of alcohol to acetic acid increases so also does the amount of ester formed at equilibrium. When the initial mixture consists of 1 mole of alcohol to 1 mole of acid, only 0.667 mole of ester is formed; that is, 66.7 per cent of the acetic acid is esterified. However, when the proportion of alcohol is increased to 8 moles to 1 mole of acid, it is seen that 96.6 per cent of the acid is converted into ester. This is an illustration of the concentration or "mass action" effect in reversible reactions. Since the equilibrium constant must always be maintained, the presence of excess of any reactant will tend to increase the proportion of the products formed at equilibrium. Similarly, if the products are already present, the extent of the forward reaction is diminished. An example of this latter type of behavior was considered in § 31c, dealing with the repression of dissociation by a reaction product. In the present case, the proportion of ester formed at equilibrium can be greatly decreased if the system initially contains an appreciable amount of water, which is one of the reaction products.

Example: Calculate the per cent of acid that is esterified when a mixture consisting initially of 1 mole of acetic acid, 1 mole of ethanol and 1 mole of water attains equilibrium at 100°C.

Let y be the number of moles of ester formed; the system at equilibrium then contains $1 - y$ mole of acid, $1 - y$ mole of alcohol, y mole of ester and $1 + y$ mole of water. Since the equilibrium constant at 100°C is 4.0,

$$K_x = 4.0 = \frac{y(1 + y)}{(1 - y)(1 - y)}$$

$$y = 0.54.$$

The other value of y is impossible. Consequently 54 per cent of the acid is esterified, compared with 66.7 per cent in the absence of the water.

32b. Reversible Reactions in Dilute Solution.—When a reaction occurs in dilute solution molar concentrations may be employed in place of mole fractions. The dissociation of nitrogen tetroxide into the dioxide has been studied in dilute solutions in chloroform, and the results may be used to evaluate the equilibrium constant. The extent of dissociation was determined from the darkening in color of the solution; the tetroxide is almost colorless while the dioxide has a dark brown color. The equilibrium constant K_c [equation (32.2)] is given by the expression

$$K_c = \frac{c_{\mathrm{NO_2}}^2}{c_{\mathrm{N_2O_4}}}$$

and the results in Table 32.2 are for concentrations in moles per liter of chloroform solution at 8.2°C. The constancy of the values in the last column shows

TABLE 32.2. THE DISSOCIATION OF NITROGEN TETROXIDE IN SOLUTION AT 8.2°C

$c_{N_2O_4}$	c_{NO_2}	K_c
0.129 mole liter^{-1}	1.17×10^{-3} mole liter^{-1}	1.07×10^{-5}
0.227	1.61	1.14
0.324	1.85	1.05
0.405	2.13	1.13
0.778	2.84	1.04

that in the solutions studied the molar concentrations may be used in place of the activities without incurring serious error. As in other cases, a knowledge of the equilibrium constant makes it possible to calculate the composition of the system at equilibrium for any given initial composition of the system.

Example: A solution is made up of 0.50 mole N_2O_4 in 450 ml of chloroform; calculate the concentration of NO_2 in the solution at equilibrium at 8.2°C.

Let y be the number of moles that have dissociated, leaving $0.5 - y$ mole N_2O_4 and forming $2y$ mole NO_2 in 450 ml, i.e., 0.45 liter. The mean value of K_c from Table 32.2 is 1.08×10^{-5}, with concentrations in moles per liter; hence,

$$K_c = 1.08 \times 10^{-5} = \frac{c_{NO_2}^2}{c_{N_2O_4}} = \frac{\left(\dfrac{2y}{0.45}\right)^2}{\dfrac{0.5 - y}{0.45}} = \frac{4y^2}{0.45(0.5 - y)},$$

$$y = 7.8 \times 10^{-4} \text{ mole.}$$

The concentration of NO_2 is $2y/0.45$, i.e., $2 \times 7.8 \times 10^{-4}/0.45 = 3.5 \times 10^{-3}$ mole per liter.

HETEROGENEOUS CHEMICAL EQUILIBRIA

33a. Activity of Solid Phase.—When a reaction involves one or more solids, in addition to a gas or a liquid phase, i.e., the reaction is **heterogeneous,** the activity of each solid in the expression for the equilibrium constant has a constant value, irrespective of the amount of solid present. By convention, *the activity of a pure solid substance is always taken as unity.* Consider, for purposes of illustration, the dissociation of solid calcium carbonate to form solid calcium oxide and carbon dioxide gas; if this reaction occurs in a closed space, the equilibrium

$$CaCO_3(c) \rightleftharpoons CaO(c) + CO_2(g)$$

is established. Utilizing the general equation (30.10) for the equilibrium constant, it is seen that

$$K = \frac{a_{CaO} \times a_{CO_2}}{a_{CaCO_3}}, \tag{33.1}$$

where the a's represent the activities. According to the convention given above, the activities of the two solids, $CaCO_3$ and CaO, are unity, so that equation (33.1) becomes

$$K = a_{CO_2}. \tag{33.2}$$

If the pressures are not too high and the temperatures are not too low, the carbon dioxide gas may be regarded as behaving ideally; the activity is then proportional to its partial pressure in the equilibrium system, i.e., to p_{CO_2}. It is then possible to write equation (33.2) in the form

$$K_p = p_{CO_2},$$

the subscript p in K_p being used to indicate that the activity has been expressed in terms of partial pressures. It follows, therefore, according to these arguments that the partial pressure of carbon dioxide in equilibrium with solid calcium carbonate and calcium oxide, generally called the **dissociation pressure** of calcium carbonate, should have a constant value at each temperature. This is exactly what has been found to be true experimentally, and some of the values obtained are given in Table 33.1. The dissociation pressure is independent of the quantities of the two solids, provided they are both present.

TABLE 33.1. DISSOCIATION PRESSURES (EQUILIBRIUM CONSTANTS) OF CALCIUM CARBONATE

773°K	0.073 mm
873	1.84
973	22.2
1073	167
1173	793
1273	2942

Apart from the fact that it leads to correct results, there are several ways of showing that the activity of a pure solid is constant, irrespective of its amount. For example, it was seen in § 26e that the activity of a liquid is proportional to its vapor pressure, and the same is true of a solid. Every pure solid has a definite and constant vapor pressure, however small, at each temperature (§ 21b); like the vapor pressure of a liquid, this does not depend on the quantity of the solid phase. Consequently, the activity of the pure solid has a constant value which depends only on the temperature. By defining the activity as the vapor pressure relative to that of the pure substance, as in equation (26.13), it is seen that the activity of a pure solid is unity at all temperatures. This is in fact the convention adopted above and always employed in physical chemistry.

It is evident from the foregoing discussion that when writing the equilibrium constant for a heterogeneous reaction between solids and gases, the terms for the solids are all taken as unity, and hence may be ignored; each gas, however, is represented by its partial pressure at equilibrium. If these rules are borne in mind the derivation of the expression for the equilibrium constant for a heterogeneous reaction is a very simple matter, as will now be shown.

33b. Reactions between Solids and Gases.—The dissociation of solid ammonium hydrosulfide, NH_4HS, has been studied in some detail. This salt dissociates into ammonia and hydrogen sulfide at quite low temperatures, viz.,

$$NH_4HS(c) \rightleftharpoons NH_3(g) + H_2S(g),$$

and remembering that the activity of the solid is to be taken as unity, the equilibrium constant is

$$K_p = p_{NH_3} \times p_{H_2S}.$$

When solid ammonium hydrosulfide was heated at 20°C, the total pressure of the vapor was found to be 0.468 atm. The actual vapor pressure of the solid salt is small and may be neglected; hence, the 0.468 atm is due to the ammonia and hydrogen sulfide gases. Since these are produced in equimolecular amounts when the ammonium hydrosulfide dissociates, the partial pressure of each must be one half of 0.468, i.e., 0.234 atm; thus,

$$p_{NH_3} = p_{H_2S} = 0.234 \text{ atm},$$

and consequently,

$$K_p = p_{NH_3} \times p_{H_2S} = 5.48 \times 10^{-2}.$$

The same value for the equilibrium constant should be obtained if the hydrosulfide is vaporized into a space already containing some ammonia or hydrogen sulfide gas. Let p be the initial pressure of one of these gases, e.g., the ammonia, and let y be the pressure of each gas resulting from the dissociation of the solid ammonium hydrosulfide; it follows then that

$$p_{NH_3} = p + y \qquad \text{and} \qquad p_{H_2S} = y$$

$$K_p = p_{NH_3} \times p_{H_2S} = (p + y)y. \tag{33.3}$$

Neglecting, as before, the actual vapor pressure of the solid, the total pressure is equal to the sum of the partial pressures of the two gases, i.e., to $p + 2y$. If the value of p, the initial excess pressure of ammonia, or of hydrogen sulfide, is known, and the total pressure at equilibrium, i.e., $p + 2y$, is measured, y can be calculated; it is thus possible to evaluate K_p from equation (33.3). The results obtained in this manner by J. P. Magnusson (1907) are recorded in Table 33.2; the values of K_p in the last column are seen to be almost constant, and approximately equal to the result, i.e., 5.48×10^{-2}, obtained above from the dissociation of the pure hydrosulfide.

The figures in Table 33.2 illustrate, once again, the repression of dissociation by excess of either of the reaction products. The normal dissociation pressure of each gas is 0.234 atm at 20°C. In the first three lines the systems contain an excess of hydrogen sulfide, and the partial pressure of ammonia, i.e., p_{NH_3}, is seen to be less than the normal dissociation pressure. Similarly, in the last three lines, where the ammonia is in excess, p_{H_2S} is smaller than 0.234 atm in each case.

TABLE 33.2. DISSOCIATION OF AMMONIUM HYDROSULFIDE AT 20°C

p_{NH_3}	p_{H_2S}	$p_{NH_3} \times p_{H_2S}$
0.0509 atm	1.084 atm	5.52×10^{-2}
0.115	0.481	5.54
0.140	0.397	5.43
0.531	0.104	5.50
0.711	0.0748	5.60
0.924	0.0587	5.42

A different kind of process involving one solid and two gases is the industrially important equilibrium,

$$C(c) + CO_2(g) \rightleftharpoons 2CO(g),$$

for which

$$K_p = \frac{p^2_{CO}}{p_{CO_2}}. \qquad (33.4)$$

Example: When the reaction $C(c) + CO_2(g) = 2CO(g)$ takes place at 850°C and 1.00 atm total pressure, the equilibrium mixture contains 93.77% CO and 6.23% CO_2 by volume. Calculate (i) the value of K_p and (ii) the equilibrium composition at 5.00 atm.

(i) By Avogadro's law, the relative composition by volume is equal to the molar composition; then the mole fractions are 0.9377 for CO_2 and 0.0623 for CO. With the total pressure at 1.00 atm, these are also the respective partial pressures in atm. Hence, by equation (33.4),

$$K_p = \frac{(0.9377)^2}{0.0623} = 14.11.$$

(ii) Let x be the mole fraction of CO and $1 - x$ that of CO_2, when the total pressure is 5.00 atm. Then $p_{CO} = 5.00x$ and $p_{CO_2} = 5.00(1 - x)$; hence,

$$K_p = 14.11 = \frac{(5.00x)^2}{5.00(1 - x)}$$

$$x = 0.783.$$

The composition is thus 78.3% CO and 21.7% CO_2 by volume.

In the reaction between solid carbon and steam represented by

$$C(c) + H_2O(g) \rightleftharpoons CO(g) + H_2(g),$$

three gases and one solid are present at equilibrium; in this case,

$$K_p = \frac{p_{CO} \times p_{H_2}}{p_{H_2O}}. \qquad (33.5)$$

Attention may be called to the fact that the combination of the equilibrium constants in equations (33.4) and (33.5) gives that for the water gas reaction. Thus, if the former is divided by the latter, the result is identical with equation (31.14). This is an interesting illustration of the combination of two heterogeneous equilibria to yield the constant for a homogeneous equilibrium. Many other examples of a similar nature are to be found in the chemical literature.

TEMPERATURE AND EQUILIBRIUM

34a. The van't Hoff Equation.—The qualitative effect of temperature on chemical equilibrium is given by the principle of Le Chatelier, but an exact relationship can be derived by means of thermodynamics. Comparison of equations (30.9) and (30.10) shows that the former can be written as

$$\Delta F^0 = -RT \ln K. \tag{34.1}$$

For a gas reaction in which the gases approach ideal behavior, the activities in equation (30.10) may be replaced by the corresponding partial pressures; K then becomes K_p and equation (34.1) takes the form

$$\Delta F^0 = -RT \ln K_p. \tag{34.2}$$

The left-hand side refers to a process in which each of the reactants and products is in its standard state of 1 atm pressure, assuming ideal behavior; the right-hand side contains two variables T and K_p and is, of course, independent of pressure. It is thus possible to differentiate equation (34.2) with respect to temperature at constant pressure; the result is

$$\left(\frac{\partial(\Delta F^0)}{\partial T}\right)_P = -R \ln K_p - RT\frac{d \ln K_p}{dT},$$

the subscript P implying constant pressure. Multiplying through by T, and substituting ΔF^0 for $-RT \ln K_p$, according to equation (34.2), this becomes

$$T\left(\frac{\partial(\Delta F^0)}{\partial T}\right)_P = \Delta F^0 - RT^2\frac{d \ln K_p}{dT}. \tag{34.3}$$

The Gibbs-Helmholtz equation (9.34), modified by the introduction of the superscript zero for the special case when all the substances taking part in the process are in their standard states, is

$$\Delta F^0 = \Delta H^0 + T\left(\frac{\partial(\Delta F^0)}{\partial T}\right)_P \tag{34.4}$$

Comparison of equations (34.3) and (34.4) immediately leads to the result

$$RT^2\frac{d \ln K_p}{dT} = \Delta H^0,$$

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^0}{RT^2}. \tag{34.5}$$

Equation (34.5) is known as the **van't Hoff equation,** and ΔH^0 is the change in enthalpy for the reaction, i.e., the heat of reaction at constant pressure, with the reactants and products in their standard states. It is a matter of experience that the enthalpy change does not vary appreciably with the pressures of the substances concerned, and so ΔH^0 may be replaced by ΔH without specifying the conditions, thus making the result more general; thus,

(34.6)

Stated in words, this equation means that if $\ln K_p$ is plotted against the absolute temperature, the slope of the curve at any temperature is equal to $\Delta H/RT^2$.

Since K_p is equal to $K_c(RT)^{\Delta n}$, by equation (30.15), while $\Delta H = \Delta E + RT(\Delta n)$, by equation (7.2), it can be readily shown that a modified form of equation (34.5) giving the variation of K_c with temperature is

$$\frac{d \ln K_c}{dT} = \frac{\Delta E^0}{RT^2}. \tag{34.7}$$

It will be observed that equation (34.6) is of the same form as the Clapeyron-Clausius equation (11.7); the latter may, in fact, be regarded as a special case of the former. When a liquid or a solid is in equilibrium with its own vapor, i.e., for the equilibria

$$\text{liquid} \rightleftharpoons \text{vapor} \qquad \text{or} \qquad \text{solid} \rightleftharpoons \text{vapor},$$

$K_p = p_{\text{vapor}}$ in each case. Hence, K_p in equation (34.6) may be replaced by the vapor pressure; further, the change in enthalpy accompanying vaporization at constant pressure is the heat of vaporization L_v(or L_s). If these substitutions are made, the van't Hoff equation becomes identical with the special form of the Clapeyron-Clausius equation that is applicable to liquid-vapor and solid-vapor equilibria. It may be noted that in this form the equation cannot be applied to solid-liquid equilibria, i.e., to melting, since the external pressure may not be regarded as the equilibrium constant of the melting process.

The general agreement between the van't Hoff equation (34.6) and the Le Chatelier principle is at once evident; according to the former, K_p must increase with temperature if ΔH is positive, whereas it will decrease with increasing temperature if ΔH is negative. These are equivalent to the conclusion reached in § 30f.

34b. Integration of the van't Hoff Equation.—In order to utilize equation (34.5) for purposes of calculation, it must be integrated, just as was the Clapeyron-Clausius equation in § 11e. If the heat of reaction ΔH^0 is taken as constant over a small range of temperature, general integration of the van't Hoff equation gives

$$\ln K_p = -\frac{\Delta H^0}{RT} + \text{constant}, \tag{34.8}$$

or

$$\log K_p = -\frac{\Delta H^0}{2.303RT} + \text{constant}, \tag{34.9}$$

which are exactly analogous to equations (11.9) and (11.10), respectively. These expressions show that the plot of log K_p against $1/T$, i.e., the reciprocal of the absolute temperature, should yield a straight line; the slope of this line will be $-\Delta H^0/2.303R$. The experimental data for a number of reversible reactions have been found to satisfy this requirement, provided the temperature range is not too large, so that ΔH^0 remains almost constant.

For practical purposes it is more convenient to integrate equation (34.5) between the definite temperature limits of T_1 and T_2 or, what is the same thing, to subtract the two forms of equation (34.9) for these two temperatures; the result is

$$\log \frac{(K_p)_2}{(K_p)_1} = -\frac{\Delta H^0}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{\Delta H^0}{4.576}\left(\frac{T_2 - T_1}{T_1 T_2}\right), \qquad (34.10)$$

where $(K_p)_1$ and $(K_p)_2$ are the equilibrium constants at the temperatures T_1 and T_2, respectively, and ΔH^0 is expressed in calories. It should be noted that the equilibrium constants $(K_p)_1$ and $(K_p)_2$ must be expressed in the same pressure units, the actual units being immaterial, since equation (34.10) involves the ratio of these constants. By means of equation (34.10) it is possible to calculate the equilibrium constant $(K_p)_2$ at the absolute temperature T_2, from the value $(K_p)_1$ at the temperature T_1, provided the heat of reaction ΔH^0 at constant pressure is known. Alternatively, if the equilibrium constants have been determined at two temperatures, the heat of reaction can be evaluated. These procedures can be applied to both homogeneous and heterogeneous equilibria, as will be seen in the examples given below.

It should be emphasized that equation (34.10) is based on the approximation of a constant value of ΔH^0 over the temperature range from T_1 to T_2. For exact calculations allowance must be made for the possible variation of the heat of reaction with temperature, although for approximate purposes a mean value of ΔH^0 may be employed. It was seen in § 7i that the variation of the heat of reaction with temperature can be expressed by means of equation (7.16), viz.,

$$\Delta H^0 = \Delta H_0^0 + \Delta a T + \tfrac{1}{2}\Delta b T^2 + \tfrac{1}{3}\Delta c T^3 + \cdots,$$

where Δa, Δb, Δc, etc., are determined by the heat capacities of the substances taking part in the reaction. This value for ΔH^0 may be substituted in the van't Hoff equation (34.5) with the result,

$$= \frac{\Delta H_0^0}{RT^2} + \frac{\Delta a}{RT} + \frac{\Delta b}{2R} + \frac{\Delta c}{3R} T + \cdots. \qquad (34.11)$$

Integration of this equation then gives a complete expression for the variation of the equilibrium constant with temperature [see equation (35.10)].

Example: The equilibrium constant K_p for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 1.64×10^{-4} at 400°C and 0.144×10^{-4} at 500°C. Calculate the mean heat of formation of 1 mole of ammonia from its elements in this temperature range.

Let T_1 be 400°C, i.e., 400 + 273 = 673°K, and T_2 be 500°C, i.e., 773°K; then $(K_p)_1$ is 1.64×10^{-4} and $(K_p)_2$ is 0.144×10^{-4}. These values may be inserted into equation (34.10) to evaluate ΔH^0 in calories for the reaction; thus,

$$\log 0.144 \times 10^{-4} - \log 1.64 \times 10^{-4} = \frac{\Delta H^0}{4.576}\left(\frac{773 - 673}{673 \times 773}\right)$$

$$\Delta H^0 = -25{,}140 \text{ cal.}$$

This is the heat of the reaction as written, in which two moles of NH_3 are formed; the mean heat of formation of one mole of NH_3 is thus −12,570 cal or −12.57 kcal.

In applying the van't Hoff equation to a heterogeneous reaction, the dissociation of a carbonate may be considered. In this case, the equilibrium constant is equivalent to the dissociation pressure of carbon dioxide. It follows, therefore, from equation (34.9) that the plot of log p_{CO_2} for various temperatures against $1/T$ should be a straight line, at least as long as ΔH^0 remains constant. The results for the dissociation of calcium carbonate in the temperature range from 600°C to 1000°C are plotted in Fig. 34.1; the points fall approximately on a straight line, and from its slope, which is equal to $-\Delta H^0/2.303R$, the enthalpy change accompanying the reaction is found to be 40.4 kcal in the given range of temperature.

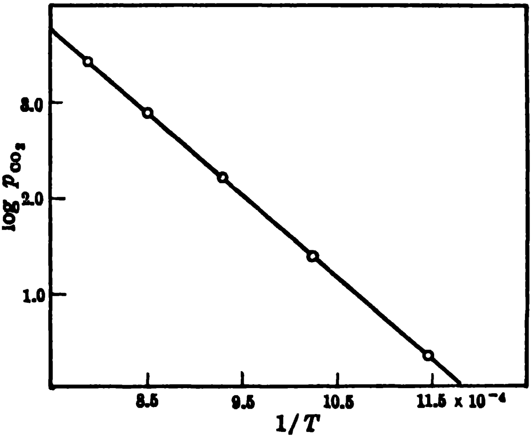

FIG. 34.1. Dissociation of calcium carbonate

Example: The total pressure developed when solid HgO is heated so as to form mercury vapor and oxygen gas, according to the reaction $2HgO(c) \rightleftharpoons 2Hg(g) + O_2(g)$, is 141 mm at 380°C, and 387 mm at 420°C. Assuming ΔH^0 to remain constant, calculate the temperature at which HgO dissociates freely in air. (This occurs when the equilibrium partial pressure of the oxygen is equal to its partial pressure in the air, i.e., 0.21 atm.)

The first step is the evaluation of ΔH^0 for the reaction. Since both the mercury and the oxygen are in the gaseous state, K_p is given by

$$K_p = p_{\text{Hg}}^2 \times p_{\text{O}_2}.$$

The partial pressure of mercury is twice that of the oxygen, and since these two together make up the total observed pressure, it follows that at 380°C, i.e., 653°K,

$$p_{\text{Hg}} = \tfrac{2}{3} \times 141 = 94 \text{ mm}, \qquad \text{and} \qquad p_{\text{O}_2} = 47 \text{ mm},$$

while at 420°C, i.e., 693°K,

$$p_{\text{Hg}} = \tfrac{2}{3} \times 387 = 258 \text{ mm}, \qquad \text{and} \qquad p_{\text{O}_2} = 129 \text{ mm}.$$

Hence,

$$(K_p)_1 \text{ at } 653°\text{K} = (94)^2 \times 47 = 4.15 \times 10^5$$

$$(K_p)_2 \text{ at } 693°\text{K} = (258)^2 \times 129 = 8.59 \times 10^6$$

and by equation (34.10)

$$\log 8.59 \times 10^6 - \log 4.15 \times 10^5 = \frac{\Delta H^0}{4.576}\left(\frac{693 - 653}{653 \times 693}\right)$$

$$\Delta H^0 = 68{,}110 \text{ cal.}$$

If the partial pressure of oxygen is to be 0.21 atm, i.e., 160 mm, the partial pressure of the mercury vapor must be 2 × 160 = 320 mm; K_p is then $(320)^2 \times 160 = 1.64 \times 10^7$. Taking ΔH^0 as 68,110 cal, the temperature T must now be found at which K_p has this value; combining this with either of the experimental K_p's, e.g., $(K_p)_1$, equation (34.10) gives

$$\log 4.15 \times 10^5 - \log 1.64 \times 10^7 = \frac{68{,}110}{4.576}\left(\frac{653 - T}{653 \times T}\right)$$

$$T = 702°\text{K}.$$

Mercuric oxide should thus dissociate freely in air when the temperature reaches 702°K, i.e., 702 − 273 = 429°C.

The appropriate form of the van't Hoff equation for reactions in solution at constant pressure is

$$\frac{d \ln K_x}{dT} = \frac{\Delta H^0}{RT^2}. \tag{34.12}$$

If the substances taking part are all in dilute solution, this expression becomes

$$\frac{d \ln K_c}{dT} = \frac{\Delta H^0}{RT^2}. \tag{34.13}$$

Attention should be called to the difference between equations (34.7) and (34.13); although both are concerned with K_c, the former, for gases, has ΔE^0 on the right hand side, while the latter, for dilute solutions, has ΔH^0. Actually, for reactions in solution ΔH^0 and ΔE^0 are not appreciably different, and so a general equation of the form of (34.7) might be regarded as applicable to both gases and solutions. The equations (34.12) and (34.13) may be integrated in the usual manner, and the results are exactly similar to those already obtained for gas reactions. Since the subject presents no new features it need not be discussed further here, but an important application of equation (34.13) will be given in § 52e.

FREE ENERGY CHANGES

35a. The Reaction Isotherm.—If the expression for ΔF^0 given by equation (34.1) is inserted into equation (30.7), it is seen that the free energy change for the reaction with reactants and products in any arbitrary states is given by

$$\Delta F = -RT \ln K + RT \ln \frac{a_L^l \times a_M^m \times \cdots}{a_A^a \times a_B^b \times \cdots}, \tag{35.1}$$

where the a's refer to the activities in these arbitrary states. It will be noted that the quantity whose logarithm is involved in equation (35.1), which may be called the arbitrary **reaction quotient,** is exactly similar in form to the expression for the equilibrium constant. It should be clearly understood, however, that in the latter the activities of reactants and products are the values when the system as a whole is in equilibrium, whereas in the reaction quotient in equation (35.1) the activities correspond to the actual conditions of the reaction, and *these may or may not correspond to a state of equilibrium.*

The arbitrary reaction quotient in terms of activities may be represented by the symbol Q_a, that is,

$$Q_a = \frac{a_L^l \times a_M^m \times \cdots}{a_A^a \times a_B^b \times \cdots}, \tag{35.2}$$

so that equation (35.1) becomes

$$\Delta F = -RT \ln K + RT \ln Q_a, \tag{35.3}$$

which is a form of what is known as the **reaction isotherm** (J. H. van't Hoff, 1886). It is evident that if the arbitrary states happen to correspond to those for the system at equilibrium, Q_a will become identical with the equilibrium constant K, since the expressions for both these quantities are of exactly the same form [compare equations (30.10) and (35.2)]. By equation (35.3), the value of ΔF would then be zero, as indeed it should be for an equilibrium system at a given temperature and pressure.

It was seen in § 26c that the standard state of unit activity may be defined in any convenient manner, and so it is obvious that the standard free energy change ΔF^0 must depend upon the particular choice of standard states. For gases, it is the usual practice to choose the state of unit activity as the ideal gas at 1 atm pressure; consequently, for gas reactions equation (35.3) becomes

$$\Delta F = -RT \ln K_p + RT \ln Q_p, \tag{35.4}$$

where K_p is the equilibrium constant with partial pressures expressed in atm, and Q_p is now the reaction quotient with the arbitrary states of reactants and products given in the same pressure units. From this form of the reaction isotherm the free energy change for a reaction taking place between gaseous reactants, at specified pressures, to form gaseous products, also at specified pressures, can be calculated. The same equation is applicable to heterogeneous reactions involving gases and solids.

Attention may be drawn to the fact that, although ΔF^0 depends on the particular standard states that are chosen, the value of ΔF is, as it should be, independent of their nature. This may be readily seen by writing equation (35.4) in the simple form

$$\Delta F = RT \ln \frac{Q_p}{K_p}, \tag{35.5}$$

from which it is evident that ΔF is determined by the *ratio* of Q_p to K_p. Consequently, as long as both of these quantities are expressed in terms of the same standard states, that is, in terms of the same units, the result will be independent of the particular standard states employed.

Example: The equilibrium constant K_p for the reaction $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$ at 2000°K is 1.55×10^7 with partial pressures in atm. Calculate (i) the free energy change accompanying the reaction of two moles of hydrogen at 0.100 atm and one mole of oxygen at 0.100 atm to form water vapor at 1.00 atm; (ii) the standard free energy change for the same reaction at 2000°K, assuming ideal behavior of the gases.

(i) The arbitrary reaction quotient Q_p in terms of pressures in atm is given by

$$Q_p = \frac{p^2_{H_2O}}{p^2_{H_2} \times p_{O_2}} = \frac{1.00}{(0.100)^2 \times (0.100)} = 1.00 \times 10^3.$$

Converting equation (35.5) to common logarithms, this becomes

$$\Delta F = 2.303RT \log \frac{Q_p}{K_p} = 2.303R \times 2000 \times \log \frac{1.00 \times 10^3}{1.55 \times 10^7},$$

since T is 2000°K. If ΔF is required in calories, R may be taken as 1.987 cal deg^{-1} mole^{-1}, so that

$$\Delta F = 2.303 \times 1.987 \times 2000 \log \frac{1.00 \times 10^3}{1.55 \times 10^7}$$

$$= -38{,}300 \text{ cal} = -38.3 \text{ kcal}.$$

(ii) The standard free energy change ΔF^0_p, for standard states of 1 atm, is merely $-RT \ln K_p$; hence,

$$\Delta F^0_p = -RT \ln K_p = -2.303 \times 1.987 \times 2000 \log 1.55 \times 10^7$$

$$= -65{,}800 \text{ cal} = -65.8 \text{ kcal}.$$

For reactions in dilute solution, the standard state is chosen as the (hypothetical) ideal solution of unit concentration, i.e., 1 mole (or 1 gram ion) per liter, or of unit molality, i.e., 1 mole per 1000 grams of solvent. Under these conditions the reaction isotherm becomes

$$\Delta F = -RT \ln K_c + RT \ln Q_c = RT \ln \frac{Q_c}{K_c}, \tag{35.6}$$

where Q_c is the arbitrary reaction quotient with the states of the reactants and products expressed in terms of concentrations in their ideal solutions. If the solutions are sufficiently dilute, the actual concentrations may be employed in place of the ideal values.

35b. Criteria of Spontaneous Reaction.—The essential importance of the reaction isotherm lies in the fact that it provides a means of determining whether a particular reaction is possible or not, under a given set of conditions. It was seen in § 9b that for a thermodynamically irreversible process taking place at constant temperature and pressure, ΔF must be negative, that is, the free energy of the system diminishes. If a particular physical or chemical change is to be theoretically possible it must be able to occur spontaneously; spontaneous processes are, however, irreversible in the thermodynamic sense (§ 8b), and hence it follows that *a reaction can take place spontaneously only if it is accompanied by a decrease of free energy*, i.e., ΔF must be negative, at constant temperature and pressure. This result applies to any process, physical or chemical; it is immaterial whether the latter is reversible, in the chemical sense, or if it goes to virtual completion.

If the value of ΔF under a given set of conditions is positive, the reaction cannot possibly occur spontaneously under those conditions, although it may be able to do so if the conditions are altered. In the problem of the preceding section, it was seen that for the combination of hydrogen and oxygen at 0.1 atm pressure to form water vapor at 1 atm pressure at 2000°K, the free energy change was negative. The reaction can therefore take place spontaneously under these conditions. Suppose, however, the hydrogen and oxygen pressures were greatly reduced, or that of the water vapor was increased, so that Q_p became greater than K_p, the value of ΔF would be positive and the reaction would not be possible. Under these conditions the reverse reaction, i.e., the dissociation of water vapor, will tend to occur. By writing the reaction isotherm in the general form

$$\Delta F = RT \ln \frac{Q}{K}, \tag{35.7}$$

it is seen that a particular process will be possible theoretically if the reaction quotient Q is less than the corresponding equilibrium constant K; ΔF will then involve the logarithm of a fraction and hence will be negative. If, however, the arbitrary pressures or concentrations are such as to make Q greater than K, the value of ΔF will be positive, and the reaction will not be possible under these conditions.

It should be borne in mind, of course, that a change in temperature may affect the value of the equilibrium constant K to such an extent that a reaction which previously could not occur spontaneously, for a given value of the quotient Q, can now do so. At some temperatures K is less than Q, but as the temperature is altered K may become greater than Q; the sign of ΔF will thus reverse from positive to negative, and the reaction becomes possible when the temperature is changed.

It is of interest to consider the physical significance of the conclusion that a reaction will be able to take place spontaneously if Q is less than K, but not if Q is greater than K. A comparison of equations (30.10) and (35.2), which define K and Q, respectively, shows that when $Q < K$, the arbitrary activities (or concentrations) of the products are relatively less than those in the equilibrium state. The occurrence of the reaction will mean that the amounts of products are increased, while those of the reactants decrease correspondingly; in other words, the state of the system will tend to move spontaneously towards the state of equilibrium. On the other hand, if $Q > K$, the products will be present in excess of the equilibrium activities, and for the reaction to continue would mean a still greater departure from equilibrium; such a change would never occur spontaneously. In these circumstances, of course, the reaction would tend to take place in the reverse direction.

The foregoing conclusions may be illustrated in another manner by means of Fig. 35.1 which shows how the free energy varies with the course of a reaction; the points R at the left, and P at the right, represent the free energies of reactants and products, respectively. In a reversible reaction, the forward reaction will occur when the initial state consists of the reactants and the reverse reaction when starting with the products. Since each reaction occurs spontaneously, each must be accompanied by a decrease in free energy, at constant temperature and pressure. The variations in free energy during the forward and reverse reactions will then be of the form of the curves RE and PE, respectively, where E represents the equilibrium condition. It is seen that E is a state of minimum free energy, in harmony with the criterion that $(\partial F)_{T,P} = 0$ at equilibrium given by equation (9.25).

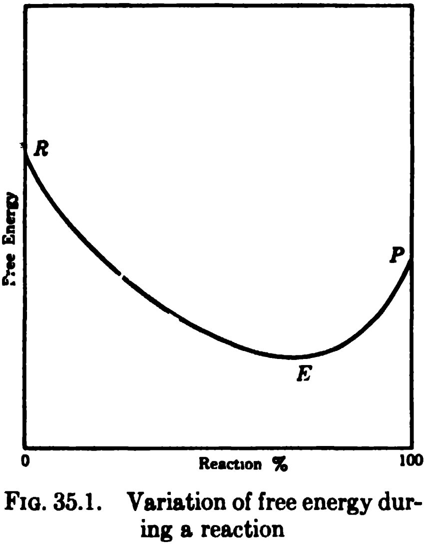

FIG. 35.1. Variation of free energy during a reaction

Since K is constant at a fixed temperature, the free energy change will depend on the value of Q, as seen from equation (35.7); when Q is equal to K, the system is in equilibrium, i.e., at E in Fig. 35.1. For $Q < K$, the free energy will be to the left of the minimum in Fig. 35.1 and the forward reaction will occur; if $Q > K$, on the other hand, the free energy will be to the right of the minimum and the reverse reaction will take place.

Although any reaction accompanied by a decrease of free energy is theoretically possible, this is no indication that the process will actually occur with a measurable speed. For example, at ordinary temperatures and pressures the free energy change for the combination of hydrogen and oxygen to form water has a very large negative value, yet the reaction, in the absence of a catalyst, is so slow that no detectable amount of water would be formed in years. The passage of an electric spark or the presence of a suitable catalyst, however, facilitates the occurrence of a reaction which the free energy change shows to be theoretically possible. The factors which determine the rate of a reaction, as distinct from its theoretical possibility, will be considered in Chapter 16.

35c. Standard Free Energy of Reaction.—The significance of the standard free energy change ΔF^0 is that it is the increase of free energy associated with a reaction taking place under such conditions that each of the reactants and products is in its standard state, e.g., for a reaction involving ideal gases every gas taking part is at a partial pressure of 1 atm. Consequently, the sign of the standard free energy gives an indication of whether the process is possible or not under these conditions; if the value is negative it means that the reaction with reactants and products in their standard states can take place at the particular temperature.

In addition to the application just described, the quantity ΔF^0 has other uses which make it an important property in the study of reactions. In the first place, it has a definite value at every temperature for any given reaction, and it is related to the equilibrium constant at the same temperature by the familiar equation (34.1). The tabulation of standard free energies is thus equivalent to the tabulation of equilibrium constants. In the second place, since the free energy, like the enthalpy, is a property which depends only on the state of a system, *it is possible to add and subtract free energy changes for different reactions*, just as was done for enthalpy changes in § 7e. Further, reversal of a particular reaction does not alter the standard free energy change but merely reverses the sign.

By utilizing these facts the ΔF^0 values of reactions which cannot be studied directly can be obtained by combining the known values for other reactions. For example, it is known that,

$$2H_2O(g) = 2H_2(g) + O_2(g) \qquad \Delta F^0_{298} = 109.28 \text{ kcal.}$$

$$CO_2(g) + H_2(g) = H_2O(g) + CO(g) \qquad \Delta F^0_{298} = 6.82$$

Multiplication of the second equation by two and addition of the first equation then gives for the reaction

$$2CO_2(g) = 2CO(g) + O_2(g)$$

$$\Delta F^0_{298} = (2 \times 6.82) + 109.28 = 122.92 \text{ kcal.}$$

In view of the definition of ΔF^0 in terms of the negative logarithm of the equilibrium constant, the addition and subtraction of standard free energies is equivalent to the multiplication and division of equilibrium constants, respectively, as in § 31d. In other words, the use of free energies is analogous to the treatment of equilibrium constants by means of a slide rule.

If the standard free energy for a reaction involving a substance in a particular state, e.g., gaseous, is known, and that for another state, e.g., liquid, is required, the difference can usually be calculated and appropriate allowance made. Suppose it is required to determine ΔF^0_{298} for the reaction

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(l).$$

This may be obtained by addition of the standard free energy changes of the reactions

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(g)$$

and

$$H_2O(g) = H_2O(l).$$

For the first of these two reactions, ΔF^0 is half of that given above for the dissociation of two moles of water vapor, with the sign changed, i.e., -54.64 kcal. The standard free energy change for the second process is obtained in the following manner. The standard state of the water as vapor is at a pressure of 1 atm, assuming ideal behavior, whereas the standard state of liquid water is pure water (§ 26d). At 25°C, pure liquid water is in equilibrium with vapor at a pressure of 23.76 mm of mercury, i.e., $23.76/760.0 = 0.0313$ atm; hence, for the process

$$H_2O(g, 0.0313 \text{ atm}) = H_2O(l),$$

ΔF_{298} is zero. The required standard free energy, for $H_2O(g, 1 \text{ atm})$ to $H_2O(l)$ is thus equal to that for the process

$$H_2O(g, 1 \text{ atm}) = H_2O(g, 0.0313 \text{ atm})$$

as may be seen by adding the two equations. By inserting 1 atm for P_1 and 0.0313 atm for P_2 in equation (9.22), the required value of ΔF^0_{298} is found to be -2050 cal, i.e., -2.05 kcal. The standard free energy change for the formation of 1 mole of liquid water from its elements at 25°C is thus $-54.64 - 2.05$, i.e., -56.69 kcal.

Various procedures have been employed for the evaluation of the standard free energies of reactions. When the equilibrium constant can be determined experimentally, ΔF^0 can of course be calculated from equation (34.1). On the other hand, if the reaction is one that goes virtually to completion, so that it is not possible to measure the equilibrium constant, the value of ΔF^0 may often be obtained by the combination of results for two or more reactions for which the data are available, as described above. For a reaction that can be made to take place in a suitable galvanic cell, the standard free energy can be derived from the electromotive force of the cell (§ 48f). Another approach, which has received much attention in recent years, is based on the determination of entropy; this subject will be treated in the latter part of the present chapter.

35d. Standard Free Energy and Temperature.—Just as the equilibrium constant changes with temperature so also must the standard free energy, and the expression for this variation can be readily obtained. If both sides of equation (34.8), obtained by the integration of the van't Hoff equation on the assumption that ΔH^0 is constant, are multiplied by RT and the sign changed, the result is

$$-RT \ln K_p = \Delta H^0 - IT, \qquad (35.8)$$

where the gas constant R has been multiplied by the integration constant in equation (34.8) to give the new constant I. The value of this constant can evidently be calculated if the equilibrium constant K_p and the change of enthalpy ΔH^0, at the same temperature T, are known. The left-hand side of equation (35.8) is equal to ΔF^0, and hence

$$\Delta F^0 = \Delta H^0 - IT. \tag{35.9}$$

If ΔH^0 were independent of temperature, this equation would provide a very simple method for determining ΔF^0 (or K_p) at any temperature, provided K_p was known at one particular temperature; all that would be necessary is a knowledge of the heat of reaction ΔH^0, and the constant I, obtained in the manner just described.

For a relatively small range of temperature, equation (35.9) may be employed in conjunction with a mean value of ΔH^0 to give a fair indication of the variation of ΔF^0 with temperature. When the temperature range is considerable, however, it is necessary to make allowance for the fact that ΔH^0 is not constant. General integration of equation (34.11), in which ΔH^0 has been expressed as a function of the temperature, gives

$$\ln K_p = -\frac{\Delta H_0^0}{RT} + \frac{\Delta a}{R}\ln T + \frac{\Delta b}{2R}T + \frac{\Delta c}{6R}T^2 + \cdots + \text{constant}. \tag{35.10}$$

If this is treated in the same manner as was equation (35.8) above, it is found that the variation of ΔF^0 with temperature is represented by

$$\Delta F^0 = \Delta H_0^0 - \Delta a T \ln T - \tfrac{1}{2}\Delta b T^2 - \tfrac{1}{6}\Delta c T^3 + \cdots - IT. \tag{35.11}$$

The values of ΔH_0^0, Δa, Δb, Δc, etc., are derived from measurements of the heat of reaction and from the heat capacities of the substances taking part in the reaction; the constant I can then be calculated from a knowledge of ΔF^0, or K_p, at any one temperature. In this way it is possible to obtain an expression which gives the standard free energy change of a particular reaction over a considerable range of temperature.

Example: Utilizing the data given in the example in § 7i, for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, together with the fact that K_p is 1.43×10^{-5}, with partial pressures in atm, at 500°C, derive a general expression for the variation with temperature of ΔF^0 for the formation of 1 mole of NH_3 from its elements.

From the results in § 7i, it is seen that ΔH_0^0 is $-18{,}280$ cal, $\Delta a = -14.912$, $\Delta b = +14.961 \times 10^{-3}$ and $\Delta c = -28.18 \times 10^{-7}$; these values may be inserted in equation (35.11). The constant I may then be calculated by utilizing the fact that K_p is 1.43×10^{-5} at 500°C, i.e., 773°K. It is more instructive, however, to follow through the detailed treatment, instead of merely substituting in a formula. The expression for ΔH^0 is

$$\Delta H^0 = -18{,}280 - 14.912T + 7.481 \times 10^{-3}T^2 - 9.39 \times 10^{-7}T^3 \text{ cal},$$

and hence

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^0}{RT^2} = -\frac{18{,}280}{RT^2} - \frac{14.912}{RT} + \frac{7.481 \times 10^{-3}}{R} - \frac{9.39 \times 10^{-7}}{R} T.$$

Upon integration this gives

$$\ln K_p = \frac{18{,}280}{RT} - \frac{14.912}{R} \ln T + \frac{7.481 \times 10^{-3}}{R} T - \frac{4.70 \times 10^{-7}}{R} T^2 + \text{const.}$$

Multiplication through by RT and changing the sign gives $-RT \ln K_p$, which is equal to ΔF^0, so that

$$\Delta F^0 = -18{,}280 + 14.912T \ln T - 7.481 \times 10^{-3}T^2 + 4.70 \times 10^{-7}T^3 - IT$$

in calories.

At 773°K, the value of K_p is 1.43×10^{-5}, so that

$$\Delta F^0 = -RT \ln K_p = -2.303 \times 1.987 \times 773 \log 1.43 \times 10^{-5}$$

$$= 17{,}140 \text{ cal.}$$

If this is substituted in the expression for ΔF^0 with T equal to 773°, it is found that I is 47.86.

The problem requires an expression for ΔF^0 for 1 mole of NH_3; that given above is for 2 moles, as in the chemical equation. It is necessary, therefore, to divide by two; the final result is

$$\Delta F^0 = -9{,}140 + 7.456 \ln T - 3.741 \times 10^{-3}T^2 + 2.35 \times 10^{-7}T^3 - 23.93\, T \text{ calories.}$$

From this expression ΔF^0 can be calculated for any temperature, within the range for which the equation for ΔH^0 is applicable.

35e. Standard Free Energies of Compounds.—For purposes of calculation it is convenient to tabulate the molar free energies of substances in their standard states, i.e., 1 atm pressure for (ideal) gases and the pure state for liquids and solids. Since these are employed to calculate standard free energy *changes* in reactions, it is not necessary to know the *absolute* free energies of the various substances concerned. The situation is exactly similar to that considered in connection with the study of enthalpy in § 7c. Just as in the latter case, a convention is adopted according to which *the free energy of all elements in their standard states is arbitrarily taken as zero at all temperatures.* The standard free energy change ΔF^0 for the reaction between hydrogen and oxygen at 25°C to form 1 mole of water in the gaseous state is −54.64 kcal, as seen in § 35c. By convention, the free energies of the hydrogen and oxygen gases are both taken as zero, and hence the molar standard free energy of water vapor, i.e., at 1 atm pressure, would be −54.64 kcal at 25°C.

By the use of the methods referred to in § 35c and § 35d, the standard free energy changes accompanying the formation of various compounds from their elements have been determined, and these, in accordance with the convention given above, represent the standard (molar) free energies of the substances. Some of the results obtained in this manner are recorded in Table

TABLE 35.1. STANDARD MOLAR FREE ENERGIES OF FORMATION OF COMPOUNDS AT 25°C

Solids and Liquids	ΔFf^0_{298}	Gases	ΔFf^0_{298}
$H_2O(l)$	−56.6902 kcal	H_2O	−54.6357 kcal
$CH_3OH(l)$	−39.73	HCl	−22.769
$C_2H_5OH(l)$	−41.77	CH_4	−12.140
$C_6H_6(l)$	+29.756	C_2H_2	+50.000
$C_6H_5 \cdot CH_3(l)$	+27.282	C_2H_4	+16.282
$CH_3COOH(l)$	−93.8	C_2H_6	−7.860
$NaCl(c)$	−91.785	H_2S	−7.892
$AgCl(c)$	−26.224	CO_2	−94.2598
$AgI(c)$	−15.85	NH_3	−3.976
$HgO(c, \textit{red})$	−13.990	CO	−32.8079
$HgO(c, \textit{yellow})$	−13.959	SO_2	−71.79
$PbO(c, \textit{red})$	−45.25	SO_3	−88.50
$PbS(c)$	−22.15	NO	+20.719
$PbSO_4(c)$	−193.89	NO_2	+12.390

35.1 for a temperature of 25°C. The physical meaning of these data may be understood more clearly by writing out the equations in full, e.g.,

$$\tfrac{1}{2}H_2(g, 1 \text{ atm}) + \tfrac{1}{2}Cl_2(g, 1 \text{ atm}) = HCl(g, 1 \text{ atm}) \qquad \Delta Ff^0_{298} = -22.69 \text{ kcal}$$

$$C(c) + O_2(g, 1 \text{ atm}) = CO_2(g, 1 \text{ atm}) \qquad \Delta Ff^0_{298} = -94.2598$$

$$C(c) + 2H_2(g, 1 \text{ atm}) + \tfrac{1}{2}O_2(g, 1 \text{ atm}) = CH_3OH(l) \qquad \Delta Ff^0_{298} = -39.73$$

By indicating the pressures of the gases it is perhaps unnecessary to insert the zero superscript in the symbol ΔF^0, since they represent alternative methods of stating the same facts. However, both are given here for the sake of completeness, and to facilitate an understanding of the significance of the results; in any event the standard state of a gas refers to the *ideal* gas at 1 atm.

The standard free energies in Table 35.1 can be used to calculate the standard free energy changes for reactions at 25°C, in the same way as the enthalpies were employed in § 7c to calculate heats of reaction. For example, in the reaction

$$\begin{array}{ccccccc} CH_4(g) & + & 2O_2(g) & = & CO_2(g) & + & 2H_2O(l), \\ -12.14 & & 0 & & -94.26 & & 2(-56.69) \end{array}$$

the standard free energy values, allowing for the number of moles in each case, are inserted below the formula for each reactant and product. The standard free energy change for the complete reaction at 25°C is then given by

$$\Delta F^0 = [(-94.26) + 2(-56.69)] - [(-12.14) + 0] = -195.50 \text{ kcal.}$$

If the value of ΔF^0 for a reaction is known at one temperature, it is theoretically possible to derive the values for other temperatures by the procedure described in § 35d.

Example: Calculate the equilibrium constant K_p at 25°C for the reaction

$$2H_2S(g) + SO_2(g) = 2H_2O(g) + 3S(c).$$

From Table 35.1 it is seen that for this reaction

$$\begin{aligned}\Delta F^0 &= [2(-54.64) + 0] - [2(-7.89) + (-71.79)] \\ &= -21.71 \text{ kcal or } -21{,}710 \text{ cal.}\end{aligned}$$

Since $-\Delta F^0 = RT \ln K_p$, it follows that $\ln K_p = -\Delta F^0/RT$, or

$$\log K_p = -\frac{\Delta F^0}{2.303RT} = \frac{21{,}710}{2.303 \times 1.987 \times 298.2} = 15.91$$

$$K_p = 8.1 \times 10^{15} \text{ at } 25°\text{C}.$$

The high value of K_p indicates that the reaction as written above goes virtually to completion.

The example just given emphasizes the importance of the interpretation of ΔF^0 as a measure of the equilibrium constant of a reaction. It is seen from equation (34.1) that ΔF^0 will be negative when K is greater than unity, i.e., when at equilibrium the products exceed the reactants. On the other hand, ΔF^0 will be positive when K is less than unity, so that at equilibrium there will be more reactants than products. A reaction with positive ΔF^0 may still take place spontaneously by suitable choice of conditions so that the Q term in the expression

$$\Delta F = \Delta F^0 + RT \ln Q,$$

obtained by combining equations (34.1) and (35.3), is small enough to make ΔF negative. However, the larger the positive value of ΔF^0, the less favorable is the equilibrium constant and, even if the conditions are determined under which the reaction will occur, i.e., Q very small, the yield of products at equilibrium would be so small as to make the process worthless. As a rough criterion, it may be stated that if ΔF^0 exceeds +10,000 cal, the reaction will be of doubtful utility.

ENTROPY AND FREE ENERGY

36a. The Third Law of Thermodynamics.—It was seen in § 9a that the free energy change associated with a given process is related to the corresponding enthalpy and entropy changes by the equation $\Delta F = \Delta H - \Delta(TS)$ and at constant temperature T this becomes

$$\Delta F = \Delta H - T\Delta S. \tag{36.1}$$

If all the substances concerned are in their standard states at the temperature T, equation (36.1) takes the form

$$\Delta F^0 = \Delta H^0 - T\Delta S^0. \tag{36.2}$$

The standard enthalpy changes ΔH^0 of many reactions are known or can be determined from calorimetric measurements, as seen in Chapter 3; hence, if the entropy changes were known there would be available a method for determining free energy changes. This would be particularly useful for reactions which go to virtual completion; for such reactions it is not possible to determine the equilibrium constant, and hence ΔF^0, by direct experiment.

If the *absolute entropies* of elements and their compounds in their standard states could be measured or their values calculated, the standard entropy change for a reaction involving these substances could be determined. The matter of evaluating standard free energy changes thus reduces itself to one of obtaining the absolute entropies of the materials taking part in the reaction.* The fundamental problem lies in the establishment of an entropy zero for each substance, but this has been overcome by the enunciation of what has become known as the **third law of thermodynamics.** Like the other laws of thermodynamics, this is largely a law of experience; in other words, it leads to results which are in agreement with those obtained by direct experiment. In addition, however, it has a certain amount of theoretical support. In its simplest terms the law may be stated in the following manner: *the entropy of a perfect crystalline solid of a pure substance is zero at the absolute zero of temperature.* With this postulate the problem of obtaining absolute entropies may be regarded as solved, for in principle the change of entropy with temperature can be determined by experimental methods; hence, the actual entropy of an element or compound at any desired temperature may be obtained.

36b. Determination of Entropy from Thermal Measurements.—If equation (8.11) for a small entropy change at constant pressure is integrated between the absolute temperatures of zero and T, the result is

$$S_T - S_0 = \int_0^T C_P \frac{dT}{T} = \int_0^T C_P \, d \ln T, \tag{36.3}$$

where S_T and S_0 are the entropies at the temperature T and at the absolute zero, respectively; C_P is the heat capacity of the substance at constant pressure. According to the third law of thermodynamics, S_0 is zero for a perfect crystalline solid, and hence *the entropy of a solid substance* at any temperature is given by

$$S = \int_0^T C_P \frac{dT}{T} = \int_0^T C_P \, d \ln T. \tag{36.4}$$

The molar entropy can thus be determined by plotting the experimental values of the heat capacity C_P against $\ln T$ (or C_P/T against T) for a number of temperatures, and measuring the area beneath the curve from zero to the temperature at which the entropy is required (see § 8e). Reliable heat capacity determinations cannot be made below about 10° or 15°K; it is

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* It should be pointed out that the situation with regard to ΔS^0 is quite different from that with ΔF^0 and ΔH^0; the evaluation of ΔS^0 is generally based on the absolute entropies of elements and compounds. Since absolute values of free energy and enthalpy cannot be determined experimentally, the convention adopted is to take the values for elements to be zero.

fortunate, therefore, that at very low temperatures the necessary data can be obtained from the Debye equation (20.2), the value of the characteristic temperature θ being readily derived from measurements at higher temperatures. Actually the Debye equation gives C_V, but the difference between C_P and C_V at low temperatures is so small as to be negligible. The evaluation of the entropy of a crystalline solid may be illustrated by reference to Fig. 36.1; the

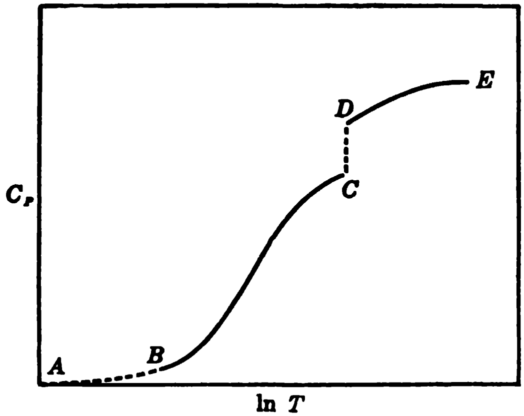

Fig. 36.1. Evaluation of entropy of crystalline solid

heat capacities plotted on the curve *BC* are the experimental values, the point *B* corresponding to the lowest temperature, i.e., 10° or 15°K, at which satisfactory measurements are possible. The portion *AB*, down to the absolute zero, is then derived from the low-temperature form of the Debye specific heat equation, i.e., equation (20.2). It is evident from this equation that the heat capacity of a solid must approach zero rapidly at temperatures below about 10°K, and so this part of the curve has little influence on the accuracy of the results. The area enclosed by the curve *ABC*, the ln *T* axis and the ordinate corresponding to any given temperature is equivalent to the entropy of the solid at that temperature.

If the solid undergoes an enantiotropic change of crystalline form on heating (§ 37d), the heat capacity curve will not be continuous, but will show a break, e.g., *CD* in Fig. 36.1, at the transition point. To the entropy obtained from the area under the two curves *ABC* and *DE* must now be added the entropy of transition, that is, the heat absorbed in the transition divided by the transition temperature on the absolute scale (§ 8f).

If the substance being studied is a liquid or a gas at the temperature at which the entropy is required, the heat capacity measurements on the crystalline solid are made up to its melting point, and the entropy at that temperature is determined in the manner just described. Heat capacity data of the liquid up to its boiling point are now plotted, in the same way, against ln *T*, and the area under the curve gives the increase in entropy in passing from the melting point to the boiling point; this is then added to the entropy of the solid at its melting point. The addition of the entropies of fusion and vaporization (§ 8f) to this total gives the entropy of the *gas* (vapor) at the boiling point. An illustration of the results obtained in this manner for nitrogen is given in Table 36.1 (W. F. Giauque and J. O. Clayton, 1933); the values are in e.u., i.e., cal per deg, per mole. The entropy of nitrogen gas at 77.32°K and 1 atm pressure is thus 36.31 e.u. per mole.

TABLE 36.1. THE MOLAR ENTROPY OF NITROGEN GAS AT THE BOILING POINT

0° to 10°K from Debye equation ($\theta = 68$)	0.458 e.u.
10° to 35.61°K (transition point) from heat capacities (graphical)	6.034
Entropy of transition, from heat of transition (54.71/35.61)	1.536
35.61° to 63.14°K (melting point) from heat capacities (graphical)	5.589
Entropy of fusion, from heat of fusion (172.3/63.14)	2.729
63.14° to 77.32°K (boiling point) from heat capacities (graphical)	2.728
Entropy of vaporization, from heat of vaporization (1332.9/77.32)	17.239
Total	36.31 e.u.

It is the general practice to record entropies of substances in their standard states at 25°C. Two additions must, therefore, be made to the entropy of nitrogen gas given above. First, that due to the increase of entropy of the gas as the temperature is raised from the boiling point to 25°C and second, a correction for departure from ideal behavior at 1 atm pressure. The effect of the temperature change may be obtained in the usual manner, by plotting the heat capacity of the gas against ln T. Alternatively, the heat capacity of the gas at atmospheric pressure may be expressed as a function of the temperature (§ 7i), and the resulting expression can be integrated with respect to ln T between the limits of the boiling point and 25°C. When accurate heat capacity measurements of the gas are not available, the values for the ideal gas may be obtained by calculations involving statistical methods (§ 36c). In this event, the ideal gas correction is determined at the boiling point by means of a convenient equation of the gas. For nitrogen at 77.32°K this is found to be +0.22 e.u. per mole. Then the increase in entropy from 77.32° to 298.15°K (25°C) is obtained from the ideal gas statistical heat capacities at 1 atm pressure; the value is 9.36 e.u. per mole. Hence, the standard molar entropy of nitrogen gas at 25°C is $36.31 + 0.22 + 9.36 = 45.89$ e.u. This result is probably slightly too large due to small experimental errors in the results quoted in Table 36.1.

36c. Entropy of Gases by the Statistical Method.—During recent years remarkable progress has been made in the calculation of entropy and other thermodynamic properties of gases by methods based on the quantum theory of energy and the science of statistical mechanics. The total energy of a molecule is made up of various kinds, e.g., translational, rotational, vibrational and electronic; there is also nuclear energy, but this need not be considered for the present purpose.

As already seen, since each of these energies is quantized, only certain definite values of the various forms of energy, i.e., specific energy levels, are permitted. The relative number of molecules in each level can be expressed in terms of the Boltzmann equation (3.20). Let N_0 be the number of molecules in the lowest energy state present in a given volume of gas, and let N_i be the number of molecules in this volume possessing energy ϵ_i in excess of the lowest level; then at the temperature T, the Boltzmann equation requires that

$$\frac{N_i}{N_0} = e^{-\epsilon_i/kT}, \tag{36.5}$$

where ϵ_i is the energy per molecule and k, the Boltzmann constant, is the gas constant for a single molecule (§ 3d). Quantum mechanics indicates that a slight modification of equation (36.5) is necessary to allow for the fact that some energy states consist of two or more closely spaced (or identical) levels. A **statistical weight** factor g_i is defined, for each energy state, as *the number of levels having essentially the same energy* ϵ_i. The appropriate form of the Boltzmann equation is then

$$\frac{N_i}{N_0} = \frac{g_i}{g_0} e^{-\epsilon_i/kT}$$

or

$$N_i = \frac{N_0}{g_0} g_i e^{-\epsilon_i/kT}, \tag{36.6}$$

where g_0 is the statistical weight of the lowest energy state.

The total number of molecules N in the given volume is equal to the sum of all the N_i values for all the possible energy states, so that, from equation (36.6)

$$N = \Sigma N_i = \frac{N_0}{g_0} \Sigma g_i e^{-\epsilon_i/kT}, \tag{36.7}$$

where the factor N_0/g_0 has been taken outside the summation sign since it is a constant. The quantity defined by the sum in equation (36.7) is called the **partition function** of the molecule; it will be represented here by the symbol Z so that

$$Z = \Sigma g_i e^{-\epsilon_i/kT}. \tag{36.8}$$

The partition function is then the sum of the $g_i e^{-\epsilon_i/kT}$ terms for every possible energy state of the molecules.*

Since there are N_i molecules in each state of energy ϵ_i, referred to the lowest energy state, the total energy of all the molecules, on this basis, is the sum of all the $N_i\epsilon_i$ terms. Strictly speaking, this summation assumes that the energies of the molecules are independent of one another, and this requires the system to be an ideal gas. Hence, if E is the total energy of all the molecules

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* Although some writers use Z for the partition function, the symbol Q is perhaps more frequently employed; it is avoided here, however, because this letter has been used to indicate the "reaction quotient" in the earlier part of this chapter.

in a given volume of ideal gas at the temperature T, and E_0 is the total energy when all the molecules occupy the lowest possible energy level, then

$$E - E_0 = \Sigma N_i \epsilon_i.$$

Utilizing equation (36.6) to express the N_i values, this becomes

$$E - E_0 = \frac{N_0}{g_0} \Sigma g_i \epsilon_i e^{-\epsilon_i/kT} \tag{36.9}$$

If equation (36.8) defining the partition function is differentiated with respect to temperature, at constant volume, it can be readily shown that

$$kT^2 \left(\frac{\partial Z}{\partial T}\right)_V = \Sigma g_i \epsilon_i e^{-\epsilon_i/kT}, \tag{36.10}$$

where the summation is the same as in equation (36.9). Now upon combining equations (36.7), (36.9) and (36.10), the result is

$$E - E_0 = \frac{NkT^2}{Z}\left(\frac{\partial Z}{\partial T}\right)_V = NkT^2 \left(\frac{\partial \ln Z}{\partial T}\right)_V. \tag{36.11}$$

If the volume under consideration contains 1 mole of gas, N is the Avogadro number and Nk is equal to R, the molar gas constant. Hence, equation (36.11) for the energy of 1 mole of ideal gas becomes

$$E - E_0 = RT^2 \left(\frac{\partial \ln Z}{\partial T}\right)_V. \tag{36.12}$$

Further, by equation (6.20) differentiation with respect to temperature, noting that E_0 is a constant, gives for the molar heat capacity at constant volume

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \left[\frac{\partial}{\partial T}\left(RT^2 \frac{\partial \ln Z}{\partial T}\right)_V\right]. \tag{36.13}$$

Utilizing equation (8.12) an expression is obtained for the molar entropy of the ideal gas, with reference to the value at the absolute zero; thus,

$$\begin{aligned} S - S_0 &= \int_0^T \frac{C_V}{T}\, dT \\ &= RT\left(\frac{\partial \ln Z}{\partial T}\right)_V + R \ln Z - R \ln Z_0. \end{aligned} \tag{36.14}$$

In order to apply this result to determine absolute entropies, it is necessary to find an expression for S_0, the entropy of an ideal gas at the absolute zero. For this purpose use is made of the Boltzmann-Planck equation (8.22). If a gas could exist at the absolute zero, all the molecules would be in the lowest energy level. The thermodynamic probability W for a single molecule would then be equal to the statistical weight of this state. i.e., to g_0. For N distinguishable molecules, the total probability would be g_0^N, but since the molecules in a gas are not distinguishable, this probability must be divided by $N!$, so that for N molecules (or 1 mole) of gas at the absolute zero, the entropy would be given by equation (8.22) as

$$\begin{aligned} S_0 &= k \ln \frac{g_0^N}{N!} \\ &= R \ln g_0 - k \ln N! \qquad (36.15)^* \end{aligned}$$

At the absolute zero, the energies of all the molecules are zero with reference to the lowest energy state; that is, the only energy state is the one for which $\epsilon_i = 0$. Consequently, by equation (36.8), the partition function Z_0 for the gas at absolute zero is given by

$$Z_0 = g_0 e^{-0/kT} = g_0.$$

Hence, equation (36.15) may be written as

$$S_0 = R \ln Z_0 - k \ln N!$$

and substitution into equation (36.14) leads to the required result for the absolute entropy of an ideal gas at temperature T, namely,

$$S = RT\left(\frac{\partial \ln Z}{\partial T}\right)_V + R \ln Z - k \ln N! \qquad (36.16)$$

It is apparent that if the partition function for a given molecular species were known at a number of temperatures, it would be possible to evaluate the entropy. The molar energy and heat capacity could also be determined, if required, from equations (36.12) and (36.13), respectively. The method used to evaluate Z is based on the supposition that, in any specified electronic state, the contributions of translation, rotation and vibration to the total energy are independent. If these energies are strictly additive, it can be shown from equation (36.8) that the total partition function is the product of the partition function for the various individual forms of energy. Further, since the expressions for entropy, etc., involve $\ln Z$, it is evident that the various thermodynamic quantities may be determined for each type of energy and the results added. In applying equation (36.16) to evaluate the entropy, the term $-k \ln N!$ is included with the translational contribution.

With the notable exception of oxygen, diatomic and simple polyatomic molecules occupy the lowest electronic level at all reasonable temperatures. The electronic partition function is thus unity and since ln 1 is zero, the contribution to the thermodynamic functions is zero. For oxygen molecules, the electronic partition function is 3, due to a triply degenerate electronic ground state.

In determining the translational partition function, an expression for the

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[*] In a perfect crystal, the arrangement of the molecules in a lattice makes them distinguishable; in this case $W = g_0^N$ and $S_0 = R \ln g_0$. If the statistical weight g_0 of the molecules in the lowest energy state of the crystal is 1, then $S_0 = 0$ in accordance with the third law of thermodynamics.

permitted energy levels is obtained from wave mechanics. As these levels are close together, the summation equation (36.8) is replaced by integration and the result obtained is

$$Z_{tr} = \frac{(2\pi mkT)^{3/2}}{h^3} V, \tag{36.17}$$

where m is the actual mass of the molecule, h is the Planck constant (§ 15b) and V is the volume of the gas. If this value for Z is inserted into equations (36.12) and (36.13) it is found that $E_{tr} = \frac{3}{2}RT$, since the translational energy at the absolute zero is zero, and that $C_V = \frac{3}{2}R$. These are identical with the results obtained in Chapter 2 from the kinetic molecular theory of ideal gases.

The translational entropy is obtained by combining equations (36.16) and (36.17) and utilizing the Stirling approximation for large numbers, i.e.,

$$\ln N! = N \ln N - N.$$

The result is

$$S_{tr} = R\left[\ln \frac{(2\pi mkT)^{3/2}}{h^3 N} V + \frac{5}{2}\right] \tag{36.18}$$

or, inserting the known values of k, h, N and noting that $m = M/N$, where M is the molecular weight, the result for a pressure of 1 atm is

$$\begin{aligned} S^0_{tr} &= \tfrac{3}{2}R \ln M + \tfrac{5}{2}R \ln T - 2.311 \\ &= \tfrac{3}{2}(4.576 \log M) + \tfrac{5}{2}(4.576 \log T) - 2.311 \text{ e.u. mole}^{-1} \end{aligned} \tag{36.19}$$

for the molar translational entropy in the standard state. Since a monatomic gas possesses no rotational or vibrational energy, only electronic and translational energy, equations (36.18) and (36.19) give the actual entropy of an ideal monatomic gas, except for a possible electronic contribution.

Example: Determine the standard molar entropy at 25°C of mercury vapor, which is a monatomic gas. (All the molecules (atoms) are in a single electronic state, so that the electronic partition function is unity.)

For mercury, M is 200.61, so that at 25°C ($T = 298.15$),

$$\begin{aligned} S^0_{tr} &= \tfrac{3}{2}(4.576 \log 200.61) + \tfrac{5}{2}(4.576 \log 298.15) - 2.311 \\ &= 41.800 \text{ e.u. mole}^{-1}. \end{aligned}$$

The electronic partition function Z_{el} is 1, so that $S_{el} = 0$. Hence, the required standard entropy is 41.800 e.u. mole^{-1}.

The most accurate method for determining the rotational and vibrational partition functions is to sum the $g_i e^{-\epsilon_i/kT}$ terms using the ϵ_i values obtained by analysis of the band spectra of the molecules, as explained in Chapter 9. Because the number of terms to be included, especially at high temperatures, can be large, the computations are often very laborious. Although the procedure has been simplified to some extent by means of mathematical devices and by the aid of electronic computers, it is used only where spectroscopic data of sufficient precision are available to make the detailed calculation worth while.

In many cases reasonably good results for the rotational contribution can be obtained by using the simple, although not exact, equation (29.3), to express the rotational energy, the statistical weight factor for the level J being $2J + 1$. Again, replacing summation by integration, the result obtained for a diatomic molecule is

$$Z_{\text{rot}} = \frac{8\pi^2 IkT}{\sigma h^2}, \tag{36.20}$$

where I is the moment of inertia of the molecule and σ is a symmetry number which is 1 for an unsymmetrical diatomic molecule and 2 for a symmetrical one. From equations (36.20) and (36.16) and the known values of the constants k and h, it is found that

$$S^0_{\text{rot}} = 4.576(\log I + \log T - \log \sigma + 38.82) \text{ e.u. mole}^{-1}, \tag{36.21}$$

where I, in cgs units, can be obtained from spectroscopic data.

A similar treatment can be applied to the vibrational energy contribution using equation (29.6) minus the zero-point energy to give the possible ϵ_i values for vibrational states with respect to the lowest ($v = 0$) state. The expression for the summation can be evaluated directly, without integration, and it is found that for a diatomic molecule

$$Z_{\text{vib}} = (1 - e^{-x})^{-1} \tag{36.22}$$

$$x = \frac{hc\omega}{kT} = 1.439\,\frac{\omega}{T},$$

in which ω, in cm^{-1}, is the equilibrium vibration frequency of the molecule. From equation (36.16) it then follows that

$$S^0_{\text{vib}} = \frac{1.987x}{e^x - 1} - 4.576 \log (1 - e^{-x}) \text{ e.u. mole}^{-1}. \tag{36.23}$$

Example: From the spectrum of molecular nitrogen, it is found that the moment of inertia of the molecules is 13.9×10^{-40} g cm^2 and the equilibrium vibration frequency is 2360 cm^{-1}. Determine the standard entropy of the gas at 25°C.

Since the ground state of molecular nitrogen is a single level, Z_{el} is unity, and the molecular weight M being 28.00, the combined standard translational and electronic entropy, the latter being actually zero, is given by equation (36.19) as

$$\begin{aligned} S^0_{\text{tr}} &= \tfrac{3}{2}(4.576 \log 28.00) + \tfrac{5}{2}(4.576 \log 298.2) - 2.311 \\ &= 35.9 \text{ e.u. mole}^{-1}. \end{aligned}$$

The vibrational frequency is 2360 cm^{-1}, and hence x, i.e., $1.439\,\omega/T$, is 11.4. Insertion of this result into equation (36.23) gives a value for S_{vib} that is negligibly small. The vibrational contribution to the entropy of molecular nitrogen at 25°C may thus be taken as zero.

The moment of inertia is 13.9×10^{-40} g cm^2, and σ is 2, since the nitrogen molecule is symmetrical; hence, by equation (36.21),

$$S^0_{\text{rot}} = 4.576\,[\log (13.9 \times 10^{-40}) + \log 298.2 - \log 2 + 38.82]$$
$$= 9.8 \text{ e.u. mole}^{-1}.$$

The total entropy of nitrogen gas in its standard state at 25°C is thus the sum of 35.9 and 9.8 e.u., i.e., 45.7 e.u. mole^{-1}, which may be compared with the thermal, i.e., third law, value of 45.89 e.u. mole^{-1} given in § 36b.

The principles described above for diatomic molecules have been extended to polyatomic molecules. The expression for the translational entropy is the same for all atoms and molecules. The rotational contribution for a nonlinear polyatomic molecule is

$$S^0_{\text{rot}} = 4.576(\tfrac{1}{2} \log ABC + \tfrac{3}{2} \log T - \log \sigma + 58.51) \text{ e.u. mole}^{-1},$$

where A, B, and C are the three moments of inertia of the molecule in cgs units. The vibrational entropy is obtained by a sum of terms like equation (36.23), one for each of the $3n - 6$ (or $3n - 5$) vibrational modes of the molecule.

In general, where entropy values of gases have been obtained by both the statistical and heat capacity (thermal) methods the results are in excellent agreement, thus providing experimental support for the third law of thermodynamics upon which the latter method is based. For example, the statistical entropy of nitrogen gas in its standard state at 25°C is 45.77, compared with the thermal value of 45.89 e.u. per mole obtained above; the former is believed to be the more accurate. There are, however, a few cases, notably hydrogen, water, nitric oxide, carbon monoxide and nitrous oxide, where the thermal entropies are lower than the statistical values. The discrepancies in these instances are due to the fact that the solids do not constitute perfect crystals in the sense required by the third law of thermodynamics. The correct entropies are, in fact, those obtained by the statistical method based on spectroscopic data.

With hydrogen, the thermal entropy is in error because of the presence of both ortho- and para-forms (§ 29j) in the liquid and solid used for the heat capacity measurements. Since orthohydrogen can have only odd values of the rotational quantum number, it follows that the lowest level is the one for which $J = 1$. Consequently, the presence of the ortho-form in the solid means that some of the hydrogen molecules must still be rotating even at the absolute zero. Such a solid is not a perfect crystal and its entropy cannot be zero. By making allowance for the rotational contribution to the entropy of the solid, the thermal entropy can be corrected and the results so obtained are in agreement with the statistical value.

The discrepancies observed with NO, CO and N_2O, i.e., NNO, are attributed to the similarity of the atoms present. As a result, the molecule can be oriented in the crystal in two alternative ways, viz., NO and ON, CO and OC, and NNO and ONN. The solids are thus, in effect, a mixture of two species and the entropy of a mixture is always greater than that of the separated components. Hence, the entropy at the absolute zero is finite, and not zero as is assumed in determining the thermal entropy. From the point of view which relates entropy to the degree of disorder (§ 8h), it is seen that the alternative orientations of the solid implies a degree of disorder and hence a finite, not zero, entropy.*

36d. Application of Entropy Data.—By the use of thermal and statistical methods, the standard molar entropies of a number of elements and compounds have been determined; some of the values at 25°C are recorded in Table 36.2 in the usual entropy units, i.e., cal per deg, per mole. From these data it is possible to derive the standard entropy change ΔS^0 for any reaction involving the substances concerned. For such a reaction as the formation of liquid benzene from its elements, viz.,

TABLE 36.2. STANDARD MOLAR ENTROPIES AT 25°C

Solids and Liquids				Gases			
	S^0_{298}		S^0_{298}		S^0_{298}		S^0_{298}
Graphite	1.3609 e.u.	Hg(l)	17.8 e.u.	H_2	31.211 e.u.	CO_2	51.061 e.u
Zn(c)	9.95	$Br_2(l)$	36.4	O_2	49.003	HCl	44.617
Ag(c)	10.206	NaCl(c)	17.30	N_2	45.767	CH_4	44.50
Na(c)	12.2	AgCl(c)	22.97	Cl_2	53.286	C_2H_2	47.997
$I_2(c)$	27.9	AgI(c)	27.3	Br_2	58.639	C_2H_4	52.45
$H_2O(l)$	16.716	$CH_3OH(l)$	30.3	I_2	62.280	C_2H_6	54.85
HgO(c, red)	17.2	$C_2H_5OH(l)$	38.4	H_2O	45.106	CH_3OH	56.8
HgO(c, yellow)	17.5	$C_6H_6(l)$	41.30	NH_3	46.01	H_2S	49.15
PbO(c, red)	16.2	$C_6H_5\cdot CH_3(l)$	52.48	CO	47.301	SO_2	59.40
PbS(c)	21.8	$CH_3COOH(l)$	38.2				
$PbSO_4(c)$	35.2						

$$6\text{C (graphite)} + 3\text{H}_2(g) = \text{C}_6\text{H}_6(l),$$

the value of ΔS^0 is seen to be given by

$$41.30 \text{ (for } C_6H_6) - [6 \times 1.36 \text{ (for 6C)} + 3 \times 31.21 \text{ (for } 3H_2)] = -60.49 \text{ e.u.}$$

As seen in § 36a, a knowledge of the standard entropy change, in conjunction with the change of enthalpy in the reaction, permits the evaluation of the standard free energy change of the process. In this way it is possible to determine the equilibrium constant of a reaction from purely thermal measurements or from thermal measurements, which give ΔH^0, in conjunction with statistical calculations based on spectroscopic information. It is of interest to mention that in certain cases accurate ΔH^0 values have been obtained from spectroscopic data (§ 29h), and since the entropy can also be obtained from similar measurements, it has been found possible to calculate free energy changes and equilibrium constants of some reactions with great precision merely from a study of the spectra of the molecules concerned.

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* From the statistical point of view, for a solid $S_0 = R \ln g_0$ and in the cases mentioned g_0 approaches 2, since there are two permitted orientations; hence S_0 is roughly 1.38 e.u. mole^{-1}.

Example: **The standard heat of formation of liquid benzene at 25°C is 11.72 kcal per mole (Table 7.1); calculate the standard free energy of formation of this substance at 25°C.**

The value of ΔH^0 for the reaction $6\text{C}(c) + 3\text{H}_2(g) = \text{C}_6\text{H}_6(l)$ is 11,720 cal, and since ΔS^0 has been found above to be -60.49 cal deg^{-1} mole^{-1}, it follows from equation (36.2) that at 25°C, i.e., 298.2°K,

$$\Delta F^0 = 11{,}720 - 298.2 \times (-60.49) = 29{,}760 \text{ cal mole}^{-1}.$$

The use of entropy data makes possible the determination of standard free energies of formation and the standard free energy changes of reactions which could not be obtained by the direct experimental methods described in § 35c. In fact many of the values quoted in Table 35.1, especially for organic compounds, were actually derived in this manner.

36e. Free Energy Function.—With the tabulated values of standard state enthalpies and free energies of formation and molar entropies at 25°C (Tables 7.1, 35.1 and 36.2), together with the information concerning the variation of heat capacity with temperature (Table 7.4), it is possible to calculate enthalpy, free energy and entropy changes for any desired temperature. An alternative procedure, which owes its use largely to the development of statistical methods for calculating thermodynamic quantities, involves the free energy function, defined by

$$\text{Free energy function} = -\left(\frac{F^0 - H_0^0}{T}\right), \tag{36.24}$$

where F^0 is the standard molar free energy of the substance at the temperature T and H_0^0 is the standard molar enthalpy at a reference temperature, generally the extrapolated value for 0°K such as is implied in ΔH_0^0. The free energy function is generally expressed in cal deg^{-1} mole^{-1} units, which are the same as for entropy.

Before proceeding to show how the free energy function is determined, the method of using it will be described. The change in free energy function $-\Delta(F^0 - H_0^0)/T$ for a specified reaction can be determined in the usual manner by taking the sum of these functions for the reaction products and subtracting the sum for the reactants at the temperature T. By separating the two terms in the free energy function it is seen that

$$-\Delta\left(\frac{F^0 - H_0^0}{T}\right) = -\frac{\Delta F^0}{T} + \frac{\Delta H_0^0}{T}$$

or

$$\Delta F^0 = T\Delta\left(\frac{F^0 - H_0^0}{T}\right) + \Delta H_0^0. \tag{36.25}$$

The first term on the right can be determined from tables of the free energy function at various temperatures and the second, as seen earlier, is a constant for the given reaction, which can be derived from enthalpy and heat capacity measurements. Hence, ΔF^0 can be evaluated directly at any desired temperature. Because the free energy function does not vary greatly with temperature, values are generally tabulated at intervals of a few hundred degrees and data for intermediate temperatures are easily obtained by interpolation.

Free energy functions and ΔH_0^0 are determined by two general procedures; one, applicable to gases only, is a statistical method involving partition functions whereas the other, based on experimental heat capacities, is commonly restricted to solids, although it can also be used for gases if necessary. For 1 mole of ideal gas PV in the equation $H = E + PV$, which defines the enthalpy (§ 6e), may be replaced by RT; the result is

$$H = E + RT.$$

At the absolute zero ($T = 0$), RT is zero and then

$$H_0 = E_0,$$

so that, upon subtraction

$$H - H_0 = (E - E_0) + RT. \tag{36.26}$$

Finally, upon adding equation (9.2), i.e.,

$$F = H - TS,$$

and dividing by T, it follows that

$$-\left(\frac{F - H_0}{T}\right) = -\left(\frac{E - E_0}{T}\right) + S - R.$$

If the various quantities apply to the standard states, i.e., ideal gas at 1 atm pressure, the left side of this equation is then the free energy function. Upon introducing equation (36.12) for $E - E_0$, equation (36.16) for S, and using the Stirling approximation for $\ln N!$, it is readily found that

$$-\left(\frac{F^0 - H_0^0}{T}\right) = R \ln \frac{Z^0}{N}, \tag{36.27}$$

where Z^0 is the partition function for 1 atm pressure.

The evaluation of ΔH_0^0 is based on the relationship

$$\Delta H_0^0 = \Delta H^0 - \Delta(H^0 - H_0^0),$$

so that if $H^0 - H_0^0$ for substances were known at the series of temperatures ΔH_0^0 could be easily obtained from the value of ΔH^0 at any temperature. By combining equations (36.12) and (36.26) it is seen that

$$H^0 - H_0^0 = RT^2\left(\frac{\partial \ln Z^0}{T}\right)_V + RT. \tag{36.28}$$

Where high precision is required the partition functions must be determined by the detailed summation procedure using spectroscopic energy values. To a good approximation, however, the partition function may be split up into the factors for translational, rotational and vibrational energies, the terms $R \ln 1/N$ in equation (36.27) and RT in equation (36.28) being retained with the translational contribution. Using the expressions for the respective partition functions, namely, equations (36.17), (36.20) and (36.22), the following results are obtained:

$\underline{-(F^0 - H_0^0)/T \text{ cal deg}^{-1} \text{ mole}^{-1}}$

Translational: $4.576(\frac{3}{2} \log M + \frac{5}{2} \log T) - 7.282$

Rotational: $4.576(\log I + \log T - \log \sigma) + 175.7$

Vibrational: $4.576 \log(1 - e^{-x})^{-1}$ where $x = 1.439\omega/T$

$\underline{H^0 - H_0^0 \text{ cal mole}^{-1}}$

Translational: $\frac{5}{2}RT = 4.968T$

Rotational: $RT = 1.987T$

Vibrational: $Rx(e^x - 1)^{-1} = 1.987x(e^x - 1)^{-1}$ where $x = 1.439\omega/T$

It should be noted that the expression for the rotational and vibrational contributions apply to diatomic molecules only. Similar expressions can be derived for polyatomic molecules. As in § 36c, it is assumed that all the molecules are in the lowest electronic state with a statistical weight of unity, so that the electronic contribution to the functions given above is zero.

The basis of the thermal method for determining the free energy function is the expression

$$-\left(\frac{F^0 - H_0^0}{T}\right) = S^0 - \left(\frac{H^0 - H_0^0}{T}\right)$$

obtained by utilizing the relationship $F^0 = H^0 - TS^0$. Since S^0 can be derived from heat capacity measurements, the problem is reduced to that of determining $H^0 - H_0^0$. For solids, to which the statistical method given above is not applicable, as well as for gases, use is made of equation (6.22), i.e., $C_P = (\partial H/\partial T)_P$, which, upon integration, gives

$$H^0 - H_0^0 = \int_0^T C_P^0 \, dT,$$

where C_P^0 refers to the heat capacity at constant pressure in the standard state, e.g., pure solid at 1 atm pressure. Hence, C_P is plotted against T and the area under the curve, between 0°K and T, gives the required $H^0 - H_0^0$. If there is a transition in the solid state, the heat of transition must be included. The procedure can be extended to gases by including the heats of fusion and vaporization and the integral of C_P^0 against T for the (ideal) gas up to the required temperature T. Because of the greater accuracy of the statistical treatment, the thermal method is rarely used for gases.

The values of $-(F^0 - H_0^0)/T$ at several temperatures and of ΔHf_0^0 for a

TABLE 36.3. FREE ENERGY FUNCTION AT SEVERAL TEMPERATURES AND STANDARD ENTHALPY OF FORMATION AT 0°K

	$-(F^0 - H_0^0)/T$ cal deg^{-1} mole^{-1}						ΔHf_0^0
Substance	298.15°	400°	600°	800°	1000°	1500°K	kcal mole^{-1}
$H_2(g)$	24.423	26.422	29.203	31.186	32.738	35.590	0
$O_2(g)$	42.061	44.112	46.968	49.044	50.697	53.808	0
$N_2(g)$	38.817	40.861	43.688	45.711	47.306	50.284	0
C(c, graphite)	0.5172	0.824	1.477	2.138	2.771	4.181	0
$CO(g)$	40.350	42.393	45.222	47.254	48.860	51.864	−27.2019
$CO_2(g)$	43.555	45.828	49.238	51.895	54.109	58.481	−93.9686
$H_2O(g)$	37.165	39.505	42.766	45.128	47.010	50.598	−57.107
$Cl_2(g)$	45.934	48.130	51.278	53.594	55.432	58.851	0
$HCl(g)$	37.692	39.721	42.545	44.554	46.127	49.052	−22.019
$NO(g)$	42.980	45.134	48.090	50.202	51.864	54.964	+21.477
$H_2S(g)$	41.17	43.52	46.85	49.31	51.29	55.16	−4.123
$CH_4(g)$	36.46	38.86	42.39	45.21	47.65	52.84	−15.987
$C_2H_6(g)$	45.27	48.24	53.08	57.29	61.11	69.46	−16.517
$C_2H_4(g)$	43.98	46.61	50.70	54.19	57.29	63.94	+14.522
$C_2H_2(g)$	39.976	42.451	46.313	49.400	52.005	57.231	+54.329
$NH_3(g)$	37.989	40.380	43.826	46.450	48.634	53.033	−9.36
$SO_2(g)$	50.82	53.36	57.09	59.94	62.28	66.82	−70.36
$SO_3(g)$	51.89	54.76	59.26	62.94	66.08	72.40	−93.06

number of substances, obtained as described above, are collected in Table 36.3. With these data, standard free energy changes and equilibrium constants can be readily determined at any required temperature within the range given in the table.

Example: Determine the equilibrium constant, with pressures in atm. for the reaction $C(c) + H_2O(g) = CO(g) + H_2(g)$ at 1000°K.

The required data from Table 36.3 are as follows:

	$CO(g)$	$H_2(g)$	$C(c)$	$H_2O(g)$	
$-(F^0 - H_0^0)/T$	48.86	32.74	2.77	47.01	cal deg^{-1}
ΔHf_0^0	−27.20	0	0	−57.11	kcal

Hence, $\Delta[(F^0 - H_0^0)/T]$ for the reaction at 1000°K is

$$-[(48.86 + 32.74) - (2.77 + 47.01)] = -31.82 \text{ cal deg}^{-1}$$

and ΔH_0^0 for the reaction is

$$[(-27.20 + 0) - \{0 + (-57.11)\}] = 29.91 \text{ kcal} = 29{,}910 \text{ cal.}$$

Hence, by equation (36.25)

$$\Delta F^0 = 1000 \times (-31.82) + 29{,}910 = -1910 \text{ cal.}$$

Since the standard state is 1 atm pressure

$$\Delta F^0 = -RT \ln K_p$$

$$-1910 = -4.576 \times 1000 \times \log K_p$$

$$K_p = 2.61$$

with pressures in atm.

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PROBLEMS

1. Derive equation (34.7) starting with equation (34.6).

2. An equimolar mixture of hydrogen, iodine and hydrogen iodide is heated in a closed vessel to 457.6°C. What will be the composition of the mixture when equilibrium is established? $K = 48.7$ for the reaction $H_2(g) + I_2(g) = 2HI(g)$.

3. The following data are available for the dissociation of iodine molecules into atoms, $I_2(g) = 2I(g)$:

°K	1073	1173	1274
Pressure, atm	0.0750	0.0918	0.1122
Degree of dissociation, α	0.189	0.342	0.523

(*a*) Determine the mean heat of dissociation for the temperature range 1073–1274°K. (*b*) What will be the degree of dissociation at 1274°K and a pressure of 0.5 atm?

4. For the reaction $C(\text{graphite}) + H_2O(g) = CO(g) + H_2(g)$, the equilibrium constant, K_p, is 2.78×10^{-2} at 800°K. (*a*) Calculate ΔF for the reaction of steam at 100 atm with carbon to form carbon monoxide and hydrogen, each at 50 atm. (*b*) Will the reaction occur spontaneously under these conditions?

5. The equilibrium constant for the reaction $Fe(c) + H_2O(g) = FeO(c) + H_2(g)$ at 700°C is 2.35 with pressures in atm. If FeO is treated at 700° with an equimolecular mixture of H_2O and H_2 at a total pressure of 1 atm, will reduction occur?

6. What is the minimum weight of solid NH_4HS which must be added to a 5.00 liter container so that equilibrium is established between solid NH_4HS and its decomposition products at 20°C? $K_p = 5.48 \times 10^{-2}$, with pressures in atm.

7. The dissociation pressure of beryllium carbide is given by $\log p\ (\text{atm}) = 7.03 - \frac{19{,}700}{T}$ in the temperature interval 1430–1669°K. The reaction is $\frac{1}{2}Be_2C(c) = Be(g) + \frac{1}{2}C(\text{graphite})$. Determine ΔH^0, ΔF^0 and ΔS^0 at 1600°K.

8. Calculate the standard free energy of methanol vapor at 25°C. The vapor pressure of liquid methanol is 122 mm at 25°.

9. (*a*) Derive equations for the variation of K_p and ΔF^0 with temperature for the reaction, $CO(g) + 2H_2(g) = CH_3OH(g)$. $C_P(CH_3OH,g) = 4.398 + 24.274 \times 10^{-3}\,T - 68.55 \times 10^{-7}\,T^2$, $L_v = 8.94$ kcal mole^{-1} at 298°K, $\Delta Ff^0_{298} = -38.69$ kcal mole^{-1}; all other required data are available in previous chapters. (*b*) If the reaction is run at 500°C starting with carbon monoxide and hydrogen in equivalent amounts, what pressure will be required to obtain a 25% yield of methanol at equilibrium?

10. The equilibrium constant, K_p, is 1.10×10^{-3} at 2200°K for the reaction $N_2 + O_2 = 2NO$. What percent by volume of NO will be produced if air at 1 atm pressure is heated to 2200°? Assume air contains 79.1% nitrogen and 20.9% oxygen by volume.

11. (*a*) Determine whether the reaction $2H_2S(g) + CH_4(g) = 4H_2(g) + CS_2(g)$ is feasible thermodynamically under standard state conditions at 25°C. $\Delta Hf^0_{298} = 27.55$ kcal mole^{-1} and $S^0_{298} = 56.84$ e.u. mole^{-1} for $CS_2(g)$; all other data will be found in the tables of the text. (*b*) When a 2 : 1 mixture of H_2S and CH_4 at a total pressure of 1 atm was reacted at 700°C, a sample of the equilibrium mixture was found to contain 325.1 mg H_2S and 54.1 mg CS_2. Calculate K_p and ΔF^0 at 700°.

12. Calculate the standard entropy of HCl(*g*) at 25°C. The moment of inertia is 2.65×10^{-40} g cm^2, the characteristic vibration frequency is 2989 cm^{-1} and the symmetry number is 1.

13. Determine the standard entropy of $Cl_2(g)$ at 25°C. $I = 115.2 \times 10^{-40}$ g cm^2, $\omega = 561$ cm^{-1}, $\sigma = 2$.

14. Calculate the degree of dissociation of $SO_3(g)$ at 400°K and 10 atm pressure. Use Table 36.3 for necessary data.

15. The following heat capacities in cal deg^{-1} mole^{-1} have been recorded for solid chlorine:

°K	C_P	°K	C_P	°K	C_P	°K	C_P
14.05	0.810	33.94	4.804	79.71	9.201	134.06	11.47
17.40	1.331	42.37	6.018	98.06	10.03	145.19	11.92
19.81	1.842	58.59	7.879	112.99	10.57	155.45	12.41
26.37	3.192	70.50	8.720	123.53	11.00	164.99	12.93

Determine the entropy of solid chlorine at its melting point, 172.12°K. Evaluate the entropy contribution below 14°K by applying the Debye equation.

16. (*a*) The density of trifluoroacetic acid vapor at 118.0°C and 418.2 mm total pressure is 2.448 g l^{-1}. Determine K_p for the dimerization process $2CF_3COOH = (CF_3COOH)_2$, with pressures in mm Hg. (*b*) $\log K_p = -10.800 + \frac{3053}{T}\cdot$ Calculate the mean value of ΔH^0 in the temperature range 80–130°C.

17. When a mixture of $SrCO_3(c)$, SrO(*c*) and C(graphite) is heated, a gas phase containing CO_2 and CO is produced. At 850°C in a previously evacuated vessel, a pressure of 171 mm is produced. At the same temperature the measured dissociation pressure of $SrCO_3$ is 2.47 mm. Calculate K_p for the reaction $C(\text{graphite}) + CO_2(g) = 2CO(g)$.

18. Calculate the value of the translational partition function for 1 mole of oxygen at 1 atm and 25°C. Show that it leads to the classical value of $\frac{3}{2}RT$ for the translational energy of an ideal gas.

19. Spectroscopic studies indicate that at 298.15°K gaseous carbon atoms occupy the following energy states:

$\bar{\nu}_i$ cm^{-1}	0	16.4	43.5	10193.7
g_i	1	3	5	5

Calculate the value of the partition function of gaseous carbon at this temperature.

11

Phase Equilibria

THE PHASE RULE

37a. The Phase Diagram.—It was pointed out in § 34a that there is no essential difference between a chemical equilibrium and the physical equilibrium involving the vapor and the liquid (or solid) phase of a substance as measured by the vapor pressure. It is nevertheless desirable to treat physical equilibria between phases separately from chemical equilibria. The present chapter will therefore be devoted to a consideration of the phenomena associated with phase equilibria, particularly in systems of two components. In place of the law of mass action and the equilibrium constant, use will be made of the phase rule to study the conditions of equilibrium. In certain cases, however, the van't Hoff equation will be applied to determine the influence of temperature.

A diagram which illustrates the conditions of equilibrium between various forms, or phases, of a substance is called a **phase diagram** or **equilibrium diagram.** An example of such a diagram is given in Fig. 37.1; this is actually a slight elaboration of the vapor pressure curves of Fig. 21.1. It will be recalled that *OA* and *OB* represent the variation of vapor pressure of the liquid and solid, respectively, with temperature, whereas *OC* shows the dependence of the melting point on pressure. Alternatively, it may be said that two phases, viz., liquid and vapor along *OA*, solid and vapor along *OB*, and solid and liquid along *OC*, are in equilibrium at temperatures and pressures represented by each of the curves in the diagram. Three phases, viz., solid, liquid and vapor, are in equilibrium at the triple point *O* where the three curves meet; there is consequently only one point at which the three phases can coexist. In the areas lying between the curves, the conditions are such that there can be but one phase, either solid or liquid or vapor. In the region

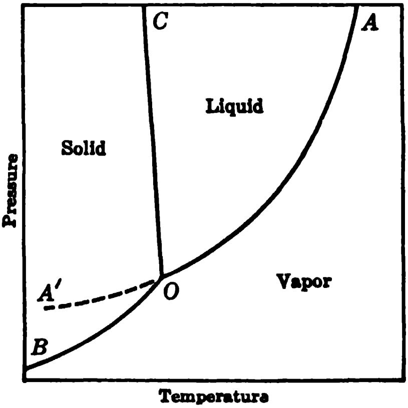

FIG. 37.1. Phase equilibrium diagram

between the curves *OA* and *OC*, for instance, only liquid can exist; the temperatures are seen to be above the melting point (curve *OC*) for any pressure, and the pressures are greater than the equilibrium vapor pressure of the liquid (curve *OA*) for any temperature. Similarly, the region to the left of the curves *OB* and *OC* represents temperatures and pressures at which solid only exists, while in the area below *OB* and *OA* the conditions are such that the only possible phase is the vapor. The phase diagram for a single substance, such as water, thus consists of three regions in each of which only one phase can occur; these regions meet at three lines, along which two phases can be in equilibrium, and the three lines intersect at a single point where all three phases can coexist.

If a liquid, free from dust particles, is cooled in a clean, smooth vessel, the temperature can frequently be brought below the normal freezing point without solid appearing; the liquid is then said to be **supercooled.** At each temperature the supercooled liquid will have a definite vapor pressure, and the vapor pressure curve is actually a continuation, without a break, of the curve for the liquid. For example, the curve *OA′* in Fig. 37.1 represents the variation with temperature of the vapor pressure of the supercooled liquid. The liquid-vapor system along *OA′* is said to be in a condition of **metastable equilibrium.** The term "metastable" is used to describe *a definite equilibrium which is, nevertheless, not the most stable equilibrium at the given temperature;* the change from metastable to stable equilibrium frequently occurs either spontaneously or upon addition of the stable phase. Thus, the introduction of a small amount of solid to the supercooled liquid along *OA′* will usually result in immediate separation of solid from the liquid; the temperature and pressure will change to a point on the stable curve *OB*. In any event, the realizable portion of the metastable curve *OA′* is generally short, because a point is soon reached at which the supercooled liquid undergoes spontaneous change to the stable, i.e., solid, state. It may be remarked that although a liquid can be supercooled, the corresponding metastable extension of the curve *BO*, to indicate the superheating of a solid without melting, has been observed only in a few special instances.

37b. The Phase Rule.—The general conditions of equilibrium between phases can be conveniently summarized in the form of a simple generalization known as the **phase rule.** This rule was deduced theoretically by J. Willard Gibbs (1876), but its application to physical chemistry may be attributed to H. W. B. Roozeboom (1884 *et seq.*). Before the rule can be stated it will be necessary to define and explain the terms involved, viz., phase, component and degrees of freedom (or variance).

A **phase** is defined as *any homogeneous and physically distinct part of a system which is separated from other parts of the system by definite bounding surfaces.* Ice, liquid water and water vapor, for example, are three phases, as has been already implied; each is physically distinct and homogeneous, and there are definite boundaries between them. In general, every solid constitutes a separate phase, although a solid solution (§ 19f) is a single phase no matter how many individual substances it may contain. In the same way, one liquid layer constitutes one phase, whether it is a pure substance or a mixture. Two liquid layers in contact represent two phases, for there is a definite surface of separation between them. A gas or a mixture of gases always constitutes one phase, for the system is homogeneous, and there is obviously no bounding surface between the different gases that may be present.

The number of **components** is *the smallest number of independent chemical constituents by means of which the composition of every possible phase can be expressed.* The water system, for example, consists of one component; the composition of each of the three phases, viz., solid, liquid and vapor, can be expressed in terms of the component H_2O. Any system consisting of a single chemical individual is always a one-component system. A salt and water, to quote a simple case, form a familiar type of two-component system. For example, copper sulfate and water can yield solid $CuSO_4 \cdot 5H_2O$, $CuSO_4 \cdot 3H_2O$, $CuSO_4 \cdot H_2O$ and $CuSO_4$ anhydrous, ice, solution and vapor as separate phases, but the composition of each phase can be expressed in terms of two independent components, such as $CuSO_4$ and H_2O. One component would be insufficient to express *every possible* composition, e.g., that of a solution, and three would be more than necessary.

Another type of system is that represented by the equilibrium

$$\underset{\text{solid}}{CaCO_3} \rightleftharpoons \underset{\text{solid}}{CaO} + \underset{\text{gas}}{CO_2},$$

in which there are three phases, viz., solid $CaCO_3$, solid CaO and gaseous CO_2. It might appear, at first sight, that there are three components, viz., $CaCO_3$, CaO and CO_2, but it is evident that these substances are *not independent*, as required by the definition of component, given above; thus, $CaCO_3$ is really equivalent to $CaO + CO_2$. The two components may consequently be taken as CaO and CO_2, so that the composition of the calcium carbonate phase can be represented as $x\ CaO + x\ CO_2$, that of the calcium oxide as $y\ CaO + 0\ CO_2$, while that of the carbon dioxide gas phase is $0\ CaO + z\ CO_2$. The two components might equally have been chosen as $CaCO_3$ and CaO, when the composition of the gas phase would be given by $z\ CaCO_3 - z\ CaO$. The actual nature of the components is not important; it is their number that is significant, and this should always be the same for a given system if the components are chosen properly.

The number of components in a system can be determined in the following general manner. Let C′ be the number of chemical constituents in the system and let r be the number of restrictions imposed on the independent variation of these constituents. The number of components C is then given by

$$C = C' - r.$$

For the dissociation of $CaCO_3$, for example, the three constituents $CaCO_3$, CaO and CO_2 are subject to the restriction that they take part in a chemical reaction; hence, $C = 3 - 1 = 2$.

The number of **degrees of freedom** or **variance** of a system is *the number of variable factors, such as temperature, pressure and concentration, which need* *to be fixed in order that the condition of a system at equilibrium may be completely defined.* Systems possessing one, two, three, etc., degrees of freedom are said to be univariant, bivariant, trivariant, etc., respectively. The significance of the number of degrees of freedom will be explained more fully below.

Provided the equilibrium between the phases is not influenced by gravity, by electrical or magnetic forces, or by surface action, and only by temperature, pressure and concentration, then the **phase rule** states that the number of degrees of freedom (F) of the system is related to the number of components (C) and of phases (P) present at equilibrium by the equation

$$\mathrm{F = C - P + 2.} \tag{37.1}$$

The simplest application of the phase rule is to a one-component system, such as that to which Fig. 37.1 applies. In this case, C is 1, and so the phase rule takes the form

$$\mathrm{F = 3 - P} \quad \text{or} \quad \mathrm{F + P = 3.}$$

That is to say, the sum of the number of phases and of the degrees of freedom should always be equal to 3, if the system is in equilibrium.

It will now be shown that this is in agreement with the conclusion to be reached from the experimental phase diagram.

A system consisting of *one phase only,* e.g., solid, liquid or vapor, is represented by an area in Fig. 37.1; in order to define such a system completely, it is obviously necessary to state both the temperature and pressure of the phase. The temperature or pressure alone is insufficient to define the condition of the system, for two coordinates, i.e., temperature and pressure, are required to specify precisely any point lying in a particular region of the diagram. A system of a single phase (P = 1) thus has two degrees of freedom (F = 2) and is bivariant; consequently, F + P = 3, as predicted by the phase rule.

When two phases are in equilibrium, however, the conditions must correspond to a point on one of the lines *OA*, *OB* or *OC* in Fig. 37.1; in order to define such a system completely, it is sufficient to state either the temperature or the pressure. The fact that the system must be represented by a point situated on a definite curve makes it unnecessary to state both temperature and pressure; by arbitrarily fixing one of these variables, the other is automatically determined by the appropriate curve *OA*, *OB* or *OC*. The one-component system of two phases (P = 2) in equilibrium is thus univariant, having one degree of freedom (F = 1); again, it is seen that F + P = 3. Finally, since three phases (P = 3) can coexist only at the triple point, the system will then have no degrees of freedom (F = 0) and will be invariant. The fact that the three given phases are in equilibrium means that the system must be at the triple point, and it is consequently unnecessary to prescribe either the temperature or pressure.

37c. Theoretical Derivation of the Phase Rule.—The phase rule can be derived from the thermodynamic result that for a small change in a system at equilibrium, the free energy change is zero (§ 9b). Since individual phases may contain two or more components in variable amounts, it is necessary to use partial molal free energies, i.e., chemical potentials μ, to make the treatment general. If the extensive property X in equation (7.5) is the free energy, this equation becomes

$$dF = \mu_1 dn_1 + \mu_2 dn_2$$

for a phase containing two components. In general, if there are C components, the corresponding expression for a small change in composition of a single phase, at constant temperature and pressure, is

$$dF = \mu_1 dn_1 + \mu_2 dn_2 + \cdots + \mu_c dn_c.$$

At equilibrium $dF = 0$, so that

$$\mu_1 dn_1 + \mu_2 dn_2 + \cdots + \mu_c dn_c = 0,$$

or, in general,

$$\Sigma \mu_i dn_i = 0.$$

Consider, next, a system of two phases, distinguished by the symbols a and b in equilibrium at constant temperature and pressure. Suppose a small quantity dn_i moles of any component i is transferred from phase a in which its chemical potential is $\mu_{i(a)}$ to phase b in which the chemical potential is $\mu_{i(b)}$. The total free energy of phase a thus changes by $-\mu_{i(a)}dn_i$ and that of the phase b by $+\mu_{i(b)}dn_i$. The net change dF is therefore

$$dF = -\mu_{i(a)}dn_i + \mu_{i(b)}dn_i = 0;$$

it is equal to zero because the system is in equilibrium. Consequently,

$$\mu_{i(a)} = \mu_{i(b)},$$

so that the chemical potentials of the component i are equal in the two phases. This important conclusion can be generalized for any number of phases: *for a system in equilibrium at constant temperature and pressure, the chemical potential of any given component has the same value in every phase.*

In a system of phases at equilibrium, the total quantity of material in any phase does not matter; it is the composition of the phase which is important. A simple illustration is provided by a saturated solution of a pure solid. As long as saturated solution and solid are in equilibrium, at a given temperature and pressure, the composition of the solution is independent of the total quantity of the solution phase or of the amount of undissolved solid phase. In any phase containing C components, the composition is completely defined by C − 1 concentration terms, for if the concentrations, e.g., in weight per cent or in mole fractions, of all but one of the components is known, that of the last one is automatically determined, e.g., by the remaining percentage or mole fraction. For a system of P phases, therefore, P(C − 1) concentration terms must be specified in order to define the composition completely. In addition to the composition, the temperature and pressure of the system, which are the same in all phases, must be known. Hence, assuming that other factors, such as gravity or surface forces, do not influence the equilibrium, the total number of independent variables which must be specified is $P(C - 1) + 2$. The requirement that the chemical potential of any component is the same in all phases at equilibrium leads to the equations

$$\begin{array}{ccccccc} \mu_{1(a)} & = & \mu_{1(b)} & = & \cdots & = & \mu_{1(P)} \\ \mu_{2(a)} & = & \mu_{2(b)} & = & \cdots & = & \mu_{2(P)} \\ \cdots & & \cdots & & \cdots & & \cdots \\ \mu_{C(a)} & = & \mu_{C(b)} & = & \cdots & = & \mu_{C(P)} \end{array}$$

for the C components in P phases. Each line of this array contains $P - 1$ independent equations, and the total number is thus $C(P - 1)$. The number of independent variables defined by this set of simultaneous equations is $C(P - 1)$, and so the number of variables remaining undetermined for the system at equilibrium is

$$[P(C - 1) + 2] - [C(P - 1)] = C - P + 2.$$

In order to define the system completely, therefore, this number of variables must be arbitrarily fixed, and hence it must be equal to the number of degrees of freedom; thus,

$$F = C - P + 2,$$

which is phase rule as given above.

If, as is often the case, a component does not occur in all the phases, the final result will still be the same. The number of composition variables is reduced and there is a corresponding decrease in the number of chemical potential equations. The net difference, which determines the number of degrees of freedom, is thus unaffected.

37d. Phase Equilibria in the Sulfur System.—A one-component system of a somewhat more complicated type than that considered earlier is provided by the element sulfur. This substance exists in two crystalline forms, namely, rhombic and monoclinic sulfur. At a specified pressure, there is a definite temperature, called the **transition point,** at which one form changes reversibly into the other. The stable form of sulfur at ordinary temperatures belongs to the rhombic system, but if heated to 95.6°C, i.e., the transition point at 1 atm pressure, the rhombic crystals change to the monoclinic form. On cooling from above 95.6°, the monoclinic crystals change back to rhombic at this temperature. *Crystalline forms that can undergo reversible changes of this type at the transition temperature* are said to be **enantiotropic,** the phenomenon being referred to as **enantiotropy** (Greek: *opposite change*). The transition point is then somewhat similar to a melting point, as will be seen below.

The complete phase diagram, representing the temperature and pressure conditions of equilibrium between the various possible phases of sulfur, is shown schematically in Fig. 37.2; *AB* is the vapor pressure curve of the rhombic crystals, and *BC* is that of the monoclinic form. The point *B* is the transition temperature under a pressure equal to the vapor pressure at that temperature. The melting points of the two forms are at *E* (113°) and *C* (119°), respectively; the former can be realized only if sulfur is heated rapidly, so that the transition to the monoclinic form does not occur at *B*. The curves *BF* and *CF* show the effect of pressure on the transition point and on the melting point of the monoclinic solid, respectively; in other words, they give the conditions of equilibrium of the rhombic and monoclinic forms (along *BF*), and of the monoclinic solid and liquid (along *CF*). It will be observed that both curves slope to the right so that the transition point and the melting point of monoclinic sulfur increase with increasing pressure. However, because the former happens to change more rapidly than the latter the two curves meet at the point *F*.

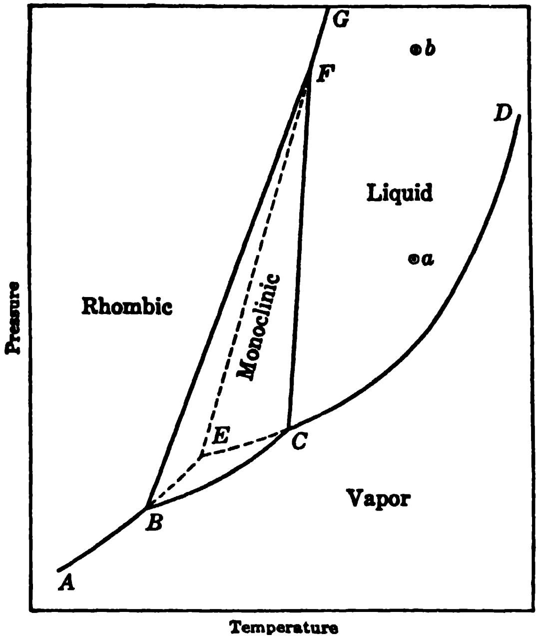

FIG. 37.2. Phase equilibrium diagram of sulfur (schematic)

The dashed curves *BE*, *EC* and *EF* represent metastable equilibria; *BE* is the metastable vapor pressure curve for the rhombic system which can be realized if this substance is heated rapidly past the transition point. The system then continues along *ABE*, without a break, instead of passing on to the stable curve *BC*. At *E*, the metastable melting point, the sulfur liquefies, and *EC* is the metastable vapor pressure curve of the liquid; this is continuous with the stable vapor pressure curve *CD* for the liquid form. The influence of pressure on the melting point of the rhombic solid is indicated by *EFG*, and the portion *EF* gives the conditions of the metastable equilibrium between rhombic sulfur and the liquid form. The curve *FG*, which is a continuation of *EF*, represents stable equilibrium between these two phases of sulfur.

An examination of Fig. 37.2 shows that the sulfur system has four observable triple points at each of which three phases are in equilibrium; the four points and the corresponding phases are as follows:

B	Rhombic, monoclinic, vapor
C	Monoclinic, liquid, vapor
E	Rhombic, liquid, vapor
F	Rhombic, monoclinic, liquid.

For these points, C = 1, P = 3, and so, by the phase rule,

$$\begin{aligned} F &= C - P + 2 \\ &= 1 - 3 + 2 = 0. \end{aligned}$$

They are, therefore, all invariant points, with no degrees of freedom; the very fact of the three particular phases being in equilibrium automatically fixes both the temperature and pressure of the system.

The diagram also shows six curves representing the conditions of equilibrium of two phases; these are:

AB(*E*)	Rhombic, vapor
BC	Monoclinic, vapor
(*E*)*CD*	Liquid, vapor
BF	Rhombic, monoclinic
(*E*)*FG*	Rhombic, liquid
CF	Monoclinic, liquid.

Since P = 2, the phase rule requires that F = 1 − 2 + 2 = 1; there are thus six kinds of univariant system. By specifying the nature of the two phases that are in equilibrium, and the temperature *or* the pressure, the state of the system will be completely defined. The nature of the phases indicates which of the six curves is applicable, and one coordinate, i.e., temperature or pressure, will then exactly identify the particular point representing the system that is being described.

The four single phases of sulfur, namely rhombic solid, monoclinic solid, liquid and vapor, each occupy a region of the equilibrium diagram. A single phase must be a bivariant system, since F = 1 − 1 + 2 = 2; hence, both temperature and pressure must be given if the exact state of the system is to be defined.

It will be observed from Fig. 37.2 that if rhombic sulfur is heated rapidly, so that the transition to the monoclinic form does not occur, the phase diagram consists of but three lines, *AE*, *ED* and *EG*, meeting at the triple point *E*. Such a diagram is then, as it should be, of the same form as Fig. 37.1 for a one-component system with a single solid phase.

Attention may be called to the triple point *F*, at 151°C and 1290 atm; it owes its existence to the fact that the slopes of the curves *BF* and *CF* are such that they intersect, as mentioned previously. The result is that the region of stability of monoclinic sulfur is definitely bounded by the lines *BF*, *CF* and *BC*, and this form of solid sulfur cannot exist at temperatures and pressures lying outside the triangular region *BCF*. Above *F*, therefore, solid sulfur can be obtained in one solid modification only, namely rhombic crystals. If liquid sulfur represented by a point such as *a* in Fig. 37.2 is cooled at constant pressure, monoclinic solid will separate out when the conditions fall on the curve *FC*. On the other hand, if the initial temperature and pressure of the liquid are given by a point such as *b*, then upon cooling, at constant pressure, rhombic crystals must form along *FG*. It is believed that the large crystals of rhombic sulfur found in nature were obtained by direct crystallization from the liquid under these conditions, that is, at temperatures above 151°C and pressures in excess of 1290 atm.

It should be pointed out that the phase rule is unable to distinguish between a metastable system, e.g., the point *E*, and a stable system, for the former still represents an equilibrium, even if not the most stable. Further, the phase rule predicts the *possible* equilibria, but it cannot tell whether they are observable or not. For example, the triple point *F* in the sulfur system can be observed because the lines *BF* and *CF* happen to slope toward one another with increasing temperature. If the slopes had been in the opposite direction, the lines would have intersected at some very low pressure, in the region where vapor alone is stable. The triple point would then be possible theoretically, as predicted by the phase rule, but it could not be realized experimentally.

SOLUTIONS OF GASES IN LIQUIDS

38a. Solubility of Gases.—A solution of a gas in a liquid is a simple example of a two-component system. The gas dissolves in the liquid and a state of equilibrium is reached when the liquid is saturated with gas. Since there are two components (C = 2) and two phases, i.e., P = 2 (liquid and gas), the phase rule requires that F = 2 − 2 + 2 = 2. There are thus two degrees of freedom, namely, temperature and pressure. The composition of the saturated solution, i.e., the solubility of the gas, thus depends on the temperature and pressure, as well as on the nature of the gas and the liquid solvent.

At a given temperature and pressure the solubilities of a series of gases in a given liquid generally increase in the order of their ease of liquefaction; thus, in any solvent, hydrogen and helium are generally the least soluble gases, whereas carbon dioxide and ammonia are much more soluble. Chemical reaction between the gas and the solvent, as undoubtedly occurs when ammonia, hydrogen chloride or carbon dioxide is dissolved in water, results in an increased solubility.

There are no universally accepted units for expressing the solubilities of gases; as will be seen later, there are theoretical reasons for employing mole fractions, but as the latter are often small they are not convenient for general use. Since the solubility of a gas is usually determined by measuring the volume, rather than the weight, that has dissolved, the **absorption coeffi-**

cient of R. Bunsen (1857) is frequently used. This is defined as *the volume of gas, reduced to 0°C and 1 atm pressure, dissolved by unit volume of solvent at the temperature of the experiment under a partial pressure of 1 atm of the gas.* The absorption coefficients of a few common gases at 20°C in three solvents of different types are quoted in Table 38.1. Although the actual values vary from one solvent to another, the order of increasing solubilities of gases is approximately the same in each case.

TABLE 38.1. BUNSEN ABSORPTION COEFFICIENTS OF GASES AT 20°

Solvent	H_2	He	N_2	O_2	CO	CO_2
Water	0.017	0.009	0.015	0.028	0.025	0.88
Ethanol	0.080	0.028	0.130	0.143	0.177	3.0
Benzene	0.066	0.018	0.104	0.163	0.153	—

It will be noted that in the evaluation of the absorption coefficient the volume of dissolved gas is supposed to be measured at 0°C and 1 atm pressure. Since 1 mole of any gas under these conditions occupies approximately 22.4 liters, it follows that *if the absorption coefficient is divided by 22.4, the result gives the solubility of the gas expressed in moles per liter*, at the experimental temperature and 1 atm pressure.

Most gases dissolve in water with a liberation of heat; hence, the Le Chatelier principle indicates that increase of temperature should result in a decrease of solubility. It is for this reason that gases may be readily expelled from solution by boiling. Certain solutions of the hydrogen halides in water are apparent exceptions to this rule, but chemical reaction between the gas and the solvent is undoubtedly a complicating factor in these cases. There are, however, other cases in which the solubility of a gas increases with temperature when chemical reaction is not involved; examples are the solutions of hydrogen, helium and oxygen in certain organic liquids.

The solubiluty of a gas expressed in moles per unit volume of liquid, at a constant pressure, may be regarded as the constant of the equilibrium existing between the gas molecules in solution and those in the gas phase. As seen above, the absorption coefficient divided by 22.4 gives the solubility in moles per liter; hence, this coefficient, represented by α, may be regarded as a measure of the equilibrium constant, and if this replaces K in the van't Hoff equation (34.13), the influence of temperature on the solubility of a gas can be expressed by

$$\frac{d \ln \alpha}{dT} = \frac{\Delta H}{RT^2}, \tag{38.1}$$

or after integration between the limits of T_1 and T_2, assuming ΔH to be constant,

$$\log \frac{\alpha_2}{\alpha_1} = \frac{\Delta H}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right). \tag{38.2}$$

In these equations ΔH is the change of enthalpy accompanying the solution of 1 mole of gas, and its value may be calculated from the solubilities α_1 and α_2 at two temperatures T_1 and T_2. It may be mentioned that ΔH is actually the *differential* heat of solution of the gas (§ 7g) in the saturated solution.

The absorption coefficients of helium, nitrogen, oxygen and carbon dioxide at 0° and 30°C, in water as solvent, are recorded in Table 38.2. The relative influence of temperature is seen to be greater for carbon dioxide than for the other gases; this means that the heat of solution is largest in this instance, a fact which is no doubt related to the chemical reaction which occurs between carbon dioxide and water.

TABLE 38.2. INFLUENCE OF TEMPERATURE ON SOLUBILITIES OF GASES IN WATER

Bunsen Absorption Coefficients

Temperature	He	N_2	O_2	CO_2
0°	0.0094	0.0235	0.0489	1.713
30°	0.0081	0.0134	0.0261	0.665

38b. Influence of Pressure: Henry's Law.—The influence of pressure on the solubility of a gas was expressed by W. Henry (1803); his conclusions, generally known as Henry's law, may be stated in the following form: *the mass of gas dissolved by a given volume of solvent, at constant temperature, is proportional to the pressure of the gas in equilibrium with the solution.* If w is the mass of gas dissolved by unit volume of solvent at the equilibrium pressure p, then according to Henry's law

$$w = kp, \tag{38.3}$$

where k is a proportionality constant. If a gas obeys equation (38.3) the plot of the solubility against the pressure should give a straight line passing through the origin. The results for the solubility of hydrogen chloride in dry benzene at 30°C are represented by Fig. 38.1; the points are seen to fall close

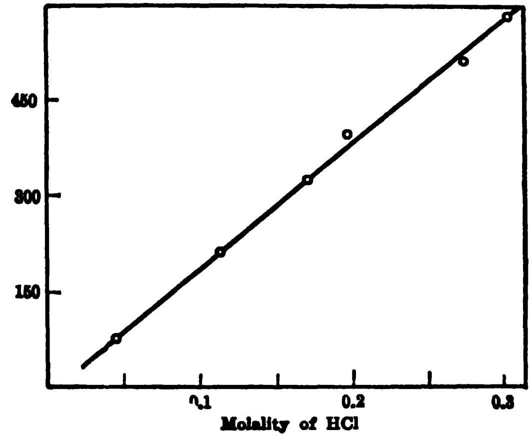

FIG. 38.1. Solubility of hydrogen chloride in benzene at 30°C

to a straight line, as required by Henry's law. Provided the pressures are not too high or the temperatures too low, most gases obey Henry's law, especially if they are not very soluble. When chemical reaction takes place between the gas and the solvent, e.g., hydrogen chloride, ammonia or carbon dioxide in water, Henry's law fails to hold if the total solubility is considered. However, if an estimate is made of the quantity of gas that is in the free, or uncombined, state in the solution, this is found to increase in proportion to the pressure as required by equation (38.3).

When gases dissolve from a mixture, instead of from the pure gas, the solubility of each constituent is proportional to its own partial pressure; in other words, Henry's law applies to each gas independently of the pressure of the others present in the mixture. The Bunsen absorption coefficient, as seen above, is proportional to the molar concentration of the gas dissolved at constant pressure, viz., 1 atm. It follows, then, that the solubility of a gas in a mixture, expressed either in terms of the volume at 0°C and 1 atm, or of moles, dissolved by unit volume, is proportional to αp, where α is the absorption coefficient and p is the partial pressure of the gas.

Example: Air consists of 78.06 per cent by volume of nitrogen and 21.00 per cent of oxygen, the remainder being inert gases. Utilizing the absorption coefficients in Table 38.1 calculate the molar composition of the gas dissolved in water saturated with air at 20°C, assuming ideal behavior of the oxygen and nitrogen. (The solubility of the inert gases is small and may be ignored.)

If the gases behave ideally, their partial pressures are proportional to the number of moles of each, and hence to the volume composition; if the total pressure of the air is 1 atm, the partial pressure of the nitrogen is consequently 0.7806 atm, whereas that of the oxygen is 0.2100 atm. The absorption coefficients are 0.0150 and 0.0280, respectively; the solubilities are therefore in the ratio of 0.7806 × 0.0150 volumes (or moles) of nitrogen to 0.2100 × 0.0280 volumes (or moles) of oxygen, i.e., 0.0117 to 0.00588. Neglecting the inert gases, the mole per cent of nitrogen in the dissolved gas is given by

$$\frac{0.0117}{0.0117 + 0.00588} \times 100 = 66.6 \text{ mole per cent.}$$

The dissolved gas therefore contains 66.6 moles of nitrogen to 33.4 moles of oxygen.

38c. Henry's Law and Raoult's Law.—In equation (38.3) the quantity w is the mass of gas dissolved in unit volume, and hence it may be taken as equal to the concentration of gas molecules in the saturated solution. If this solution is moderately dilute, the concentration is proportional to the mole fraction of the dissolved substance, and so it is possible to write the Henry's law equation (38.3) as

$$x_2 = k'p_2 \qquad \text{or} \qquad p_2 = \frac{x_2}{k'}, \tag{38.4}$$

where x_2 is the mole fraction of solute (gas) in the solution when the pressure of the gas above the solution is p_2; k' is a proportionality constant which is related to k in equation (38.3). Although equation (38.3) represents the historical form of Henry's law, this name is now frequently applied to equation (38.4) and related expressions.

In an ideal solution of a volatile solvent and volatile solute, Raoult's law (§ 22a) applies to the solute as well as the solvent; hence the pressure p_2 of the volatile solute in equilibrium with a solution in which the mole fraction of the solute is x_2 is given by

$$p_2 = x_2 p_2^0, \tag{38.5}$$

where p_2^0 is the vapor pressure of the pure solute, in this case a liquefied gas at the temperature of the solution. Comparison of equations (38.4) and (38.5) shows a distinct similarity; in fact the two equations would become identical if k' were equal to $1/p_2^0$. This condition is approached in a few cases, representing *ideal* solutions of gases in liquids; for such solutions Henry's law and Raoult's law, as applied to the solute, may be regarded as identical. For the majority of solutions of gases in liquids, however, the behavior is not ideal, and although k' in equation (38.4) is approximately constant, in accordance with Henry's law, it is not equal to $1/p_2^0$, as would be required by Raoult's law.

The relationship between Henry's law and Raoult's law shows that the solubility of a gas may be considered from two points of view; by equation (38.4), x_2 may be regarded as the solubility of the gas, in mole fractions, under the pressure p_2, and by equation (38.5), p_2 may be taken as the vapor pressure of a volatile solute when it is present to the extent of mole fraction x_2 in the solution. From the latter aspect it is possible to calculate the ideal solubility of a gas in a liquid. For example, at 25°C, pure liquid ethane has a vapor pressure of 42 atm, i.e., $p_2^0 = 42$ atm. Consequently, by equation (38.5), the ideal solubility of ethane *in any solvent* at 25°C and a pressure p_2 of 1 atm is given by

$$x_2 = \tfrac{1}{42} = 0.024 \text{ mole fraction.}$$

The observed solubility of ethane in n-hexane at 25°C is 0.017 mole fraction at 1 atm pressure; the difference between the observed and calculated values shows that the solution of ethane in n-hexane does not behave ideally.

MIXTURES OF TWO LIQUIDS

39a. Ideal Systems and Raoult's Law.—A system consisting of a mixture of two volatile liquids is essentially similar to a solution of a gas in a volatile liquid, the temperature being low enough for the gas to liquefy under the applied pressure. For practical purposes, however, it is best to consider mixtures of liquids from the aspect of vapor pressure, whereas in the previous section the solution of a gas was treated mainly from the point of view of solubility. Nevertheless, it should be realized, as indicated above, that there is no real difference between these two approaches to the study of systems of two components involving gaseous and liquid phases. The particular method employed is the one which happens to lead to the most useful results.

When a system consists of two liquids, such as water and alcohol, or benzene and toluene, which are soluble (miscible) in one another in all proportions, no distinction can, or need, be drawn between solvent and solute. With such systems, therefore, the practice is to replace the subscripts 1 and 2 by the letters A and B. The symbol p_A then represents the partial pressure of the component A in the vapor, while p_B is that of the component B, when the vapor and liquid phases are in equilibrium. The total vapor pressure P is equal to the sum of the two partial pressures, i.e., $p_A + p_B$, in accordance with Dalton's law of partial pressures (§ 2h). The tacit assumption is made here that the vapors behave as ideal gases; the pressures are generally so low that this approximation does not cause appreciable errors.

The partial pressures of the vapors in equilibrium with a mixture of two volatile liquids are determined from measurements of the total pressure P and the composition of the vapor. If the latter is stated in terms of the respective mole fractions x'_A and x'_B, it follows from equation (2.25) that*

$$p_A = x'_A P \qquad \text{and} \qquad p_B = x'_B P, \tag{39.1}$$

where $P = p_A + p_B$. The partial vapor pressures vary with the nature of the substances and their proportions present in the mixture, and also, of course, with the temperature.

By definition, an **ideal system of two liquids** is described as *one in which both constituents obey Raoult's law over the whole range of concentrations and at all temperatures*, i.e.,

$$p_A = x_A p_A^0 \qquad \text{and} \qquad p_B = x_B p_B^0 \tag{39.2}$$

for all values of the mole fractions x_A and x_B in the liquid, and at all temperatures; p_A^0 and p_B^0 are the vapor pressures of the pure liquids A and B, respectively, at each temperature.

In a general way, it appears that Raoult's law might be expected to hold for a mixture in which the presence of the molecules of B has no effect on the forces existing between the molecules of A, and vice versa (§ 26a). A mixture of two liquids behaving in this manner with respect to each other will show no volume or heat change upon mixing, and its behavior is ideal. The vapor pressure of the pure liquid A is determined essentially by two factors; first, the "escaping tendency" of the molecules, which depends on the van der Waals forces acting between the A molecules in the liquid and, second, the number of A molecules available. If the molecular forces remain unchanged in a mixture, the escaping tendency of the A molecules will be the same in the solution as in the pure liquid; however, the proportion of A molecules in the liquid is less in the former case, and hence the vapor pressure of A will be reduced in proportion. If n_A is the number of molecules (or moles) of A, and n_B is the number of molecules (or moles) of B in the mixture, the proportion of A mole-

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[*] It should be noted that the primed quantities x'_A and x'_B refer to the mole fractions of A and B in the vapor and the unprimed quantities x_A and x_B to the mole fractions in the liquid.

cules in the mixture is $n_A/(n_A + n_B)$, which is the mole fraction x_A of A. The vapor pressure p_A of the component A in the mixture should thus be proportional to x_A, viz.,

$$p_A \quad \frac{n_A}{n_A + n_B} \quad kx_A \tag{39.3}$$

where k depends on the escaping tendency of the A molecules in the solution. As postulated above, this escaping tendency is the same as in the pure liquid for which $x_A = 1$ and $p_A = p_A^0$. Substitution of these values into equation (39.3) shows that k is equal to p_A^0, and so this equation becomes

$$p_A \quad x_A p_A^0,$$

which is the statement of Raoult's law as applied to the component A [equation (39.2)]. Exactly the same result is obtained for the component B, so that if the intermolecular forces remain unchanged when A and B are mixed, Raoult's law should apply to both substances in the mixture.

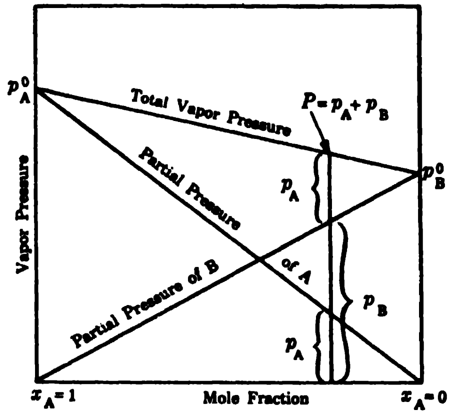

FIG. 39.1. Vapor pressures of ideal liquid system at constant temperature

The variation with the composition of the liquid of the partial and total vapor pressures at a given temperature for an ideal system, to which the Raoult equations (39.2) are applicable, is shown in Fig. 39.1. The plot of the partial pressure of each constituent against its respective mole fraction in the liquid is a straight line passing through the origin, as seen in the figure; the total vapor pressure, equal to the sum of the partial vapor pressures, is then also a straight line, as shown. If the mixture is really ideal, a similar diagram, but with different actual pressures, would be obtained at any temperature at which the liquids can exist. As seen in § 38a, the phase rule requires that a two-component system in two phases have two degrees of freedom. If the temperature is prescribed as in Fig. 39.1, then the composition of the liquid, representing the second degree of freedom, automatically determines the pressures in the system.

As is to be anticipated, from the discussion of intermolecular forces and Raoult's law, ideal, or approximately ideal, behavior is exhibited almost exclusively by mixtures of two similar liquids. The following are examples of mixtures which have been found experimentally to obey Raoult's law over the whole range of compositions, at least at one temperature: ethylene bromide and ethylene chloride, *n*-hexane and *n*-heptane, *n*-butyl chloride and *n*-butyl bromide, and carbon tetrachloride and silicon tetrachloride.

Example: The vapor pressures of pure CCl_4 and $SiCl_4$ at 25°C are 114.9 mm and 238.3 mm, respectively. Assuming ideal behavior, calculate the total vapor pressure of a mixture of equal weights of the two liquids.

Let w be the weights of both CCl_4 (A) and $SnCl_4$ (B). The molecular weights are 153.8 for A and 169.9 for B, so that the mixture consists of $w/153.8$ moles of A and $w/169.9$ moles of B; the mole fraction of CCl_4 is thus

$$x_A = \frac{w/153.8}{(w/153.8) + (w/169.9)} = 0.525.$$

The mole fraction x_B of $SiCl_4$ is then $1 - x_A$, i.e., 0.475. The partial vapor pressures are consequently,

$$p_A = x_A p_A^0 = 0.525 \times 114.9 = 60.3 \text{ mm}$$

$$p_B = x_B p_B^0 = 0.475 \times 238.3 = 113.2 \text{ mm},$$

and the total vapor pressure is therefore $60.3 + 113.2 = 173.5$ mm.

39b. Nonideal Mixtures of Miscible Liquids.—If the two components A and B of a liquid mixture are different in character, the molecular forces between the A molecules will differ from those acting between the B molecules. The result of this circumstance will be that the presence of B will affect the escaping tendency of the A molecules, and vice versa; Raoult's law will then not be applicable. A mixture of two dissimilar liquids would thus be expected to behave in a nonideal manner, and this has been found to be the case. If the attraction between the B molecules is much stronger than that between the A molecules, the effect is to force the latter out of the liquid into the vapor; in other words, the escaping tendency of the A molecules will be increased by the presence of B. The partial vapor pressure of A will consequently be greater than is to be expected from Raoult's law; such behavior is known as **positive deviation** from the ideal law. Theoretical treatment shows that when one component of a mixture exhibits positive deviations, the other component must do the same; the nonideal system as a whole is then said to show positive deviations from Raoult's law. The type of vapor pressure curves obtained at a given temperature for mixtures of this kind is shown in Fig. 39.2, where the dotted lines indicate ideal behavior. If the positive deviations are large, and especially if the vapor pressures of the pure liquids are not very different, the curve for the total vapor pressure of the mixture will exhibit a maximum. Such behavior is not uncommon and is of importance in connection with distillation, as will be seen later (§ 39d).

If the two liquids constituting the mixture are both nonpolar, e.g., carbon tetrachloride and heptane, or if both are moderately polar, e.g., ether and acetone, the positive deviations from ideal behavior are not large. On the other hand, if one component is slightly polar while the other is highly polar or, more particularly, if the mixture consists of a polar and a nonpolar compound, e.g., an alcohol and a hydrocarbon, considerable positive deviations may occur. Such large deviations may lead to the liquids becoming partially immiscible (§ 39e).

If the two constituents of a mixture are such that the molecules of A and B *attract one another strongly*, and particularly if a compound between A and B is formed to some extent in the liquid, the vapor pressure of each constituent will be less than that required by the Raoult equation. This type of nonideal behavior is described as **negative deviation** from Raoult's law. The vapor pressure curves at constant temperature are then of the form shown in Fig. 39.3, where, as before, the dotted lines indicate ideal behavior. It will be observed that the vapor pressure curve may well have, and in fact frequently does have, a minimum for a particular composition. Systems exhibiting negative deviations from Raoult's law are pyridine and acetic acid, chloroform and ethyl ether, and the halogen acids and water; in every case there are good reasons for believing that the molecules of the two components attract one another strongly, even to the extent of interaction or partial compound formation in the liquid state.

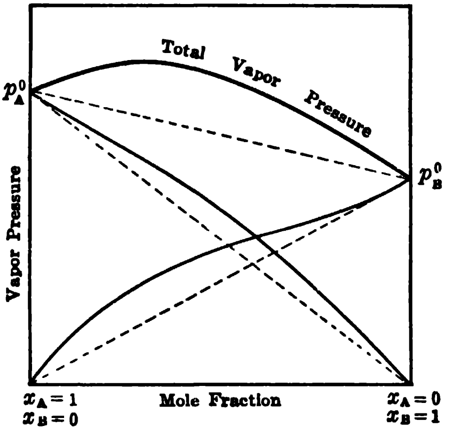

FIG. 39.2. Vapor pressure at constant temperature in a system exhibiting positive deviations from Raoult's law

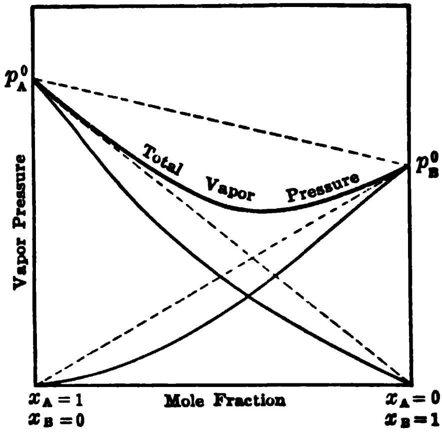

FIG. 39.3. Vapor pressure at constant temperature in a system exhibiting negative deviations from Raoult's law

An examination of Figs. 39.2 and 39.3 shows that as the system approaches pure A, i.e., very dilute B, or pure B, i.e., very dilute A, in composition, the partial vapor pressure of A or B, respectively, approximates the ideal (Raoult law) value, irrespective of whether positive or negative deviations occur at other compositions. This is the justification for the statement in § 26a that for dilute solutions Raoult's law is almost invariably applicable to the solvent. Further, it is found that Henry's law applies to the constituent present in small amount, i.e., the solute, over the same range that Raoult's law holds for the one present in excess, i.e., the solvent. A system of this kind is sometimes called an "ideal dilute solution."

39c. Composition of Liquid and Vapor.—If the vapors behave ideally, then by equation (39.1), since $P = p_A + p_B$,

$$x'_{\mathrm{A}} \quad \frac{p_{\mathrm{A}}}{p_{\mathrm{A}} + p_{\mathrm{B}}} \tag{39.4}$$

If the liquid mixture in equilibrium with the vapor also behaves ideally, then by equation (39.2) p_{A} and p_{B} may be replaced by $x_{\mathrm{A}}p^0_{\mathrm{A}}$ and $x_{\mathrm{B}}p^0_{\mathrm{B}}$, respectively, where x_{A} and x_{B} refer to the mole fractions in the liquid; equation (39.4) consequently becomes

$$x'_{\mathrm{A}} = \frac{x_{\mathrm{A}}p^0_{\mathrm{A}}}{x_{\mathrm{A}}p^0_{\mathrm{A}} + x_{\mathrm{B}}p^0_{\mathrm{B}}} \tag{39.5}$$

$$\frac{x'_{\mathrm{A}}}{x_{\mathrm{A}}} = \frac{1}{x_{\mathrm{A}} + x_{\mathrm{B}}\dfrac{p^0_{\mathrm{B}}}{p^0_{\mathrm{A}}}},$$

or since x'_{A} and x_{A} represent the mole fractions of A in the vapor and liquid phases, respectively,

$$\frac{\text{Mole fraction of A in vapor}}{\text{Mole fraction of A in liquid}} = \frac{1}{x_{\mathrm{A}} + x_{\mathrm{B}}\dfrac{p^0_{\mathrm{B}}}{p^0_{\mathrm{A}}}}. \tag{39.6}$$

It can be seen from equation (39.6) that, since $x_{\mathrm{A}} + x_{\mathrm{B}}$ is equal to unity, the proportion of A will be the same in the liquid and vapor only if p^0_{A} is equal to p^0_{B}, that is, if the pure liquids A and B have the same vapor pressure. If the vapor pressure of pure B is greater than that of A, the ratio $p^0_{\mathrm{B}}/p^0_{\mathrm{A}}$ will be greater than unity, and hence so also will be the value of the denominator in equation (39.6). The quotient in the equation will thus be less than unity; the mole fraction of A in the vapor phase will consequently be less than in the liquid phase. This means that if the pure liquid B has a higher vapor pressure than pure A, the vapor will contain relatively more B than does the liquid with which it is in equilibrium. The general conclusion, derived here for a system obeying Raoult's law, is that *the vapor always contains relatively more of the more volatile, i.e., higher vapor pressure, component than does the liquid phase.* The same result is applicable to all liquid mixtures whether they behave ideally or not; for ideal liquid systems the composition of the vapor can be calculated by means of equations (39.5) or (39.6), but for nonideal solutions further information is necessary.

Example: Calculate the composition of the vapor in equilibrium at 25°C with the mixture of CCl_4 and $SiCl_4$ referred to in the example in § 39a.

From the data and results of the previous example, $p^0_{\mathrm{A}} = 114.9$ mm, $p^0_{\mathrm{B}} = 238.3$ mm, $x_{\mathrm{A}} = 0.525$ and $x_{\mathrm{B}} = 0.475$; hence, by equation (39.5),

$$x'_{\mathrm{A}} = \frac{0.525 \times 114.9}{(0.525 \times 114.9) + (0.475 \times 238.3)} = 0.348$$

$$x'_{\mathrm{B}} = 1 - x'_{\mathrm{A}} = 0.652.$$

The vapor thus contains 0.348 mole fraction of CCl_4 and 0.652 mole fraction of $SiCl_4$. The same result may be obtained directly from the example in § 39a, since the number of moles of each constituent in the vapor is proportional to its partial pressure. (It should be noted that the vapor is relatively richer in B, i.e., $SiCl_4$, than is the liquid; pure $SiCl_4$ has a higher vapor pressure than CCl_4 at 25°C.)

The composition of the vapor in equilibrium with a liquid containing known amounts of two components can either be calculated, as shown above for an ideal system, or determined experimentally. In either event, the results for a definite temperature can be plotted in the manner shown in Fig. 39.4. At any value of the total pressure P, the point l on the curve marked "liquid" gives the composition x of the liquid in equilibrium with vapor whose composition x' is indicated by the point v on the curve marked "vapor." The line vl is called a **tie line,** because it connects (or ties together) phases in equilibrium.

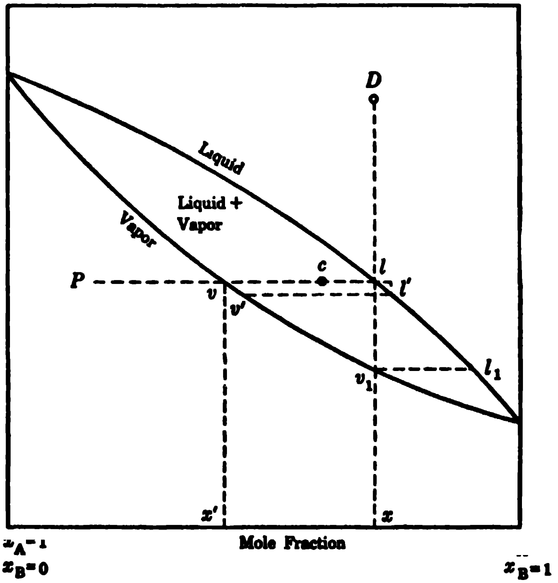

FIG. 39.4. Liquid-vapor equilibria (temperature constant)

It is seen from the figure that the vapor in equilibrium with any liquid (except pure A or pure B) is relatively richer in the component having the higher vapor pressure, viz., A in this instance.

The curves in Fig. 39.4 are typical of systems which behave ideally or which show small deviations from ideal behavior. Corresponding curves can be obtained for systems in which the total vapor pressure has a maximum or minimum, at a given temperature; the "liquid" and "vapor" curves are always related to one another in such a way as to satisfy the condition that the vapor of the mixture shall contain a relatively larger proportion of the more volatile component. At the maximum or minimum point, however, the liquid and vapor curves touch; at such points, therefore, the liquid and vapor in equilibrium with each other have the same composition.

The area above the "liquid" curve in Fig. 39.4 represents the pressure-composition conditions under which only liquid phase can exist and the area under the "vapor" curve indicates the condition for vapor alone. The area between the curves corresponds to the coexistence of liquid and vapor. The phase rule requires that, for a two-component ($C = 2$) system, the maximum number of degrees of freedom when only one phase ($P = 1$) is present is $F = 2 - 1 + 2 = 3$. In Fig. 39.4, the temperature has been fixed so that two degrees of freedom remain; hence, the pressure and composition are independently variable as long as the mixture is all liquid or all vapor. In the two-phase region, there is only one degree of freedom, and so if the composition is fixed, the two phases can coexist only at a particular pressure. If a mixture of over-all composition c is brought to the pressure P, it will be found to consist of a liquid phase of composition x and a vapor phase of composition x'; the relative number of moles of liquid to vapor will be in the ratio of the linear distances vc to cl.

Consider a solution of composition x at a pressure such as D in Fig. 39.4; only liquid will be present. As the pressure is decreased, no phase change will occur until the point l is reached at the pressure P. Vapor of composition v will then be produced. Since this is richer than the liquid in component A, the removal of a finite amount of vapor will make the liquid relatively richer in B; its composition will be l' to the right of l in the figure. Consequently, if vaporization is to continue, the pressure must be lowered still further; the liquid l' will then be in equilibrium with vapor v' at the lower pressure. As the pressure is steadily decreased, the composition of the liquid changes gradually from l to l_1, and the composition of the vapor from v to v_1. The composition of the last trace of liquid to evaporate is represented by l_1; the equilibrium vapor at v_1 then has the composition of the original liquid. The process just described is called an **isothermal distillation.**

39d. Distillation of Liquid Mixtures.—Instead of distillation at constant temperature and varying pressure, as described above, it is the general practice to perform distillations at constant pressure, frequently 1 atm. The boiling point of a mixture is the temperature at which the total vapor pressure is 1 atm, and hence the distillation is carried out at the boiling point. Since the vapor pressure varies with the composition of the mixture, so also will the boiling point. Three main types of such variation may be distinguished.

First, if the system is one which is ideal or which does not deviate greatly from ideal behavior, the vapor pressure will vary regularly with the composition and there will be no maximum or minimum (see Fig. 39.4). In this case the boiling point also will vary in a regular manner from that of one pure component to that of the other. Second, if the system exhibits positive deviations from Raoult's law to such an extent that the vapor pressure-composition curve has a maximum, the corresponding boiling point curve will exhibit a minimum. Since there is at each temperature a particular mixture having a total vapor pressure higher than that of any other mixture, there must be a corresponding mixture having a lower boiling point than any other. Third, if the system is of the type showing negative deviations from ideal behavior, the vapor pressure curve may have a minimum; in this case there will be a particular mixture possessing a maximum on the boiling point-composition curve. These three types of variation of boiling point with composition will be considered in turn.

I. The Boiling Point Increases Regularly.—The properties of a system of this type may be depicted by the experimental curves in Fig. 39.5, for a constant pressure of 1 atm. These curves should be compared with those in Fig. 39.4, which are for a constant temperature; the two sets of curves are related to one another in an inverse manner. The higher the vapor pressure of a liquid at a given temperature, the lower will be its boiling point. In Fig. 39.4 the component A has the higher vapor pressure, and this falls regularly as the proportion of B is increased; consequently, in Fig. 39.5 the boiling point increases regularly from A to B.

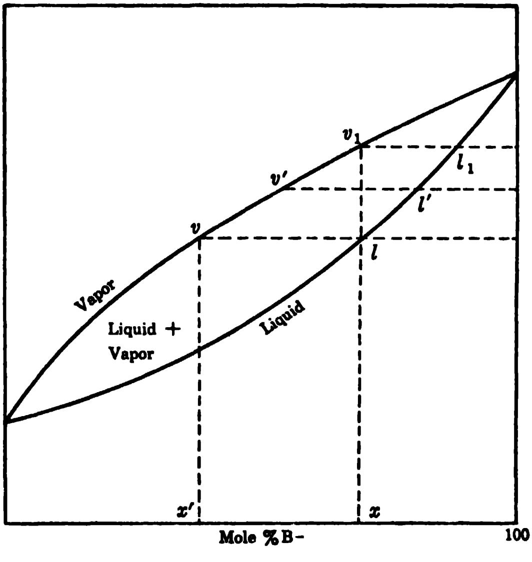

FIG. 39.5. Variation of boiling points of mixtures with composition (pressure constant)

The curve marked "liquid" in Fig. 39.5 gives the temperature at which liquids of different compositions attain a vapor pressure of 1 atm; in other words, this represents the variation of boiling point with composition. The "vapor" curve gives the composition of the vapor that is in equilibrium with any liquid at its boiling point. For example, the tie line at the temperature t shows that the liquid represented by l (mole fraction x) and vapor represented by v (mole fraction x') are in equilibrium at this temperature. If a liquid of composition x is heated, it will boil at the temperature t, and the vapor which comes off at the commencement has the composition x'; if the vapor is condensed, the resulting liquid condensate will also have this composition.

It is evident from the curves that the vapor is relatively richer in A, the component of higher vapor pressure, than is the liquid; hence, the residual liquid will become richer in B, and its boiling point must consequently rise. This accounts for the gradual increase of temperature observed when a liquid mixture is distilled. If the vapor is not condensed nor allowed to escape, but is kept in equilibrium with the boiling liquid at constant pressure, the temperature will continue to rise as evaporation proceeds. At the temperature t', for example, the composition of the liquid remaining will be represented by l' and that of the vapor in equilibrium with it by v'. The liquid is seen to be considerably richer in B, the less volatile component, than was the original liquid; on the other hand, the vapor is appreciably richer in A, the more volatile component of the system. When vaporization of the liquid is complete, at temperature t_1, the equilibrium vapor (at v_1) will have the composition x while the last trace of liquid will be represented by l_1.

The results described in the preceding paragraph form the basis for the process of **fractional distillation** or **rectification,** whereby a mixture of two or more liquids having appreciably different boiling points can be separated from one another. For this purpose a fractionating (or rectifying) column is generally used, a common type employed in industry being the bubble-cap column shown diagrammatically in Fig. 39.6. The column, which is attached to the boiler B, contains a number of shallow trays (or plates) P capable of holding a thin layer of liquid. Each plate has an overflow, which allows excess liquid to flow to the plate below, and several bubble caps C, through which vapor rising upward can escape only after bubbling through the liquid. The vapor is condensed at the top of the column and part, called the reflux, is allowed to flow back down the column. In order to make the separation process continuous, liquid feed enters at an intermediate stage in the column and the two liquid products (of a binary mixture) are withdrawn from the top and bottom of the column, respectively.

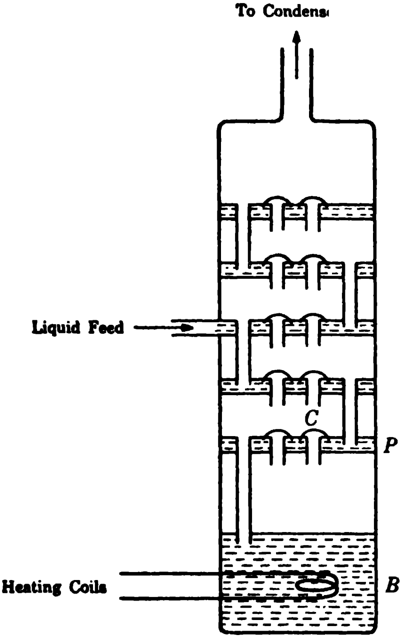

FIG. 39.6. Schematic bubble cap distillation column

As the vapor from the boiler ascends, it is brought into contact with the cooler liquid flowing downward. It can be seen from Fig. 39.5 that if the temperature of the vapor is lowered, it will condense to some extent giving a vapor richer in the more volatile constituent A, whereas the proportion of B in the liquid increases. At the same time, the temperature of the liquid is raised so that it partially vaporizes. Again, the proportion of A in the vapor is increased relative to that in the liquid. The condensation-vaporization exchange between vapor and liquid occurs at each plate and the net result is that the ascending vapor becomes increasingly richer in A whereas the descending liquid contains more and more B. If the column is properly designed, essentially pure A (more volatile) can be drawn off from the top of the column and almost pure B (less volatile) from the bottom.

The performance of a fractionating column is often expressed in terms of the height equivalent to a **theoretical plate.** This is defined as the length of the column from the top of which rises a vapor of the composition that would be in phase equilibrium with the liquid leaving at the bottom. If complete equilibrium were established at the plates in a bubble-cap column, each would be equivalent to a theoretical plate. However, because of insufficient contact between liquid and vapor and of nonuniformity of composition of the liquid, equilibrium is incomplete. The height equivalent of a theoretical plate (or H.E.T.P.) is thus greater than the actual distance between the plates.

A graphical method for the determination of the H.E.T.P. or the number of theoretical plates in a column has been proposed by W. L. McCabe and E. W. Thiele (1925). It can be applied to plate-type columns as well as to packed columns which have no actual plates but, instead, are filled with small, inert objects, such as beads, rings or helices of glass or ceramic. The method makes use of a diagram, such as Fig. 39.7, in which the mole fraction of the more volatile constituent A in the vapor is plotted as ordinate against the corresponding mole fraction in the liquid at equilibrium as abscissa. The information for the figure is obtained from the vapor and liquid curves in Fig. 39.5. Suppose the feed liquid has the composition indicated by l; this will be in equilibrium with vapor v. If the vapor v is now condensed, the composition of the liquid will be l_1. The equilibrium vapor will then be v_1 condensing to liquid l_2, and so on. Each equilibrium stage of vaporization and condensation represents a

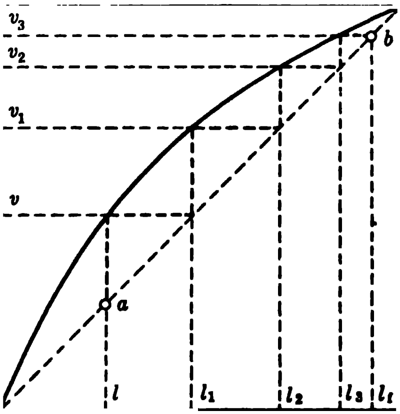

FIG. 39.7. Vapor-liquid equilibrium (pressure constant)

theoretical plate. Suppose that in a given fractionating column, l_f represents the experimentally determined composition of the condensate at the top of the column. This has been attained in four theoretical stages; one of these is represented by the boiler and so the column is equivalent to three theoretical plates. The H.E.T.P. is thus equal to the length of column between the feed entry and the top divided by three. With the foregoing explanation in mind, it is seen that to determine the number of theoretical stages, the broken line at 45° is drawn bisecting the diagram. The points *a* and *b* indicate the compositions of the feed and the A-rich product. The number of steps between *a* and *b* is then one more than the number of theoretical plates.

Any mixture of two liquids giving a boiling point-composition curve of the type shown in Fig. 39.5 can, theoretically, be separated into its components by fractional distillation. The greater the difference in the boiling points, that is to say, the steeper the boiling point curve, the more readily can the separation be achieved. The fractional distillation of liquid air, petroleum, benzene-toluene mixtures, and alcohol-water mixtures are all processes of industrial importance in which partial or complete separation of the components can be achieved.

II. Systems with a Boiling Point Minimum.—When there is a particular mixture having a boiling point lower than any other, the boiling point-composition curves are of the form shown in Fig. 39.8. The liquid and vapor curves touch at the minimum *M*, since here liquid and vapor in equilibrium have the same composition. The liquid mixture represented by *M* will, therefore, boil at a constant temperature and will distil over completely without change of composition. Liquids of this kind *which are not pure substances but which nevertheless distil unchanged at a definite temperature* are called **constant boiling mixtures** or **azeotropic mixtures** (Greek: *to boil without change*). The compositions as well as the boiling points of such mixtures change with pressure, thus proving that they are not definite compounds. Some instances of minimum constant boiling point mixtures at 1 atm pressure are given in Table 39.1.

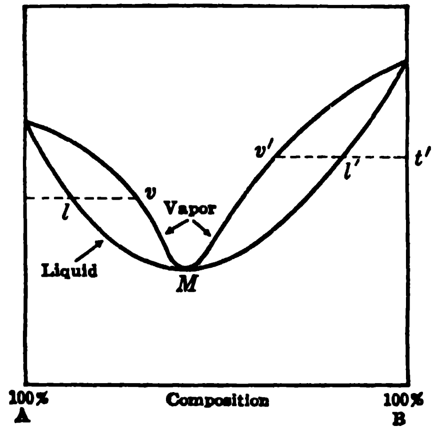

FIG. 39.8. System with minimum boiling point (pressure constant)

The results to be expected when a system of the type having a boiling point curve with a minimum is distilled may be seen from Fig. 39.8. When the liquid *l* boils at the temperature *t*, the vapor first evolved has the composition *v*, and is consequently relatively richer in B than is the liquid. As dis-

TABLE 39.1. MINIMUM CONSTANT BOILING MIXTURES AT 1 ATM

				Constant Boiling Mixture	
A	B. Pt.	B	B. Pt.	A (mole %)	B. Pt.
Ethyl acetate	77.1°C	Ethanol	78.26°C	53.6	71.8°C
Ethyl acetate	77.1°	Water	100.00°	69.5	70.4°
Ethanol	78.26°	Water	100.00°	89.4	78.15°
Carbon tetrachloride	76.5°	Ethanol	78.26°	60.3	64.95°

tillation proceeds, the residual liquid in the flask tends toward pure A in composition. If the condensate is redistilled, however, it is apparent that the vapor approaches in composition that of the mixture at the minimum boiling point. Fractional distillation will thus ultimately result in a distillate of composition M, although the final residue will approach pure A. Complete separation of the two constituents is thus impossible. An analogous conclusion is reached by consideration of the liquid l'; the composition of the distillate will again tend toward M, while the residue now approaches pure B. For systems having a minimum boiling point it is consequently possible to obtain in a pure state by fractional distillation only the component present in excess of the amount required to give the constant boiling mixture; this component remains in the final residue in the flask. The composition of the distillate always tends toward that of the mixture having the minimum boiling point, i.e., maximum vapor pressure.

If Fig. 39.8 is divided into two parts by a vertical line through M, it is seen that each part has the appearance of the simple system in which the boiling point charges regularly with composition. The components of the two parts are A and M (the azeotropic mixture) for the left side and B and M for the right. The behavior of any mixture can then be interpreted in the same manner as for a simple system.

A somewhat similar situation exists in connection with a plot of the compositions of the liquid and vapor in equilibrium analogous to Fig. 39.7. The curve is in two parts, one above and one below the 45° line bisecting the figure. The curve crosses this line at the point representing the azeotropic system, since the liquid and vapor then have the same composition.

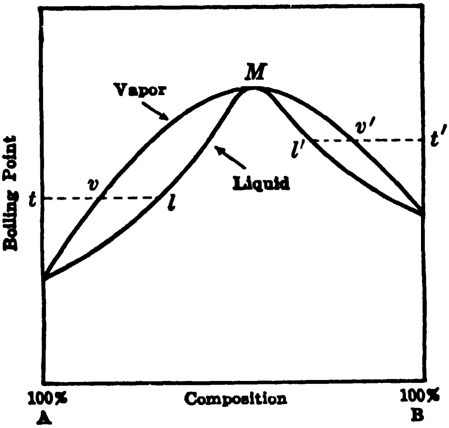

FIG. 39.9. System with maximum boiling point (pressure constant)

III. Systems with a Boiling Point Maximum.—Mixtures which exhibit marked negative deviations from Raoult's law often yield systems for which the vapor pressure curve has a minimum, and hence the boiling point-composition curve has a maximum, as in Fig. 39.9. The liquid and vapor curves meet at the maximum boiling point M, where again the two phases have the same composition. The liquid M is thus an azeotropic mixture of maximum boiling point; it distils without change of composition at a definite temperature. Here, again, the composition varies regularly with the external (total) pressure, indicating that the constant boiling mixture is not a definite compound, as was at one time considered possible.* Maximum boiling point systems are not common, the most familiar being those formed by water and a halogen acid. It is of interest to mention that the composition of the constant boiling mixture is so definite, *at a given external pressure*, that the distillate is used for the purpose of making standard solutions of hydrochloric acid for quantitative analysis.

A vertical line through M in Fig. 39.9 gives two simple systems; to the left the components are A and M, to the right they are B and M. It is thus evident that separation of the components of a maximum boiling point system by fractional distillation is not possible. The composition of the vapor, and hence of the condensate, will tend toward A if the original mixture lies to the left of M, while it will approach pure B if the mixture was originally to the right of M. In every case, however, the composition of the residue in the distilling flask will tend toward that of the mixture M of maximum boiling point. It is thus possible to obtain in a pure state only that constituent which is present in excess of the amount required by the azeotropic mixture.

The phase rule shows that the boiling point of an azeotropic mixture must be constant at a given pressure. For a two-component system of two phases there are, in general, two degrees of freedom. But in the case under consideration, two restrictions are imposed: constant pressure and equal liquid-vapor compositions. The azeotropic system is thus effectively invariant, so that equilibrium between liquid and vapor can exist only at a specified temperature.

39e. Partially Miscible Liquids.—When two liquids are so markedly different in nature that the system exhibits large positive deviations from ideal behavior, there occurs the phenomenon of **partial miscibility,** that is, limited solubility of each liquid in the other. If alcohol is added to acetic acid or to water, or vice versa, there is no limit to the proportion of one liquid that can be added to the other without the formation of two separate layers. Such liquids are said to be completely miscible. On the other hand, if a small quantity of phenol, ether or aniline is added to water, the substance will at first dissolve completely, but if the addition is continued, a condition is reached when no further solution occurs, and two liquid layers are formed. The two liquids are then only partially miscible with one another. Among

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* It may seem, at first sight, that the statement at the end of § 39b, referring to negative deviations from Raoult's law as being sometimes due to partial compound formation in the liquid, is a contradiction of the conclusion that the mixture of maximum boiling point is not a compound. Actually there is no such contradiction. Interaction between the components of the mixture may lead to a vapor pressure minimum, and hence a boiling point maximum, but the composition of the system at which this occurs bears no simple relationship to the nature of the compound, if any, or to the extent of its presence in the mixture.

other pairs of liquids that are partially miscible at ordinary temperatures are aniline and hexane, carbon disulfide and methyl alcohol, and water and amyl or butyl alcohol. When the relative quantities of the two components A and B are such that two liquid layers coexist, one of the layers is a saturated solution of A in B while the other is a saturated solution of B in A, e.g., aniline in water and water in aniline. The two liquid layers or phases in equilibrium are called **conjugate solutions.** Since the conjugate solutions are in equilibrium, they will have the same vapor pressures.

The compositions of the conjugate solutions at a given temperature and pressure are quite definite, and may be determined experimentally. As long as two liquid layers are present in equilibrium, at the particular temperature, their compositions are independent of the actual or relative amounts of the layers. If the values of these compositions for a number of different temperatures and a constant pressure, e.g., 1 atm, are plotted, a curve of the kind shown in Fig. 39.10 is obtained; the one given is actually for the aniline-hexane system. At any temperature *t* the tie line points l_1 and l_2 give the compositions of the two conjugate solutions; l_1 is the solution richer in aniline and l_2 is the one richer in hexane. It is seen from the shape of the curve *ACB* that as the temperature is raised the compositions of the two layers become closer; this is because the solubility of each liquid in the other increases with increasing temperature. At the temperature t_c the two layers have become identical in composition; they are, in fact, one layer the composition of which is represented by the point *C*, the maximum of the curve. The temperature t_c is known as the **critical solution temperature** or as the

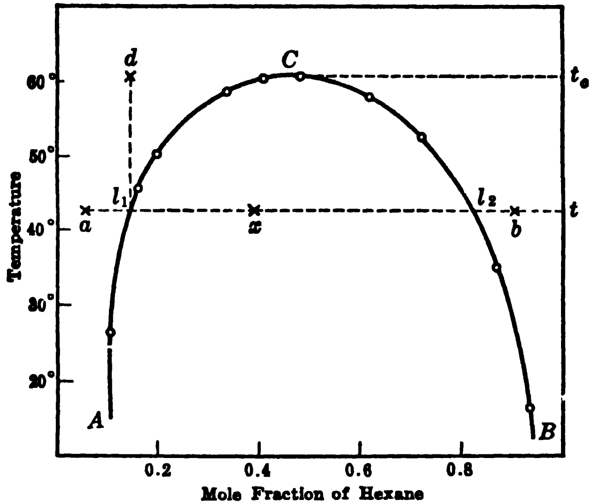

FIG. 39.10. Partially miscible liquids: the aniline-hexane system at atmospheric pressure

(upper) **consolute temperature** of the system. *Above this temperature the two liquids, which had previously been partially miscible, become completely miscible in all proportions*, and only one liquid layer is then possible. The consolute temperatures, and the corresponding compositions, expressed in weight per cent, for a number of systems are recorded in Table 39.2.

TABLE 39.2. CONSOLUTE TEMPERATURES AND COMPOSITIONS IN WEIGHT PER CENT

System		Consolute	Composition	
A	B	Temperature	A	B
Aniline	Hexane	59.6°C	52%	48%
Methanol	Cyclohexane	49.1°	29	71
Methanol	Carbon disulfide	40.5°	20	80
Water	Phenol	65.9°	66	34
Benzene	Sulfur	163°	35	65
Water	Aniline	167°	15	85

Actually all systems whose compositions lie outside the curve ACB consist of only one liquid layer, while those represented by points within the curve are made up of two layers, the compositions of which are given by the points on the curve for the same temperature. Thus, the point x, for example, indicates a system of two layers whose respective compositions are represented by l_1 and l_2. The amount of the layer l_1, relative to that of the layer l_2 is equal to the ratio of the distances xl_2 to xl_1. These facts may be used to draw a number of interesting conclusions. A mixture whose composition and temperature are given by the point a consists of a single layer; it is an unsaturated solution of hexane in aniline. If more hexane is now added the temperature remaining constant, the point representing the composition of the system will move to the right along the horizontal line. When the composition just falls on the curve ACB, i.e., at l_1, the second layer of composition l_2 will just commence to form. As the mole fraction of hexane is increased still further, the relative amount of the layer l_1 will decrease while the l_2 layer will increase; but, *the composition of each layer will remain unchanged as long as the two phases are present*, at the given temperature. Eventually, when sufficient hexane has been added for the system to have the composition l_2, the layer l_1 will have just ceased to exist. From l_2 to b, and beyond, the mixture of hexane and aniline then consists of a single layer which is now an unsaturated solution of aniline in hexane. Conclusions similar to the foregoing can, of course, be derived at any temperature lying below the consolute temperature t_c, or for the addition of either component of the system.

Another way in which a single layer may be converted into two layers, or vice versa, is by changing the temperature. Consider, for instance, the point d lying outside the curve ACB; it is immaterial whether this point is above or below the critical solution temperature t_c.* The system consists of a single

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* In order to simplify the figure, d has been chosen vertically above the point l_1; this is, however, not necessary. The general conclusions are applicable to any point outside the curve ACB.

layer; in the particular case chosen it happens to be an unsaturated solution of hexane in aniline. Suppose that the composition of the mixture is maintained constant, but the temperature is lowered. The state of the system will move vertically downward in Fig. 39.10, and it will remain one layer until the curve *ACB* is reached, at the point l_1; here the second layer, composition l_2, just commences to form. Experimentally, this point is indicated by the clear solution becoming opalescent due to formation of minute droplets of solution l_2. *If the temperature is lowered still further, the compositions of the conjugate layers will no longer remain unchanged;* the representative points will move down the curve from l_1 toward *A* for the first (aniline rich) layer, and from l_2 toward *B* for the second (hexane rich) layer. Incidentally, it can be shown that the proportion of the aniline layer to the hexane layer will decrease as the temperature is lowered.

Although systems with an upper consolute temperature, such as in Fig. 39.10, are probably of more common occurrence, there are instances in which the curve is reversed, so that there is a **lower consolute temperature.** That is to say, the two liquids become completely miscible *below* a certain temperature. In systems of this type the mutual solubilities of the two components decrease with increasing temperature. However, there is experimental evidence to show that this decrease of solubility does not continue as the temperature is raised, for after a certain point a normal solubility behavior, similar to Fig. 39.10, commences. Where the liquids are such that measurements over a considerable temperature range are possible, it is found that systems possessing a lower consolute temperature also exhibit an upper consolute temperature. There are thus two temperature limits outside which the liquids are completely miscible, and between which they are partially miscible (Fig. 39.11). Most of the systems of this type that have been studied hitherto consist of water and an amine, e.g., nicotine or methyl piperidine, or water and an ether or ketone, e.g., methyl ethyl ketone. The increased solubility as the temperature is lowered is undoubtedly due to increasing compound formation between the two components in the liquid state. The system, which shows positive deviations from ideal behavior at one temperature, thus tends to exhibit negative deviations as the temperature is lowered.

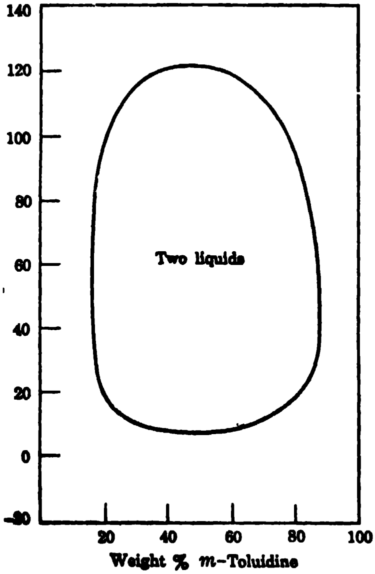


FIG. 39.11. The *m*-toluidine-glycerol system at 1 atm pressure

For the sake of clarity, it should be noted that mixtures with a lower consolute temperature probably always have an upper temperature of this kind, although it may not be accessible experimentally if it is above the temperature at which either of the liquids ceases to exist. A system with an upper consolute temperature, however, does not necessarily have a lower consolute point; it is very doubtful, for example, whether aniline and hexane, or methyl alcohol and carbon disulfide, would unite to a sufficient extent to give an increased mutual solubility with decreasing temperature. An alcohol or phenol with water might conceivably do so, but the temperatures would then be below those at which the liquids solidify.

39f. Distillation of Partially Miscible Liquids.—As long as only one liquid layer is present, distillation of a system of partially miscible liquids is the same in principle as for a completely miscible pair. The vapor always contains relatively more than the residual liquid of the component, or mixture of components, having the highest vapor pressure. When the liquid being distilled consists of two layers, or if two layers are formed in the flask during the course of the distillation as a result of the change in composition, the situation is different. *As long as the two layers are present, irrespective of their relative amounts, the total vapor pressure remains constant,* and the system boils, i.e., distils, at a definite temperature. The composition of the vapor is also constant, as long as the two layers are present, and so the distillate has a constant composition. This composition will, in general, not be the same as that of the mixture being distilled, and so the proportions of the two components in the residual liquid will alter. This means that the relative amounts of the two layers will alter, but their respective compositions, as well as the temperature and vapor pressure, will remain unchanged. The distillate of constant composition will thus continue to be collected, and the boiling point will be constant, as long as there are two conjugate layers in the flask. Eventually, one or other of the two layers will be used up completely, leaving one only; then the boiling point will rise, and the composition of the vapor, and distillate, will change continuously, just as for completely miscible liquids.

When there are two conjugate solutions in equilibrium with vapor, as exists in the process of distillation, the system consists of three phases, namely, two liquids and one vapor; hence, for the two component system, the phase rule then requires that $F = 2 - 3 + 2 = 1$, and so the system is univariant, having one degree of freedom. This result implies that only one of the variables, either temperature, pressure or composition, needs to be fixed in order to define the system completely. In the present case, the distillation is presumably carried out at the fixed pressure of 1 atm and this is the one degree of freedom. Consequently, the mere act of distilling the system of two liquid layers at a definite pressure means that the temperature and compositions of the three phases, viz., two liquid and one vapor, are fixed. The phase rule says nothing about the relative amounts of the layers, but it clearly indicates that as long as the two liquid layers are present, each will have a definite composition, and the composition of the vapor in equilibrium with them will, likewise, be constant. Further, the temperature, that is, the boiling point, will not change.

When one of the liquids has disappeared, so that there is now only one liquid and one vapor phase, P is equal to 2; the phase rule then gives F = 2 − 2 + 2 = 2, and the system is bivariant, with two degrees of freedom. Even if the pressure is fixed at 1 atm, there is still one variable; the equilibrium temperature, i.e., the boiling point of the mixture, can then vary, and as this changes corresponding changes occur in the compositions of both liquid and vapor. The phase rule thus provides a concise summary of the experimental facts.

39g. Completely Immiscible Liquids: Steam Distillation.—It is probably true that no two liquids are absolutely insoluble in each other, but with certain pairs, e.g., mercury and water and carbon disulfide and water, the mutual solubility is so small that the liquids may be regarded as virtually immiscible. For systems of this type, each liquid exerts its own vapor pressure, independent of the other, and the total vapor pressure is the sum of the separate vapor pressures of the two components in the pure state at the given temperature. The composition of the vapor can be readily calculated by assuming that the gas laws are obeyed; the number of moles of each constituent in the vapor will then be proportional to its partial pressure, that is to say, to the vapor pressure of the substance in the pure state. If p_A^0 and p_B^0 are the vapor pressures of the pure liquids A and B, respectively, at the given temperature, and n'_A and n'_B are the numbers of moles of each present in the vapor, the total pressure P at the same temperature is given by

$$P = p_A^0 + p_B^0, \tag{39.7}$$

and the composition of the vapor by

$$\frac{n'_A}{n'_B} = \frac{p_A^0}{p_B^0}. \tag{39.8}$$

To express the ratio of A to B in the vapor in terms of the actual weights w_A and w_B, the numbers of moles must be multiplied by the respective molecular weights, M_A and M_B; hence, from equation (39.8),

$$\frac{w_A}{w_B} = \frac{n'_A M_A}{n'_B M_B} = \frac{p_A^0 M_A}{p_B^0 M_B}. \tag{39.9}$$

A system of two immiscible liquids will boil, that is, distil freely, when the total vapor pressure P is equal to the atmospheric pressure. The boiling point of the mixture is thus lower than that of either constituent, since the total pressure of the vapor is the sum of the two separate vapor pressures. Further, since the total vapor pressure is independent of the relative amounts of the two liquids, the boiling point, and hence the composition of the vapor and distillate, will remain constant as long as the two layers are present. The same conclusion can be readily derived from the phase rule, as in the case of a system of two partially miscible liquids.

The properties just described are utilized in the process of **steam distillation,** whereby a substance that is immiscible, or almost immiscible, with water, and that has a relatively high boiling point, can be distilled at a much lower temperature by passing steam through it. The same result should, theoretically, be obtained by boiling a mixture of water and the particular immiscible substance, but by bubbling steam through the latter the system is kept agitated, and equilibrium is attained between the vapor and the two liquids. The mixture distils freely when the total pressure of the two components is equal to that of the atmosphere. For example, when a mixture of water and chlorobenzene is distilled at an external pressure of 740.2 mm, the liquid is found to boil at a temperature of 90.3°C; at this temperature the vapor pressure of pure water is 530.1 mm, and that of chlorobenzene is 210.1 mm, making a total of 740.2 mm. The composition of the distillate, which is equal to that of the vapor, as given by equation (39.9), is then

$$\frac{\text{Wt. of chlorobenzene } (w_A)}{\text{Wt. of water } (w_B)} = \frac{p_A^0 M_A}{p_B^0 M_B} = \frac{210.1 \times 112.5}{530.1 \times 18.02} = 2.47.$$

The distillate should thus contain 2.47 parts by weight of chlorobenzene to one part of water, that is, 71.2 per cent by weight of the former; the actual value found by experiment was 71.4 per cent.

It is seen that chlorobenzene, which has a normal boiling point of 132°C, can be distilled with steam at a temperature about 40° lower, the distillate containing over 70 per cent of the organic compound. An examination of the calculation shows that the high proportion by weight of chlorobenzene in the steam distillate is due largely to the high molecular weight of this substance, viz., 112.5, as compared with that of water. In addition, this case is a particularly favorable one because chlorobenzene has a relatively high vapor pressure in the region of 90° to 100°C. In order that a liquid may be distilled efficiently in steam, it should therefore be immiscible with water, it should have a high molecular weight, and its vapor pressure should be appreciable in the vicinity of 100°C. A liquid which is partially miscible with water, such as aniline, may be effectively distilled in steam, provided the solubility is not very great. In calculating the composition of the distillate, however, the pressures p_A^0 and p_B^0 in equation (39.9) would have to be replaced by the actual partial pressures.

Attention may be called to the fact that equation (39.9) can be employed to determine the approximate molecular weight of a substance that is almost immiscible with water. This can be done provided the composition of the steam distillate and the vapor pressures of the two components are known.

Example: The hydrocarbon terpinene was found to distil freely in steam at a temperature of 95°C, when the atmospheric pressure was 744 mm; the vapor pressure of pure water at this temperature is 634 mm. The distillate contained 55 per cent by weight of terpinene; calculate its molecular weight.

If the terpinene is designated by A, and the water by B, it follows that at 95°C, the boiling point of the mixture, p_B^0 is 634 mm, and hence p_A^0 is equal to $P - p_B^0$, i.e., 744 − 634 = 110 mm. The ratio w_A/w_B in equation (39.9) is 55/45, since the distillate contains 55 per cent of terpinene (A) and 45 per cent of water (B); it follows, therefore, from equation (39.9) that

$$\frac{55}{45} = \frac{110 \times M_A}{634 \times 18}$$

$$M_A = 127.$$

(The actual value is 136.)

39h. The Distribution Law.—If to a system of two liquid layers, consisting of two immiscible or slightly miscible components, there is added a third substance which is soluble in both layers, this substance is found to distribute, or divide, itself between the two layers in a definite manner. It has been shown experimentally that at equilibrium, at constant temperature, the ratio of the concentrations in the two layers has a definite value, independent of the actual amount of the dissolved substance; thus, if c_1 and c_2 are the concentrations of this substance in the two layers, then

$$\frac{c_1}{c_2} = \text{constant}. \qquad (39.10)$$

In words, therefore, *the dissolved substance, irrespective of its total amount, distributes itself between the two layers in a constant concentration ratio, at constant temperature.* This may be regarded as the statement of the **distribution law;** the ratio, equal to the constant in equation (39.10), is referred to as the **distribution ratio.**

An interesting conclusion may be drawn by considering the two liquid layers to be in contact with excess of the pure solute, either solid or liquid, so that when equilibrium is attained both solutions are saturated with the dissolved substance. If the saturation solubilities in the two liquid layers are s_1 and s_2, respectively, the distribution law then gives

$$\frac{c_1}{c_2} = \frac{s_1}{s_2} = \text{distribution ratio}. \qquad (39.11)$$

The distribution ratio should thus be equal to the ratio of the solubilities of the substance in the two layers. It will be shown below that the distribution law in the form of equation (39.10) can usually be applied only to dilute solutions; hence, equation (39.11) will hold only if the solute is sparingly soluble in both solvents, so that the saturated solutions are dilute. In any event, even if the equation is not exact, it is generally true that the solute distributes itself in such a manner as to have a higher concentration in the layer in which it normally has the larger saturation solubility. This fact is made use of in the familiar process employed in the organic laboratory of extracting an aqueous solution with ether or other solvent that is immiscible. or partially miscible, with water.

The distribution law is actually one of wide applicability, for it should hold for the distribution of a dissolved substance between any two phases, e.g., liquid-liquid, gas-liquid, liquid-solid, etc. Henry's law for the influence of pressure on the solubility of a gas is, in fact, a form of the distribution law; this follows directly from equation (38.3). According to this equation w/p is a constant; w is the mass of gas in unit volume of the solution, and hence it is proportional to the concentration of gas in the solution, while the pressure p is related to the concentration in the gas phase. The ratio of the concentrations of the gas in the two phases, viz., liquid and gas, is thus constant by Henry's law.

It was seen earlier that when two phases are in equilibrium, at constant temperature and pressure, the chemical potential of a given substance will be the same in both phases. By means of equation (26.6) the chemical potential of the dissolved substance in any two phases may be represented by

$$\mu_1 = \mu_1^0 + RT \ln a_1 \qquad \text{and} \qquad \mu_2 = \mu_2^0 + RT \ln a_2,$$

where a_1 and a_2 are the activities of the solute in the two phases. When the system is at equilibrium at a given temperature and pressure, μ_1 and μ_2 must be equal, so that

$$RT \ln \frac{a_1}{a_2} = \mu_2^0 - \mu_1^0.$$

At constant temperature the standard chemical potentials μ_1^0 and μ_2^0 are constant, and so also are R and T; it follows, therefore, that

$$\frac{a_1}{a_2} = \text{constant}, \tag{39.12}$$

which is the exact form of the distribution law. For systems which are ideal or do not depart appreciably from ideal behavior, the ratio of the activities may be replaced by the ratio of the mole fractions, i.e., x_1/x_2 should be constant. Further, for dilute solutions or for gases, the ratio of the concentrations may be used in place of the ratio of the mole fractions, and so in these circumstances c_1/c_2 should be constant, in agreement with the simple form of the distribution law equation (39.10).

In spite of the theoretical limitations of the simple form of the law to dilute, almost ideal solutions, it has been found to hold in many cases, *provided the dissolved substance has the same molecular weight in both solvents.* The results obtained in some experiments on the distribution of succinic acid between water (c_1) and ether (c_2) are given in Table 39.3; the ratio c_1/c_2 is seen to be approximately constant over an appreciable range of concentrations.

TABLE 39.3. DISTRIBUTION OF SUCCINIC ACID BETWEEN WATER AND ETHER AT 15°C

c_1	0.191	0.370	0.547	0.749 mole liter^{-1}
c_2	0.0248	0.0488	0.0736	0.101
c_1/c_2	7.69	7.58	7.43	7.41

When the dissolved substance does not have the same molecular weight in the two liquid phases, the simple form of the distribution law breaks down.

The reason for this is that the law is applicable only to the molecular species that is common to the two layers. Consider, for example, the distribution of benzoic acid between water and benzene. In the former liquid the acid consists mainly of C_6H_5COOH molecules; there is some ionization, but this is small and may be ignored here. In the benzene solution, on the other hand, the benzoic acid is largely associated (§ 26a) to form double molecules, $(C_6H_5COOH)_2$, with a relatively small proportion of single molecules, C_6H_5COOH. The distribution law, as expressed by equation (39.10), holds for the species present in both layers, namely the single C_6H_5COOH molecules. If allowance is made for this modification, the law is found to be obeyed in a satisfactory manner.

Suppose a given solute A has a normal molecular weight in one solvent, in which the concentration is c_1, while in the second solvent it exists mainly as the associated molecule A_n, the total concentration being c_2. In the latter solvent there will be an equilibrium between associated and simple molecules, i.e.,

$$A_n \rightleftharpoons nA,$$

and assuming the solution to be dilute, the equilibrium constant is

$$K_c = \frac{c_A^n}{c_{A_n}}, \tag{39.13}$$

where c_A is the concentration of simple molecules and c_{A_n} of associated molecules in the second solvent. It then follows from equation (39.13) that

$$c_A = \text{constant} \times \sqrt[n]{c_{A_n}}. \tag{39.14}$$

If the solute is mainly in the associated form, c_{A_n} may be identified with c_2, the total concentration in the second layer; hence, from equation (39.14),

$$c_A \approx \text{constant} \times \sqrt[n]{c_2}. \tag{39.15}$$

As stated above, the distribution law applies to the species that the two liquid phases have in common, namely the simple A molecules; in this case, therefore, it should take the form

$$\frac{c_1}{c_A} = \text{constant},$$

and upon introducing the value of c_A given by equation (39.15), the result is

$$\frac{c_1}{\sqrt[n]{c_2}} = \text{constant}. \tag{39.16}$$

The modified distribution law derived in this manner may be tested by means of the data for the distribution of benzoic acid between water and benzene, quoted in Table 39.4. It can be seen that c_1/c_2 is far from constant, but $c_1/\sqrt{c_2}$ remains almost unchanged over a range of concentrations. It is apparent that n in equation (39.16) is equal to 2, so that benzoic acid exists

TABLE 39.4. DISTRIBUTION OF BENZOIC ACID BETWEEN WATER AND BENZENE AT 20°

c_1	c_2	c_1/c_2	$c_1/\sqrt{c}$
4.88×10^{-2} mole liter^{-1}	3.64×10^{-1} mole liter^{-1}	0.134	0.025
8.00	8.59	0.093	0.027
16.0	33.8	0.047	0.027
23.7	75.3	0.030	0.027

mainly as $(C_6H_5COOH)_2$ molecules in the particular benzene solutions used in these experiments.

The fact that the simple distribution law applies only to the molecular species common to the two layers has found a number of useful applications in physical chemistry. For example, when iodine is dissolved in an aqueous solution of potassium iodide it combines to some extent with the iodide ions to form the I_3^- ion, viz.,

$$I_2 + I^- = I_3^-,$$

and it is of interest to know how much of the free iodine I_2 is left in the solution. This can be found by studying, first, the distribution of iodine between water and an organic solvent, e.g., carbon disulfide, carbon tetrachloride or chloroform, and finding the distribution ratio. The experiments are then repeated with the same organic liquid and a solution of iodine in potassium iodide. By determining the concentration of iodine in the organic solvent, in which I_2 molecules only are present, and assuming the distribution ratio just found, the concentration of free iodine in the iodide solution can be calculated.

Example: The distribution ratio of iodine between carbon disulfide and water is found to be 625. When iodine is distributed between carbon disulfide and a 0.125 molar solution of KI, the concentration of iodine in the former layer is found to be 0.1896 mole per liter; the total concentration in the aqueous KI layer is 0.02832 mole per liter. What is the concentration of I_3^- ions in the latter layer?

The concentration of free I_2 in the KI layer must be equal to the concentration in the carbon disulfide divided by the distribution ratio for free iodine, i.e., 0.1896/625 mole per liter; hence,

$$\text{Conc of } I_2 \text{ in KI layer} = \frac{0.1896}{625} = 0.000303 \text{ mole per liter.}$$

The total concentration of iodine in this layer is 0.02832 molar, and so the concentration of I_3^- ions is $0.02832 - 0.00030 = 0.02802$ mole per liter.

GAS-SOLID SYSTEMS

40a. Salt Hydrates: Application of Phase Rule.—The nature of the equilibrium between a gas and a solid depends on whether the two combine to form compounds or not; the discussion here will be restricted to cases in which compounds are formed, since these are of wider interest. Simple examples of gas-solid equilibria of this type are the dissociation of solid calcium carbonate to form calcium oxide and carbon dioxide, and the dissociation of salt hydrates. These systems have already been studied in Chapter 10 from the aspect of the equilibrium constant; in the present chapter the point of view will be somewhat different, use being made of the phase rule and of equilibrium diagrams.

Consider the dissociation of solid $CuSO_4 \cdot 5H_2O$ to form solid $CuSO_4 \cdot 3H_2O$ and water vapor, thus

$$CuSO_4 \cdot 5H_2O(c) \rightleftharpoons CuSO_4 \cdot 3H_2O(c) + 2H_2O(g).$$

This is a system of two components (C = 2), since the proportions of two independent substances, e.g., $CuSO_4$ and H_2O, must be specified in order that the composition of each phase may be defined. There are three phases (P = 3), namely two solids and one gas; hence, by the phase rule $F = 2 - 3 + 2 = 1$. The system at equilibrium is consequently univariant; this means that only one variable, e.g., the temperature, need be fixed to define the equilibrium completely. At a given temperature, therefore, there should be a definite pressure of water vapor in equilibrium with the two hydrates. This conclusion is, of course, identical with that derived from a consideration of the equilibrium constant in § 33a. Once again, it is apparent that the two solid phases must be present in addition to the vapor, for otherwise the system would not be univariant. It is necessary therefore in speaking of the aqueous vapor pressure or dissociation pressure of a *salt hydrate system, to name the two solid phases;* the bare expression "dissociation pressure of a salt hydrate" generally has no exact significance.

An examination of the variation of the equilibrium pressure with the total composition of a salt hydrate is of interest. For example, starting with pure $CuSO_4 \cdot 5H_2O$ in a closed container attached to a vacuum pump and manometer, the solid may be gradually dehydrated by evacuation and the vapor pressure determined at constant temperature, from time to time during the dehydration. The results obtained at 25°C are shown in Fig. 40.1. As pumping is started, the pressure will drop steadily until 7.8 mm of mercury is reached. The $CuSO_4 \cdot 5H_2O$ will then start to dissociate into $CuSO_4 \cdot 3H_2O + 2H_2O$ and the pressure will remain constant as long as the system contains more water than $CuSO_4 \cdot 3H_2O$. When only the latter remains, the pressure will fall sharply to 5.6 mm. It then stays constant at this value until the composition of the system is $CuSO_4 \cdot H_2O$, when it falls again, to 0.8 mm, where it remains until the salt is completely anhydrous; the pressure of the water vapor then sinks to zero. It is evident from these results that there are three consecutive equilibria involving the hydrates of copper sulfate, viz.,

$$CuSO_4 \cdot 5H_2O(c) \rightleftharpoons CuSO_4 \cdot 3H_2O(c) + 2H_2O(g) \qquad p = 7.8 \text{ mm at } 25°\text{C}$$

$$CuSO_4 \cdot 3H_2O(c) \rightleftharpoons CuSO_4 \cdot H_2O(c) + 2H_2O(g) \qquad 5.6 \text{ mm}$$

$$CuSO_4 \cdot H_2O(c) \rightleftharpoons CuSO_4(c) + H_2O(g) \qquad 0.8 \text{ mm}$$

It is seen from Fig. 40.1 that as long as the two particular solid phases are present, the equilibrium pressure remains constant, irrespective of the rela-

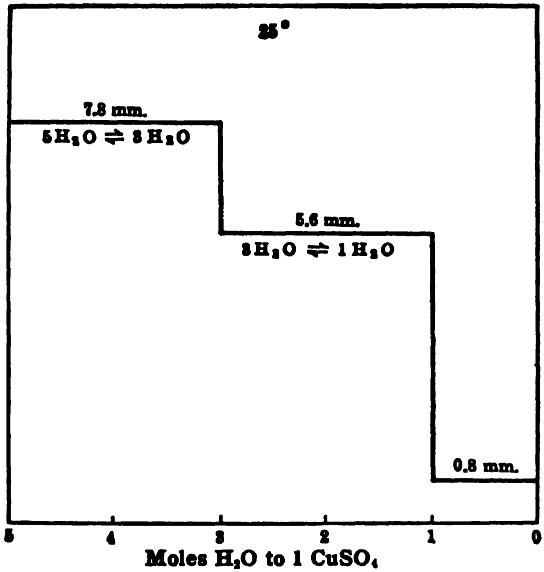


FIG. 40.1. Dehydration of copper sulfate at 25°

tive amounts of these two phases; this result is in agreement with the phase rule and the equilibrium constant.

If the starting material is anhydrous copper sulfate and water vapor is gradually added, the same variation of pressure with composition as in Fig. 40.1 would be obtained as step-wise hydration takes place. In this case, the state of the system is initially at the right and it moves to the left as water is added.

40b. Salt Hydrate Equilibria and Temperature.—At other temperatures, similar results to those described above have been obtained; the vapor pressures are, however, higher the higher the temperature. At 50°C, for example, the three systems mentioned above give equilibrium vapor pressures of 45.4, 30.9 and 4.5 mm, respectively. It appears that above 102°C the pentahydrate is not stable, and $CuSO_4 \cdot 3H_2O$ is then the first stable hydrate; at such temperatures only two horizontal portions would appear in the vapor pressure-dehydration curve.

The variation of vapor pressure of the salt hydrate system with temperature may be represented in the manner depicted in Fig. 40.2; this diagram is not quantitative, as is Fig. 40.1, but it is of the proper form. The lowest three curves show the variation with temperature of the equilibrium vapor pressure of the indicated systems; the uppermost curve gives the vapor pressure of an aqueous saturated solution of $CuSO_4 \cdot 5H_2O$. The data in Fig. 40.2 may be correlated with those in Fig. 40.1; in fact each of the two diagrams is a section, at a definite composition and at a definite temperature, respectively, of a three-dimensional model in which the variations of vapor pressure, temperature and concentration are shown simultaneously.

Suppose water vapor is gradually added to the anhydrous salt while the system is kept at a constant temperature; starting from *a* (Fig. 40.2), where the vapor pressure is zero (anhydrous salt), the pressure increases along the vertical line *af* (constant temperature). Between *a* and *b* the anhydrous salt and vapor exist without interaction; at *b*, which is the vapor pressure of the $CuSO_4$-$CuSO_4 \cdot H_2O$ system at the given temperature, the monohydrate commences to form, and the pressure remains constant although water vapor is being added, as long as some anhydrous salt remains. The point *b* in Fig. 40.2 thus corresponds to the lowest horizontal step in Fig. 40.1. When the formation of $CuSO_4 \cdot H_2O$ is complete, further addition of water causes the vapor pressure to rise suddenly to *c* in Fig. 40.2. Here again the pressure remains constant until the whole salt is in the form of trihydrate. The point *c* is equivalent to the second step in Fig. 40.1. If more water is now added the vapor pressure rises to *d*, and remains unchanged until the whole solid is converted into pentahydrate. The point *d* is consequently equivalent to the uppermost line in Fig. 40.1.

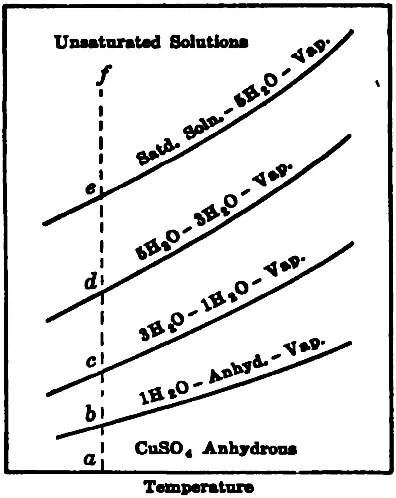


FIG. 40.2. Variation of vapor pressure with temperature

If the addition of water is continued further, the pentahydrate commences to dissolve, a saturated solution being formed; the vapor pressure, at the stipulated constant temperature, is then given by the point *e*. Although there is now only one solid phase, there is still a total of three phases present, viz., solid $CuSO_4 \cdot 5H_2O$, solution and vapor; the system is still univariant, according to the phase rule, and the vapor pressure will have a definite value at each temperature as long as the three phases coexist in equilibrium. Ultimately, the addition of sufficient water results in the whole of the solid salt being dissolved and the solution is unsaturated. There are now two phases only, and hence the vapor pressure varies with the concentration of the solution, the values falling on the line *ef*.

SOLID-LIQUID SYSTEMS

41a. Freezing Point and Solubility Curves.—The conditions of equilibrium between solid and liquid phases in a system of two components may be considered from two points of view. If the liquid mixture (solution) is in equilibrium with the solid phase of the component present in excess, that is, the solid solvent, the solution is said to be at its freezing point. The curve representing the variation of the equilibrium temperature with the composition of the liquid phase is referred to as the **freezing point curve.** On the other hand, if the solid phase in equilibrium with the solution is that of the substance present in smaller amount, that is, the solid solute, the liquid phase is said to be a **saturated solution,** and the curve showing the variation of its composition with temperature is called a **solubility curve.**

It was pointed out earlier that there is no fundamental difference between solute and solvent, and the distinction between solubility and freezing point curves is merely a matter of convenience. When the two components of the system are similar chemically, e.g., both are metals or oxides, or when they are organic compounds of not very different melting point, it is not possible to distinguish clearly between solvent and solute. The curves representing the conditions of equilibrium of solid and liquid phases at different temperatures are called freezing point curves, irrespective of which component constitutes the solid phase. On the other hand, if one of the substances differs from the other, e.g., a salt and water, or if the system consists of two organic compounds with very different melting points, e.g., benzene and naphthalene, it is generally possible to make the conventional distinction between solvent and solute. In this case the term "solubility" is used when the solid phase is the solute, and "freezing point" when it is the solvent.

In the experimental study of both solubility and freezing points of solutions, what is determined is a temperature and the composition of a solution in equilibrium with excess solid at that temperature. Whether the data are interpreted as a solubility or freezing point measurement depends upon the purpose of the experiment. In any event, by combining equations (24.2) and (24.3), and replacing p/p^0 by the mole fraction x, in accordance with Raoult's law, the result

$$\ln x = -\frac{L_f}{R}\left(\frac{T_0 - T}{T_0 T}\right) \tag{41.1}$$

gives either the variation of the freezing point of an ideal solution with composition (mole fraction of solvent) or the dependence of the ideal solubility (mole fraction of solute) on the temperature. It is possible, therefore, by means of equation (41.1) to calculate the ideal solubility of a solid. Since L_f is now the molar heat of fusion of the solute, T_0 is its freezing point and T is the temperature at which the solubility is to be calculated, it is seen that, expressed in mole fractions, the ideal solubility of a solid at a given temperature is independent of the solvent.

Example: The heat of fusion of naphthalene is 4540 cal mole^{-1}, and its freezing point is 80.0°C. Calculate its ideal solubility, in any solvent, at 25.0°C.

In equation (41.1), L_f is 4540, T_0 is $273.2 + 80.0 = 353.2$°K and T is $273.2 + 25.0 = 298.2$°K; hence

$$2.303 \log x = -\frac{4540 \times 55.0}{1.987 \times 353.2 \times 298.2}$$

$$x = 0.304 \text{ mole fraction.}$$

The ideal solubility of naphthalene in any solvent at 25°C is 0.304 mole fraction. Some experimental values in various solvents are as follows: benzene 0.292, toluene 0.289, carbon bisulfide 0.290, nitrobenzene 0.295, carbon tetrachloride 0.257, chlorobenzene 0.313, hexane 0.121 and ethanol 0.024. Except for the last two solvents, where the departure from ideal behavior is considerable, the agreement between observed and calculated solubilities may be considered to be good.

41b. Condensed Systems.—In the study of liquid-solid equilibria it is the practice to disregard the vapor phase and to fix an arbitrary constant pressure, generally 1 atm. Experimental studies are then made with vessels open to the atmosphere. It should be understood that since the pressure is generally not the equilibrium value, the system as a whole is not strictly in true equilibrium. For a solid-liquid system, however, the effect of pressure is relatively small (§ 21a), and so the results at atmospheric pressure will be very little different from those which would be obtained if the system were in equilibrium with vapor. A system in which only solid and liquid phases are considered is called a **condensed system.**

Since the maximum number of degrees of freedom in a two-component system is three, fixing the pressure leaves two adjustable variables, temperature and composition. It is thus possible to use ordinary rectangular coordinates for the graphical representation of the conditions of equilibrium in a condensed system of two components. Solid-liquid equilibria of a number of types and of varying degrees of complexity are known; some of the more important simpler cases will now be described.

41c. Solid Phases Consist of Pure Components.—If a liquid mixture of two similar components A and B is cooled, solid will commence to separate at a definite temperature, namely the freezing point. The actual value of the freezing point will depend on the composition of the liquid mixture, and if the results for a series of such mixtures of components varying from pure A to pure B are plotted against the corresponding compositions, two curves, like *AC* and *BC* in Fig. 41.1, are obtained. The points *A* and *B* are the freezing points of the pure components; the addition of B to A lowers the freezing point along *AC*, and similarly A added to B lowers the freezing point of the latter along *BC*. If the freezing point and composition of a given mixture are such as to fall on the curve *AC*, the solid which separates is pure A; on the other hand, if the freezing system is represented by a point on *BC*, pure solid B will separate from the liquid. The curves *AC* and *BC* may be regarded as representing the conditions of temperature under which liquid phases of various compositions are in equilibrium with the solid phase A or the solid phase B, respectively. Since it gives the conditions of equilibrium of different phases, Fig. 41.1 is an example of a two-component phase diagram.

At the point *C*, where the curves *AC* and *BC* meet, *both solids* A and B are in equilibrium with the liquid phase. There are consequently three phases present, and since the system involves two components, there can be only one degree of freedom, according to the phase rule; thus $P = 3$, $C = 2$, and hence, $F = 2 - 3 + 2 = 1$. Since the pressure is arbitrarily fixed at 1 atm,

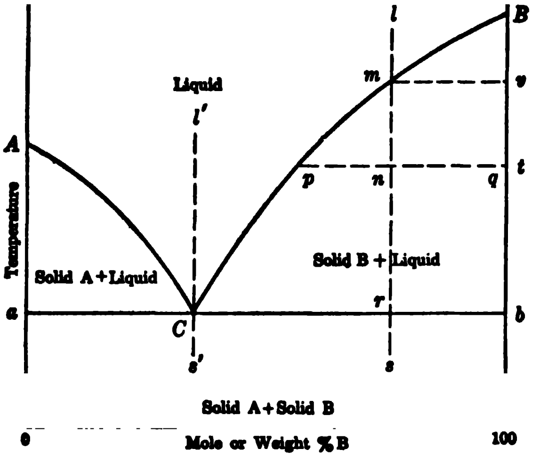


FIG. 41.1. Solid-liquid phase equilibria

this represents the one degree of freedom; the system has thus effectively no degrees of freedom, that is to say, it is then an invariant condensed system. This means that the mere fact of the existence of the two solid phases A and B in equilibrium with the liquid, at 1 atm pressure, completely defines the point *C*; there is thus only one temperature where this equilibrium is possible, as the phase diagram actually indicates. The point *C*, where the freezing point curves *AC* and *BC* meet, is the lowest temperature at which any liquid mixture can be in equilibrium with solid A or B; consequently, it is the lowest temperature at which any mixture of solid A and B will melt. For this reason *C* has been called the **eutectic point** (Greek: *easily melting*). It is the lowest temperature at which the existence of liquid phase for the given system is possible at the arbitrarily fixed pressure, viz., 1 atm.

A number of examples of two-component systems which give equilibrium diagrams of the type in Fig. 41.1 are mentioned in Table 41.1. It is seen that the components may both be metals, or one may be a metal and the other a nonmetal. In some cases both are salts, while in others they are organic compounds. Systems involving a salt and water are sometimes of this type, as will be seen in § 41e.

TABLE 41.1. TWO-COMPONENT SYSTEMS WITH SIMPLE EUTECTIC

A	M. Pt.	B	M. Pt.	Eutectic
Antimony	630°C	Lead	326°C	246°C
Bismuth	268°	Cadmium	317°	146°
Silicon	1412°	Aluminum	657°	578°
Potassium chloride	790°	Silver chloride	451°	306°
o-Nitrophenol	44.1°	*p*-Toluidine	43.3°	15.6°
Benzene	5.4°	Methyl chloride	−63.5°	−79°

By means of the phase diagram it is possible to predict the behavior of any system upon heating or cooling. Consider, for purposes of illustration, a system of composition represented by the line *ls* in Fig. 41.1; *l* represents the system above its freezing point, when it consists of liquid phase only, and *s* is the same system completely solidified, since it is below the eutectic temperature. If the liquid *l* is cooled, no solid will separate until the temperature corresponding to the point *m* on the freezing point curve *BC* is reached; at this temperature solid B will commence to deposit, as indicated by the tie line *mv*. As the temperature continues to fall, the state of *the system as a whole* will be represented by points lying between *m* and *r*, since the total amount of A and B in the various phases remains constant. Such points, of which *n* may be chosen as an example, indicate mixtures of solid B and of liquid whose composition changes, becoming relatively richer in A, as the temperature falls. At the typical point *n*, at the temperature *t*, the composition of the liquid phase is given by the point *p*, while the solid consists of pure B, as indicated by the other end *q* of the constant temperature tie line passing through *n*. The relative amounts of solid B to liquid mixture are in the ratio of the distances *np* to *nq*.

It is apparent that as the temperature falls from *m* to *r*, the composition of the liquid phase must correspondingly change from *m* to *C*, pure solid B separating all the time. When the eutectic temperature is reached at *r*, the second solid, that is A, commences to deposit in addition to B; the temperature must now remain constant until all the liquid has solidified, since the phase rule shows that there is only one temperature at which the liquid can be in equilibrium with two solid phases. This is indicated by the tie line through *C* ending at *a* and *b*. When the whole system has solidified completely, the temperature of the mixed solids A and B can fall from *r* to *s*. If the solid *s* is heated until it liquefies completely, the changes described above take place exactly in the reverse order.

If the original liquid *l* were on the left side of the eutectic point, that is to say, if it were richer in the component A, there would be a similar series of changes on cooling. In this case, however, solid A would separate first; the temperature would then continue to fall, while the composition of the liquid changed, until the eutectic was reached. The second solid B would now deposit, and the temperature would again remain constant until the system was completely solid.

In the special case in which the composition of the liquid *l′* coincides exactly with that of the eutectic point, solid will separate on cooling only when the eutectic temperature is reached at *C*. The two solid phases A and B will deposit simultaneously, and the temperature will remain constant until the liquid has disappeared. Microscopic examination shows that solid of eutectic composition consists of small individual crystals of the two components in a random mixture. Solids of any other composition are found to contain relatively large crystals of one component embedded in a matrix of the eutectic mixture of small crystals.

In general, the term **liquidus curve** is given to the curve representing the composition of the liquid phase in equilibrium with solid. Correspondingly, the composition of the latter is indicated on the **solidus curve.** Thus, in Fig. 41.1, the liquidus curves are *AC* and *BC*, and the corresponding solidus curves are *AaC* and *BbC*, respectively.

41d. Cooling Curves: Thermal Analysis.—It is apparent from the results described in the preceding section that upon cooling a liquid mixture, solid A or B commences to separate when the temperature reaches a point on the curve *AC* or *BC*, respectively. The solid continues to deposit as the temperature falls, but when the eutectic is reached, and both solids separate, the temperature remains constant. The separation of solid A or B is always accompanied by the evolution of heat, equal in amount but opposite in sign to the heat of fusion; consequently, at the point equivalent to *m* in Fig. 41.1, the rate of cooling will be diminished. The cooling will thus continue from *m* to *r* at a slower rate than before, until the eutectic point is attained when the temperature remains constant. If the temperature of the system while cooling, starting with the molten liquid *l*, were plotted against the time, a **cooling curve,** such as is shown in Fig. 41.2, would be expected; the letters in this figure correspond to those in Fig. 41.1. From *l* to *m* the liquid cools rapidly, then at *m* solid commences to separate and the rate of cooling is slowed down; the cooling curve thus shows a break at the temperature *m*, i.e., the freezing point, where solid first commences to form. As the composition of the liquid phase changes, the temperature falls from *m* to *r*; at *r*, the eutectic point, the temperature remains constant, along *rr′*, until solidification is complete. When no more liquid is left, cooling of the solid can proceed from *r′* to *s*. Frequently, owing to the absence of crystallization nuclei, supercooling occurs and the temperature drops slightly below *m* without solid separating. However, as soon as solid begins to form, heat is evolved and there is a transient increase of temperature as shown by the dotted region in Fig. 41.2. Subsequently, the behavior is the same as if no supercooling had occurred.

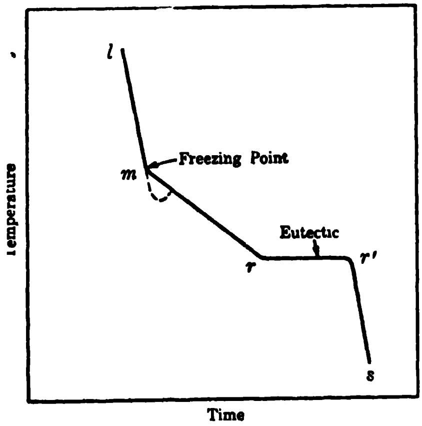
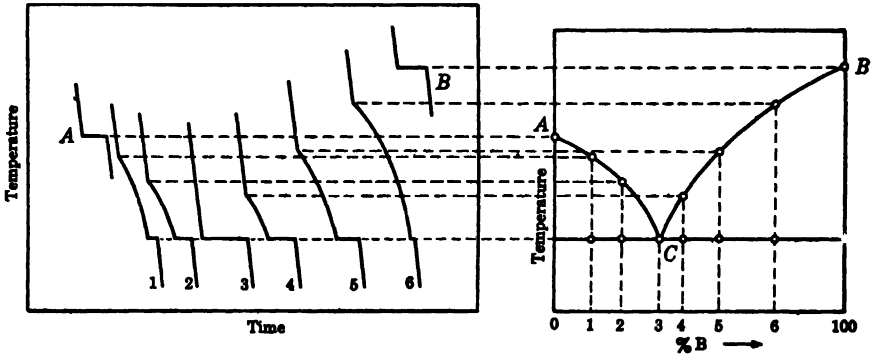


FIG. 41.2. Cooling curve

From the cooling curve for a mixture of any definite composition, it is thus possible to obtain the freezing point of that mixture and the eutectic temperature for the system. The former will, of course, vary with the composition, but the latter remains the same throughout. The closer the composition of the original system is to that of the eutectic, the shorter will be the portion *mr* and the longer the halt *rr′* at the eutectic temperature. If the liquid mixture coincides exactly with the composition at the eutectic point, the region *mr* will not exist; the cooling curve will then not show a break until the eutectic temperature is reached.

The facts described above form the basis of the method of **thermal analysis** for the study of solid-liquid phase equilibria, especially those involving metals. A series of mixtures of known amounts of the two constituents A and B are made up, and each mixture is heated until it melts to a homogeneous liquid. It is then allowed to cool steadily, and the temperature is recorded at regular intervals so as to obtain the cooling curve, as in Fig. 41.2. The first break in the curve occurs at the freezing point of the particular mixture; this temperature is plotted against the composition of the mixture, thus giving the appropriate point on the curve *AC* or *BC* of the equilibrium (phase) diagram, Fig. 41.1. The second break, where the temperature remains constant, gives the eutectic point, and for a system of the type under consideration this should be the same for all the mixtures. In order to complete the diagram it is necessary to know the freezing points (or melting points) of pure A and B; these can be determined by means of cooling curves, for the pure liquid will solidify at a constant temperature. The general nature of the procedure is represented schematically in Fig. 41.3.



(a) (b)

FIG. 41.3. Construction of phase diagram by thermal analysis, (a) cooling curves of pure A, B and mixtures of composition 1-6, (b) phase diagram

41e. Systems Involving a Salt and Water: Freezing Mixtures.—Although there is no fundamental difference between the properties of a system involving a salt and water, and that of a binary system of two metals, or two salts, etc., it is of interest to give special attention to the former. There is one limitation to the complete study of many salt-water systems: the melting point of the salt is often so high that it is above the critical temperature of the water in the solution. It is consequently then impossible to follow the two-component system up to the melting points of both components. The complete phase diagrams have been obtained in a few cases, however, by working at high pressures to prevent evaporation of the water.

The equilibrium diagram for potassium iodide and water is depicted in

Fig. 41.4; it is seen to be of the general type being considered, although the melting point of potassium iodide, at the extreme right, is not attained. Ice separates from the potassium iodide solutions along *AC*, and so this curve is usually regarded as giving the freezing points of the solutions; on the other hand, *BC* may be considered as the *solubility curve* of potassium iodide, since the solid is in equilibrium with solutions that are obviously saturated with this salt. The relatively steep rise of the curve *CB* shows that the solubility of potassium iodide increases slowly with temperature. The dependence of solubility on temperature varies with the nature of the salt and the solvent, for reasons which will be examined in § 41h.

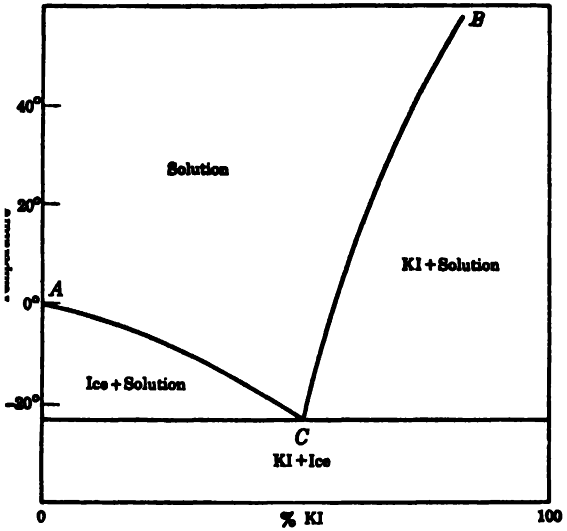


FIG. 41.4. System of a salt (KI) and water

The freezing point and solubility curves meet at *C*, the eutectic point, where both ice and potassium iodide deposit from solution at −23°C; this is the lowest temperature at which an aqueous solution of potassium iodide can exist, at atmospheric pressure. All solutions when cooled will ultimately show a halt in temperature at this point until the liquid phase has disappeared. Since a system having the same composition as the eutectic freezes at a constant temperature, as seen above, the salt-water mixture depositing at this point was at one time considered to be a definite compound, i.e., a salt hydrate. The physical properties, such as heat of solution and density, of the solid are, however, equal to the mean values of the two components, suggesting that it is really a mixture. If a compound were formed the actual values would differ appreciably from the respective means. Further, the separate crystals of ice and salt can be observed when the eutectic solid is placed under the microscope. There is no doubt, at the present time, that the solid separating at the eutectic point is a mixture and not a definite salt hydrate.

41f. The Two Components Form a Solid Compound.—If the components A and B form a stable solid compound AB, the phase diagram obtained by plotting the results of a thermal analysis, or of any equivalent procedure, is of the type shown in Fig. 41.5. In addition to the branches *AC* and *BE*, which represent the compositions of liquids in equilibrium with solid A and B, respectively, at different temperatures, there is a central portion *CDE* rising to a maximum. This portion of the phase diagram gives the conditions of equilibrium of liquid systems with the solid compound AB; in accordance with both theory and experiment, the maximum *D* of the curve occurs when the composition of the liquid is identical with that of the compound. The particular diagram in Fig. 41.5 shows the formation of a compound containing equimolecular amounts of A and B; hence, the point *D'* vertically below *D*, is midway between pure A and pure B on the molecular composition axis.* From the position of the maximum, i.e., *D* or *D'*, it is consequently possible to derive, without the necessity for chemical analysis, the formula of the solid compound which separates from the liquid phase along the curve *CDE*.

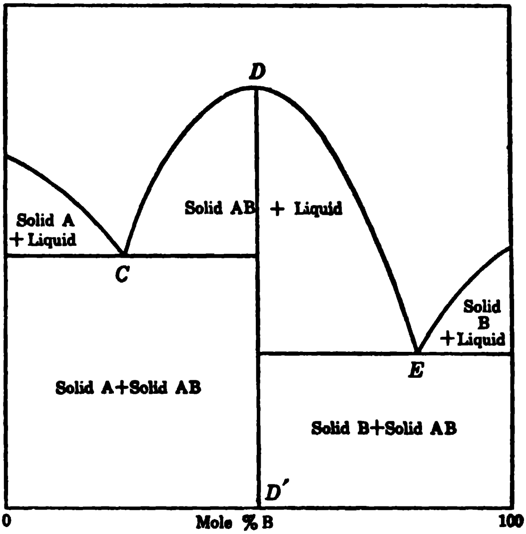


FIG. 41.5. Compound with congruent melting point

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[*] In order to simplify the interpretation of the phase diagram the composition of the liquid in Fig. 41.5 is assumed to be in mole per cent; this makes the point *D'*, representing the compound AB, fall midway along the composition axis. It should be noted, however, that it is a common practice to represent the compositions in weight per cent, as in Fig. 41.1; in this event, the molecular composition at *D'* would have to be calculated instead of being read off by inspection.

Since the liquid at the maximum point *D* has the same composition as the solid with which it is in equilibrium, the temperature at *D* is actually the melting point of the compound. In this case, the compound is fairly stable at its melting point, and *solid and liquid of the same composition can coexist;* the compound AB is then said to have a **congruent melting point.** It will be noted that at the temperature *D* the two-component system has become virtually a one-component system, the one component being the compound AB; the temperature at *D* is consequently just as definite as are the melting points of the pure components A and B, and its cooling curve will have the same form. The melting point of the compound may lie above, below or between the melting points of the two single components; instances of all three types are well known.

It will be evident that in Fig. 41.5 there are now two eutectic points, viz., *C* and *E*; at the former the solids A and AB deposit, while at the latter the solid phases are B and AB. The details of the phase diagram can best be understood by regarding it as made up of two diagrams of the simple eutectic type shown in Fig. 41.1 placed side by side. To the left of the dividing line *DD′* in Fig. 41.5 the figure gives the conditions of solid-liquid phase equilibrium of the two-component system A and AB, while to the right of the line the two components may be regarded as AB and B. The details in each part of the diagram correspond exactly with those in Fig. 41.1, and bearing these facts in mind it is a simple matter to determine the behavior of any liquid upon cooling, or of any mixture of solids when heated.

There are many examples of binary systems in which stable solid compounds are formed. The plotting of the phase diagram is the recognized method for investigating if the two components combine to yield such compounds, and if so to determine their composition. Instances of systems in which solid compounds are formed are given in Table 41.2.

TABLE 41.2. TWO-COMPONENT SYSTEMS WITH SOLID COMPOUNDS

A	M. Pt.	B	M. Pt.	Compound	M. Pt.
Aluminum	657°C	Magnesium	650°C	A_3B_4	463°C
Gold	1064°	Tin	232°	AB	425°
Calcium chloride	777°	Potassium chloride	790°	AB	754°
Diphenylamine	52.8°	Benzophenone	47.7°	AB	40.2°
Urea	132°	Phenol	43°	AB_2	61°

When two components form more than one compound there will be a curve on the equilibrium diagram analogous to *CDE* for each compound. In each case the composition of the maximum of any curve is identical with that of the solid compound depositing from liquid phases represented by that curve, and the temperature of the maximum gives the melting point of the particular compound. A phase diagram of this type, involving ferric chloride and water, will be referred to presently (Fig. 41.8); four stable compounds are formed in this system.

The sharpness of the maximum in a phase diagram gives an indication of the stability of the compound at its melting point; if the maximum is flat, it means that the compound tends to decompose to a great extent. Sometimes the compound is so unstable that it decomposes completely at a temperature below its melting point; *the solid cannot then be in equilibrium with a liquid having the same composition as itself.* The compound is then said to have an **incongruent melting point** or **peritectic point.**

The equilibrium (phase) diagram for this type of behavior is represented in Fig. 41.6, in which it is supposed that a 1:2 compound AB_2 is formed. At

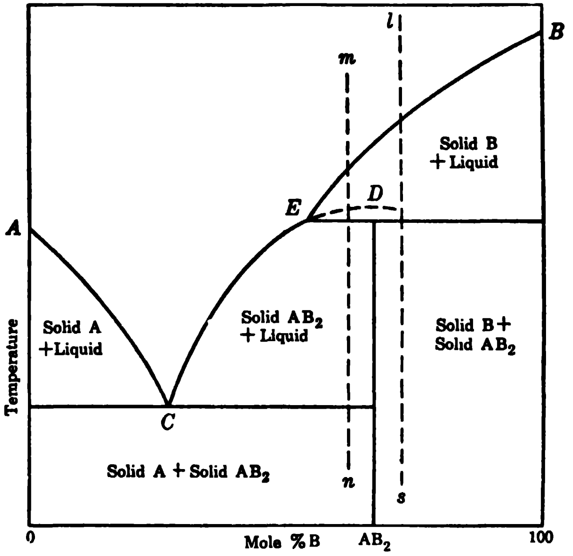

FIG. 41.6. Compound with incongruent melting point

E, which is the peritectic point, the temperature is below the hypothetical melting point *D*; the compound AB_2 then dissociates completely into its constituents, giving pure solid B and a solution of composition *E*. Along the curve *CE* solid AB_2 separates, but along *EB* the solid phase consists of pure B. If a liquid such as *l*, lying to the right of *D*, is cooled, solid B will separate at first and the liquid composition will tend towards *E*; then when the temperature reaches *E* the compound AB_2 commences to form. There are now one liquid and two solid phases and so the condensed system is invariant; the temperature at *E* will thus remain constant. Since the overall composition at *l* corresponds to more B than is present in the compound, some solid B will be left when all the liquid has been converted into solid AB_2. This is also shown by the fact that the line *ls* ends in the region of solid B + solid AB_2. On the other hand, when a liquid of composition lying between *E* and *D*, e.g., *m*, is cooled, the solid B formed will be completely replaced at the peritectic point by solid AB_2 and liquid *E*. Upon further cooling to *n*, the behavior is typical of a eutectic system, the solids A and AB_2 being formed.

Compounds with incongruent melting points are found in the following systems: gold-antimony ($AuSb_2$); magnesium-nickel (Mg_2Ni, congruent; $MgNi_2$, incongruent); sodium-bismuth (NaBi, congruent; Na_3Bi, incongruent); potassium chloride-cupric chloride ($2KCl \cdot CuCl_2$); picric acid-benzene (AB); and acetamide-salicylic acid (AB).

41g. The Formation of Salt Hydrates.—For systems consisting of a salt and water, the compounds are salt hydrates; these generally have incongruent melting points, since they decompose into anhydrous salt and water, or into a lower hydrate and water, below their melting points, i.e., the appropriate maxima in the phase diagram. A case which has been well studied is the system consisting of sodium sulfate and water; part of the phase diagram is reproduced in Fig. 41.7. Along the curve *AB* the liquid solution is in equilibrium with ice, while along *BC* the solid phase is $Na_2SO_4 \cdot 10H_2O$; the latter curve may thus be regarded as the solubility curve of this salt. Before a maximum is attained, an incongruent melting point, or **transition point**, is reached at *C*; here the decahydrate $Na_2SO_4 \cdot 10H_2O$ decomposes into the anhydrous salt Na_2SO_4 and water. At the point *C* the decahydrate and anhydrous salts are in equilibrium with saturated solution; there are thus two solid phases and one liquid, and so the condensed system is invariant. The equilibrium will thus occur at one particular temperature, the transition point, at each pressure. The transition temperature for the $Na_2SO_4 \cdot 10H_2O$-Na_2SO_4 system at 1 atm pressure is 32.383°C; it is so definite that it has been suggested as a fixed point in thermometry. The curve *CD* gives the compositions of solutions in equilibrium with anhydrous sodium sulfate, and so it is the solubility curve of this salt. It will be noted that this curve slopes to the left, indicating that the solubility *decreases* with increasing temperature.

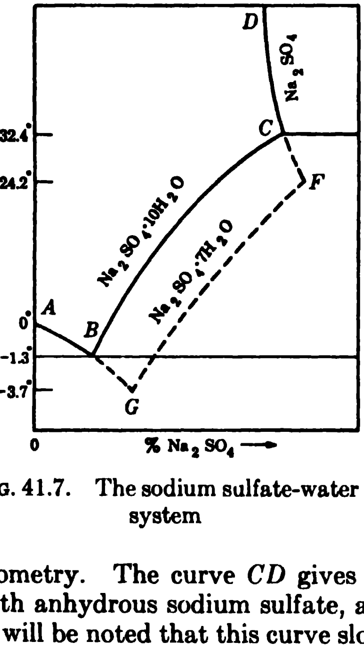

FIG. 41.7. The sodium sulfate-water system

If a solution, saturated with respect to anhydrous sodium sulfate along the curve *DC*, is cooled from above the transition temperature, then when this point is reached the decahydrate should commence to deposit. Sometimes, however, this does not happen; the anhydrous form remains, in metastable equilibrium (§ 37a), and the composition of the solution continues along *DC*, beyond *C*, until *F* is reached at 24.2°C. At this point a new hydrate $Na_2SO_4 \cdot 7H_2O$ separates. This substance is always metastable with respect to the decahydrate, and it can be formed only if the latter is completely absent. In these circumstances the metastable curves *BG* and *GF* can be realized; *GF* is the solubility curve of the heptahydrate $Na_2SO_4 \cdot 7H_2O$, and

G is a metastable eutectic. The point *F* is the transition point at which heptahydrate and anhydrous salt are in metastable equilibrium with saturated solution. The fact that the metastable solubility curve *GF* lies to the right of the stable curve *BC*, shows that at a given temperature the metastable form is more soluble than the stable form. The addition of a small crystal of the decahydrate will cause the excess salt to precipitate as $Na_2SO_4 \cdot 10H_2O$, and the concentration will fall from *GF* to *BC*. The statement that *a metastable form is more soluble than the stable form at the same temperature* represents a rule of universal applicability.

One of the best known systems involving salt hydrates with congruent melting points is that formed by ferric chloride and water, the phase diagram for which is given in Fig. 41.8. Four stable hydrates are known, namely

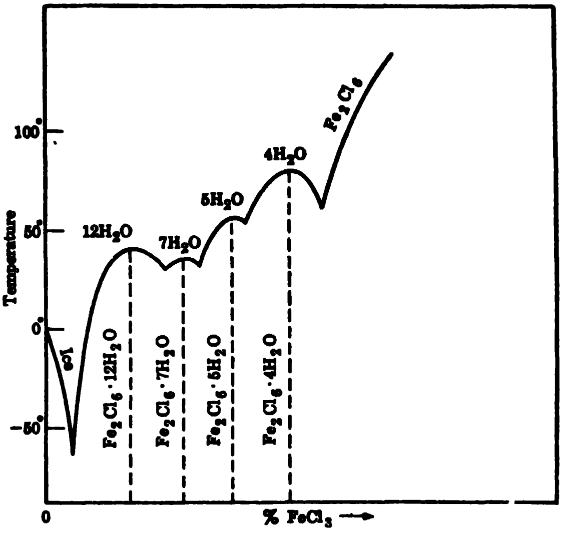

FIG. 41.8. Salt hydrates with congruent melting points ($FeCl_3$-H_2O)

$Fe_2Cl_6 \cdot 12H_2O$, $Fe_2Cl_6 \cdot 7H_2O$, $Fe_2Cl_6 \cdot 5H_2O$ and $Fe_2Cl_6 \cdot 4H_2O$; the double formula Fe_2Cl_6 is used for ferric chloride in order to avoid the use of fractional numbers of molecules of water in two of the four cases. It will be evident from Fig. 41.8 that each hydrate has a definite (congruent) melting point; this point may be alternatively regarded, in each case, as the temperature at which the saturated solution of the hydrate has the same composition as the solid phase.

41h. Influence of Temperature on Solubility of Salts.—It was stated in § 41a that when a solid forms an ideal solution in a liquid, heat should be absorbed when it dissolves, the amount being numerically equal to the heat of fusion of the pure solid solute. Although solutions of salts do not behave ideally, it is true that in the majority of cases heat is absorbed when a salt dissolves in water; the solubility of that particular salt then increases with increasing temperature in accordance with the requirement of the Le Chatelier principle. There are a few salts, such as anhydrous sodium sulfate, referred to above, and calcium sulfate and chromate, for which the solubility decreases as the temperature is raised. This means that when these substances dissolve, in the region of the saturated solutions, there is an evolution of heat, just as is the case with gases. An examination of the nature of the compounds showing the reversed temperature effect on solubility reveals the fact that they are usually anhydrous salts. When a solid dissolves in a liquid, two distinct processes occur; in the first place, work must be done against the electrostatic and other forces that hold the ions together in the crystal, and in the second place, the ions unite with the molecules of water to form **hydrated ions.** There are many reasons for expressing the belief that ions in solution do not consist merely of bare units, such as Na^+, Cl^-, SO_4^{-2}, etc., but are combined with, or in some way associated with, a number of water molecules. There may be definite compound formation, such as in $Cu(H_2O)_4^{+2}$, but in any event there are also probably a number of water dipoles which are held to the ion by forces of electrostatic attraction. A positive ion, for example, will attract the negative parts of a number of dipolar molecules, and similarly a negative ion will attract the positive regions of such molecules. The process of hydration is accompanied by the liberation of energy, and it is this factor which makes it possible for salts to dissolve in water while they are insoluble in nonpolar organic liquids, such as hydrocarbons, etc. In the latter, no process analogous to hydration, that is, solvation, is possible, and no means is available to supply some, or all, of the energy required to break up the salt crystal into individual ions in solution; the salt thus remains in the solid state and does not dissolve.

If the ions are largely hydrated in the crystal, as is the case with $Na_2SO_4 \cdot 10H_2O$, the energy which must be supplied to overcome the forces in the solid is greater than that which is gained in the hydration stage in the solution. When such substances dissolve, there is an absorption of heat and the solubility increases with temperature. On the other hand, if the salt is anhydrous, there is a possibility, although not an absolute necessity, that the heat evolved when the ions are hydrated will exceed the heat absorbed in disintegrating the solid. If this occurs, as it evidently does in the cases mentioned above, there is an evolution of heat when the salt dissolves, and hence there is a decrease of solubility as the temperature is raised. Provided there is appreciable hydration in the solution, the solubility of an anhydrous salt will increase only slightly, as with sodium chloride, or it will decrease with increasing temperature.

41i. Continuous Series of Solid Solutions.—When the solid that separates from the liquid phase is not a pure substance, as it is in the preceding cases, but a homogeneous solid solution (§ 19f), there are some important changes in the phase diagram. First, *it is possible for the freezing point of one component to be raised by the addition of the other;* second, if the two solids A and B are completely soluble in each other, like two completely miscible liquids, *it is not possible to have more than one solid phase.* A homogeneous solid solution constitutes a single phase, irrespective of its composition, and since there is only one liquid phase, the condensed system can never consist of more than two phases. By the phase rule, therefore, the minimum number of degrees of freedom, corresponding to the maximum number of phases, is thus given by

$$F = C - P + 2 = 2 - 2 + 2 = 2.$$

Even after fixing the pressure, for the condensed system, there still remains one degree of freedom; an invariant system is thus impossible in the present case and there will be no singular point or discontinuity, such as a eutectic, on the phase diagram. Three types of freezing point curves have been obtained, depending on whether the freezing points of all mixtures lie between those of the pure components, or whether there is a mixture with a maximum or a minimum freezing point.

I. The Freezing Point Varies Regularly.—A typical equilibrium diagram of the kind in which the freezing points of all mixtures lie between those of the pure components A and B is shown in Fig. 41.9. The upper (liquidus) curve gives the composition of the liquid phase in equilibrium with solid solution whose composition is indicated by the corresponding point on the lower (solidus) curve. At any temperature t, for example, the liquid represented by the point y will be in equilibrium with solid solution z; it is evident that *the composition of the solid phase changes continuously with that of the liquid from which it separates.* At any temperature, however, the liquid phase always contains relatively more of the component by the addition of which the freezing point is depressed, namely A in the present case.

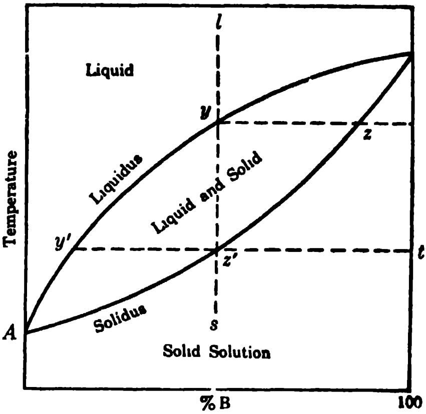

FIG. 41.9. Continuous series of solid solution

If the liquid represented by the point l is cooled, freezing will commence at y (temperature t) and the composition of the solid phase separating will be given by z. As cooling proceeds, the composition of the system as a whole will be represented by points on the vertical line ls between y and z'; these will represent mixtures of liquid and solid solutions whose compositions are given by the appropriate points on the liquidus and solidus curves. The composition of the liquid changes steadily from y to y', while at the same time that of the solid goes from z to z'. It should be noted that if the system is to remain in equilibrium upon cooling, the compositions of both liquid and solid phases must change continuously. When the composition of the liquid reaches the point y', at the temperature t', the solid phase with which it is in equilibrium, namely z', has the same composition as the original liquid. In other words, at this temperature solidification is complete, and $z's$ represents the cooling of the solid. Separation of solid thus commences at y, and is complete at z'; for this reason the liquidus curve is sometimes called the *freezing point curve*, while the solidus curve is called the *melting point curve*. When the liquid l is cooled, solid first separates at the freezing point t; on the other hand, when the solid s, of the same composition, is heated liquid first appears at the melting point t'.

The cooling curve of a liquid from which a solid solution separates differs from that considered previously (§ 41d). Upon cooling the liquid l, solid first separates at y, and hence there will be a change in the rate of cooling which will be indicated by a break in the cooling curve at the temperature t. As cooling proceeds, and solid continues to separate, the temperature will fall steadily. Finally, at the temperature t', when solidification is complete, the solid will commence to cool more rapidly (Fig. 41.10). There are thus two breaks in the curve, in opposite directions, at t and t'; in this way the points y and z', on the liquidus and solidus curves, respectively, are obtained for any mixture of known composition. By carrying out these cooling observations with a number of mixtures, as well as with pure A and B, that is by thermal analysis, the complete phase diagram can be plotted. It will be noted that since the system has no invariant point, there is no complete arrest in the cooling curves, such as is obtained at a eutectic.

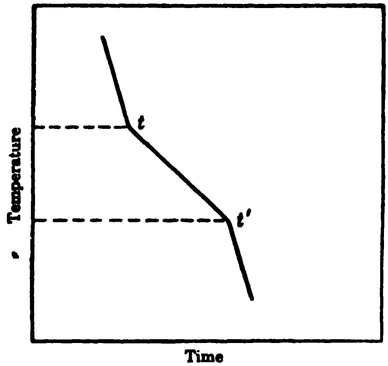

FIG. 41.10. Cooling curve indicating formation of solid solution

Substances of similar constitution or closely related elements are usually isomorphous and form completely miscible solid solutions, provided their lattice dimensions are not very different (§ 19f); examples are cobalt-nickel, gold-silver, gold-platinum, silver chloride-sodium chloride, lead bromide-lead chloride, and naphthalene-β-naphthol.

II. The Freezing Point Curve Has a Maximum.—The type of equilibrium diagram depicted in Fig. 41.11 is not common; it is seen that each component *raises* the freezing point of the other, and that the liquidus and solidus curves touch at the maximum M. At this point the liquid and solid in equilibrium evidently have the same composition; the liquid solution will then freeze, and the solid solution will melt sharply at a definite temperature, given by the maximum M, just like a pure substance. Nevertheless, the maximum point does not represent a compound; it is merely a consequence of the fact that the liquidus and solidus curves must touch at the maximum.

One of the rare cases of a freezing point curve with a maximum is the system *d*- and *l*-carvoxime; the components have the same melting point (72°C), and the curve is symmetrical with a maximum at 91.4°C. The composition at the maximum in this case corresponds to equimolecular amounts of the two components; the solid phase is, however, not a compound but a solid solution.

III. The Freezing Point Curve Has a Minimum.—A number of systems yielding completely miscible solid solutions have freezing point curves with a minimum, as in Fig. 41.12. Here, as in other cases, the liquidus curve lies above the solidus curve, and the two touch at the minimum *M*. At this point the solid and liquid in equilibrium again have the same composition, and the solid will melt and the liquid will freeze sharply, like a pure substance. The solid phase is actually a solid solution of definite composition, but the molecular proportions of the constituents A and B do not necessarily correspond to simple whole numbers as would be the case for a definite compound.

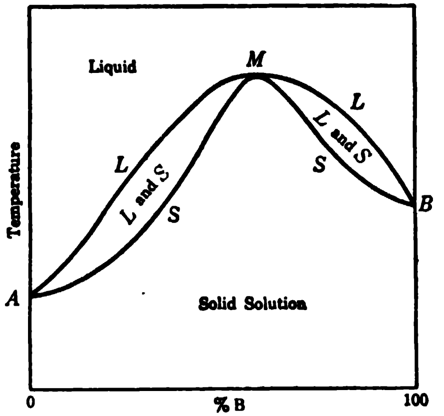

Fig. 41.11. Solid solutions with maximum melting point

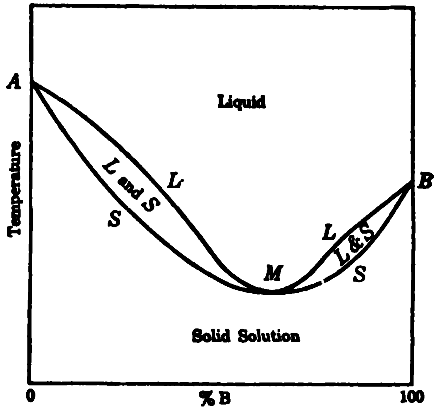

Fig. 41.12. Solid solutions with minimum melting point

Among systems forming a continuous series of solid solutions and giving phase diagrams with minima the following may be mentioned: copper-manganese, copper-gold, cobalt-manganese, arsenic-antimony, mercuric bromide-mercuric chloride, potassium chloride-potassium bromide, and *p*-chloroiodobenzene-*p*-dichlorobenzene.

41j. Partially Miscible Solid Solutions.—It frequently happens that two substances can form solid solutions with one another to a limited extent only, so that between definite concentration limits, depending upon the temperature, two conjugate solid solutions can exist. The phenomenon of partial miscibility of solids is analogous to that occurring with partially miscible liquids. Solid A can dissolve a certain quantity of solid B to form a single solid solution, and similarly solid B can dissolve a limited amount of A, but if these concentrations are exceeded two solid phases, each of which is a homogeneous solution of A and B, are produced. Since it is now possible to have three phases, viz., two solid solutions and one liquid, the condensed system can be invariant, and so the solid-liquid equilibrium curves will exhibit a discontinuity. Two types of behavior are found in practice, the nature of the discontinuity being somewhat different in the two cases.

I. The Discontinuity Is a Eutectic Point.—In Fig. 41.13, *AC* and *BC* are the liquidus curves, and *ADC* and *BEC* are the corresponding solidus curves; along *AD* the solid phases may be regarded as solid solutions of B in excess of A (S_1 type), and along *BE* the solid solutions are of A in excess of B

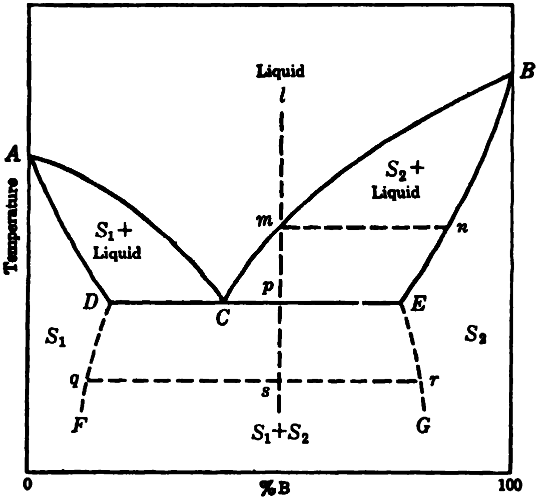

FIG. 41.13. Partially miscible solid solutions with eutectic point

(S_2 type). All points along the line *DCE*, except the extremes *D* and *E*, represent mixtures of the solid solutions *D* and *E*. The liquidus curves meet at *C* which is the eutectic point for the system. It differs in one respect from the ordinary eutectic of Fig. 41.1; the solid phases in equilibrium are not the pure components A and B, as in the latter case, but the conjugate solid solutions whose compositions are represented by the points *D* and *E*. The eutectic *C* is, however, a true invariant point for the condensed system of two components; it is the lowest temperature at which liquid can exist. Just as the compositions of two conjugate liquid solutions vary with the temperature (see Fig. 39.10), so also do those of the conjugate solid solutions. This variation is indicated by the curves *DF* and *EG*. Theoretically, a consolute temperature might be expected above *DE*, but in this region liquid only occurs, and the solids have no real existence.

If a liquid *l* is cooled, solid solution commences to separate at *m*, the composition of the solid being given by the point *n*. Upon further cooling, the composition of the liquid phase moves down the line *mC*, while that of the solid solution changes correspondingly along *nE*, assuming equilibrium to be continuously attained. When the temperature of the system reaches the point *p*, two solid solutions, represented by the points *D* and *E*, separate from the eutectic liquid *C*. The condensed system of three phases is now invariant, and the temperature remains constant at the eutectic point until the liquid has completely solidified. On further cooling, the compositions of the two solid solutions will change along *DF* and *EG*, provided equilibrium exists. When the system as a whole has reached *s*, there are two solid solutions whose compositions are *q* and *r*, respectively. Unless the cooling below the eutectic temperature is very slow, to permit redistribution of the components among the solid solutions, equilibrium is not established and the mixtures corresponding to *D* and *E* are "frozen in."

Phase diagrams similar to that in Fig. 41.13 have been obtained for the systems gold-nickel, bismuth-lead, cadmium-tin, potassium nitrate-thallous nitrate, silver chloride-cuprous chloride, and naphthalene-monochloroacetic acid.

II. The Discontinuity Is a Transition Point.—When the addition of one component raises the melting point of the other, and the solids are only partially miscible, the phase diagram is of the form of Fig. 41.14. The liquidus curve *AC* gives the compositions of the liquids in equilibrium with solid solutions (S_1 type) given by *AD* on the solidus curve *ADC*; similarly, *BC* is the liquidus curve corresponding to *BE* (S_2 type of solid solutions) on the solidus curve *BED*. The point *C* represents an invariant condensed system, for there are here three phases, viz., two solid solutions and one liquid,

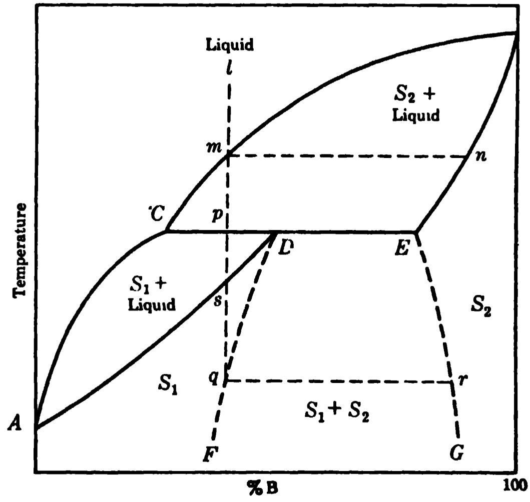

Fig. 41.14. Partially miscible solid solutions with transition point

in equilibrium. It is not a eutectic point, since it is not the lowest temperature at which liquid exists, but it is frequently called a *transition point*, for reasons which will be evident shortly. The compositions of the conjugate solid solutions in equilibrium with liquid at the transition point are indicated by D and E. Upon cooling, these change along the lines DF and EG, respectively, in a manner analogous to that observed for partially miscible liquids.

The behavior upon cooling mixtures lying to the right of D or to the left of C can be readily derived from previous considerations, but in the region between C and D the phenomena are unusual. When the liquid l is cooled, solid solution of composition n commences to separate at m; the composition of the liquid phase moves down mC, while that of the solid in equilibrium with it changes correspondingly along nE. When the transition point is reached at p, two solid solutions, D and E, are in equilibrium with liquid of composition C. Since the condensed system is now invariant, the temperature remains constant until one of the phases disappears. In this case, however, it is not the liquid that is removed by complete solidification. The liquid remains, but the solid solution E (S_2 type) gradually diminishes in amount while D (S_1 type) increases; it is for this reason that the temperature is described as a transition point. When the former solid solution has completely disappeared the system is again univariant; the temperature can then continue to fall once more from p to s, the composition of the liquid changing along CA, and that of the solid solution (S_1 type) along DA. At the point s, the system has completely solidified in the form of a single solid solution. The temperature of the solid may now fall to q when two solid solutions, of composition q and r, respectively, will form if the system attains equilibrium.

Systems forming two series of solid solutions with a transition point are cadmium-mercury, silver chloride-lithium chloride, silver nitrate-sodium nitrate, and *p*-iodochlorobenzene-*p*-diiodobenzene.

SYSTEMS OF THREE COMPONENTS

42a. Graphical Representation of Three-Component Systems.—

For systems of three components it is possible to have four degrees of freedom, since temperature, pressure and the concentrations of two components may be independently variable.* In order to simplify the graphical representation of the conditions of equilibrium for three components, the procedure usually adopted is to consider a condensed system, that is, the vapor is ignored. This reduces the number of degrees of freedom to three, and hence a three-dimensional model can be used to represent the compositions of equilibrium systems at different temperatures.

In order to understand the type of figure that is used, it is convenient to consider, in the first place, the condition of constant temperature; it is then required to indicate in a simple manner the composition of a system of three

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* Although there are three components, the concentrations of two components define the composition of the system completely; thus, x per cent of A, and y per cent of B, means $100 - x - y$ per cent of C.

independent components. For this purpose it is the common practice to use a diagram consisting of an equilateral triangle; the property which is utilized is that the sum of the distances from any point within this triangle drawn perpendicular to the three sides is always equal to the height of the triangle. By taking this length as unity, and expressing the amounts of the three components of a given system as fractions of the whole, it is possible to represent the composition of any system by a point in the diagram. To facilitate the plotting of the points corresponding to various compositions on the triangular diagram, the height is divided into ten, or more, equal parts, and a series of lines are drawn parallel to the three sides, thus producing a network of small equilateral triangles within the large one. Special graph paper, based on these principles, can be purchased for use in plotting the experimental results for three-component systems. In Fig. 42.1 the corners *A*, *B*, *C* of the triangle represent the pure components A, B, C, respectively; the perpendicular distance from a point *P* to any side gives the proportion of the component occupying the opposite corner. Thus, the distances *Pa*, *Pb* and *Pc* give the

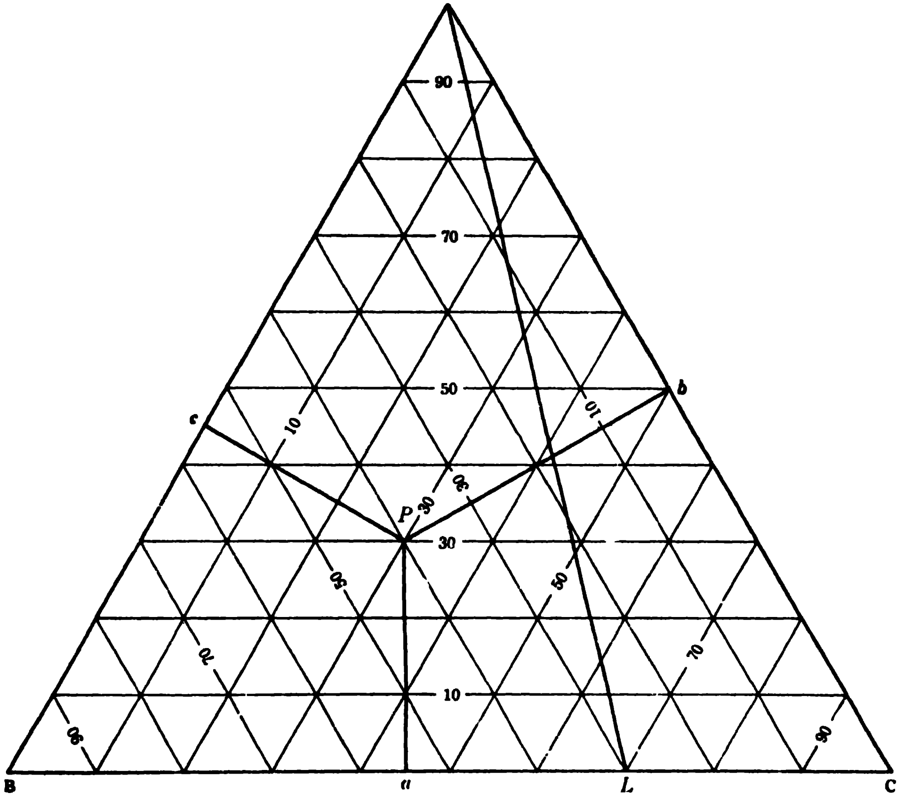


FIG. 42.1. Principle of the triangular diagram

fractional amounts of A, B and C, respectively, in the system represented by the point *P*, where the composition is seen to be 0.3A, 0.4B and 0.3C in mole fractions or in weight fractions; multiplied by 100, these become molar or weight per cent, respectively.

Any point within the triangle indicates a system of three components, but a point situated on one of the sides represents two components only; a point on the edge *BC* would mean the amount of A is zero, and similarly along *AC* there is no B, whereas on the line *AB* the component C would be absent. A point on the edge *AB* of the triangle, for example, would imply a two-component system containing definite amounts of A and B only. One of the properties of the triangular diagram is that a line such as *AL* drawn through an apex, represents mixtures in which the *ratio* of two components, in this case B and C, remains constant although the proportion of the third component, A, varies from zero at *L* to 100% at *A*.

If it is required to represent variations of temperature as well as composition, a prism having an equilateral triangular cross-section is used, the temperature being measured vertically; an illustration of such a model is given in Fig. 42.2. A section through the prism at any definite temperature is an isotherm and gives a triangular diagram of the type just described.

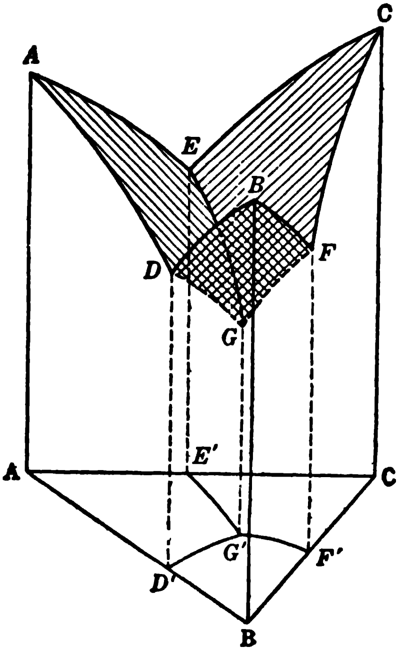


FIG. 42.2. Three component system with solid phases

42b. Systems with Solid Phases.—The maximum number of phases which can coexist for a system of three components, excluding the vapor, is four; this represents an invariant condensed system, i.e., one with no degrees of freedom. Since C = 3, the phase rule leads to the result F = 3 − 4 + 2 = 1, for a system of four phases (P = 4); the one remaining degree of freedom is the pressure, and as this is fixed for the condensed system, the system is effectively invariant. It is thus possible for as many as four phases to be in equilibrium at any arbitrary pressure. Consequently, in the study of three-component systems considerable complexity can arise. In addition to the vapor, which is neglected, there may be one, two or three liquid phases, and three different solid phases, apart from the possibility of solid compounds formed by combination of two or more of the components.

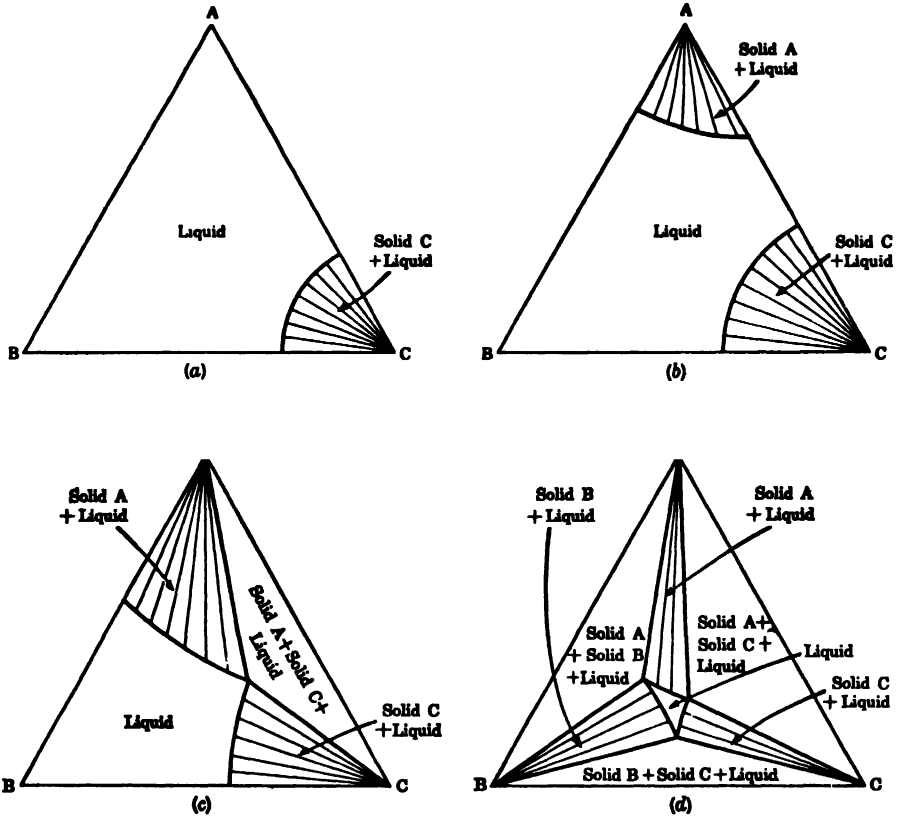
Only two of the many possible three-component systems will be considered here; they are of interest because they have a bearing on problems of industrial importance. The first type of system to be examined is that in which the three components A, B and C are completely miscible when liquid, so that only one liquid phase can exist; further, it is supposed that the solids A, B and C separate out in the pure state, and there is no formation of compounds or of solid solutions. The conditions of equilibrium of solid and liquid phases for each pair of components, that is, for A and B, B and C, and C and A, respectively, is then given by a simple eutectic curve of the type considered in Fig. 41.1. The phase equilibria in the three-component system are then represented by means of a triangular prism, as shown in Fig. 42.2. Each vertical face of the prism depicts a two-component system; thus for A and B, the solid-liquid equilibrium (freezing point) curve is *ADB*, and for the binary systems B and C, and A and C, the equilibrium curves are *BFC* and *CEA*, respectively. The points *D*, *E* and *F* are the binary (two-component) eutectics, at which two solid phases can exist in contact with binary liquid.

If now the ternary (three-component) system is considered, the conditions of equilibrium are given by points within the prism. Points lying on the surfaces *AEGD*, *BFGD* and *CFGE* represent the conditions under which one of the solids, A, B and C, respectively, is in equilibrium with ternary liquid; the position of the point on the surface gives the composition of the latter. The lines along which two surfaces join are the **ternary eutectic curves,** and they indicate the conditions of temperature and liquid composition for the separation of two solid phases from the liquid; thus, along *DG*, *FG* and *EG* the pairs of solids are A and B, B and C, and A and C, respectively. These three lines meet at *G*, the **ternary eutectic point** for the system; it is the only temperature at which the liquid phase can be in equilibrium with three solids, at the given pressure. At the ternary eutectic there are four phases, viz., three solid and one liquid, in equilibrium; hence, as seen above, the condensed system is invariant, and it must consequently be represented by a definite point on the diagram. Below the temperature *G* the ternary liquid, i.e., liquid containing all three components, cannot exist.

Because of the inconvenience of a three-dimensional model, an attempt is made to indicate the essential results on a planar diagram. For this purpose the three binary and one ternary eutectic points, and the curves joining them, are projected on a horizontal plane, as shown at the base of the prism in Fig. 42.2. Sections taken through the prism at a number of temperatures are also projected on the base, and the values of the temperatures are indicated. A few typical sections through Fig. 42.2, drawn as separate figures for clarity, are shown in Fig. 42.3; (*a*) represents a section at a temperature between points *A* and *C*, (*b*) at a temperature between points *E* and *A*, (*c*) at a temperature between points *F* and *E*, and (*d*) at a temperature between points *G* and *D*.

An example of the type of system just considered is that involving the metals lead (A), bismuth (B) and tin (C); the melting points are 326° for A, 270° for B, and 232° for C; the binary eutectics are 128° for A-B, 134° for B-C, and 182° for A-C; the ternary eutectic temperature is 96°C.

42c. Systems of Two Salts and Water.—An interesting type of three-



(a) (b) (c) (d)

FIG 42.3. Isothermal sections of Fig. 42.2 at several temperatures

component system is that consisting of water and two salts having an ion in common; if the salts do not possess a common ion the system is one of four components.* Fundamentally the system of two salts and water does not differ from the type considered in the preceding section; the essential distinction, however, lies in the fact that the melting points of the two salts are so much higher than that of the water that the complete phase-equilibrium diagram cannot be realized. It is found more convenient to study the salt-water system at constant temperature, as well as at a definite pressure, and to plot the curves representing the conditions of equilibrium of the solid salts and

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* The reasons for this is as follows. For a system of two salts with an ion in common, e.g., KCl and NaCl, and water, there are four constituents, H_2O, K^+, Na^+ and Cl^-, but these may not vary independently because they are subject to the restriction that $(K^+) + (Na^+) = (Cl^-)$; hence the number of components is $4 - 1 = 3$. If the two salts have no ion in common, e.g., KCl and $NaNO_3$, the constituents are five in number, H_2O, K^+, Na^+, Cl^- and NO_3^-, but they are subject to the restriction that $(K^+) + (Na^+) = (Cl)^- + (NO_3^-)$; as a result the components are $5 - 1 = 4$ in number.

the ternary liquids at that temperature. This means that the solubility of each salt is determined in an aqueous solution containing varying amounts of both, at constant temperature and pressure. The experimental method used is to make up various mixtures of the two salts with an ion in common, and dissolve them in water at a temperature slightly higher than that at which the system is to be studied. The solution is then allowed to come to equilibrium at the experimental temperature; the clear liquid and the residual solid are removed, and both are analyzed. In this way the composition of the liquid containing the two salts in solution, and the nature of the solid salt in equilibrium with it are determined; the results for a number of solutions are then plotted on a triangular diagram in the usual manner.

When the two salts S_1 and S_2 do not form a compound, i.e., double salt, or solid solution, the solubility curves giving the compositions of the solutions in equilibrium with either solid are of the type shown in *AC* and *CB* in Fig. 42.4. For purposes of illustration, it is supposed that the solid phase containing S_2 is a hydrated salt having the formula $S_2 \cdot nH_2O$. The solubility of S_1 in water is given by the point *A* and that of $S_2 \cdot nH_2O$ by *B*; these are, of course, two-component systems involving S_1 and H_2O and S_2 and H_2O, respectively.

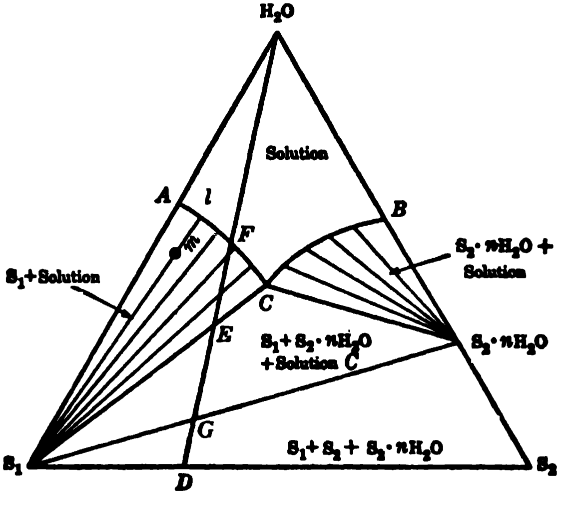

FIG. 42.4. Two salts and water

The significance of the curves in Fig. 42.4 may be understood by considering an arbitrary mixture of S_1, S_2 and H_2O represented by *m*. When this attains equilibrium, at the given temperature, analysis shows the saturated solution to have the composition *l*. If *m* and *l* are connected by a tie line, its extension will give the composition of the solid in equilibrium with the solution *l*. In this instance the solid is evidently S_1, and this is confirmed by analysis and by the fact that the tie lines for other mixtures in the area ACS_1

converge at S_1, as shown in the figure. Hence, points along the curve *AC* give the compositions of saturated solution in equilibrium with the solid phase S_1. Similarly, for mixtures in the area $BCS_2 \cdot nH_2O$, the tie lines converge on the point marked $S_2 \cdot nH_2O$. The hydrate is consequently the solid phase in equilibrium with solutions along the curve *BC*.

The point *C*, where the two solubility curves meet, gives the composition of the solution in equilibrium with the two solids S_1 and $S_2 \cdot nH_2O$ at the given temperature; this point is referred to as an **isothermal invariant point.** At *C* there are, apart from vapor, three phases, viz., two solid and one liquid, and the phase rule shows that the three-component system then has two degrees of freedom. These are the pressure and temperature which have been fixed, and so the condensed system is effectively invariant.

It is instructive to consider the behavior of a mixture of solid S_1 and S_2 as water is added. Suppose the mixture is represented by the point *D* in Fig. 42.4; the line *D*-H_2O then gives the composition of all possible ternary mixtures of *D* and H_2O. The first addition of water converts the S_2 into its hydrate; this is completed when the system reaches the composition *G*. From *G* to *E* the solids dissolve producing the invariant saturated solution *C* in increasing amounts. At *E* the system enters the two-phase area ACS_1 in which only solid S_1 can exist in equilibrium with solution; at this point all of the $S_2 \cdot nH_2O$ has dissolved but some solid S_1 remains, the relative amount of saturated solution to solid S_1 being in the ratio of ES_1 to *EC*. It is then possible to separate pure S_1 from the mixture *D* by adding enough water to reach *E* and filtering. From *E* to *F*, as more water is added, increasing amounts of S_1 dissolve, the composition of the saturated solution changing steadily from *C* to *F*. At *F*, the last trace of S_1 will have dissolved.

Conversely, isothermal evaporation of an unsaturated solution of S_1 and S_2 in water, initially somewhere along the line *F*-H_2O, will result in the deposition of S_1 when the composition reaches *F*. As more water is vaporized and the over-all composition changes from *F* to *E*, the composition of the solution varies from *F* to *C* while increasing amounts of S_1 are deposited. At the over-all composition *E* and solution composition *C*, solid $S_2 \cdot nH_2O$ commences to deposit, and from *E* to *G* the solids S_1 and $S_2 \cdot nH_2O$ separate from the invariant solution *C*. From *G* to *D*, the hydrate decomposes forming S_2.

The system $NaCl$-Na_2SO_4-H_2O gives a phase-equilibrium diagram of the type shown in Fig. 42.4 at temperatures below 17.9°C; S_1 is NaCl, which separates in the anhydrous form, and $S_2 \cdot nH_2O$ is $Na_2SO_4 \cdot 10H_2O$. The shape and position of the curves and the nature of the solid phases change with temperature; thus, between 17.9° and 32.4° the anhydrous solid Na_2SO_4 can separate from the solution, as well as $Na_2SO_4 \cdot 10H_2O$, and the solubility curve has three parts. Above 32.4°C the hydrated salt cannot exist in contact with solution, and then the solid phases are NaCl and Na_2SO_4.

If, in addition to the pure components S_1 and S_2, or their hydrates, one or more compounds, i.e., double salts, can separate from the solution at the experimental temperature, the solubility curve will have an additional portion, e.g., *CD* in Fig. 42.5, along which the solid phase is the compound of

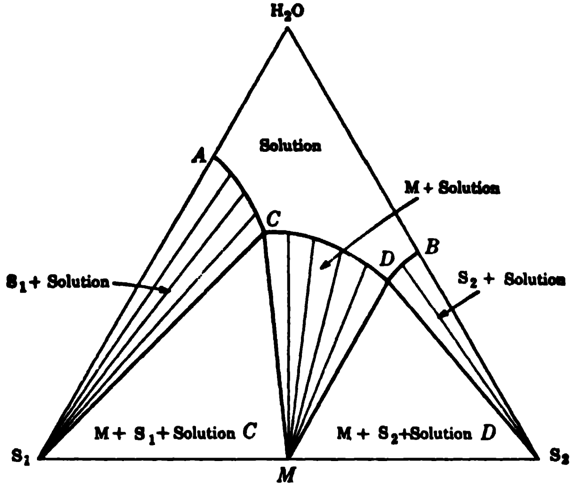

FIG. 42.5. Two salts and water: formation of a double salt

composition indicated by the point *M*. In this case it is seen that the compound, or double salt, like the single salts S_1 and S_2, is anhydrous; if it were hydrated the tie lines from *CD* would meet at a point within the triangle, as required for a phase containing all three components. In Fig. 42.5, the line joining *M* to the apex of the triangle, representing pure water, cuts the curve *CD*; this indicates that the double salt is stable in solution. If the line had cut *AC* or *BD*, as is sometimes the case, it would indicate that solid *M* decomposes into S_1 or S_2, respectively, in contact with water.

A diagram of the type shown in Fig. 42.5 is given by the system NH_4NO_3-$AgNO_3$-H_2O at ordinary temperatures; the compound *M* has the composition $NH_4NO_3 \cdot AgNO_3$. If more than one double salt is formed, there will be an additional portion of the solubility curve for each one that can separate from solution at the given temperature. Thus, for the system $(NH_4)_2SO_4$-NH_4NO_3-H_2O, there are two compounds, viz., $(NH_4)_2SO_4 \cdot 2NH_4NO_3$ and $(NH_4)_2SO_4 \cdot 3NH_4NO_3$, for each of which, in addition to the pure components $(NH_4)_2SO_4$ and NH_4NO_3, there is a curve in the equilibrium diagram. By changing the temperature the nature of the curves is changed, and there is generally a definite transition point above or below which each double salt can no longer exist in contact with solution.

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PROBLEMS

1. Argon is slightly soluble in a molten mixture of lithium, sodium and potassium fluorides. (*a*) Determine the Henry's law constant from the following data at 800°C:

Pressure, atm	2.03	1.51	1.00
Solubility $\times 10^8$, moles cc^{-1}	6.84	5.16	3.40

(*b*) At 600°C, $k = 0.90 \times 10^{-8}$. Evaluate the mean heat of solution of argon in the melt for the temperature range 600–800°C.

2. Estimate the lowering in the freezing point of water when saturated with air (79% nitrogen, 21% oxygen by volume) at atmospheric pressure.

3. The vapor pressure of liquid ethylene is 40.6 atm at 0°C and 24.8 atm at −20°C. (*a*) Estimate the ideal solubility of ethylene in a liquid at 25°C and 1 atm pressure. (*b*) How many grams of ethylene will ideally dissolve in 1000 g of hexane?

4. A mixture of one mole of ethyl bromide and two moles of ethyl iodide at 40°C is placed in an evacuated vessel. (*a*) Determine the composition and pressure of the initial vapor. (*b*) If the container is large enough, what will be the vapor composition and pressure when the last drop of liquid vaporizes? The vapor pressures of the pure liquids are 802 and 252 mm respectively.

5. Mixtures of methylcyclohexane (M), b.p. 100.8°, and toluene (T), b.p. 110.7°C, are frequently used to determine the number of theoretical plates in fractionating columns. The equilibrium data for this system at 760 mm are

Mole fraction M in liquid		0	0.100	0.200	0.300	0.400
Mole fraction M in vapor		0	0.143	0.270	0.378	0.470
Mole fraction M in liquid	0.500	0.600	0.700	0.800	0.900	1.000
Mole fraction M in vapor	0.560	0.650	0.737	0.818	0.906	1.000

Determine the number of theoretical plates in a column which produces (*a*) a distillate containing 0.70 mole fraction M from a feed of 0.30 mole fraction M and (*b*) a distillate of 0.74 M from a feed of 0.20 M. (*c*) If a solution containing 15 mole percent T is distilled until the residue is 65 mole percent T, what will be the composition of the distillate?

6. *Iso*-butyl alcohol, b.p. 107.9°, and *iso*-butyl bromide, b.p. 91.0°, form an azeotrope boiling at 88.8°C and containing 12% by weight of the alcohol. (*a*) Sketch the boiling point-composition curve. (*b*) Which component can be obtained pure by fractional distillation of a 50% mixture? (*c*) What weight of the bromide would be obtained by fractional distillation of the mixture obtained when 150 g of the alcohol are converted to the bromide in 95% yield?

7. Methylethylketone and water are partially miscible. At 30°C the two layers contain 21.9 and 89.9% by weight of ketone. What will be the weight of each layer when 50 g each of ketone and water are equilibrated at this temperature?

8. The distribution ratio of ammonia between water and chloroform at 18°C is 25.8. When a 0.0250 M copper sulfate solution was equilibrated with ammonia and chloroform, the aqueous solution contained 0.385 mole l^{-1} of ammonia and the chloroform 0.0112 mole l^{-1}. Determine how much ammonia is complexed with the Cu^{+2} ion and the value of x in the formula $Cu(NH_3)_x^{+2}$.

9. The following data were obtained when quinine $C_{20}H_{24}O_2N_2$ was distributed between ether and water at 0°:

Water layer, g per 100 ml	0.0547	0.0590	0.0622
Ether layer, g per 100 ml	1.1142	1.2901	1.4281

Quinine exists as a monomer in water. Determine its molecular complexity in ether.

10. Lithium borohydride (*c*) and dimethyl ether (*g*) react to form compounds of the general formula $[LiBH_4]_x[(CH_3)_2O]_y$. From the data below, for the reaction in a closed container at 0°C, determine (*a*) the composition of the compounds formed and (*b*) K_p and ΔF^0 for the dissociation of each compound.

Mole fraction $LiBH_4$	0.331	0.334	0.351	0.407	0.493	0.500
Pressure, mm	423.9	354.2	193.7	193.8	193.8	97.0
Mole fraction $LiBH_4$	0.518	0.569	0.672	0.679	0.809	0.968
Pressure, mm	8.3	7.9	5.8	2.9	2.8	2.9

11. Cooling curves for the binary alloy system, gold-antimony, give the following information:

Wt % antimony	0	10	20	30	40	50
Start of freezing, °C	1063	730	470	400	445	455
Completion of freezing, °C	1063	360	360	360	360	360
Wt % antimony	55	60	70	80	90	100
Start of freezing, °C	460	495	545	580	610	631
Completion of freezing, °C	460	460	460	460	460	631

(*a*) Plot the phase diagram for the system and identify all areas and phases. (*b*) Describe the sequence of events when liquid melts of 20, 50 and 80 atom percent antimony are cooled from 800° to 300°C.

12. When mixtures of silicon and germanium are heated, melting occurs over a range of temperature; thus,

Atom % silicon	0	25	40	62	80	90	100
Start of melting, °C	940	1010	1070	1170	1275	1340	1412
Completion of melting, °C	940	1160	1235	1310	1370	1395	1412

(*a*) Draw the phase diagram. (*b*) What is the nature of the solid formed when any melt of silicon and germanium is cooled?

13. The data below give the compositions of the liquid and solid phases in equilibrium at 25°C in the system ammonium sulfate-beryllium sulfate-water in weight per cent.

Liquid Phase		Wet Solid Phase	
$\%(NH_4)_2SO_4$	$\%BeSO_4$	$\%(NH_4)_2SO_4$	%BeS
43.45	0	—	—
38.60	8.62	82.29	2.82
35.88	16.04	71.09	7.59
37.56	19.72	—	—
34.26	22.08	42.93	32.83
32.20	24.04	42.84	33.64
28.09	26.79	—	—
24.99	26.68	9.12	46.90
15.66	27.26	3.07	52.18
5.77	28.56	1.37	51.16
0	29.94	0	59.35

In each case the difference from 100% represents water. (*a*) Plot the phase diagram indentifying all phases. (*b*) What will be the composition of the first crystals to deposit when solutions containing 10%$(NH_4)_2SO_4$ + 20% $BeSO_4$ and 20%$(NH_4)_2SO_4$ + 10% $BeSO_4$ are evaporated?

12

The Conductance of Electrolytes

THE LAWS OF ELECTROLYSIS

43a. Electrolytic Conduction.—Solid and liquid substances which are able to conduct the electric current can be divided roughly into two categories. There are, first, the **metallic conductors** or **electronic conductors** in which the electricity is carried by the electrons. It was seen in Chapter 7 that a metal consists of a relatively rigid lattice of positive ions, i.e., atoms which have lost some electrons, and a system of mobile electrons removed from the atoms. When an electrical potential is applied, the electrons are forced to stream in one direction, while the positive ions remain stationary; the flow of electricity is thus not accompanied by any appreciable movement of matter. Since the electrons carry negative charges, the direction in which they stream is opposite to that conventionally regarded as the direction of the positive current.

Conducting materials of the second type are known as **electrolytic conductors** or **electrolytes**, and the properties of these conductors will be given detailed consideration in this and succeeding chapters. *Electrolytes are distinguished from metallic conductors by the fact that the current is carried by ions and not by electrons.* As already seen, ions consist of atoms or groups of atoms which have lost or gained electrons, thus acquiring positive or negative charges, respectively. The application of an electrical potential causes these charged particles of matter to move, the positive ions in the direction of the current and the negative ions in the opposite direction.* It follows, therefore, that passage of an electric current through an electrolyte is always accompanied by a transfer of matter. This transfer is manifested by changes of concentration, and also by visible separation of material at the points where the electric current enters and leaves the electrolyte. Although many molten salts and hydroxides are electrolytic conductors, the treatment here will be restricted to electrolytes consisting of a salt, acid or base dissolved in a suitable solvent, such as water. In accordance with the theory of electrolytic dissociation (§ 26b), such solutions contain ions produced by the spontaneous dissociation of the dissolved acid, base or salt.

In order to pass a current of electricity through an electrolyte, two suitable

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* The term **ion** originates from a Greek word meaning "to go"; it was applied to charged particles because of their movement under the influence of an electrical force.

pieces of metal (or carbon), called **electrodes,** are inserted in the solution; these are connected to a source of **electromotive force** (abbreviated to E.M.F.). The electrode at which the positive current enters the solution is called the positive electrode or **anode** (Greek: ana, *up*), while that at which the current leaves is known as the negative electrode or **cathode** (Greek: cata, *down*). The ions which carry a positive charge move through the solution in the direction of the positive current, that is, toward the cathode; these ions are consequently called **cations.** Similarly, the negative ions travel in the opposite direction, toward the anode; they are thus referred to as **anions.** The function of the applied E.M.F. is to direct the ions to the appropriate electrodes, and also to cause a movement of electrons, from the anode to the cathode, *outside the cell,* as indicated in Fig. 43.1. The flow of current is thus accompanied by a removal of electrons from the anode and their transfer through the external connecting wire, to the cathode. As will be seen below, the supply of electrons at the anode is provided by the negatively charged anions, while the same number of electrons at the cathode are removed by the positively charged cations.

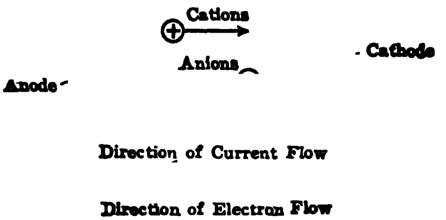

FIG. 43.1. Flow of current and electrons

When a cation, carrying a positive charge, reaches the cathode it acquires (negative) electrons which are available at this electrode, thus having its charge neutralized. Since cations generally consist of a positively charged atom of a metal or of hydrogen, the neutralization of the charge leaves the neutral metal or hydrogen deposited upon the cathode. This result is in accord with the statement made above that the passage of an electric current through an electrolyte is usually associated with the visible separation of matter. Similarly, when an anion, which is negatively charged, reaches the anode, the electrons are removed, leaving the discharged neutral atom or group of atoms. If the anion is a halogen or hydroxyl ion, the discharged material may appear as the free halogen or as oxygen, respectively. Some anions, such as sulfate and nitrate, are not usually discharged from aqueous solutions, and so other processes, accompanied by the removal of electrons, take place at the anode. One of these is the liberation of oxygen from water. Another is the abstraction of electrons from the atoms of the actual metal constituting the anode; the atoms are thus converted into the corresponding positively charged cations which pass into solution. Such attackable metals as copper, zinc and cadmium usually dissolve when they are made anodes. On the other hand, platinum and gold fall into the category of "unattackable metals" that pass into solution to a small extent, or not at all, when they are used as anodes.

In the foregoing discussion it has been supposed, for the sake of simplicity, that the ions which carry the current are the ones discharged at the anode or cathode; this is, however, not necessarily the case. The ions carrying most of the current are generally those present in largest quantity, but these may not be actually discharged. The factors determining the order in which ions have their charges neutralized at the electrodes will be considered in §§ 50b, 50c.

43b. Faraday's Laws of Electrolysis.—The decomposition of electrolytic solutions by means of the electric current, in the manner just described, is known as **electrolysis.** While investigating the phenomena of electrolysis, M. Faraday (1833) discovered certain relationships between the quantity of electricity passing through an electrolyte and the amount of any material liberated at the electrode. The **quantity of electricity** *is equal to the product of the current strength and the time for which it is passed;* the nature of the units employed will be described more fully below. In the meantime, the results obtained by Faraday may be considered in the form of the two **laws of electrolysis,** as follows.

I. *The amount of chemical change produced by an electric current, that is, the amount of any substance deposited or dissolved, is proportional to the quantity of electricity passed.*

II. *The amounts of different substances deposited or dissolved by the same quantity of electricity are proportional to their chemical equivalent weights.*

Combination of the two laws of electrolysis leads to the conclusion that the weight w in grams of material deposited or dissolved at an electrode is proportional to $I \times t \times e$, where I is the current strength, usually expressed in amperes, t is the time in seconds and e is the equivalent weight of the material. It is thus possible to write

$$w = \frac{I \times t \times e}{F}, \tag{43.1}$$

where $1/F$ is the proportionality constant. The significance of this constant may be seen by taking the quantity $I \times t$ equal to F; then the weight w of substance deposited (or dissolved) is equal to e, the equivalent weight. In other words, F, called the **faraday,** *is the quantity of electricity which must be passed in order to deposit or dissolve 1 gram equiv. of any substance.* It is important to note that this quantity of electricity is always the same, irrespective of the nature of the substance deposited or dissolved.

The practical unit quantity of electricity, called the **coulomb,** is defined in terms of the practical unit of current, the ampere;* thus, *the coulomb is the quantity of electricity passing through a conductor when 1 ampere flows for 1*

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* Prior to 1948, electrical measurements were made in terms of "international" units. The international ampere was defined as that current which in 1 second would deposit 1.11800 milligrams of silver. At the present time, instruments are calibrated in "absolute" units based on the cgs system. The absolute ampere is then equal to 1.000165 int. amperes. Similar small differences exist between other absolute and international electrical units, e.g., the ohm and the volt, but the maximum discrepancy is only 0.05 per cent and is negligible for most experimental purposes.

second. By making precise measurements of current, time and weight of silver deposited from a solution of a silver salt, it is possible to evaluate the faraday by equation (43.1). The best value at the present time is $F = 96,495.6 \pm 1.1$ absolute coulombs. However, the experimental uncertainties connected with ordinary measurements make it satisfactory to write

$$F = 96{,}500 \text{ coulombs},$$

the error thus introduced being only about 0.005 per cent. Insertion of this value in equation (43.1) then gives a complete summary of Faraday's laws in the form

$$w = \frac{I \times t \times e}{96{,}500} \tag{43.2}$$

An important use of equation (43.2) lies in its application to the measurement of quantity of electricity or of current strength. The apparatus used for the purpose is known as a **coulometer,** and by its means the amount of a given material, e.g., silver, copper, iodine or a mixture of hydrogen and oxygen, set free in electrolysis can be measured. Thus, if w is determined in this way, and the equivalent weight e of the substance is known, the quantity of electricity passed, i.e., $I \times t$, can be derived from equation (43.2). If the time t is measured, the current strength I, assumed to be constant, can be calculated.

Example: The passage of a constant current through a dilute solution of sulfuric acid, with platinum electrodes, for 1 hr resulted in the liberation of 336 ml of mixed hydrogen and oxygen, reduced to S.T.P. Calculate the strength of the current.

The passage of 1 faraday, i.e., 96,500 coulombs, results in the simultaneous liberation of 1 equiv., i.e. 8 grams, of oxygen, and 1 equiv., i.e., 1 gram, of hydrogen; this represents $\frac{1}{4}$ mole of O_2 and $\frac{1}{2}$ mole of H_2, making a total of $\frac{3}{4}$ mole of gas per faraday. The volume of $\frac{3}{4}$ mole of gas at S.T.P. is $\frac{3}{4} \times 22.4 = 16.8$ liters; hence

$$16.8 \text{ liters of } H_2 + O_2 \text{ gases are liberated by } 96{,}500 \text{ coulombs.}$$

The actual volume of gas obtained in the experiment was 0.336 liter; hence,

$$0.336 \text{ liters of } H_2 + O_2 \text{ gases are liberated by } \frac{96{,}500}{16.8} \times 0.336 \text{ coulombs.}$$

Since the current is passed for 1 hr, i.e., 3600 sec, the current in amp is obtained by dividing the number of coulombs by 3600; thus

$$\text{Current strength} = \frac{96{,}500 \times 0.336}{16.8 \times 3600} = 0.536 \text{ amp.}$$

There is little doubt that Faraday's laws are exact; they have been found to hold at high and low temperatures, as well as under normal conditions, for nonaqueous solutions and fused salts, as well as for aqueous solutions. Provided the correct equivalent weight is employed, there are no exceptions to equation (43.2). The laws also apply to chemical changes at the anode and cathode which do not involve deposition on, or solution of, the electrode; for example, ions are frequently oxidized at the anode or reduced at the cathode.* For such reactions equation (43.2) may still be employed if the appropriate equivalent weight is used; thus, in the reduction of ferric (Fe^{+3}) to ferrous (Fe^{+2}) ions, or the reverse oxidation process, the equivalent weight is equal to the atomic weight of iron, i.e., 55.85.

Apparent exceptions to Faraday's laws sometimes arise when two or more processes occur simultaneously at an electrode; for example, the deposition of a metal, such as zinc or nickel, may be accompanied by the evolution of hydrogen. The quantity of metal liberated at the cathode is then not in accord with equation (43.2); however, if allowance is made for the fact that part of the current is utilized in an alternative process, the laws are found to be obeyed.

43c. Significance of Faraday's Laws.—Apart from their practical value, Faraday's laws have an important theoretical significance. The discharge at a cathode, or formation at an anode, of 1 g equiv. of any ion requires the passage of one faraday of electricity; hence, it is reasonable to suppose that this represents the charge carried by 1 g equiv. of any ion. If the ion has a valence of z, then 1 mole or 1 gram ion of these ions will contain z gram equiv., and will consequently carry z faradays, i.e., zF coulombs, where F is 96,500. The number of individual ions in 1 gram ion is equal to the Avogadro number, and so the electrical charge carried by a single ion is equal to zF/N. Since z is an integer, one for a univalent ion, two for a bivalent ion, and so on, it follows that the charge of electricity carried by a single ion is a multiple of a fundamental unit charge whose value is F/N. This result, derived from Faraday's laws, implies that *electricity, like matter, is atomic in nature*, and that F/N is the "atom" or unit of electric charge. There are many reasons for identifying this unit charge with the charge of an electron, i.e., ϵ, so that

$$\epsilon = \frac{F}{N}.$$

This conclusion is supported by the value of the electronic charge calculated from this relationship in § 13b; the result derived in this manner is virtually identical with that obtained from the most accurate oil drop experiments. Conversely, from the measured values of the faraday and the electronic charge, an accurate determination of the Avogadro number can be made.

One final consequence of Faraday's laws may be mentioned; since equivalent amounts of different ions are discharged at the anode and cathode, for a given current, it follows that when a solution is electrolyzed the number of electrons taken up by the cations at the cathode must be equal to the number released simultaneously at the anode. This will, presumably, be also equal to the number of electrons which pass through the external connection from the anode to the cathode.

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* Strictly speaking all processes occurring at anode and cathode are oxidation and reduction in the most general sense, since they all involve the removal or addition of electrons, respectively (see § 46c).

THE MIGRATION OF IONS

44a. Transference Numbers.—Although positive and negative ions are discharged in equivalent amounts at the two electrodes, these ions do not necessarily move at the same speed toward the cathode and anode, respectively, under the influence of an applied E.M.F. This can be seen in a simple pictorial manner by considering Fig. 44.1, which represents an electrolytic vessel containing an equivalent number of positive and negative ions, indicated by plus and minus signs. Since the solution must always be electrically neutral, the cations and anions must always remain equivalent in number; if they are both univalent, then the numbers must be equal. The condition of the solution at the commencement of electrolysis is shown in Fig. 44.1, I. Suppose that the *cations only* are able to move under the influence of an applied potential, and that two of these ions move from left to right in a given time; the condition attained will then be as in Fig. 44.1, II. At each electrode the two unpaired ions are discharged; two electrons are given up at the anode and the same number are taken up at the cathode. It is seen, therefore, that although only positive ions are assumed to be able to move, equivalent amounts of positive and negative ions are discharged at the cathode and anode, respectively. A condition of this kind actually exists in certain solid and fused electrolytes, where all the current is carried by the cations; for example, in solid silver chloride and bromide and sodium chloride the positive ions carry the current, whereas in barium and lead chlorides all the current is carried by the negative ions.

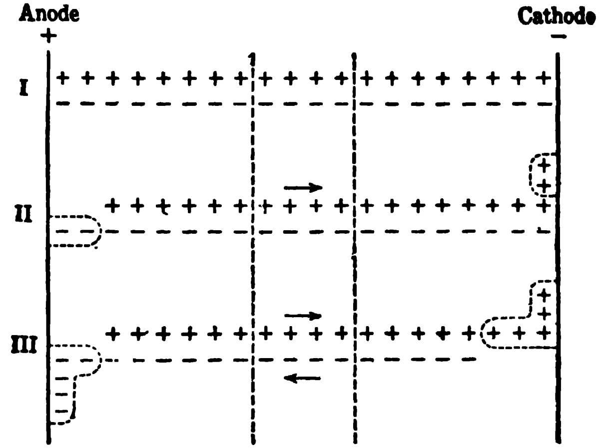

FIG. 44.1. The migration of ions

If, while the cations are moving in one direction, three anions are carrying electricity in the opposite direction, so that the ionic velocities are in the ratio of 2 to 3, the result will be as shown in Fig. 44.1, III. Five ions, equal to the sum of two and three, are seen to be discharged at each electrode, in spite of the difference in the speeds of the ions. Exactly analogous results would be obtained for any speeds of the two ions, and so there is no difficulty in correlating Faraday's laws with the fact that the oppositely charged ions in a solution may have different velocities.

It can be seen from the two cases just considered and, in fact, from any particular choice of the ionic speeds, that the total number of ions discharged, and hence the total quantity of electricity carried through the solution, is proportional to the sum of the speeds of the two ions. If u_+ is the velocity of the cations and u_- that of the anions in the same solution, and under the same conditions, the quantity of electricity passing will be proportional to the sum, $u_+ + u_-$. The amount carried by each ion is proportional to its own speed, i.e., to u_+ or to u_-, as the case may be, and so *the fraction of the total current carried by each ionic species*, which is called its **transference number**, is given by

$$t_+ = \frac{u_+}{u_+ + u_-} \quad \text{and} \quad t_- = \frac{u_-}{u_+ + u_-}, \tag{44.1}$$

so that

$$t_+ + t_- = 1,$$

where t_+ and t_- are the transference numbers of the cations and anions, respectively, in the given electrolyte. It is evident from equation (44.1) that the faster the speed of one ion relative to that of the other, the greater will be the fraction of the total current carried by the former. It should be noted that the actual ionic velocities are not important in determining the transference numbers; the relative velocities are the significant quantities.

44b. Determination of Transference Numbers: The Hittorf Method. —An examination of Fig. 44.1 shows that in II, where two cations have moved while the anions were stationary, the number of positive and negative ions in the vicinity of the anode, i.e., in the anode compartment, has decreased from 8 to 6, i.e., by two ions, while there is no change in the region of the cathode, i.e., in the cathode compartment. Similarly, when the speeds of the cations and anions are in the ratio of 2 to 3, there is a decrease of two units in the material in the anode compartment, while that in the cathode compartment decreases by three units. In general, *the number of equivalents of electrolyte migrating from any compartment during the passage of current is proportional to the speed of the ion moving away from it;* thus,

$$\frac{\text{Equivalents migrating from anode compartment}}{\text{Equivalents migrating from cathode compartment}} = \frac{\text{Speed of cation}}{\text{Speed of anion}} = \frac{u_+}{u_-}. \tag{44.2}$$

The total number of equivalents migrating from both compartments, which is proportional to $u_+ + u_-$, is seen to be equal to the number of equivalents deposited on each electrode, that is to say, to the number of equivalents passed through the electrolyte; hence, it follows from equations (44.1) and (44.2),

$$\frac{u_+}{u_+ + u_-} = t_+ = \frac{\text{Equivalents migrating from anode compartment}}{\text{Equivalents of current passed}}, \tag{44.3}$$

and

$$\frac{u_-}{u_+ + u_-} = t_- = \frac{\text{Equivalents migrating from cathode compartment}}{\text{Equivalents of current passed}}. \tag{44.4}$$

These two expressions provide a basis for the experimental determination of transference numbers by the method proposed by W. Hittorf (1853).

In order to determine the number of equivalents of current passed, a coulometer (§ 43b) is generally included in the same circuit as the experimental solution, so that the same quantity of electricity passes through them both. The number of equivalents of metal, e.g., silver or copper, deposited in the coulometer gives the denominator of equations (44.3) and (44.4). The numerators can then be obtained by measuring the change in concentration of the solution in the vicinity of the anode and cathode, respectively, in the experimental vessel. Since the sum of the two transference numbers t_+ and t_- must be unity, it is not necessary to measure the concentration changes in both anode and cathode compartments, except for confirmatory purposes; the determination of the transference number of one ion thus automatically gives the value for the other ion.

When carrying out transference number measurements by means of the Hittorf (analytical) method, precautions must be taken to avoid the possibility of mixing between the anode and cathode solutions; for this reason it is desirable to have a "middle compartment," analogous to that depicted between the dashed lines in Fig. 44.1, in which the concentration remains unchanged when current is passed. Diffusion and convection must be made negligible, so that the measured concentration changes can really be ascribed to ionic transference and not to extraneous factors. In addition, evolution of gases during electrolysis, which would stir the solution, must be avoided.

One form of apparatus, which has been used for the study of solutions of alkali and alkaline earth chlorides, is shown diagrammatically in Fig. 44.2; two right-angle bends are introduced below the anode A and also above the cathode C, in order to minimize the possibility of mixing of the solutions in different parts of the apparatus. The latter is filled with the experimental solution whose *weight concentration* must be known; suitable electrodes A and C are inserted, and these are connected in series with a coulometer and a source of current. A current of 0.01 to 0.02 amp is passed for two or three hours, so as to produce appreciable, but not too large, changes of concentration; the stopcocks S_1 and S_2 are then closed. The liquid isolated above S_1 represents the anode solution, while that below S_2 is the cathode solution; these are removed and analyzed. The concentration of the "middle compartment," between the two stopcocks, should be unchanged after the electrolysis. The quantity of material, e.g., silver, deposited by the current in the coulometer is determined, and from this the number of equivalents can be calculated. Since the change in concentration of the solution is accompanied by a change of density, and hence of volume, the loss of material from anode or cathode compartment must be determined with reference to a definite *weight* of solvent present after current has passed.

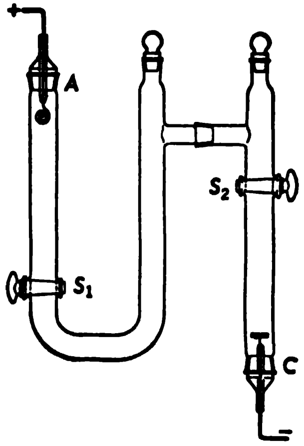

FIG. 44.2. Apparatus for application of Hittorf method

During electrolysis the concentration of electrolyte around the electrodes will always change due to the migration of ions and frequently also as a result of electrode reactions. Suppose a solution of silver nitrate is being electrolyzed between silver electrodes and let N_e be the number of faradays of electricity passed through the solution. In the anode compartment the electrode reaction will cause N_e g equiv. of silver metal to dissolve and form silver ions, instead of discharging this number of nitrate ions; at the same time N_m g equiv. of silver ions will migrate out of the compartment. Since N_m is less than N_e there will be an increase in the number of equiv. of silver nitrate in the anode compartment during the electrolysis, equal to $N_e - N_m$. If the number of g equiv. of silver ion in the solution initially is N_i and the number in the same weight of water at the end, i.e., finally, is N_f, then $N_f - N_i = N_e - N_m$ or $N_m = N_i - N_f + N_e$. By equation (44.3) $t_+ = N_m/N_e$ and so

$$t_+ = \frac{N_i - N_f + N_e}{N_e}. \tag{44.5}$$

The calculation is simplified if the nitrate ion is considered. Since the electrode reaction does not affect this ion, N_m, the number of g equiv. migrating into the anode compartment (or out of the cathode compartment) is equal to $N_f - N_i$. Hence, by equation (44.4)

$$t_- = \frac{N_f - N_i}{N_e}. \tag{44.6}$$

The same result can be obtained from equation (44.5) by utilizing the fact that $t_- = 1 - t_+$. The values of N_i and N_f are, of course, the same irrespective of whether they represent g equiv. of silver ions or of nitrate ions in the initial and final solutions.

If the concentration changes in the cathode compartment are considered, then N_e g equiv. of silver are removed (by deposition) in the electrode reaction while N_m g equiv. migrate into the compartment. The concentration of electrolyte will therefore be less at the end than at the beginning of electrolysis. Let the initial and final amounts of silver ion in the cathode compartment be N'_i and N'_f g equiv., respectively. Then $N_m - N_e = N'_f - N'_i$ or $N_m = N'_f - N'_i + N_e$; hence

$$t_+ = \frac{N'_f - N'_i + N_e}{N_e}.$$

The change in the nitrate ion will be a decrease due entirely to migration out of the cathode compartment, so that $N_m = N'_i - N'_f$ and

$$t_- = \frac{N'_i - N'_f}{N_e}.$$

Example: A solution containing 3.654 g KCl per 100 g (exactly) was electrolyzed, using a cathode consisting of Ag coated with AgCl. After the passage of current which resulted in the deposition of 1.9768 g Ag in a coulometer, 122.93 g of the cathode solution was found to contain 5.136 g KCl. Calculate the transference number of the K^+ ion in the KCl solution.

In this experiment the K^+ ions are not discharged (and removed) at the cathode; instead Cl^- from the AgCl passes into solution, according to the reaction $AgCl + \epsilon \rightarrow Ag + Cl^-$, in amount exactly equivalent to the quantity of electricity, i.e., to the Ag deposited in the coulometer. Allowance for this must be made in determining the loss from the cathode compartment. The equiv. wt. of Ag is 107.88; hence,

$$\text{Number of g equiv. of Ag deposited} = \frac{1.9768}{107.88} = 0.01832.$$

This gives the number of g equiv. of Cl^- from the cathode which have entered the cathode solution.

After electrolysis the cathode solution contains 122.93 − 5.14 = 117.79 g of H_2O to 5.136 g KCl; the equiv. wt. of KCl is 74.56, and consequently,

$$\text{Number of g equiv. of KCl (or } Cl^-\text{) in cathode solution} = \frac{5.136}{74.56} = 0.06888.$$

If the Cl^- had not been added from the cathode, the number of g equiv. of KCl, associated with 117.79 g H_2O, would have been 0.06888 − 0.01832 = 0.05056.

Before electrolysis 100 g solution contained 3.654 g KCl, so that the weight of H_2O was 100.00 − 3.65 = 96.35 g; this was associated with 3.654/74.56 = 0.04900 g equiv. KCl. Hence 117.79 g H_2O (present in the cathode solution after electrolysis) was associated before electrolysis with

$$\frac{0.04900 \times 117.79}{96.35} = 0.05991 \text{ g equiv. KCl (or } Cl^-\text{)}.$$

The loss of Cl^- from the cathode compartment due to migration is thus 0.05991 − 0.05056 = 0.00935 g equiv. Since 0.01832 g equiv. was deposited in the coulometer, it follows that the transference number of the ion leaving the cathode compartment, i.e., the anion Cl^-, is given by

$$t_- = \frac{0.00935}{0.01832} = 0.510.$$

The transference number t_+ of the cation K^+ is thus 1.000 − 0.510 = 0.490.

44c. The Moving Boundary Method.—Although the Hittorf method is simple, accurate results are difficult to obtain, especially with fairly dilute solutions; one reason is the small concentration changes which occur when the current is passed. It has, therefore, been largely replaced by a more direct method for the determination of transference numbers, based on a study of the rate of movement of the boundary between two ionic solutions. If it is required to determine the transference numbers of the ions in the electrolyte MA, e.g., potassium chloride, it is necessary to have another, i.e., "indicator," electrolyte, M′A, e.g., lithium chloride, having an ion in common with the experimental substance. Further, the indicator ion M′ must have a smaller velocity than M; this condition is satisfied, in the case under consideration, by the lithium ion, which migrates more slowly than the potassium ion under the influence of the same applied E.M.F.

Imagine the two solutions, i.e., of MA and M′A, in an electrolysis apparatus, part of which consists of a uniform vertical tube, as depicted in Fig. 44.3. A suitable anode is placed in the indicator solution M′A, and a cathode is inserted in the experimental solution. The actual nature of the anode and cathode is immaterial, provided they do not cause gas evolution or other interference. By means of a special device, which constitutes an important part of the method, a sharp boundary is produced between the two solutions at *b*. Formation of a sharp boundary is especially simple with many chloride and nitrate solutions. If a silver anode is used with nitrate solutions and a cadmium anode with chloride solutions, the silver nitrate and cadmium chloride, respectively, formed during electrolysis produces a sharp boundary with the experimental solution. This is referred to as an **autogenic boundary.** The relatively slow-moving silver and cadmium ions then act as indicators.

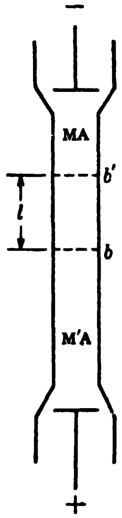

FIG. 44.3. Moving boundary method for transference numbers

When a current is passed, the M (potassium) ions move upward toward the cathode, and these are followed by the M′ (indicator) ions, thus maintaining the sharp boundary. The M′ ions are chosen with this end in view, for if they were the faster moving ions the boundary would become blurred. After the passage of a measured quantity Q of electricity, the boundary has moved from b to b', and this distance l is measured. In observing the boundary, especially between two colorless electrolytes, use is made of the difference in the refractive indices of the indicator and experimental solutions. The method of calculating the transference numbers is then as follows.

If Q coulombs of electricity are passed through the apparatus, the quantity carried by the cation (potassium ion) is t_+Q and hence t_+Q/F g equivalent of this ion must migrate upward from b to b'. If the concentration of the MA (potassium chloride) solution in the vicinity of the boundary is c gram equiv. per cc,* this boundary must move through a volume $t_+Q/F\mathrm{c}$ cc. If

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* The symbol c is used to represent concentrations in gram equiv., as distinct from concentrations in gram ions or moles, for which c is employed.

the cross section of the tube through which the boundary moves is a sq cm and the distance from b to b' is l cm, the volume through which it moves is $l \times a$ cc; hence

$$\frac{t_+Q}{F\text{c}} = la$$

or

$$t_+ = \frac{l \times a \times F \times \text{c}}{Q}. \tag{44.7}$$

It is thus possible to calculate the transference number of the cation (potassium ion) from the data available. In accurate work a correction must be applied for volume changes occurring as a result of chemical reactions at the electrodes, for these will affect the movement of the boundary. The correction is negligible except for relatively concentrated solutions.

Example: In a moving boundary experiment with 0.100 N KCl, using 0.065 N LiCl as indicator solution, a constant current of 0.005893 amp was passed for 2130 sec, and the boundary was observed to move through 5.60 cm in a tube of 0.1142 sq cm cross section. Calculate the transference numbers of the K^+ and Cl^- ions.

The values of l and a are given, while that of the faraday is known; hence, Q and c must be derived from the data to calculate t_+ by equation (44.7). The quantity of electricity Q in coulombs is the product of the current in amp and the time in sec, i.e., 0.005893×2130 coulombs. The concentration c must be expressed in g equiv. per cc, since l is in cm and a in cm^2. The solution of KCl contains 0.100 g equiv. per liter, and this is 10^{-4} g equiv. per ml, or per cc, with sufficient accuracy; hence, c is 10^{-4}, and by equation (44.7),

$$t_+ = \frac{5.60 \times 0.1142 \times 96{,}500 \times 10^{-4}}{0.005893 \times 2130} = 0.492.$$

The transference number of the K^+ ion is thus 0.492, and hence that of the Cl^- ion must be $1.000 - 0.492 = 0.508$.

A third method of determining transference numbers depends upon the measurement of the E.M.F. of certain cells. This will be described in the next chapter.

44d. Results of Transference Number Measurements.—The experimental methods referred to above determine the transference numbers of what is called the **ion constituents** rather than of the ions themselves. The ion constituent was defined by A. A. Noyes and K. G. Falk (1911) as the ion-forming portion of an electrolyte irrespective of the extent to which it may actually exist as free ions. For what are called strong electrolytes (§ 45c), such as the salts of alkali and alkaline earth metals with anions of strong acids, e.g., chlorides, nitrates and perchlorates, the ion constituent and the ion are essentially the same, since the salt exists almost entirely as free ions. For many other salts the ion constituent may include both simple and complex ions and nonionized molecules. In cadmium iodide, for example, the ion constituent probably exists as CdI^+, CdI_3^- and CdI_4^{-2} ions and CdI_2

molecules as well as Cd^{+2} ions. The measured transference number includes contributions from all these species and thus cannot be regarded as that of the Cd^{+2} ion. Although it is the general practice to refer to the transference number of an ion (cation or anion), the limitation discussed here should be borne in mind.

Some of the most recent values of the transference numbers of the cations in various electrolytes at a number of concentrations at 25°C are quoted in Table 44.1. The corresponding anion transference numbers may be obtained in each case by subtracting the cation transference number from unity. It will be noted that the transference numbers vary to some extent with the concentration of the electrolyte; this fact is of great significance, for it implies that the speeds of the ions, upon which the transference numbers depend [equation (44.1)], are not constant but may change as the concentration of the solution is altered. Transference numbers also vary with temperature. In general, as the temperature is increased the values tend to approach 0.5; this implies that the speeds of ions tend to become equal at high temperatures.

TABLE 44.1. TRANSFERENCE NUMBERS OF CATIONS AT 25°C

Concn.	HCl	LiCl	NaCl	KCl	KNO_3	$BaCl_2$	K_2SO_4
0.01 N	0.825	0.329	0.392	0.490	0.508	0.440	0.483
0.02	0.827	0.326	0.390	0.490	0.509	0.437	0.485
0.05	0.829	0.321	0.388	0.490	0.509	0.432	0.487
0.10	0.831	0.317	0.385	0.490	0.510	0.425	0.489
0.20	0.834	0.311	0.382	0.489	0.512	0.416	0.491
0.50	0.838	0.303	—	0.489	—	0.399	0.491

An examination of the cation transference numbers of the three alkali chlorides, viz., lithium, sodium and potassium chlorides, as given in Table 44.1, reveals the fact that the values increase in this order. Since these three electrolytes have the same anion, it is apparent that the speeds of the cations must increase in the order lithium, sodium, potassium. Of these ions, lithium is the smallest and potassium the largest, as may be expected from general considerations of atomic weight and atomic structure, and as has been verified by X-ray diffraction measurements on crystals. It would be anticipated, therefore, that lithium, the smaller ion, should have a higher velocity than the potassium ion, which is larger. The fact that the reverse is actually the case, as shown by transference and other measurements, is a strong argument in favor of the hydration of ions in solution (§ 41h). Because of the small size of the *bare* lithium ion, there is a strong electrostatic field in its vicinity, and so it is able to attract a relatively large number of water dipoles. The larger bare potassium ion cannot hold as many, because of the weaker field at its circumference. The result is that the highly hydrated lithium ion in solution is actually larger than the hydrated potassium ion; this explains why the former ion moves with a smaller speed than the latter.

More direct experimental evidence for the hydration of ions in solution has been obtained in connection with transference studies. If the ions carry molecules of water with them in their migration, the cations will take some water out of the anode compartment, for example, while the anions will bring some water in with them. If the anions and cations are hydrated to different extents, the net result should be a change in the amount of water in the compartment. This change will be a measure of the difference in the extents of hydration of the positive and negative ions. That such changes in the water content do occur as a result of ionic migration has been proved in two ways: first, by observations on the volumes of the anode and cathode solutions separated by a parchment membrane, and second, by showing that the concentration of a nonelectrolyte, such as urea or a sugar, which is not affected by the current, actually changes in the course of electrolysis. The volume and concentration changes are to be attributed to the net addition or removal of water by the hydrated ions. By making allowance for the water transported with the ions, so-called "true" transference numbers can be calculated from the "apparent" values in Table 44.1.

The fact that experiments give the transference number of the ion constituent makes it possible, in some instances, to use the data to throw light on the nature of the electrolyte in solution. A case of special interest is that of cadmium iodide for which the transference numbers at a number of concentrations, interpolated from experimental measurements at 18°C, are given in Table 44.2. The negative values of the transference number in the more concentrated solutions show that the cadmium ion constituent includes species that are negatively charged, e.g., CdI_3^- and CdI_4^{-2}, and migrate to the anode. In fact, in these solutions, more cadmium migrates to the anode than to the cathode as Cd^{+2} or CdI^+ ions. With increasing dilution of the cadmium iodide solution, the complex ions CdI_3^- and CdI_4^{-2} dissociate into simple Cd^{+2} and I^- ions. Consequently, the almost constant positive values of the transference number in the more dilute solutions may well be that of the Cd^{+2} ion.

TABLE 44.2. TRANSFERENCE NUMBERS OF CADMIUM ION CONSTITUENT IN CADMIUM IODIDE SOLUTIONS AT 18°C

CdI_2 g equiv./l	0.01	0.02	0.05	0.1	0.2	0.5	1.0
Transference No.	0.444	0.443	0.396	0.296	0.127	−0.003	−0.420

EQUIVALENT CONDUCTANCE

45a. Electrolytic Conductance.—Solutions, like metallic conductors, obey **Ohm's law** which relates the electrical pressure or E.M.F. applied to a conductor and the strength of the current passing. The law states that *the current strength (I) is directly proportional to the applied* E.M.F. *(E), and inversely proportional to the resistance (R)*; thus, with the appropriate units,

$$I = \frac{E}{R}. \tag{45.1}$$

Of these three quantities, the resistance in absolute ohms and the E.M.F. in absolute volts are defined in cgs units, and the unit of current, the absolute ampere, is then derived from these by means of equation (45.1); it is the current which will flow through a 1 ohm resistance when an E.M.F. of 1 volt is applied. Since absolute measurements are too time consuming for practical purposes, the ohm is represented by a group of wire-wound resistance coils and the volt by a group of Weston cells (§ 46a) at the U.S. National Bureau of Standards; these constitute the primary electrical standards of the country.

The resistance of any uniform conductor varies directly as its length (l cm) and inversely as its area of cross section (a sq cm), so that

$$R = \text{R}\frac{l}{a}\ \text{ohms}, \tag{45.2}$$

where R, a constant for the given conductor, is known as the **specific resistance** or **resistivity**; its units are ohms cm. The specific resistance is effectively *the resistance in ohms of a specimen 1 cm in length* ($l = 1$) *and 1 sq cm in cross section* ($a = 1$); that is, R is the resistance between opposite faces of a 1 cm cube of the material.

The **specific conductance** of any conductor is defined as *the reciprocal of the specific resistance*, and may be represented by the symbol κ. Since by definition κ is equal to 1/R, equation (45.2) becomes

$$R = \frac{1}{\kappa}\cdot\frac{l}{a}\ \text{ohms}, \tag{45.3}$$

and hence,

$$\kappa = \frac{l}{aR}\ \text{ohms}^{-1}\ \text{cm}^{-1}. \tag{45.4}$$

Since R is in ohms, l in cm and a in sq cm, the units of κ are ohms^{-1} cm^{-1}. The conductance C is defined as the reciprocal of the resistance, so that by equation (45.3),

$$C = \kappa\frac{a}{l}\ \text{ohms}^{-1}. \tag{45.5}$$

The specific conductance κ is thus seen from equation (45.5) to be *the conductance between opposite faces of a 1 cm cube*. The unit of conductance, indicated above as ohm^{-1}, is frequently referred to as a "reciprocal ohm" or "mho."

Following F. W. Kohlrausch (1876), it is convenient to define a quantity called the **equivalent conductance**, represented by the symbol Λ (Greek: capital *lambda*); thus

$$\Lambda = 1000\frac{\kappa}{c}\ \text{ohms}^{-1}\ \text{cm}^2, \tag{45.6}$$

where c is the concentration of the solution in *gram equiv. per liter*. If v cc is the volume of solution containing 1 gram equiv. of electrolyte, then v is equal to 1000/c, neglecting the difference between ml and cc; thus the equivalent conductance may be alternatively defined as

$$\Lambda = \kappa v \text{ ohms}^{-1} \text{ cm}^2. \qquad (45.7)$$

The equivalent conductance of a solution can thus be readily derived from its concentration (or dilution) and the measured specific conductance. Strictly speaking, the units of Λ are ohms^{-1} cm^2 equiv.$^{-1}$, but the last term is generally omitted, since it is implied in the expression equivalent conductance.

The importance of the equivalent conductance lies in the fact that it is a measure of the conducting power of all the ions produced by 1 gram equiv. of electrolyte at a given concentration. Imagine two large electrodes set 1 cm apart and suppose the whole of the solution containing 1 gram equiv. is placed between these electrodes. Since v cc is the volume of the solution, then the area of the electrodes in contact with solution will be v cm^3/1 cm $= v$ sq cm. Hence, in equation (45.5), $l = 1$ cm and $a = v$ sq cm, so that the conductance is κv; it is thus numerically equal to the equivalent conductance as defined by equation (45.7).

45b. Measurement of Conductance of Electrolyte.—The specific conductance of an electrolytic solution can be obtained by means of equation (45.4) from the resistance R of the electrolytic conductor of known dimensions l and a. The resistance is most frequently determined by means of some form of Wheatstone bridge circuit. In the earliest measurements, direct current was employed, but this caused the results to be erratic because of the so-called "polarization" due to gases liberated at the electrodes. Following the suggestion of F. W. Kohlrausch (1868), a rapidly alternating current is now generally used. The direction of the current is reversed about a thousand times per second, so that the "polarizations" produced by successive pulses counteract one another. A Wheatstone bridge arrangement is shown in Fig. 45.1; C is the cell containing the solution whose resistance is

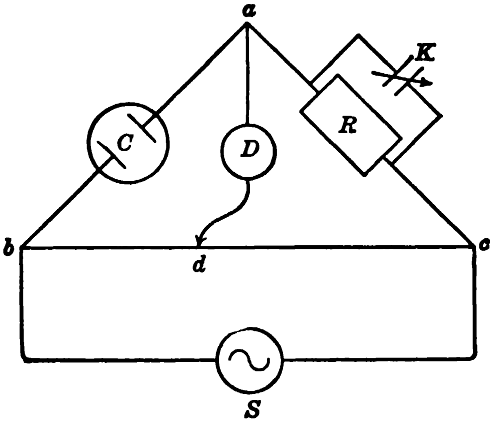


FIG. 45.1. Measurement of resistance of electrolyte

to be measured, and R is a variable standard resistance. The source of the alternating current is indicated by S, and D is a suitable current detector; K is a variable capacitor for compensating the electrical capacitance of the cell. The point of contact d is moved along the uniform wire or other resistance bc, until no current can be detected in D. When this condition is attained, the ratio of the resistances in the bridge arms, i.e., ab to ac, is equal to the ratio of bd to dc. The resistance in ab is that of the cell C, i.e., R_c, and that in the arm ac is the known resistance R, so that

$$\frac{R_c}{R} = \frac{bd}{dc}.$$

By observing the ratio bd/dc at the point of balance of the bridge, when no current passes through D, the value of R_c can be derived directly, since R is known.

For approximate measurements, an induction coil may be used as the source S of alternating current; in modern work, however, some form of vacuum-tube oscillator, with an output frequency of 1000 to 2000 cycles per sec, is almost invariably employed. The best form of detector D is a tuned telephone earpiece, but its sensitivity may be increased by means of an audio-frequency vacuum-tube amplifier. Alternatively, a cathode-ray oscilloscope may be used as a sensitive detector. Various types of cells C have been used for conductance work; Fig. 45.2, I, shows a simple cell often employed in the laboratory, while Fig. 45.2, II depicts a "dipping cell" that is useful for industrial measurements. Where accurate results are required, cells designed specially to avoid errors due to electrostatic capacity effects are used; one of these (G. Jones and G. M. Bollinger, 1931) is represented in Fig. 45.2, III. The electrodes in the cell are of stout platinum, and they are generally coated with a layer of finely divided platinum black; this tends to decrease the effect of polarization. Exceptionally pure water, known as **conductance water,** made by redistilling good distilled water in a special apparatus, should be employed in preparing solutions for conductance studies.

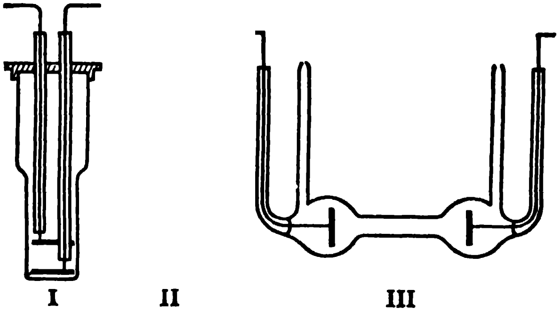


FIG. 45.2. Types of conductance cells

Instead of attempting to measure the dimensions l and a of the conductance cell, which are required for calculating the specific conductance by equation (45.4), the cell is standardized by means of a solution of known conductance. For a given cell both l and a, and hence the quantity l/a, are constant; if the constant l/a, known as the **cell constant,** is represented by k, it follows from equation (45.4) that

$$\kappa = \frac{k}{R}. \qquad (45.8)$$

A solution of potassium chloride, whose specific conductance is known accurately from measurements made in cells of known dimensions, is placed in the experimental cell and the resistance R is measured; the cell constant k for the given cell can then be calculated from equation (45.8). Once the cell constant is known, the specific conductance of any solution can be determined by measuring its resistance when filled with the given solution.

Example: The measured resistance of a cell containing exactly 0.1 g equiv. of KCl in 1000 ml at 25°C was found to be 3468.9 ohms; the specific conductance of this solution is known, with considerable accuracy, to be 0.012856 ohm^{-1} cm^{-1} at 25°C. An exactly 0.1 N solution of another substance in the same cell had a resistance of 4573.4 ohms; calculate the equivalent conductance of this electrolyte at the given concentration. (The conductance of the water is so small that it may be neglected.)

For the KCl solution, R is 3468.9 ohms and κ is 0.012856 ohm^{-1} cm^{-1}, and hence the cell constant is given by equation (45.8) as

$$k = \kappa R = 0.012856 \times 3468.9 = 44.597 \text{ cm}^{-1}.$$

Hence, for the other electrolyte,

$$\kappa = \frac{k}{R} = \frac{44.597}{4573.4} = 0.009751 \text{ ohm}^{-1} \text{ cm}^{-1}.$$

The equivalent conductance is given by equation (45.6); since the solution is exactly 0.1 N, it follows that c is 0.1000 g equiv. *per liter*, and hence

$$\Lambda = 1000\frac{\kappa}{c} = \frac{1000 \times 0.009751}{0.1000} = 97.51 \text{ ohms}^{-1} \text{ cm}^2.$$

45c. Results of Conductance Measurements.—The results of conductance measurements are usually expressed as the equivalent conductances. Some reliable values for a series of concentrations of a number of electrolytes in aqueous solution at 25°C are recorded in Table 45.1; the concentrations are in gram equiv. per liter. These data show that the equivalent conductance, and hence the conducting power of the ions in 1 gram equiv. of any electrolyte, invariably increases with decreasing concentration. The figures, however, appear to approach a limiting value in very dilute solutions. As pointed out by F. W. Kohlrausch (1885) this limiting value, which is of considerable significance, can often be obtained by extrapolating the measured equivalent conductances against the square root of the concentration. The

TABLE 45.1. EQUIVALENT CONDUCTANCES AT 25°C IN OHMS^{-1} CM^2

Concn.	HCl	NaCl	KCl	$AgNO_3$	½$BaCl_2$	½NiSO
0.0005 N	422.7	124.5	147.8	131.4	136.0	118.7
0.001	421.4	123.7	146.9	130.5	134.3	113.1
0.005	415.8	120.6	143.5	127.2	128.0	93.2
0.01	412.0	118.5	141.3	124.8	123.9	82.7
0.02	407.2	115.8	138.3	121.4	119.1	72.3
0.05	399.1	111.1	133.4	115.2	111.5	59.2
0.10	391.3	106.7	129.0	109.1	105.2	50.8

limiting equivalent conductance is represented by the symbol Λ_0, and it is called the **equivalent conductance at infinite dilution.** In a sense this expression is somewhat misleading because an infinitely dilute solution would be pure water; what is implied, however, is a solution so dilute that further dilution does not change the equivalent conductance, which then has its limiting value.

It will be seen from Table 45.1 that the equivalent conductances of substances like hydrochloric acid, alkali halides and sodium hydroxide do not change very greatly with concentration; this is also evident from Fig. 45.3 in

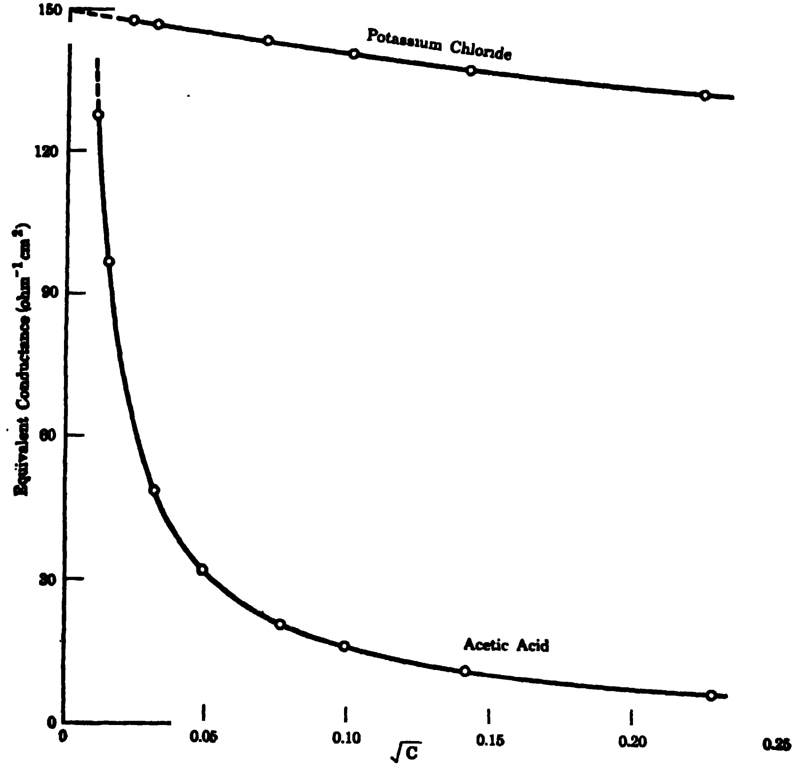


FIG. 45.3. Equivalent conductances of strong and weak electrolytes

which the equivalent conductance of potassium chloride is plotted against the square root of the concentration. Electrolytes of this type, which generally consist of solutions of strong acids and bases, and of many simple salts, are known as **strong electrolytes.** The weak acids and bases, particularly the organic carboxylic acids and amines, behave in a different manner; these are called **weak electrolytes.** An aqueous solution of acetic acid is a typical weak electrolyte, and the variation of its equivalent conductance with concentration is also shown in Fig. 45.3. The values are seen to be low at concentrations less than about 0.01 N, and then to increase very rapidly in extremely dilute solutions. It is, of course, impossible to draw a sharp distinction between strong and weak electrolytes, and many substances exhibit intermediate behavior, e.g., salts of the transition metals, such as manganese, nickel, iron, cobalt, copper, zinc, etc., particularly those of dibasic acids, such as the sulfates.

It should be pointed out that the behavior of a particular electrolyte is dependent upon the nature of *both* the solvent and solute. A particular substance which is a strong electrolyte in water may become an intermediate, or even a weak, electrolyte in a solvent of low dielectric constant. For example, tetraiosoamylammonium nitrate at a concentration of 5×10^{-4} N is a "strong" electrolyte in water ($D = 79$), its equivalent conductance being 85.1, but a "weak" electrolyte, with an equivalent conductance of 0.000129 $\text{ohm}^{-1}\ \text{cm}^2$ in dioxane ($D = 2.2$). According to Coulomb's law, the force of electrostatic attraction between two oppositely charged particles is inversely proportional to the dielectric constant of the medium separating the charges. In a solvent of high dielectric constant, such as water, the attraction between ions of opposite charge is small; hence, the ions are relatively free to carry the electric current. In a medium of low dielectric constant, however, e.g., below about 30, the ions attract one another so strongly, that they are much less free to move under the influence of an applied E.M.F. It is thus possible to account qualitatively for the change in behavior of a given electrolyte in solvents of different dielectric constants; a more quantitative treatment of this subject is described below.

45d. The Interionic Attraction Theory.—When the theory of electrolytic dissociation was first enunciated by S. Arrhenius (1887) to account for the abnormal colligative properties of salt solutions (§ 26b), the decrease of equivalent conductance with increasing concentration was attributed to the diminution in the extent to which the salt was dissociated into ions in solution. In other words, the falling off in the equivalent conductance was ascribed to a decrease in the degree (or fraction) of ionization as the concentration of the solution was increased. The conductance of a solution of a given solute depends on two factors, namely, the number of ions and their speeds. In supposing that the changes in equivalent conductance were due to the variation in the degree of ionization, the responsibility for the change was placed entirely upon the number of ions produced from 1 gram equiv. of electrolyte. The tacit assumption is involved, therefore, that the speeds of the ions do not vary appreciably with the concentration. Although this may be approximately true for weak electrolytes, it is certainly not the case for strong electrolytes. The data in Table 44.1, showing the variation of transference numbers with concentration, imply a variation of the ionic speeds. It follows, therefore, that the dependence of the speeds of the ions on the concentration of the solution must be, at least partly, responsible for the change in the equivalent conductance.

The view widely adopted at the present time is that *strong electrolytes*, such as the halides and nitrates of the alkali and alkaline earth halides, *are completely ionized at all reasonable concentrations.* This postulate is in harmony with the electronic theory of valence (§ 16b) and with the results obtained from the study of crystals of salts by X-rays (§ 18c). It is now generally accepted that even in the solid state a salt consists of positive and negative ions held together by forces of electrostatic attraction, and that the molecule, as such, does not exist in the crystal. It is reasonable to suppose, therefore, that when a salt is dissolved in water, the ions, which already exist in the solid, become free to move and conduct electricity. It follows then that substances having ionic lattices, i.e., the strong electrolytes, may be regarded as being completely ionized in solution at all reasonable concentrations.

If this is the case, the variation of equivalent conductance with concentration cannot be ascribed to a change in the number of ions obtained from 1 gram equiv. of electrolyte, for this is constant; the degree of ionization, in other words, is equal to unity at all concentrations. The falling off in the equivalent conductance must then be due to a decrease in ionic velocity with increasing concentration. This is the basis of the **interionic attraction theory** of electrolytic conductance; the theory is applicable to all types of electrolytes, but its importance lies particularly in connection with strong electrolytes. The basis of the theory in its simplest terms is that in a dilute solution the ions are relatively far apart, and so they exert little influence upon one another. As the concentration is increased, however, and the ions come closer together, the attraction between ions of opposite charge results in a decrease of their speeds, and consequently in the equivalent conductance of the solution.

The quantitative treatment of the theory of interionic attraction is due mainly to the work of P. Debye and E. Hückel (1923), and of L. Onsager (1926). The fundamental idea underlying the deductions is that as a consequence of the electrical attraction between positive and negative ions, there are, on the average, more ions of unlike sign than of like sign in the neighborhood of any ion. Every ion may, therefore, be regarded as being surrounded by a centrally symmetric **ionic atmosphere** having a resultant charge whose sign is opposite to that of the ion itself. When an E.M.F. is applied, so that the ions are caused to move, the oppositely charged ionic atmospheres take some time to readjust themselves; the result is that the ion tends to move away from its atmosphere, Fig. 45.4. Since the ion and its atmosphere have opposite charges, there is an electrostatic attraction between them which slows down the motion of the ion. This effect on the speed of an ion is known as the **asymmetry (or relaxation) effect,** because it arises from a lack of

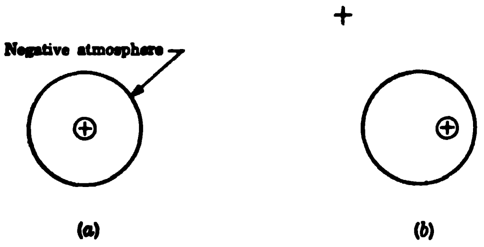


FIG. 45.4. Origin of the asymmetry effect. (*a*) Symmetric ionic atmosphere in absence of applied E.M.F. (*b*) Asymmetric atmosphere with applied E.M.F.

symmetry in the atmosphere of a moving ion, resulting from the slowness of readjustment (or relaxation) of the ionic atmosphere.

It was predicted by P. Debye and K. Falkenhagen (1928) that the existence of the asymmetry effect should lead to a variation of the conductance of a solution with the frequency of the alternating current source used in its measurement. At the low frequencies, about 10^3 cycles per sec, ordinarily used, the oscillations of the field are sufficiently slow so that the asymmetry (or distortion) of the ionic atmosphere can oscillate with the alternations of the applied field. If the frequency is increased sufficiently, the alternations will occur too rapidly for any distortion to take place and so the asymmetry effect will be virtually absent. Consequently, the retarding force on the ions due to the asymmetry effect will disappear at high frequencies of the alternating current and the conductance of the solution should be greater than at lower frequencies. This phenomenon, known as the **dispersion of conductance,** has been observed experimentally. Up to frequencies of about 10^6 cycles per sec, the conductance is independent of frequency, but at higher frequencies it increases toward a limiting value representing complete absence of the asymmetry effect. The greater the concentration of the solution and the charge of the ions, the higher the frequency at which the increase in conductance first becomes apparent.

Another factor which results in a retardation of the ionic motion is the tendency of the applied E.M.F. to move the oppositely charged ionic atmosphere, with its associated molecules of water of hydration, in a direction opposite to that in which the central ion is moving. An additional retarding influence, equivalent to an increase in viscosity of the solvent, is thus exerted on the moving ion, since the atmosphere tends to drag the ion with it. This is known as the **electrophoretic effect,** because it is somewhat analogous to that opposing the movement of a colloidal particle in an electric field (§ 55e).

By expressing the magnitudes of these effects in terms of properties of the ions and the solvent, and assuming ionization to be complete, the following equation was derived for a uni-univalent strong electrolyte, that is, an electrolyte like potassium chloride which yields two univalent ions in solution, viz.,

$$\Lambda = \Lambda_0 - \left[\frac{82.4}{(DT)^{1/2}\eta} + \frac{8.20 \times 10^5}{(DT)^{3/2}} \Lambda_0\right]\sqrt{c}, \tag{45.9}$$

where D is the dielectric constant of the solvent, η is its viscosity, and T is the absolute temperature; c is the concentration of the solution in moles per liter or gram equiv. per liter, since they are identical in this case. It is seen that equation (45.9), generally known as the **Onsager equation,** accounts for the falling off in the equivalent conductance Λ from the limiting value Λ_0 with increasing concentration of the electrolyte. The first term in the brackets is due to the electrophoretic effect, while the second represents the asymmetry effect; the sum multiplied by the square root of the concentration gives the difference between Λ_0 and Λ at any concentration.

Of the two terms the first is the larger, except for solutions of acids; thus, for 0.001 N potassium chloride at 25°C, the equivalent conductance is 2.95 $\text{ohms}^{-1}\ \text{cm}^2$ less than at infinite dilution and 1.90 of this is calculated to be due to the electrophoretic effect.

It should be noted that the dielectric constant D appears in the denominator of both terms; this means that in solvents of lower dielectric constant, such as methanol, ethanol, nitromethane, acetonitrile, etc., the equivalent conductance usually falls off with concentration more rapidly than in water. This conclusion is in general agreement with the experimental fact, referred to earlier, that a strong electrolyte approaches the behavior of a weak electrolyte in a solvent of low dielectric constant.

By writing A and B in place of the two quotients in equation (45.9), this becomes

$$\Lambda = \Lambda_0 - (A + B\Lambda_0)\sqrt{c}, \tag{45.10}$$

where A and B are constants for a given solvent that depend only on the temperature. For water at 25°C, A is 60.20 and B is 0.229, so that for solutions of strong uni-univalent electrolytes in water the theoretical treatment leads to the result

$$\Lambda = \Lambda_0 - (60.2 + 0.229\ \Lambda_0)\sqrt{c} \tag{45.11}$$

at 25°. This means that the plot of the equivalent conductance Λ against the square root of the concentration, i.e., $\sqrt{c}$, should give a straight line of slope $60.2 + 0.229\ \Lambda_0$. Such has been found to be the case for dilute solutions of a number of strong uni-univalent electrolytes, as the results in Fig. 45.5 indicate. The experimental data are represented by the small circles, while the dashed lines give the theoretical slopes as derived from equation (45.11); the agreement is seen to be excellent up to concentrations of about 2×10^{-3} gram equiv. per liter.

In more concentrated solutions deviations begin to occur, as may be seen from the figure; these are due to approximations and simplifications made in the derivation of the Onsager equation (45.9). The problem of the quantitative treatment of solutions of even moderate concentrations is too difficult to be possible at present. Nevertheless, the fact that the theoretical equa-

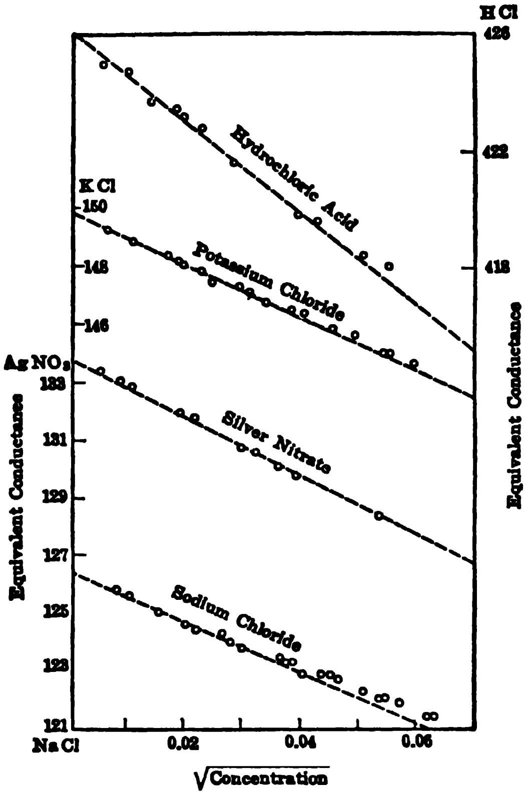


FIG. 45.5. Test of the Onsager equation

tion has been found satisfactory in dilute solutions, suggests that the fundamental postulates of complete ionization of strong electrolytes and of the mutual interaction of the ions in solution, as stated above, provide a sound basis for the interpretation of the variation of equivalent conductance with concentration.

45e. Incomplete Dissociation.—For certain electrolytes, the plot of Λ against $\sqrt{c}$ is approximately linear, but the slope is appreciably greater than would be expected from the Onsager equation. In these cases the conductance is less than required by theory, and it appears that not all the ions are available for carrying the current. A fraction α, called the **degree of dissociation** of the electrolyte, may be defined as *the fraction of the solute which is dissociated into ions that are free to carry current* at a given concentration. The appropriate form of equation (45.10) is then

$$\Lambda = \alpha[\Lambda_0 - (A + B\Lambda_0)\sqrt{\alpha c}]. \qquad (45.12)$$

This equation is particularly applicable to intermediate electrolytes, such as those consisting of ions of high valence, and to solutions in solvents of low dielectric constant. Since A, B and Λ_0 may be regarded as known, it should be possible to solve equation (45.12) in order to evaluate the degree of dissociation α of the electrolyte at any concentration c. In practice it is found convenient to do this by means of a series of approximations, because equation (45.12) involves $\alpha^{3/2}$, and so it is effectively of the third order.

For weak electrolytes, such as the weak organic acids and bases, the degree of dissociation is small, and the factor $\sqrt{\alpha c}$ in equation (45.12) is less than 0.01. Further, since the quantity $A + B\Lambda_0$ lies between 80 and 150 for most electrolytes, it follows that the correction term $(A + B\Lambda_0)\sqrt{\alpha c}$ is generally not more than 1.5 for a weak electrolyte. The equivalent conductance at infinite dilution Λ_0 is about 250 and 400 ohms^{-1} cm^2 for bases and acids, respectively, and so the value of the correction term is negligible in comparison; thus, equation (45.12) can be reduced to the simple, but somewhat approximate, form

$$\Lambda = \alpha\Lambda_0$$

for a weak electrolyte. The degree of dissociation is then given by

$$\alpha = \frac{\Lambda}{\Lambda_0}. \tag{45.13}$$

It may be pointed out that this result is equivalent to the assumption, made by Arrhenius in the early development of the ionic theory, that the falling off in equivalent conductance with concentration is due solely to incomplete dissociation of the solute into ions, and not to changes in the velocities of the latter. It can be seen from the foregoing arguments, however, that this is true only when the electrolyte is so weak, and hence the concentration αc of free ions is so small, that the correction term $(A + B\Lambda_0)\sqrt{\alpha c}$ in equation (45.12) is negligible. This term allows for the decrease of ionic velocity due to ionic interaction, and in weak electrolytes this is evidently so small that the speeds of the ions may be regarded as remaining almost constant.

It should be emphasized that equation (45.13) is applicable to weak electrolytes only; it cannot be used to calculate the degree of dissociation of strong, moderately strong, or intermediate electrolytes, for which the interionic attraction term is appreciable. For such solutions, the fraction Λ/Λ_0 is given the noncommittal name of the **conductance ratio.** It is only for weak electrolytes that the conductance ratio is *approximately* equal to the degree of dissociation; for accurate values of α, it is always necessary to employ the more complete equation (45.12).

Example: The equivalent conductance Λ of an aqueous solution of 1.0283×10^{-3} g equiv. acetic acid per liter is 48.15 ohms^{-1} cm^2 at 25°; Λ_0 is 390.7 ohms^{-1} cm^2. Calculate the degree of dissociation, from equation (45.12), and compare the result with the conductance ratio. The constants A and B for water at 25°C are 60.2 and 0.229.

For weak and moderately weak electrolytes, the value of α in equation (45.12) may be derived as follows. As a first approximation, α in the correction term $\sqrt{\alpha c}$

is taken as the conductance ratio, i.e., Λ/Λ_0; in the present case this is $48.15/390.7 = 0.1232$. Substitution in equation (45.12) then gives

$$48.15 = \alpha[390.7 - (60.2 + 0.229 \times 390.7)\sqrt{0.1232 \times 1.0283 \times 10^{-3}}],$$

since Λ is 48.15 for the concentration 1.0283×10^{-3} g equiv. per liter. The value of α is thus found to be 0.1238. This is not greatly different from the conductance ratio, i.e., 0.1232, as is to be expected for a weak electrolyte.

45f. Significance of the Degree of Dissociation.—The quantity α, referred to above as the degree of dissociation, represents the fraction of the solute which yields completely free ions. The fact that α is less than unity for many electrolytes may be due to two causes; these are, however, indistinguishable as far as conductance is concerned. Although many salts undoubtedly exist in the ionic form even in the solid state, so that they may be regarded as completely, or almost completely, ionized at all reasonable concentrations, *the ions are not necessarily free to move independently.* As a result of electrostatic attraction, ions of opposite sign may form a certain proportion of what are termed **ion-pairs**; these are not definite molecules, but they behave as if they were nonionized molecules. Any particular ion-pair has a temporary existence only, for there is a continual interchange between the various ions in the solution; nevertheless, at any instant a number of oppositely charged ions will be paired off in this manner, and so are made unavailable for carrying the electric current. In cases of this kind α will be less than unity, and *the electrolyte will be incompletely dissociated, in spite of the fact that it is completely ionized.*

It is thus seen to be essential to distinguish between "dissociation" and "ionization," a distinction which was not evident in the Arrhenius theory. The term "ionization" applies to the total number of ions, irrespective of whether they are free or are held in ion-pairs; "dissociation," on the other hand, refers only to the ions that are free to carry current. The free ions are, of course, still subject to the effects of the ionic atmosphere which results in a retardation of their velocities with increasing concentration. These effects, it must be understood, are quite distinct from, and additional to, the formation of ion-pairs.

For strong electrolytes, such as alkali and alkaline earth halides and nitrates, in particular, the ionization is complete, and there are no covalent, nonionized molecules, even though dissociation may be incomplete in fairly concentrated solutions. A solution of sodium chloride, for example, probably contains no actual nonionized NaCl molecules, although there may be transient ion-pairs (Na^+Cl^-) held together by electrostatic forces. Weak electrolytes, and also many intermediate electrolytes, however, exist to some extent in the form of nonionized molecules. A solution of acetic acid, for instance, contains neutral covalent molecules of CH_3COOH, as well as acetate (CH_3COO^-) and hydrogen (H^+) ions; some of these may be held together as ion-pairs ($CH_3COO^-H^+$). The degree of dissociation α represents the fraction of the acetic acid present as free ions capable of carrying the current; the remaining fraction $1 - \alpha$ includes both nonionized molecules and ion-pairs. Neither of these is able to transport electricity, and so the ordinary conductance measurements cannot differentiate between them.

Both theoretical and experimental observations suggest that *the extent of formation of ion-pairs for a given ionic concentration is greater the smaller the size of the ions, the higher their valence, and the lower the dielectric constant of the solvent.* The size of the ion referred to is its effective size in solution, which includes molecules of solvent; this may differ considerably from the size of the bare ion, as seen in § 44d. It follows, therefore, that hydration in aqueous solution, or solvation in general, is an important factor in ion-pair formation.

In solvents of low dielectric constant, where the force of attraction between ions of opposite sign is large, there is an increased tendency for the occurrence of ion-pairs. There are reasons for believing that even **ion-triplets** or **triple ions,** involving the association of three ions, are formed in sufficiently concentrated solutions. These triple ions, e.g. $(M^+A^-M^+)$, or $(A^-M^+A^-)$, formed from the simple ions M^+ and A^- differ from the ion-pairs (M^+A^-) in having a net charge; they are consequently able to conduct the electric current. The existence of such triple ions accounts for the observation that the equivalent conductances of some electrolytes in solvents of low dielectric constant pass through a minimum, and then increase with increasing concentration (Fig. 45.6). The initial decrease is due partly to the increased formation of nonconducting ion-pairs. As the concentration is increased, the latter are converted into conducting triple ions; consequently the equivalent conductance passes through a minimum and then increases.

45g. The Independent Conductance of Ions.—In the so-called state of infinite dilution, all forces of interaction between the ions will have ceased to exist; both ionization and dissociation are then complete, and all the ions that can possibly be derived from the given electrolyte are free to carry current. It is evident that if any relationships exist between the equivalent conductances of different electrolytes, these are the conditions under which they can best be studied. If the Λ_0 values for the sodium and potassium salts of the same anion are examined, it will be found that there is a constant difference, irrespective of the nature of the anion; the following results, for example, were obtained at 18°C:

KCl	$\Lambda_0 = 130.0$ ohms^{-1} cm^2	KNO_3	$\Lambda_0 = 126.3$ ohms^{-1} cm^2
NaCl	108.9	$NaNO_3$	105.2
Difference	21.1	Difference	21.1

The same difference of 21.1 ohms^{-1} cm^2 is found for the equivalent conductances at infinite dilution of any pair of sodium and potassium salts of the same anion. Analogous results have been obtained with other pairs of salts, having either a cation or an anion in common. The conclusion to be drawn from these observations, as pointed out by F. W. Kohlrausch (1875), is that *at infinite dilution, each ion makes a definite contribution toward the equivalent conductance of an electrolyte,* irrespective of the nature of the other ion with which it is associated in the solution. The value of *the equivalent conductance*

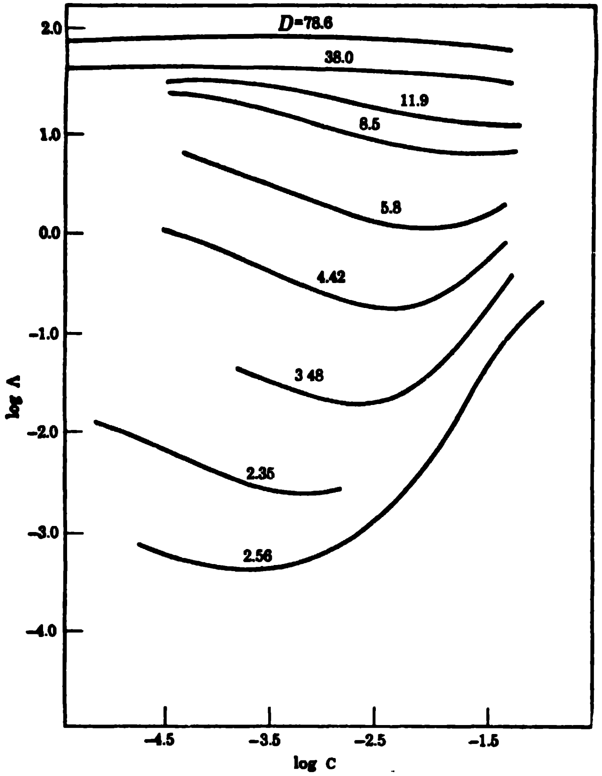


FIG. 45.6. Influence of dielectric constant on conductance. Tetraisoamylammonium nitrate in mixtures of water and dioxane at 25°C

of any electrolyte at infinite dilution is thus made up of the sum of two independent factors, one characteristic of each ionic species; hence,

$$\Lambda_0 = \lambda_+ + \lambda_-, \tag{45.14}$$

where λ_+ and λ_- (Greek: *lambda*) are known as the **ion conductances** of cation and anion, respectively, at infinite dilution. The ion conductance is a definite constant for each ion in a given solvent, the value depending only on the temperature.

The ion conductances can be determined by a method of trial and error, from the known equivalent conductances at infinite dilution, obtained from experimental data. A more satisfactory procedure, however, is to make use of the measured transference numbers. The ability of an electrolyte to transport current, and hence its conductance, is determined by the product of the total charge carried by the ions and their speeds. For equivalent solutions at infinite dilution, where ionization is complete, the total charge of the ions is constant, and hence the limiting equivalent conductance of an electrolyte must depend only on the ionic velocities. If the total conductance is the sum of the individual ion conductances, as expressed by equation (45.14), it follows that the ion conductance must be directly proportional to the ionic speed; thus,

$$\lambda_+ = ku_+ \qquad \text{and} \qquad \lambda_- = ku_- \tag{45.15}$$

$$\Lambda_0 = \lambda_+ + \lambda_- = k(u_+ + u_-), \tag{45.16}$$

where k is a universal constant for all electrolytes. It must be understood, of course, that the λ and u values in these equations refer to infinite dilution. From equations (45.15) and (45.16) it follows immediately that

$$\frac{\lambda_+}{\Lambda_0} = \frac{u_+}{u_+ + u_-} = t_+ \qquad \text{and} \qquad \frac{\lambda_-}{\Lambda_0} = \frac{u_-}{u_+ + u_-} \quad t_-, \tag{45.17}$$

which may be written in the general form

$$\frac{\lambda_0}{\Lambda_0} = t_0 \qquad \text{or} \qquad \lambda_0 = t_0\Lambda_0, \tag{45.18}$$

where the zero subscripts have been inserted to emphasize the fact that infinite dilution is to be understood. It can thus be seen that the ion conductance of any ion can be obtained from a knowledge of Λ_0 for an electrolyte containing that ion, and its transference number in the same electrolyte extrapolated to infinite dilution.

By utilizing the best conductance and transference number data at 25°C the ion conductances quoted in Table 45.2 have been obtained. It should be noted that since these are actually *equivalent* ion conductances, symbols such as $\frac{1}{2}Ba^{+2}$ and $\frac{1}{2}SO_4^{-2}$ are employed.

TABLE 45.2. ION CONDUCTANCES AT INFINITE DILUTION AT 25°C

Cation	λ_+	Anion	λ_-
H^+	349.81 ohms^{-1} cm^2	OH^-	198.6 ohms^{-1} cm^2
K^+	73.50	Br^-	78.14
NH_4^+	73.55	I^-	76.84
Ag^+	61.90	Cl^-	76.35
Na^+	50.10	NO_3^-	71.46
Li^+	38.68	ClO_4^-	67.36
$\frac{1}{2}Ba^{+2}$	63.63	HCO_3^-	44.50
$\frac{1}{2}Mg^{+2}$	53.05	$\frac{1}{2}SO_4^{-2}$	80.02

Attention may be called to the fact that although the ion conductance is a definite property of the ion, and is independent of the nature of the solute of which it is a part, the transference number of a given ion varies with the electrolyte. The reason for this apparent anomaly is that the transference number is the fraction of the current carried by the given ion, and this obviously depends on the nature of the other ion present in the solution. Thus, the value of t_0 for a given ion, e.g., the chloride ion, in equation (45.18) varies from one chloride to another; however, the limiting conductances Λ_0 of these chlorides vary correspondingly in an inverse manner, so that the product $t_0\Lambda_0$, which gives λ_0 for the chloride ion, remains constant.

45h. Application of Ion Conductances.—An important use of ion conductances is to determine the limiting conductances at infinite dilution of certain electrolytes which cannot be, or have not been, evaluated from direct experimental data. For example, with a weak electrolyte the extrapolation to infinite dilution is very uncertain (see Fig. 45.3), and with sparingly soluble salts the range of measurements is too small for extrapolation to be possible. The value of Λ_0 in these cases can, however, be obtained by adding the ion conductances. The equivalent conductance of acetic acid at infinite dilution, for instance, is the sum of the conductances of the hydrogen and acetate ions; the former is derived from a study of strong acids and the latter from measurements on acetates. It is therefore possible to write

$$\begin{aligned}\Lambda_{0(\mathrm{CH_3COOH})} &= \lambda_{\mathrm{H^+}} + \lambda_{\mathrm{CH_3COO^-}}\\ &= 349.8 + 40.9 = 390.7 \text{ ohms}^{-1}\text{ cm}^2 \text{ at } 25^\circ\text{C.}\end{aligned}$$

The same result can be derived in another manner which is often convenient, since it avoids the necessity of separating the conductance of an electrolyte into the contributions of its constituent ions. The limiting equivalent conductance of any electrolyte, that is, $\Lambda_{0(\mathrm{MA})}$, is equal to $\lambda_{\mathrm{M^+}} + \lambda_{\mathrm{A^-}}$; consequently,

$$\begin{aligned}\Lambda_{0(\mathrm{MCl})} + \Lambda_{0(\mathrm{NaA})} - \Lambda_{0(\mathrm{NaCl})} &= (\lambda_{\mathrm{M^+}} + \lambda_{\mathrm{Cl^-}}) + (\lambda_{\mathrm{Na^+}} + \lambda_{\mathrm{A^-}}) - (\lambda_{\mathrm{Na^+}} + \lambda_{\mathrm{Cl^-}})\\ &= \lambda_{\mathrm{M^+}} + \lambda_{\mathrm{A^-}} = \Lambda_{0(\mathrm{MA})},\end{aligned}$$

so that

$$\Lambda_{0(\mathrm{MA})} = \Lambda_{0(\mathrm{MCl})} + \Lambda_{0(\mathrm{NaA})} - \Lambda_{0(\mathrm{NaCl})}, \tag{45.19}$$

where $\Lambda_{0(\mathrm{MCl})}$, $\Lambda_{0(\mathrm{NaA})}$ and $\Lambda_{0(\mathrm{NaCl})}$ are the equivalent conductances at infinite dilution of the chloride of the metal M, i.e., MCl, of the sodium salt of the anion A^-, i.e., NaA, and of sodium chloride, respectively. Any convenient anion may be used instead of the chloride ion, and similarly the sodium ion may be replaced by another metallic cation or by the hydrogen ion.

45i. Ionic Mobilities.—The actual velocity of an ion is proportional to the **potential gradient**, that is, to the applied E.M.F. divided by the distance between the electrodes. For a potential gradient of 1 volt per cm the velocity is called the **ionic mobility**. The limiting value at infinite dilution can be related to the ionic conductance as follows. Consider a cube of 1 cm edge containing a dilute solution of an electrolyte of concentration c g equiv. per liter and specific conductance κ ohms^{-1} cm^{-1}. By definition, κ is also the actual conductance of the solution in the 1 cm cube and so its resistance is $1/\kappa$ ohms. If an E.M.F. of 1 volt is applied, so that the potential gradient is 1 volt per cm, then Ohm's law shows that the current strength will be κ amperes. From equation (45.6) this is seen to be $\Lambda c/1000$ amperes.

The magnitude of this current can be calculated in another manner. If

u_+ and u_- cm per sec are the mobilities of the cations and anions, respectively, then these represent the distance the corresponding ions will move under the given potential gradient. Since the cube has a cross section of 1 sq cm, the cations in a volume u_+ cc and all the anions in u_- cc will be transported in opposite directions per second. Since the dilute (completely ionized) solution contains c/1000 g equiv. of each ion per cc, and each g equiv. carries one faraday, i.e., F coulombs of electricity, the total quantity of electricity carried by the ions is $F(u_+ + u_-)c/1000$ coulombs per sec. This is the magnitude of the current in amperes, so that

$$F(u_+ + u_-)c/1000 = \Lambda c/1000$$

or

$$F(u_+ + u_-) = \Lambda.$$

For an infinitely dilute solution, Λ may be replaced by the sum of the ionic conductances, so that

$$F(u_+ + u_-) = \lambda_+ + \lambda_-$$

or, in general, for either ion

$$u_0 = \frac{\lambda_0}{F}, \tag{45.20}$$

where u_0 and λ_0 are the limiting values of the ionic mobility and the ionic conductance. Some values of ionic mobilities calculated from equation (45.20), using the ion conductances in Table 45.2, are given in Table 45.3.

TABLE 45.3. CALCULATED IONIC MOBILITIES AT 25°C

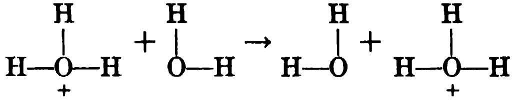
Cations	Mobility (cm per sec)	Anions	Mobility (cm per sec)
Hydrogen	36.2×10^{-4}	Hydroxyl	20.5×10^{-4}
Potassium	7.61	Sulfate	8.27
Barium	6.60	Chloride	7.91
Sodium	5.19	Nitrate	7.40

It will be observed that, apart from hydrogen and hydroxyl ions, most ions have mobilities of about 6×10^{-4} cm per sec at 25°C, under unit potential gradient. Increasing the temperature increases the speeds of nearly all ions by about 2 per cent per degree.

Example: A potential of 5.60 volts is applied to two electrodes placed 9.80 cm apart; how far would an NH_4^+ ion be expected to move in 1 hr in a dilute solution of an ammonium salt at 25°C?

The ion conductance for NH_4^+ is 73.4 ohms^{-1} cm^2 at 25° from Table 45.2; hence, the mobility is $73.4/96{,}500 = 7.61 \times 10^{-4}$ cm per sec. The potential gradient in the problem is $5.60/9.80 = 0.571$ volt per cm, and so the actual velocity of the NH_4^+ ion is $7.61 \times 10^{-4} \times 0.571 = 4.34 \times 10^{-4}$ cm per sec. In 1 hr, i.e., 3600 sec, the distance moved by the ion in dilute solution, i.e., approximately infinite dilution, would be $4.34 \times 10^{-4} \times 3600 = 1.56$ cm.

The exceptionally high mobilities, and ionic conductances, of the hydrogen and hydroxyl ions have been ascribed to an unusual type of conductance mechanism. The great affinity of the proton (or H^+) for a water molecule suggests that the hydrogen ion in water is, at least, $H^+(H_2O)$ or H_3O^+. When a hydrogen ion approaches a water molecule, a proton can be readily transferred in the manner shown below.

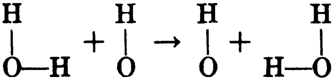


$$\mathrm{H{-}\overset{\overset{H}{|}}{\underset{+}{O}}{-}H} + \mathrm{\overset{\overset{H}{|}}{O}{-}H} \rightarrow \mathrm{H{-}\overset{\overset{H}{|}}{O}} + \mathrm{H{-}\overset{\overset{H}{|}}{\underset{+}{O}}{-}H}$$

The water molecule which remains then rotates and is ready to receive another proton. The process of proton transfer can continue through the solution and as a result there is a transfer of positive charge, toward the cathode, which is superimposed on the normal motion of the hydrogen ion in the electric field.

The additional conductivity is referred to as **Grotthuss conduction,** after T. von Grotthuss who proposed a somewhat similar mechanism for the electrical conductivity of solutions in general in 1806. The hydrogen ion also exhibits abnormal mobilities and ionic conductances in methyl and ethyl alcohol solutions in which the Grotthuss mechanism is possible. In acetone, however, where the transfer of protons in this manner cannot occur, the conductance and mobility are normal.

The high mobility of the hydroxyl ion in water is attributed to a similar proton transfer mechanism; a proton now passes from a water molecule to the hydroxyl ion



$$\mathrm{\overset{\overset{H}{|}}{O}{-}H} + \mathrm{\overset{\overset{H}{|}}{O}} \rightarrow \mathrm{\overset{\overset{H}{|}}{O}} + \mathrm{H{-}\overset{\overset{H}{|}}{O}}$$

so that there is an effective transfer of the negative charge. This is in addition to the normal transport of the hydroxyl ions in the electric field. It will be noted that in both cases illustrated above the proton moves from left to right, based on the assumption that the negative electrode (cathode) is at the right. The positive charge is, of course, transferred in the same direction, but the negative charge, on the hydroxyl ion, is seen to move in the opposite direction, as successive water molecules to the left transfer a proton and become hydroxyl ions.

Ionic mobilities have been determined by direct experiment, utilizing a principle similar to that employed in the moving boundary method for transference numbers. The concentrations of the solutions must be adjusted so that the potential gradient is uniform; the rate of movement of the boundary then gives the speed of the ion under the influence of this potential gradient. From the result the ionic mobility, i.e., the speed for a gradient of 1 volt per cm, can be calculated. The values obtained in this manner are in satisfactory agreement with those recorded in Table 45.3, derived from the ion conductances. The latter, of course, refer to infinite dilution, and hence the experimental results, which are obtained in solutions of finite concentration, will be somewhat lower.

45j. Determination of Solubilities by Conductance Measurements. —If a sparingly soluble electrolyte ionizes in a simple manner, it is possible to calculate its solubility from conductance measurements. If s is the solubility, in gram equiv. per liter, of a given salt, and κ is the specific conductance of the saturated solution, then the equivalent conductance, according to equation (45.6), is given by

$$\Lambda = 1000 \frac{\kappa}{s}. \tag{45.21}$$

If the salt is sparingly soluble the saturated solution will be so dilute that Λ will not differ appreciably from the limiting value at infinite dilution; it is thus possible to write

$$\Lambda_0 = 1000 \frac{\kappa}{s},$$

$$s = 1000 \frac{\kappa}{\Lambda_0}. \tag{45.22}$$

In these dilute solutions the conductance of the water is an appreciable part of the total; hence, it must be subtracted from the total conductance to give the contribution of the ions of the salt required in equation (45.22).

Since the specific conductance κ can be determined by experiment, and Λ_0 can be derived from the ion conductances, as shown in § 45h, it is possible to calculate the solubility of the salt. This method for determining solubilities can be used only if the solute undergoes simple dissociation into ions of known conductance. Further, the saturated solution must be dilute and dissociation must be virtually complete, so that the actual equivalent conductance is not appreciably different from the limiting value. The preliminary solubility values obtained in this manner are used to make an estimate of the equivalent conductance, by means of the Onsager equation (45.11), to determine the validity of the assumption concerning complete dissociation. If the discrepancy is larger than the experimental error, the Onsager value is used to recalculate the solubility by means of equation (45.21).

Example: For a saturated solution of AgCl at 25°C, κ was found to be 3.41×10^{-6} ohm^{-1} cm^{-1}; the value of κ for the water used to make up the solution was 1.60×10^{-6} ohm^{-1} cm^{-1}. Determine the solubility of AgCl in water, in moles per liter, at 25°C.

The actual specific conductance of the AgCl is the difference between the values for the saturated solution and for the water; hence, κ for the AgCl is $(3.41 - 1.60) \times 10^{-6}$, i.e., 1.81×10^{-6} ohm^{-1} cm^{-1}. The Λ_0 for AgCl at 25° is 138.3 ohms^{-1} cm^2, as found from the ion conductances of Ag^+ and Cl^-; hence, by equation (45.22),

$$s = \frac{1000 \times 1.81 \times 10^{-6}}{138.3} = 1.31 \times 10^{-5} \text{ g equiv. per liter.}$$

In this case g equiv. and moles are identical; the preliminary value of the solubility of AgCl is therefore 1.31×10^{-5} mole per liter at 25°. For this concentration and $\Lambda_0 = 138.3$ the Onsager equation (45.11) gives a value of 138.0 for Λ. Since this differs from Λ_0 in the fourth significant figure only, the effect on the calculated solubility is within the experimental error.

45k. Conductance Titrations.—If a solution of a strong acid is gradually neutralized by a strong base, e.g., sodium hydroxide, the hydrogen ions of the former are replaced by the metal ions, e.g., Na^+ ions, having a much lower conductance (Table 45.2). The conductance of the solution will therefore decrease steadily as the base is added. When neutralization is complete the further addition of alkali causes an increase of conductance since the excess base contributes additional ions to the solution. It follows, therefore, that the variation of the conductance with the addition of alkali will be of the form shown in Fig. 45.7, I, the minimum corresponding to the equivalence point, i.e., the theoretical end point, of the neutralization. It is evident from these curves that conductance measurements can be used to determine the equivalence point in a strong acid-base titration. The conductance is measured at six or eight points, after the addition of known amounts of alkali; two lines are then drawn through these points in a plot of the conductance against the quantity of alkali added, as in Fig. 45.7. The intersection of the lines gives the required end point. If the alkali solution is much more concentrated than, e.g., about ten times, that of the acid there is little volume change, and these lines are virtually straight. It is thus possible to determine the end point by making four observations, two each side of the equivalence point, and drawing two straight lines through the points.

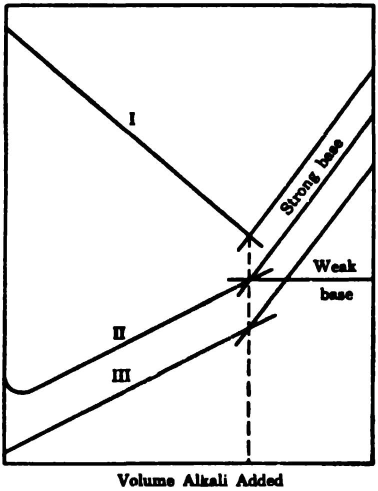


FIG. 45.7. Conductance titrations

When a moderately weak acid, e.g., acetic acid, is neutralized by a strong base the initial conductance is low, and after a small decrease which is sometimes observed, the conductance increases; this is because the salt formed, e.g., sodium acetate, is a strong electrolyte and hence is more highly ionized than the weak acid. At the equivalence point there is a further increase of conductance, since the strong base is an even better conductor than the salt because of the high conductance of the hydroxyl ion. The variation of conductance with the addition of alkali is similar to that in Fig. 45.7, II. If the acid is very weak, e.g., boric acid or phenol, the initial decrease of conductance upon neutralization is not observed, the titration curves being of the type shown in Fig. 45.7, III. In each case the end point is given by the intersection of two (almost) straight lines, provided the volume change is kept small, as stated above. When titrating a weak or very weak acid the sharpness of the intersection at the end point may be improved by using a weak base for neutralization. Such a base has a very small conductance, and so the curve is almost horizontal after the equivalence point has been attained (Fig. 45.7).

The conductance method can be used to determine the end point in the titration of a salt of a weak acid, e.g., sodium acetate, by a strong acid, e.g., hydrochloric acid. As the reaction proceeds the strong electrolyte sodium acetate is replaced by sodium chloride which has approximately the same conductance; the conductance of the solution thus remains almost constant, since the contribution of the acetic acid is negligibly small. When the equivalence point is reached the conductance commences to increase rapidly because of the free strong (hydrochloric) acid that is now present. Precipitation titrations, e.g., the addition of sodium chloride to silver nitrate, or the reverse, may also be followed by conductance measurements. Since the solubility of silver chloride is low, its contribution to the conductance is extremely small; the conductance of the solution thus remains almost constant until the equivalence point is reached, and then it commences to increase. In each instance the end point can be ascertained from the intersection of two straight lines.

The conductometric titration procedure has many advantages. It can be used for the analysis of dilute solutions, provided no extraneous electrolytes are present, and also for very weak acids, when other methods of titration fail. Mixtures of strong and weak acids, and colored solutions can be readily titrated by the conductance method. Since the end point is determined graphically there is no need to take special precautions as the equivalence point is approached, as in ordinary titrations. Finally, it is not necessary to measure the actual conductance of the solution; any quantity that is proportional to the conductance, e.g., the reading on a conductance bridge or resistance box, is adequate. This may be plotted against the volume of titrant, as in Fig. 45.7.

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PROBLEMS

1. How long would it take to plate an area of 25.0 cm² with a layer of copper 0.10 mm thick using a current of 0.500 amp? The density of copper may be taken as 8.96 g cm^{-3}.

2. In the electrolysis of a solution containing cuprous copper, nickel and zinc complex ions, a deposit of metal weighing 0.175 g was found to contain 72.8% Cu, 4.3% Ni and 22.9% Zn. Assuming 100% efficiency for the electrolysis, determine the number of coulombs which passed through the solution.

3. Anthracene can be oxidized anodically to anthraquinone according to the equation $C_{14}H_{10} + 2H_2O = C_{14}H_8O_2 + 6H^+ + 6\epsilon$. What weight of anthraquinone will be produced by 0.5 amp in 4 hours?

4. A 1.0 N solution of potassium chloride containing 7.1474 g KCl per 100 g solution, was electrolyzed using a Ag anode and AgCl cathode. After the passage of 0.03 amp for 19.5 hours, 2.4835 g of silver was deposited in a coulometer in series with the apparatus. The anode solution weighing 121.41 g was found to contain 6.5100 g KCl per 100 g of solution and the cathode solution weighing 125.66 g contained 7.7671 g of the salt per 100 g of solution. Calculate the transference number of the K^+ from the data for each solution.

5. A solution of lithium chloride containing 0.86356 g of salt per 100 g of water was electrolyzed using a Ag anode and AgCl cathode. At the end of the run 1.37588 g of silver had been deposited in a coulometer. The anode solution, weighing 124.894 g, contained 0.72899 g of salt per 100 g of water and the cathode solution, weighing 123.456 g, contained 1.00032 g of salt per 100 g of water. Calculate the transference number of lithium ion from the data for each solution.

6. A conductance cell with a constant of 2.485 cm^{-1} is filled with a KCl solution for which $\Lambda = 141.3$ ohm^{-1} cm² at 25°C. If the specific conductance of the water is 1.0×10^{-6} ohm^{-1} cm^{-1}, what was the resistance of the solution?

7. The equivalent conductance of sodium lactate solutions varies with concentration as follows:

$c \times 10^3$, mole l^{-1}	0.1539	0.3472	0.6302	1.622	2.829	4.762
Equiv. cond.	87.89	87.44	86.91	85.80	84.87	83.78

(*a*) Estimate Λ_0 by a suitable plot of the data. (*b*) Compare the experimental slope of the curve with the value required by the Onsager equation. (*c*) Determine Λ_0 for lactic acid.

8. From data available in this chapter, determine the transference number at 25°C of the Cl^- ion in an infinitely dilute solution of (*a*) NaCl, (*b*) KCl.

9. The equivalent conductance of a 0.05 N barium chloride solution is 111.5 at 25°C. Determine the ion conductance and mobility of the barium and chloride ions.

10. In a moving boundary experiment with 0.02 N NaCl using an autogenic rising boundary from a cadmium anode, a current of 0.0016001 amp was passed through the solution in a tube of 0.1115 cm² cross section. The times taken for the boundary to move various distances were as follows:

Distance, cm	0	1.00	3.00	6.00	8.00	10.00
Time, sec	0	344	1036	2070	2757	3454

Determine the transference number of the sodium ion.

11. The boundary between a 0.0998 N solution of gadolinium chloride and a lithium chloride solution swept through a volume of 1.111 cm³ in 4406 sec, using a current of 5.594×10^{-3} amp. Calculate the transference number of the Gd^{+3} ion.

12. When water with a specific conductance of 1.12×10^{-6} ohm^{-1} cm^{-1} was saturated at 25°C with barium sulfate the value rose to 4.63×10^{-6} ohm^{-1} cm^{-1}. Determine the solubility of $BaSO_4$ at this temperature.

13. When 100 ml of a HCl solution was titrated with 1.045 N NaOH, the following data were obtained:

NaOH added, ml	0	1.00	2.00	3.00	4.00	5.00
Resistance, ohms	2564	3521	5650	8065	4831	3401

Determine the normality of the acid.

13

Electromotive Force

GALVANIC CELLS

46a. E.M.F. and Its Measurement.—A **galvanic** or **voltaic cell** consists essentially of two electrodes combined in such a manner that when they are connected by a conducting material, such as a metallic wire, an electric current will flow. Each electrode, in general, involves an electronic (metallic) and an electrolytic conductor in contact; at the surface of separation between the metal and the solution there exists a difference of electrical potential, called the **electrode potential.** The E.M.F. of the cell is then equal to the algebraic sum of the two electrode potentials, appropriate allowance being made, as described later, for the sign of each potential difference.

For reliable measurement of the E.M.F. of a galvanic cell it is necessary to use some form of potentiometer, the essential principle of which can be understood from Fig. 46.1. A "working cell" C of constant E.M.F., generally a storage cell, is connected across the conductor AB of fairly high resistance. The cell X, which is being studied, is connected to A so that its E.M.F. opposes that of C, and through a galvanometer G to a contact D which can be moved along AB. The position of D is adjusted until no current flows through the galvanometer; the fall of potential between A and D due to the working cell C is then exactly compensated by the E.M.F. of the experimental cell X, that is, E_X. By means of a suitable switch the cell X is now replaced by a standard cell S, of accurately known E.M.F., equal to E_S, and the contact is adjusted

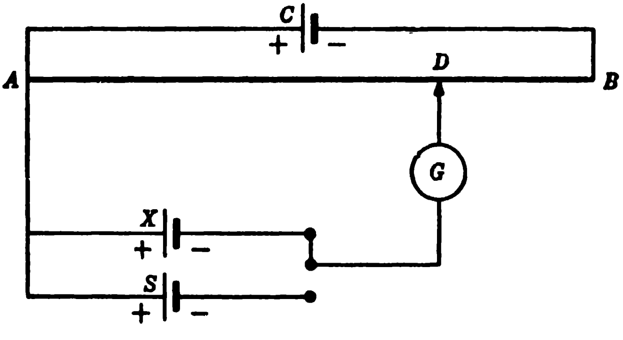

FIG. 46.1. Measurement of E.M.F.

until a point of balance is reached at D' (not shown in the figure). The fall of potential between A and D' is consequently equal to E_S. The fall of potential between A and any point on AB is proportional to the resistance of that part of the conductor; it follows, therefore, that

$$\frac{E_X}{E_S} = \frac{\text{Fall of potential between } A \text{ and } D}{\text{Fall of potential between } A \text{ and } D'}$$

$$= \frac{\text{Resistance of } AD}{\text{Resistance of } AD'}.$$

In its simplest form, AB may be a uniform wire; then the resistances AD and AD' are proportional to the lengths AD and AD'. With the ratio of the resistances AD to AD' determined, and since E_S, the E.M.F. of the standard cell is known, the E.M.F. of the experimental cell, E_X, can be calculated.

The majority of E.M.F. measurements at the present time are made by means of special potentiometers, operating on the foregoing principle, which can be purchased from instrument makers. In these, the conductor AB consists of a number of resistance coils with a movable contact, together with a slide wire for fine adjustment. After calibration with a standard cell, the E.M.F. of the cell being studied can be read directly from the instrument with an accuracy of 0.1 millivolt, i.e., 10^{-4} volt, or better.

The standard cell that is widely employed for E.M.F. measurements is some form of the **Weston cell**; it is highly reproducible, its E.M.F. remains constant over long periods of time, and it has a small temperature coefficient. In order to retain constancy of E.M.F. while in use, only very minute currents should be drawn from the cell, as is actually done if the potentiometer is operated properly. In the normal Weston cell the negative electrode consists of a 12.5 per cent cadmium amalgam in a saturated solution of cadmium sulfate, $3CdSO_4 \cdot 8H_2O$, and the positive electrode is mercury, covered with solid mercurous sulfate, in the same solution; the cell is represented by the formulation

$$12.5\% \text{ Cd in Hg} | 3CdSO_4 \cdot 8H_2O(s) | \text{saturated solution of } CdSO_4 | Hg_2SO_4(s) | Hg.$$

This is an example of the conventional method for depicting the characteristics of a galvanic cell which will be used frequently in the present chapter. Vertical lines indicate boundaries between phases or between solutions of different composition or concentration. The concentrations of solutions are usually indicated, since they generally affect the E.M.F. of the cell. Although the symbol (c) is now used to represent the solid (crystalline) state in thermochemical equations (Chapter 3), it is still the custom to employ (s) in electrochemical representations.

The Weston cell is usually set up in an H-shaped vessel, as shown in Fig. 46.2, connection to the cadmium amalgam and mercury electrodes being made by platinum wires sealed through the glass. The E.M.F. of the normal Weston cell is 1.018636 absolute volts at 20.0°C, and it decreases by the small amount of 4×10^{-5} volt for every degree rise of temperature. For ordinary laboratory work, an "unsaturated" Weston cell is often employed; it contains a solution of cadmium sulfate saturated at 4.0°C, and consequently unsaturated at room temperatures. The E.M.F. of this cell lies within the range 1.0188 to 1.0198 volts, depending upon the exact condition of manufacture, and the variation with temperature is so small as to be negligible.

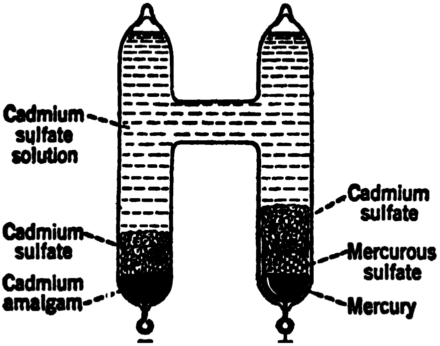

FIG. 46.2. The Weston standard cell

46b. Reversible Cells.—During the operation of a galvanic cell a chemical reaction takes place at each electrode, and it is the energy of these reactions that provides the electrical energy of the cell. If there is an overall chemical reaction, the cell is referred to as a **chemical cell.** In some cells, however, there is no resultant chemical reaction, but there is a change of energy due to the transfer of solute from one concentration to another; such cells are called **concentration cells.**

In order that the electrical energy produced by a galvanic cell may be related thermodynamically to the process occurring in the cell, it is essential that the latter should behave reversibly in the thermodynamic sense. A **reversible cell** must satisfy the following conditions. If the cell is connected to an external source of E.M.F. which is adjusted so as exactly to balance the E.M.F. of the cell, i.e., so that no current flows, there should be no chemical or other change in the cell. If the external E.M.F. is decreased by an infinitesimally small amount, current will flow from the cell, and a chemical or other change, proportional in extent to the quantity of electricity passing, should take place. On the other hand, if the external E.M.F. is increased by a very small amount, the current should pass in the opposite direction, and the process occurring in the cell should be exactly reversed.

It may be noted that galvanic cells can be expected to behave reversibly only when the currents passing are infinitesimally small, so that the system is always virtually in equilibrium (§ 6f). If large currents flow, concentration gradients arise within the cell because diffusion is relatively slow; in these circumstances the cell cannot be regarded as existing in a state of equilibrium. It is important to recall, in this connection, that in the potentiometric method of measuring E.M.F.'s, described above, an infinitesimal or zero current is drawn from the cell at the point of balance. The E.M.F. obtained in this way is as close to the reversible value as is experimentally possible. If an attempt had been made to determine the E.M.F. with an ordinary voltmeter, which takes an appreciable current, the result would have been in error.

A familiar instance of a reversible cell is the **Daniell cell,** consisting of a zinc electrode immersed in an aqueous solution of zinc sulfate, and a copper electrode in copper sulfate solution, viz.,

$$\mathrm{Zn} \mid \mathrm{ZnSO_4\ soln.} \mid \mathrm{CuSO_4\ soln.} \mid \mathrm{Cu},$$

the two solutions being usually separated by a porous partition. Provided there is no spontaneous diffusion through this partition, and the electrodes are not attacked by the solutions when the external circuit is open, this cell behaves in a reversible manner. If the external circuit is closed by an E.M.F. just less than that of the Daniell cell, the chemical reaction taking place in the cell is

$$\mathrm{Zn} + \mathrm{Cu^{+2}} = \mathrm{Zn^{+2}} + \mathrm{Cu},$$

i.e., zinc dissolves from the zinc electrode to form zinc ions in solution, while copper ions are discharged and deposit copper on the other electrode. On the other hand, if the external E.M.F. is slightly greater than that of the cell, the reverse process occurs; the copper electrode dissolves while metallic zinc is deposited on the zinc electrode.

46c. Reversible Electrodes.—The electrodes constituting a reversible cell are **reversible electrodes**, and three chief types of such electrodes are known; *the combination of any two reversible electrodes gives a reversible cell.* The first type of reversible electrode involves a *metal or a nonmetal in contact with a solution of its own ions*, e.g., zinc in zinc sulfate solution, or copper in copper sulfate solution, as in the Daniell cell. The nonmetals which, at least in principle, yield reversible electrodes are hydrogen, oxygen and the halogens, the corresponding ions being hydrogen, hydroxyl and halide ions, respectively. Since the electrode materials in these cases are nonconductors, and often gaseous, finely divided platinum or other unattackable metal, which comes rapidly into equilibrium with the hydrogen, oxygen, etc., is employed for the purpose of making electrical contact (see § 48c). Electrodes of the first kind are reversible with respect to the ions of the electrode material, e.g., metal, hydrogen, oxygen or halogen. If the electrode material is a univalent metal or hydrogen, represented by M, the electrode and the reaction which takes place when the cell of which it is part operates, are then represented by

$$\mathrm{M} \mid \mathrm{M^+} \qquad \text{and} \qquad \mathrm{M} \rightleftharpoons \mathrm{M^+} + \epsilon,$$

where ϵ indicates an electron, and $\mathrm{M^+}$ implies a *hydrated* (*or solvated*) *ion in solution.* The direction of the reaction depends on the direction of the flow of current through the cell. If the electrode material is a univalent nonmetal A, the ions are negative, and the corresponding representations are

$$\mathrm{Pt} \mid \mathrm{A^-} \mid \mathrm{A} \qquad \text{and} \qquad \mathrm{A^-} \rightleftharpoons \mathrm{A} + \epsilon.$$

Since nonmetals taking part in electrode reactions are not electrical conductors, a suitable inert metal, frequently platinum, is used as part of the electrode system. It serves to make electrical connection between the electrode and the remainder of the cell. This is why the symbol Pt is used in representing the $A^- \mid A$ electrode.

Electrodes of the second type involve *a metal and a sparingly soluble salt of this metal in contact with a solution of a soluble salt of the same anion;* an example is the important electrode consisting of silver, solid silver chloride and a solution of a soluble chloride, such as hydrochloric acid, viz.,

$$\mathrm{Ag} \mid \mathrm{AgCl}(s) \mid \mathrm{HCl\ soln.}$$

The electrode reaction in this case may be written as

$$\mathrm{Ag}(s) + \mathrm{Cl}^- \rightleftharpoons \mathrm{AgCl}(s) + \epsilon,$$

the chloride ion being that in the solution of the soluble chloride, e.g., hydrochloric acid. These electrodes behave as if they were reversible with respect to the common anion, namely, the chloride ion in this case. Electrodes of the second type have been made with other insoluble halides, e.g., silver bromide and iodide, and mercurous chloride, and also with insoluble sulfates, oxalates, etc.

The third important type of reversible electrode consists of *an unattackable metal, e.g., gold or platinum, immersed in a solution containing both oxidized and reduced states of an oxidation-reduction system,* e.g., Sn^{+4} and Sn^{+2}, Fe^{+3} and Fe^{+2}, or $\mathrm{Fe(CN)}_6^{-3}$ and $\mathrm{Fe(CN)}_6^{-4}$. The purpose of the unattackable metal is to act as a conductor for making electrical contact, just as in the case of a gas electrode. The oxidized and reduced states are not necessarily ionic; for example, an important type of reversible electrode to be considered later (§ 53d, II) involves the organic compound quinone, together with hydrogen ions, as the oxidized state, while the neutral molecule hydroquinone is the reduced state. Electrodes of the kind under consideration, consisting of conventional oxidized and reduced forms, are sometimes called **oxidation-reduction electrodes**; the chemical reactions taking place at these electrodes are either oxidation of the reduced state or reduction of the oxidized state, e.g.,

$$\mathrm{Pt} \mid \mathrm{Sn}^{+2}, \mathrm{Sn}^{+4} \qquad \mathrm{Sn}^{+2} \rightleftharpoons \mathrm{Sn}^{+4} + 2\epsilon$$

$$\mathrm{Pt} \mid \mathrm{Fe(CN)}_6^{-4}, \mathrm{Fe(CN)}_6^{-3} \qquad \mathrm{Fe(CN)}_6^{-4} \rightleftharpoons \mathrm{Fe(CN)}_6^{-3} + \epsilon,$$

depending upon the direction of the current. Here also, an electrical conductor, in the form of an inert metal, e.g., platinum, is part of the electrode system. In order that the electrode may behave reversibly it is essential that the system contain *both* oxidized and reduced states.

The three types of reversible electrodes described above differ formally as far as their construction is concerned; nevertheless, they are all based on the same fundamental principle which it is important to understand clearly. *A reversible electrode always involves an oxidized and a reduced state,* using the terms "oxidized" and "reduced" in their broadest sense; thus, oxidation refers to the liberation of electrons while reduction implies the taking up of electrons. If the electrode consists of a metal M and its ions M^+, the former is the reduced state and the latter is the oxidized state; similarly, for an anion electrode, the A^- ions are the reduced state while A represents the oxidized state. In the silver-silver chloride electrode, the metallic silver and the chloride ions together form the reduced state of the system while silver chloride is the oxidized state. It can be seen, therefore, that all three types of reversible electrode are made up from the reduced and oxidized states of a given system, and in every case the electrode reaction may be written in the general form

$$\text{Reduced State} \rightleftharpoons \text{Oxidized State} + n\epsilon,$$

where n is the number of electrons by which the oxidized and reduced states differ.

46d. Reactions in Reversible Cells.—In a reversible cell, consisting of two reversible electrodes, a flow of electrons, and hence a flow of current, can be maintained only if oxidation occurs at one electrode and reduction at the other electrode. According to the convention widely adopted, *the* E.M.F. *of the cell is positive when in its normal operation oxidation takes place at the left-hand electrode of the cell as written*, reduction occurring at the right-hand electrode. If the reverse is the case, so that reduction takes place at the left-hand electrode, the E.M.F. of the cell, by convention, will have a negative sign.

The Daniell cell, represented by

$$\text{Zn} \mid \text{M ZnSO}_4 \text{ soln.} \mid \text{M CuSO}_4 \text{ soln.} \mid \text{Cu},$$

has an E.M.F. of 1.10 volt, and by the convention its sign is positive. This means that when the cell operates oxidation occurs at the left-hand electrode; that is to say, metallic zinc atoms are being oxidized to form zinc ions in solution, i.e.,

$$\text{Zn} = \text{Zn}^{+2} + 2\epsilon.$$

At the right-hand electrode there must, therefore, be reduction of the cupric ions, from the copper sulfate solution, to copper atoms, i.e.,

$$\text{Cu}^{+2} + 2\epsilon = \text{Cu}.$$

The electrons liberated at the zinc electrode travel along the external connecting circuit and are available for the discharge (reduction) of the cupric ions at the copper electrode. The complete cell reaction, obtained by adding the separate electrode reactions, is consequently

$$\text{Zn} + \text{Cu}^{+2} = \text{Zn}^{+2} + \text{Cu},$$

as stated in § 46b. Since two electrons are involved for each zinc (or copper) atom taking part in the reaction, the whole process as written, with quantities in gram atoms or gram ions, takes place for the passage of two faradays of electricity.*

When writing the reaction taking place in a cell for which the sign of the E.M.F. is not stated, the convention is to assume that the sign is positive; thus, the oxidation is supposed to take place at the left-hand electrode. Consider, for example, the cell

$$H_2(g) \mid \text{HCl soln.} \mid AgCl(s) \mid Ag(s),$$

consisting of a hydrogen electrode at the left, and a silver-silver chloride electrode at the right, both in contact with the same solution of hydrochloric acid. Hydrogen gas is oxidized to hydrogen ions, at the left-hand electrode, viz.,

$$\tfrac{1}{2}H_2(g) = H^+ + \epsilon,$$

and silver chloride is reduced to silver at the right-hand electrode, viz.,

$$AgCl(s) + \epsilon = Ag(s) + Cl^-,$$

so that the complete reaction, with quantities in moles, gram ions or gram atoms, is

$$\tfrac{1}{2}H_2(g) + AgCl(s) = H^+ + Cl^- + Ag(s)$$

for the passage of one faraday. The H^+ and Cl^- ions, of course, represent hydrochloric acid in the aqueous solution.

If the cell just considered were written in the reverse direction, viz.,

$$Ag(s) \mid AgCl(s) \mid \text{HCl soln.} \mid H_2(g),$$

then, according to the convention, the cell reaction would be exactly opposite to that derived above, namely

$$H^+ + Cl^- + Ag(s) = \tfrac{1}{2}H_2(g) + AgCl(s).$$

In this case, it is presumed that the solid silver and the chloride ions are oxidized to solid silver chloride at the left-hand electrode, while hydrogen ions are reduced to hydrogen gas at the right-hand electrode. The correct formulation for the normal (spontaneous) operation of the cell readily becomes apparent when its E.M.F. is measured, since there is only one way in which a cell can be properly connected to a potentiometer. The left-hand electrode in the formulation is the negative pole of the cell, in the sense referred to in the footnote.

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* The practical convention, employed in connection with cells for yielding current, e.g., Daniell cell, Leclanché cell, secondary (lead-acid or iron-nickel-alkali) cells, etc., is to call the negative pole the electrode at which the process is oxidation when the cell is producing current; the positive electrode is the one at which reduction is the spontaneous process. The reason for this is that oxidation is accompanied by the liberation of electrons, and so the electrode metal acquires a negative charge; similarly, the reduction electrode will acquire a positive charge, because electrons are taken up from it. The subject will be considered further in § 48d.

FREE ENERGY CHANGES IN CELLS

47a. Free Energy and E.M.F.—It was seen in § 9a that the free energy change accompanying a process is equal to the reversible work, other than that due to a volume change, at constant temperature and pressure. When a reversible cell operates, producing an infinitesimal current, the electrical work is thermodynamically reversible in character, and does not include any work due to a volume change. Further, since the temperature and pressure remain constant, *it is possible to identify the electrical work done in a reversible cell with the free energy change accompanying the chemical or other process taking place in the cell.* The work done in a cell is equal to the product of the E.M.F. and the quantity of electricity passing. The practical **unit of electrical energy** is defined as the energy developed when one coulomb is passed under the influence of an E.M.F. of one volt; this unit is called the **volt-coulomb,** and is equivalent to 1 absolute joule or 10^7 ergs. The calorie defined by the U. S. Bureau of Standards is equivalent to 4.1840 abs. joules, and hence 1 volt-coulomb is equivalent to 1/4.1840, i.e., 0.2390 (defined), calorie.*

If the E.M.F. of a reversible cell is E volts, and the process taking place is associated with the passage of n faradays, i.e., nF coulombs, the electrical work done *by* the system is consequently nFE volt-coulombs or joules. The corresponding increase of free energy is equal to the electrical work done *on* the system; it is consequently possible to write

$$\Delta F = -nFE. \tag{47.1}$$

For a reaction to occur spontaneously, at constant temperature and pressure, ΔF must, of course, be negative and equation (47.1) shows that the E.M.F. must then be positive. Hence, if a cell is formulated to correspond to a positive value of the E.M.F., the cell reaction will be spontaneous. A negative E.M.F. would indicate that the assumed reaction will not occur spontaneously, the reverse reaction, however, would be spontaneous. A case in point is the cell given in the last paragraph of § 46d. This has a negative E.M.F. at all reasonable concentrations of hydrochloric acid. It follows, therefore, as is well known, that silver will not dissolve in hydrochloric acid to liberate hydrogen. But the reverse reaction, i.e., the reduction of solid silver chloride by hydrogen, can take place spontaneously.

It should be noted that the E.M.F. of a cell is an intensive property of the system concerned; it is independent of the size of the cell in which a particular reaction occurs. The free energy change, on the other hand, is an extensive property of the type described in § 6c. It depends, as equation (47.1) shows, on nF, the number of coulombs, i.e., the quantity of electricity, passing through the cell. In other words, the actual free energy change in the cell is determined by the E.M.F. and also by the extent to which the cell reaction occurs. The general practice is to express the value of the free energy change

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* Data published before 1948 are based on the international joule (or volt-coulomb); the conversion relationship is 1 calorie = 4.1833 int. joules.

for the quantities involved in the chemical equation used to express the cell reaction. This point must not be overlooked (see § 48f).

The identification of the free energy change of a chemical reaction with the electrical work done when the reaction takes place in a reversible cell can be justified experimentally in the following manner. By the Gibbs-Helmholtz equation (9.34),

$$\Delta F = \Delta H + T\left(\frac{\partial(\Delta F)}{\partial T}\right)_P,$$

where ΔH is the change in enthalpy accompanying the cell reaction; if ΔF is replaced by $-nFE$, the result is

$$-nFE = \Delta H - nFT\left(\frac{\partial E}{\partial T}\right)_P$$

$$\Delta H = -nF\left[E - T\left(\frac{\partial E}{\partial T}\right)_P\right] \tag{47.2}$$

It is seen from equation (47.2) that if the E.M.F. of the reversible cell, i.e., E, and its temperature coefficient $\partial E/\partial T$, at constant pressure, are known, it is possible to evaluate the enthalpy change of the reaction occurring in the cell. As seen in § 7a, this is numerically equal to the heat of reaction at constant pressure. Further, since $\Delta F = \Delta H - T\Delta S$, the same measurements can be used to calculate the entropy change of the process.

Example: The E.M.F. of the cell, which is independent of the concentration of the KCl solution,

$$\mathrm{Ag} \mid \mathrm{AgCl}(s) \mid \mathrm{KCl\ soln.} \mid \mathrm{Hg_2Cl_2}(s) \mid \mathrm{Hg},$$

is +0.0455 volt at 25°C, and the temperature coefficient is $+3.38 \times 10^{-4}$ volt per degree. What is the reaction taking place in the cell, and what are the enthalpy and entropy changes at 25°C?

Since the E.M.F. is positive, oxidation occurs at the left-hand electrode, viz.,

$$\mathrm{Ag}(s) + \mathrm{Cl^-} = \mathrm{AgCl}(s) + \epsilon,$$

while at the right-hand electrode the mercurous chloride is reduced to mercury, thus

$$\tfrac{1}{2}\mathrm{Hg_2Cl_2}(s) + \epsilon = \mathrm{Hg} + \mathrm{Cl^-},$$

so that the complete cell reaction for 1 faraday is

$$\mathrm{Ag}(s) + \tfrac{1}{2}\mathrm{Hg_2Cl_2}(s) = \mathrm{AgCl}(s) + \mathrm{Hg}.$$

For this particular cell, E is +0.0455 volt, and $\partial E/\partial T$ is $+ 3.38 \times 10^{-4}$ volt degree^{-1}; since the reaction as written requires 1 faraday, n is equal to 1. These values may be inserted into equation (47.2), and if F is taken as 96,500 coulombs, ΔH will be in volt-coulombs, i.e., joules; to convert to calories it is then necessary to multiply by 0.2390. Consequently at 25°C, when T is $273 + 25 = 298$°K,

$$\Delta H = -1 \times 96{,}500 \times 0.2390(0.0455 - 298 \times 3.38 \times 10^{-4})$$
$$= 1270 \text{ calories, i.e., } 1.27 \text{ kcal.}$$

It can be seen from equation (47.2) that

$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P$$

and so

$$\Delta S = 1 \times 96{,}5000 \times 0.2390 \times 3.38 \times 10^{-4} \text{ cal deg}^{-1}$$
$$= 7.8 \text{ e.u.}$$

An alternative procedure would be to calculate ΔF and ΔS and then determine ΔH by the relationship $\Delta F = \Delta H - T\Delta S$.

Some of the results obtained in the calculation of enthalpy changes from E.M.F. measurements at 25°C are recorded in Table 47.1; the values derived from direct thermochemical determinations are given for purposes of comparison. The agreement between the results for ΔH derived from E.M.F. measurements and from thermal data is seen to be satisfactory. It is probable, in fact, that the former are more accurate than the latter.

TABLE 47.1. ENTHALPY AND FREE ENERGY CHANGES FROM E.M.F. MEASUREMENTS

Cell Reaction	E volt	$\partial E/\partial T$ $\times 10^4$	ΔH kcal E.M.F.	ΔH kcal Thermal	ΔF kcal
$Cd + PbCl_2 = CdCl_2 + Pb$	0.1880	−4.80	−15.25	−14.65	−8.67
$Cd + 2AgCl = CdCl_2 + 2Ag$	0.6753	−6.50	−40.08	−39.53	−31.15
$Pb + 2AgCl = PbCl_2 + 2Ag$	0.4900	−1.86	−25.16	−24.17	−22.60
$Pb + Hg_2Cl_2 = PbCl_2 + 2Hg$	0.5356	+1.45	−22.72	−20.10	−24.72

In the last column of the table are given the free energy changes for the reactions as written, derived from the measured E.M.F. and equation (47.1) with $n = 2$ in each case. It is seen that when the temperature coefficient is negative, the free energy change, i.e., the energy available to perform work (other than work of expansion), is less than the enthalpy change, i.e., the total energy produced in the reaction. The difference in energy is given up to the surroundings during the reaction. When the coefficient is positive, the free energy change is the larger; the surroundings must then supply the energy for the additional work performed.

47b. E.M.F.'s of Reversible Cells.—The free energy change accompanying a given reaction depends on the concentrations or, more accurately, the activities, of the reactants and the products, as was seen in Chapter 10. It is evident, therefore, that the E.M.F. of a reversible cell, in which a particular reaction takes place when producing current, will vary with the activities of the substances present in the cell. The exact connection can be readily derived in the following manner. Suppose the general reaction

$$aA + bB + \cdots \rightleftharpoons lL + mM + \cdots$$

occurs in a reversible cell; the corresponding free energy change is then given by equation (30.7), viz.,

$$\Delta F = \Delta F^0 + RT \ln \frac{a_L^l \times a_M^m \times \cdots}{a_A^a \times a_B^b \times \cdots}, \tag{47.3}$$

where a_A, a_B, $\cdots$, a_L, a_M, $\cdots$, now represent the activities of A, B, $\cdots$, L, M, $\cdots$, *as they occur in the reversible cell.* If, as in § 35a, the arbitrary reaction quotient, in terms of activities, is represented by the symbol Q_a, then equation (47.3) may be written as

$$\Delta F = \Delta F^0 + RT \ln Q_a. \tag{47.4}$$

As before, ΔF^0 is the free energy change when all the substances taking part in the cell reaction are in their standard states.

If E is the E.M.F. of the cell under consideration when the various substances have the arbitrary activities a_A, a_B, $\cdots$, a_L, a_M, $\cdots$, as given above, and the reaction as written occurs for the passage of n faradays, it follows from equation (47.1) that ΔF, as given by equations (47.3) or (47.4), is also equal to $-nFE$. Further, if the E.M.F. of the reversible cell is E^0 when all the substances involved are in their standard states, then ΔF^0 is equal to $-nFE^0$. Substituting these values for ΔF and ΔF^0 into equation (47.4), and dividing through by $-nF$, the result is

$$E = E^0 - \frac{RT}{nF} \ln Q_a. \tag{47.5}$$

This expression is seen to relate the E.M.F. of a cell to the activities of the substances taking part; E^0, the standard E.M.F., is a constant for the given cell reaction, varying only with the temperature, at 1 atm pressure.

The foregoing results may be illustrated by reference to the cell

$$H_2(g) \mid \text{HCl soln.} \mid AgCl(s) \mid Ag,$$

for which, as seen above, the cell reaction is

$$\tfrac{1}{2}H_2(g) + AgCl(s) = H^+ + Cl^- + Ag(s)$$

for the passage of one faraday. The reaction quotient in terms of activities is

$$Q_a = \frac{a_{H^+} \times a_{Cl^-} \times a_{Ag}}{a_{H_2}^{1/2} \times a_{AgCl}},$$

but since the silver and the silver chloride are present in the solid state, their activities are unity, in accordance with the convention referred to in § 33a; hence,

$$Q_a = \frac{a_{H^+} \times a_{Cl^-}}{a_{H_2}^{1/2}}.$$

Inserting this expression into equation (48.5), with n equal to unity, the E.M.F. of the cell is given by

$$E = E^0 - \frac{RT}{F} \ln \frac{a_{H^+} \times a_{Cl^-}}{a_{H_2}^{1/2}}. \tag{47.6}$$

The E.M.F. is thus seen to be dependent upon the activities of the hydrogen and chloride ions in the solution of hydrochloric acid, and of the hydrogen gas in the cell.

REVERSIBLE ELECTRODE POTENTIALS

48a. Single Electrode Potentials.—There is at present no known method whereby the potential of a single electrode can be measured; it is only the difference in potential of two electrodes, i.e., the E.M.F. of a cell made by combining the electrodes, that can be determined experimentally. However, by choosing an arbitrary zero of potential, much as the freezing point of water is chosen as the zero of the Celsius temperature scale, it is possible to assign a potential to the individual electrodes. *The arbitrary zero of potential is taken as the potential of a reversible hydrogen electrode, with gas at 1 atm pressure, in a solution of hydrogen ions of unit activity.* This particular electrode, viz., $\mathrm{Pt} \mid \mathrm{H_2}(1\ \mathrm{atm}) \mid \mathrm{H^+}(a = 1)$, is known as the **standard hydrogen electrode,** for reasons which will be evident shortly. The convention, therefore, is to take the potential of the standard hydrogen electrode as zero; electrode potentials based on this zero are said to refer to the **hydrogen scale.** As with other electrodes involving nonmetals, platinum (or other inert conductor) is used to provide electrical contact; the surface is covered with a catalytic layer of finely divided platinum to permit rapid establishment of equilibrium between the hydrogen gas absorbed by the metal and the hydrogen ions in solution (§ 48c). If any electrode, e.g., M, M^{+n}, is combined with the standard hydrogen electrode, so as to make a complete cell, viz.,

$$\underset{E}{\mathrm{M}} \mid \mathrm{M}^{+n}\ \mathrm{soln.} \mid \mathrm{H^+}\ (a = 1) \underset{0}{\mid} \mathrm{H_2}\ (1\ \mathrm{atm}) \mid \mathrm{Pt},$$

the E.M.F. of this cell, i.e., E, is equal to the potential of the M, M^{+n} electrode on the hydrogen scale.*

In any cell which can be set up in the manner just indicated, an oxidation reaction takes place at the left-hand electrode, while the hydrogen ions are reduced to hydrogen gas at the hydrogen electrode. The oxidation process may be written in the general form given at the end of § 46c, viz.,

$$\text{Reduced state} = \text{Oxidized state} + n\epsilon,$$

and the corresponding hydrogen electrode reaction is

$$n\mathrm{H^+} + n\epsilon = \tfrac{1}{2}n\mathrm{H_2}(g).$$

The complete cell reaction for the passage of n faradays is consequently

$$\text{Reduced state} + n\mathrm{H^+} = \text{Oxidized state} + \tfrac{1}{2}n\mathrm{H_2}(g). \qquad (48.1)$$

The E.M.F. of the cell is then given by equation (47.5) as

$$E = E^0_{\mathrm{el.}} - \frac{RT}{nF} \ln \frac{(\text{Oxidized state}) \times a_{\mathrm{H_2}}^{n/2}}{(\text{Reduced state}) \times a_{\mathrm{H^+}}^{n}}, \qquad (48.2)$$

---

* Because the so-called electrode potentials are really E.M.F.'s of cells in which the potential of one electrode is arbitrarily set equal to zero, they are sometimes referred to as electrode (or half-cell) E.M.F.'s.

where parentheses have been used to represent the activities of the oxidized and reduced states as they actually occur in the cell. However, in the standard hydrogen electrode, by definition, the pressure of the gas is 1 atm, so that the activity a_{H_2} is unity (§ 35a), and the activity of the hydrogen ions a_{H^+} in the electrode is also unity. Thus equation (48.2) reduces to the simple form

$$E = E^0_{\text{el.}} - \frac{RT}{nF}\ln\frac{(\text{Oxidized state})}{(\text{Reduced state})}, \qquad (48.3)$$

E being called the **oxidation potential** *of any reversible electrode* and $E^0_{\text{el.}}$ the corresponding **standard oxidation potential,** that is, *the potential of the electrode when all the substances concerned are in their standard states of unit activity.*[*] The qualification "oxidation" is used because it describes the process taking place at the electrode; the corresponding "reduction potentials" will be considered presently.

The E.M.F. of a cell made by combining any given electrode with a standard hydrogen electrode, as represented above, may be either positive or negative depending on the nature of the electrode. If it is positive then, as seen in § 47a, the reaction (48.1) is spontaneous; the M electrode tends to lose electrons more readily than does the hydrogen electrode, i.e., the metal M oxidizes more readily than hydrogen. Conversely, negative values of the E.M.F. mean that the reverse reaction is spontaneous and that the hydrogen electrode tends to lose electrons more readily, i.e., is more easily oxidized, than the M electrode. The arrangement of electrodes in order of their oxidation potentials (see Table 48.1) thus provides a quantitative indication of their relative ease of oxidation.

48b. Expressions for Electrode Potentials.—The application of equation (48.3) may be illustrated by reference to a few simple cases of the different types of electrodes described in § 46c. Consider, first, an electrode consisting of a metal in contact with a solution of its own cations, e.g., copper in copper (cupric) sulfate solution. The electrode and oxidation reaction are

$$\text{Cu} \mid \text{Cu}^{+2} \qquad \text{and} \qquad \text{Cu} = \text{Cu}^{+2} + 2\epsilon,$$

the Cu being the reduced state and Cu^{+2} the oxidized state; in this case n is 2, and hence by equation (48.3)

$$E = E^0_{\text{el.}} - \frac{RT}{2F}\ln\frac{a_{\text{Cu}^{+2}}}{a_{\text{Cu}}}.$$

The activity a_{Cu} of the solid metal is unity, by convention, and hence

$$E = E^0_{\text{el.}} - \frac{RT}{2F}\ln a_{\text{Cu}^{+2}}, \qquad (48.4)$$

---

[*] As far as possible standard electrode potentials will be distinguished by the use of a subscript, e.g., $E^0_{\text{el.}}$, E^0_{Ag}, etc.; the standard E.M.F. of a complete cell will be indicated by E^0_{cell}.

so that the electrode potential is dependent upon the standard oxidation potential $E^0_{\text{el.}}$ of the Cu, Cu^{+2} system, and on the activity $a_{Cu^{+2}}$ of the cupric ions in the copper sulfate solution. An example of the second type of electrode is one in which a nonmetal, e.g., oxygen at 1 atm pressure, is in contact with its own anions, i.e., hydroxyl ions. The electrode and oxidation reaction are

$$\text{Pt} \mid O_2 \text{ (1 atm)} \mid OH^- \qquad \text{and} \qquad 2OH^- = \tfrac{1}{2}O_2 \text{ (1 atm)} + H_2O(l) + 2\epsilon,$$

and hence the electrode potential is given by equation (48.3) as

$$E = E^0_{\text{el.}} - \frac{RT}{2F} \ln \frac{a_{O_2}^{1/2} \times a_{H_2O}}{a^2_{OH^-}}. \qquad (48.5)$$

Since the oxygen gas is at 1 atm pressure, the activity a_{O_2} is unity, and so also is that of the water, i.e., a_{H_2O} is 1, by convention;* hence equation (48.5) becomes

$$E = E^0_{\text{el.}} - \frac{RT}{F} \ln \frac{1}{a_{OH^-}}. \qquad (48.6)$$

The third type of electrode is the so-called "oxidation-reduction" electrode, consisting of a piece of platinum or gold in contact with a solution containing both oxidized and reduced states, these terms being used in their restricted sense. A simple illustration is the ferric-ferrous system, for which the electrode and oxidation reaction are

$$\text{Pt} \mid Fe^{+2}, Fe^{+3} \qquad \text{and} \qquad Fe^{+2} = Fe^{+3} + \epsilon,$$

for the passage of one faraday. According to equation (48.3), therefore,

$$E = E^0_{\text{el.}} - \frac{RT}{F} \ln \frac{a_{Fe^{+3}}}{a_{Fe^{+2}}}, \qquad (48.7)$$

where $a_{Fe^{+3}}$ and $a_{Fe^{+2}}$ are the activities of the ferric and ferrous ions, respectively, in the given electrode solution.

Quite frequently, hydrogen ions are involved in the oxidation-reduction system, as is the case, for example, with quinone-hydroquinone; the electrode and oxidation reaction here are

$$\text{Pt} \mid H_2Q, Q \qquad \text{and} \qquad \underset{\text{hydroquinone}}{C_6H_4(OH)_2} = \underset{\text{quinone}}{C_6H_4O_2} + 2H^+ + 2\epsilon,$$

for two faradays. Writing a_{H_2Q} for the activity of the hydroquinone and

---

* Strictly speaking a_{H_2O} is equal to unity for pure water. All cells, however, and other systems of electrochemical interest, must contain electrolytes, which lower the activity of the water. According to § 26c, a_{H_2O} is equal to p/p^0, where p is the aqueous vapor pressure of the given solution and p^0 is that of water at the same temperature. For a 0.1 N solution of (total) strong electrolyte a_{H_2O} is about 0.996, and for a N solution it is approximately 0.97. Consequently, as long as the total concentration of electrolyte is not too great, e.g., 0.1 N or less, as is usually the case, a_{H_2O} is not significantly different from unity.

a_Q for that of the quinone in the electrode solution, it follows from equation (48.3) that

$$\begin{aligned} E &= E^0_{\text{el.}} - \frac{RT}{2F} \ln \frac{a_Q \times a^2_{H^+}}{a_{H_2Q}} \\ &= E^0_{\text{el.}} - \frac{RT}{2F} \ln \frac{a_Q}{a_{H_2Q}} - \frac{RT}{F} \ln a_{H^+}. \end{aligned} \tag{48.8}$$

It should be evident from the foregoing examples that it is not a difficult matter to derive the equation for the oxidation potential of any electrode; all that is necessary is to write down the electrode reaction, and then to insert the appropriate activities of *all the substances concerned* in the oxidized and reduced states into equation (48.3). The result is then simplified by using the convention of assigning unit activity to each pure liquid or solid and to each gas at 1 atm pressure. The **reduction potential** of any electrode is equal to the oxidation potential for the same electrode but *with the sign reversed.* It is thus unnecessary to write out separate formulae for reduction potentials. The procedure that is recommended is to derive the oxidation potential for the given electrode and then merely to reverse the sign. At the same time, the order of writing the electrode components is reversed. For example, the representation and reaction of the copper-cupric ion reduction electrode, would be

$$Cu^{+2} \mid Cu \qquad \text{and} \qquad Cu^{+2} + 2\epsilon = Cu,$$

and the reduction potential would be given by an equation identical with (48.4) but with the sign reversed. Similarly, for the reduction form of the ferrous-ferric electrode,

$$Fe^{+2}, Fe^{+3} \mid Pt \qquad \text{and} \qquad Fe^{+3} + \epsilon = Fe^{+2},$$

the potential is expressed by equation (48.7) with the reversed sign. It should be noted that the order of writing Fe^{+2} and Fe^{+3} in the representation of the electrode has no significance.

In every galvanic cell, oxidation occurs at one electrode and reduction at the other electrode; the equations given above give the oxidation potential, and the corresponding reduction potential is obtained by reversing the sign. *The* E.M.F. *of the complete cell is equal to the algebraic sum of the oxidation potential of one (left-hand) electrode and the reduction potential of the other (right-hand) electrode.* It follows, therefore, that the E.M.F. of the cell is equivalent to *the difference of two oxidation potentials.* As a consequence, the E.M.F. of a cell is independent of the arbitrary potential chosen as the zero of the potential scale; the actual value, whatever it may be, cancels out when taking the difference of the two oxidation potentials based on the same, e.g., hydrogen, scale. Illustrations of the calculation of the E.M.F.'s of cells from electrode potential data will be given in later sections.

48c. Reference Electrodes.—In order to measure the potential of any electrode on the hydrogen scale, all that is necessary, in principle, is to combine the electrode with a standard hydrogen electrode, i.e., one with gas at 1 atm pressure and a solution of hydrogen ions of unit activity, and to determine the E.M.F. of the resulting cell. As seen in § 48a, this value is identical with the required electrode potential. Several forms of hydrogen electrode have been designed, three of which are shown in Fig. 48.1. In each case, the platinum electrode, which may consist of a foil of 1 to 3 sq cm exposed area or a wire 2 or 3 cm in length, is coated with a deposit of finely divided metal (platinum black) by electrolysis of dilute chloroplatinic acid. Pure hydrogen gas at 1 atm pressure is bubbled through the hydrogen-ion solution in which the platinum electrode is immersed, so that about half the area is in the solution and the other half in the gas space. Electrical connection to the electrode is made by a wire attached to the platinum.

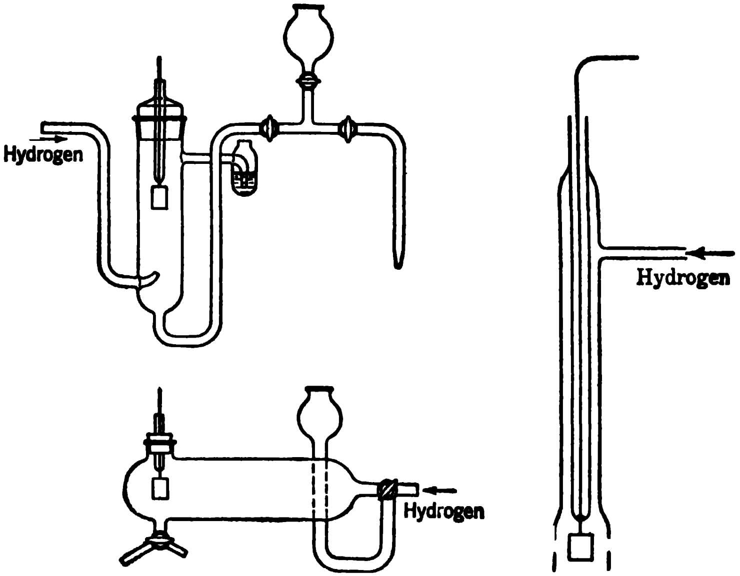

FIG. 48.1. Forms of hydrogen electrode; (*right*) Hildebrand type

The hydrogen electrode is not convenient for routine work, partly because it involves the use of a stream of gas and also because it is easily rendered inactive (or poisoned) by traces of impurities in the gas. Consequently, several secondary reference electrodes have been devised. The most common of these is the **calomel electrode**; it consists of mercury in contact with a solution of potassium chloride saturated with mercurous chloride (calomel). Three different concentrations of potassium chloride have been employed, namely 0.1 N, 1.0 N and a saturated solution. The oxidation potentials of these electrodes have been measured against the standard hydrogen electrode, so that the values are known; they are as follows on the hydrogen scale at 25°C:

Hg | $Hg_2Cl_2(s)$ | 0.1 N KCl	−0.334 volt
Hg | $Hg_2Cl_2(s)$ | 1.0 N KCl	−0.280
Hg | $Hg_2Cl_2(s)$ | Satd. KCl	−0.242.

A difficulty that arises in the determination of electrode potentials is that it is frequently necessary to have two different solutions in contact. For example, the potential of a Zn | $ZnSO_4$ soln. electrode may be measured by combining it with a calomel electrode, e.g., 0.1 N KCl | $Hg_2Cl_2(s)$ | Hg; in the resulting cell there will be a junction between two different solutions. Such a liquid-liquid contact introduces an additional potential, known as a **liquid junction potential.** In certain simple cases it is possible to calculate the value of this potential with fair accuracy, but in most instances the calculation is too difficult and uncertain to be significant. It is therefore the general practice to try to reduce the value of the liquid junction potential as much as possible, and this may be achieved by the use of a **salt bridge.** This generally consists of a tube or a convenient vessel containing a saturated solution of potassium chloride which is employed to connect the solutions in the two electrodes. It is because potassium and chloride ions have almost identical mobilities (see Table 45.3) that potassium chloride possesses the property of being able to minimize liquid junction potentials (see § 49b). When potassium chloride cannot be used, e.g., if one of the electrodes contains a silver salt, a saturated solution of ammonium nitrate is employed as a salt bridge. It is doubtful whether the potentials are ever eliminated entirely, but at least they can be reduced in magnitude so that the actual value is negligible for measurements not requiring the highest degree of accuracy. When a salt bridge is used, and it is supposed that the liquid junction potential is eliminated, a double line || is inserted between the symbols for the two solutions, e.g.,

Zn | M $ZnSO_4$ soln. || 0.1 N KCl | $Hg_2Cl_2(s)$ | Hg.

Example: The E.M.F. of the cell just given, containing molar $ZnSO_4$, was found to be 1.094 volt; determine the oxidation potential of the Zn | $ZnSO_4$ soln. electrode on the hydrogen scale.

Let E_{Zn} be the value of the required potential, i.e., of the left-hand electrode of the cell; the reduction potential of the 0.1 N KCl calomel electrode is opposite in sign to the oxidation value given above, i.e., +0.334 volt. The total E.M.F. of the cell is thus $E_{Zn} + 0.334$; hence,

$$E_{Zn} + 0.334 = 1.094, \quad \text{and} \quad E_{Zn} = +0.760 \text{ volt.}$$

The great advantage of the calomel electrode is its convenient construction; vessels of various types have been employed, some of which are shown in Fig. 48.2. In each case a small quantity of pure mercury is covered with a paste of pure mercurous chloride, mercury and potassium chloride solution.

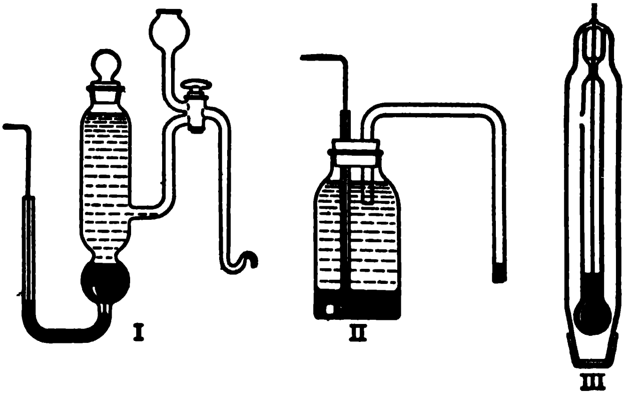

FIG. 48.2. Forms of calomel electrode

The vessel is then filled with the appropriate solution of potassium chloride which has been saturated with calomel. Electrical connection with the mercury is made by means of a platinum wire sealed into a glass tube, or through the walls of the vessel. The solution of potassium chloride is brought into contact with the other solution, e.g., in the salt bridge, by means of a siphon tube, as in Fig. 48.2, I and II. The compact form of calomel electrode (Fig. 48.2, III), as used with many commercial potentiometers, is dipped directly into the solution of the other electrode; connection between the two solutions occurs at the relatively loose ground glass joint.

For work of special accuracy where liquid junctions can be avoided by the use of a single electrolyte, e.g., a chloride solution, the silver-silver chloride electrode has been employed as a reference electrode. It usually consists of a silver wire coated with a layer of silver chloride; this is inserted directly into the solution of the chloride in the experimental electrode. The oxidation potential of the silver chloride electrode has been determined from measurements on cells consisting of this electrode combined with a hydrogen electrode in solutions of hydrochloric acid; the E.M.F. of the cell

$$\text{Ag} \mid \text{AgCl}(s) \mid \text{Cl}^- \, (a = 1) \; \text{H}^+ \, (a = 1) \mid \text{H}_2 \, (1 \text{ atm}) \mid \text{Pt}$$

has been found to be -0.2223 volt at 25°C. Since the potential of the right-hand electrode is zero, by convention, the oxidation potential of the silver chloride electrode is also -0.2223 volt; the corresponding reduction potential, with chloride ions at unit activity, is

$$\text{Cl}^- \, (a = 1) \mid \text{AgCl}(s) \mid \text{Ag}, \qquad +0.2223 \text{ volt at } 25^\circ\text{C}.$$

48d. Standard Oxidation Potentials.—According to the equations derived in § 47b, the potential of any electrode is determined by the standard potential $E^0_{\text{el.}}$, and by the activity or activities of the ions taking part in the electrode process. These activities are variable, but the standard potential is a definite property of the electrode system, having a constant value at a given temperature. The standard potentials of many electrodes have been determined, with varying degrees of accuracy, and the results have been tabulated. The principle of the method used to evaluate $E^0_{\text{el.}}$ for a given electrode system is to measure the potential E of the electrode, on the hydrogen scale, in a series of solutions of known concentration. Using the ionic concentration in place of the activity in equation (48.3) an approximate value of the standard potential is obtained for each concentration. These values are plotted against a convenient function of the concentration and the results are extrapolated to infinite dilution, where the ionic concentration is equal to the activity, to obtain the correct value of $E^0_{\text{el.}}$ at the experimental temperature. An example of the general procedure is given in § 49d. The results obtained for the **standard oxidation potentials** of a number of electrodes at 25°C are recorded in Table 48.1; the appropriate electrode process is given in each case.

TABLE 48.1. STANDARD OXIDATION POTENTIALS AT 25°C ON THE HYDROGEN SCALE

Electrode	Reaction	$E^0_{\text{el.}}$
$K \mid K^+$	$K \rightarrow K^+ + \epsilon$	+2.925 volt
$Na \mid Na^+$	$Na \rightarrow Na^+ + \epsilon$	+2.714
$Zn \mid Zn^{+2}$	$Zn \rightarrow Zn^{+2} + 2\epsilon$	+0.763
$Fe \mid Fe^{+2}$	$Fe \rightarrow Fe^{+2} + 2\epsilon$	+0.440
$Cd \mid Cd^{+2}$	$Cd \rightarrow Cd^{+2} + 2\epsilon$	+0.408
$Co \mid Co^{+2}$	$Co \rightarrow Co^{+2} + 2\epsilon$	+0.277
$Ni \mid Ni^{+2}$	$Ni \rightarrow Ni^{+2} + 2\epsilon$	+0.250
$Sn \mid Sn^{+2}$	$Sn \rightarrow Sn^{+2} + 2\epsilon$	+0.140
$Pb \mid Pb^{+2}$	$Pb \rightarrow Pb^{+2} + 2\epsilon$	+0.126
$Pt \mid \frac{1}{2}H_2(g) \mid H^+$	$\frac{1}{2}H_2 \rightarrow H^+ + \epsilon$	±0.000
$Pt \mid Sn^{+2}, Sn^{+4}$	$Sn^{+2} \rightarrow Sn^{+4} + 2\epsilon$	−0.15
$Pt \mid Cu^+, Cu^{+2}$	$Cu^+ \rightarrow Cu^{+2} + \epsilon$	−0.153
$Ag \mid AgCl(s) \mid Cl^-$	$Ag + Cl^- \rightarrow AgCl + \epsilon$	−0.2223
$Cu \mid Cu^{+2}$	$Cu \rightarrow Cu^{+2} + 2\epsilon$	−0.337
$Pt \mid Fe(CN)_6^{-4}, Fe(CN)_6^{-3}$	$Fe(CN)_6^{-4} \rightarrow Fe(CN)_6^{-3} + \epsilon$	−0.356
$Pt \mid O_2(g) \mid OH^-$	$2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2\epsilon$	−0.401
$Pt \mid I_2(s) \mid I^-$	$I^- \rightarrow \frac{1}{2}I_2 + \epsilon$	−0.5355
$Pt \mid Fe^{+2}, Fe^{+3}$	$Fe^{+2} \rightarrow Fe^{+3} + \epsilon$	−0.771
$Hg \mid Hg_2^{+2}$	$Hg \rightarrow \frac{1}{2}Hg_2^{+2} + \epsilon$	−0.789
$Ag \mid Ag^+$	$Ag \rightarrow Ag^+ + \epsilon$	−0.7991
$Pt \mid Hg_2^{+2}, Hg^{+2}$	$Hg_2^{+2} \rightarrow 2Hg^{+2} + 2\epsilon$	−0.920
$Pt \mid Br_2(l) \mid Br^-$	$Br^- \rightarrow \frac{1}{2}Br_2 + \epsilon$	−1.0652
$Pt \mid Cl_2(g) \mid Cl^-$	$Cl^- \rightarrow \frac{1}{2}Cl_2 + \epsilon$	−1.3595
$Pt \mid Ce^{+3}, Ce^{+4}$	$Ce^{+3} \rightarrow Ce^{+4} + \epsilon$	−1.61

It should be remembered that the standard potential refers to the condition in which all the substances in the cell are in their standard states of unit activity; gases such as hydrogen, oxygen and chlorine are thus at 1 atm pressure. With bromine and iodine, however, the standard states are chosen as the pure liquid and solid, respectively; the solutions are therefore saturated with these elements in the standard electrodes. For all ions the standard state of unit activity is taken as *the hypothetical ideal solution* of unit molality (see § 26c), or, in other words, a solution for which the product $m\gamma$ is unity, where m is the molality of the ion and γ its activity coefficient.

The standard reduction potentials, corresponding to the oxidation potentials in Table 48.1, but involving the reverse electrode processes, would be obtained by reversing the sign in each case; thus, for example, for the zinc electrode

$$\begin{array}{lll} \mathrm{Zn}\,|\,\mathrm{Zn}^{+2} & E^0_{\mathrm{el.}} = +0.763 \text{ volt} & \mathrm{Zn} = \mathrm{Zn}^{+2} + 2\epsilon \\ \mathrm{Zn}^{+2}\,|\,\mathrm{Zn} & E^0_{\mathrm{el.}} = -0.763 \text{ volt} & \mathrm{Zn}^{+2} + 2\epsilon = \mathrm{Zn}, \end{array}$$

whereas for the chlorine electrode

$$\begin{array}{lll} \mathrm{Pt}\,|\,\mathrm{Cl_2}(g)\,|\,\mathrm{Cl}^- & E^0_{\mathrm{el.}} = -1.3595 \text{ volt} & \mathrm{Cl}^- = \tfrac{1}{2}\mathrm{Cl_2}(g) + \epsilon \\ \mathrm{Cl}^-\,|\,\mathrm{Cl_2}(g)\,|\,\mathrm{Pt} & E^0_{\mathrm{el.}} = +1.3595 \text{ volt} & \tfrac{1}{2}\mathrm{Cl_2}(g) + \epsilon = \mathrm{Cl}^-. \end{array}$$

The reversal in sign of the standard potential also requires a change in the sign of the electrode potential, so that equation (48.3), which is

$$E_{\mathrm{ox}} = E^0_{\mathrm{ox}} - \frac{RT}{nF}\ln\frac{a_{\mathrm{ox}}}{a_{\mathrm{red}}}$$

becomes

$$E_{\mathrm{red}} = E^0_{\mathrm{red}} + \frac{RT}{nF}\ln\frac{a_{\mathrm{ox}}}{a_{\mathrm{red}}},$$

where E^0_{red} is opposite in sign to E^0_{ox}, so that E_{red} is equal in magnitude but opposite in sign to E_{ox}.

The representation of electrode processes in terms of oxidation potentials, as in Table 48.1, or sometimes in the form of reduction potentials, is based on the convention introduced by G. N. Lewis (1913). It is generally employed by physical chemists in the United States and elsewhere because it is particularly useful for the thermodynamic treatment of reactions taking place in reversible cells, such as the study of free energy changes and chemical equilibria. In this system, the sign of the potential depends upon whether there is an increase or decrease of free energy accompanying a particular reaction, e.g., the one represented in equation (48.1) when the potential is given on the hydrogen scale. Thus, since $\Delta F = -nFE$, a positive oxidation potential means that the indicated process is accompanied by a decrease of free energy, whereas a negative sign implies an increase of free energy. It is important to understand that, on this basis, the sign of the electrode potential has no direct relationship to the sign of the electrical charge on the electrode.

Analytical and practical electrochemists in the United States and many European chemists employ a different scheme for expressing the sign of the electrode potential. In the so-called European system, which is that used for giving the conventional signs to the electrodes in current-producing cells (see page 485, footnote), the sign is determined by the tendency for the metal (or conducting portion) to give up or acquire electrons. For example, the standard potential of the Zn | Zn^{+2} electrode is negative (−0.763 volt) because, when combined with a standard hydrogen electrode, the tendency is for the Zn to form Zn^{+2} ions, thus leaving the electrons on the metal which consequently has a negative charge. Correspondingly, the standard potential of the Cu | Cu^{+2} electrode is + 0.337 volt, because the tendency here is for the Cu^{+2} ions to take up electrons to form Cu atoms, thus leaving the metal with a positive charge. The positive and negative signs of the electrode potentials consequently indicate relative tendencies for electrons to be removed from or transferred to the conducting part of the electrode, but have no direct connection with the signs of the free energy changes.

It should be apparent, therefore, that, although the potentials on the two systems will be the same numerically, the signs have different meanings. By coincidence, the potentials in the European system have the same sign as reduction potentials, and so they may be treated as such, in the manner shown above. Nevertheless, it should be realized that they are not actually reduction potentials. If Benjamin Franklin, in his arbitrary assignment of the terms positive and negative to the two forms of electricity, had made the opposite choice, then the signs of all potentials in the European system including those of cell electrodes, would have been reversed. However, those used for thermodynamic (oxidation and reduction) electrode potentials would be unaffected by such a change. It should also be noted that, as seen above, the potentials on the thermodynamic scale differ in sign according as the electrode is written as M | M^+ or as M^+ | M, but in the European system the signs would be the same. It is this aspect of the situation that makes the latter less desirable for use in the application of electrode potential measurements to physiochemical problems.

48e. Applications of Electrode Potentials.—There are numerous applications of electrode potentials in various branches of chemistry; some of these will be considered here, while others will be found in later sections. In order to make practical use of the electrode potential equations developed in § 48b, it is necessary to insert values for R and F in the factor RT/nF which appears in all such equations. The potential is always expressed in volts, and since F is known to be 96,500 coulombs, the value of R must be in volt-coulombs, i.e., joules; thus R is 8.314 joules deg^{-1} mole^{-1}. Inserting these values of R and F, and introducing the factor 2.303 to convert natural logarithms to common logarithms, i.e., to the base 10, equation (48.3) becomes

$$\begin{aligned} E &= E^0_{\text{el.}} - \frac{2.303 \times 8.314}{96{,}500} \cdot \frac{T}{n} \log \frac{a_{\text{ox}}}{a_{\text{red}}} \\ &= E^0_{\text{el.}} - 1.984 \times 10^{-4} \frac{T}{n} \log \frac{a_{\text{ox}}}{a_{\text{red}}} \text{ volts.} \qquad (48.9) \end{aligned}$$

It should be understood that the quantities a_{ox} and a_{red} refer to *the product of the activities of all the substances concerned* in the oxidized and reduced states, respectively. At 25°C, i.e., T is 298.15°K, which is the temperature most frequently employed for accurate electrochemical measurements, equation (48.9) becomes

$$E = E^0_{el.} - \frac{0.05915}{n} \log \frac{a_{ox}}{a_{red}}. \tag{48.10}$$

At 20°C the numerical factor preceding the second term on the right is 0.0582 and at 30°C it is 0.0602.

I. Approximate Determination of Ionic Activities.—If the potential of a particular electrode is measured in a solution of its ions at an unknown activity, the value of the latter can be calculated. This is particularly useful for the determination of very small ionic activities, such as are encountered in the study of sparingly soluble salts and of complex ions. It is important to mention that the results obtained in this manner are not strictly ionic activities; since other ions must always be present, it is theoretically impossible to determine the activity of a single ionic species. The quantity actually measured is a kind of mean value of the activities of two or more ions. For many purposes, the value derived from electrode potential measurements may be taken as approximately equal to the corresponding molalities in gram ions per 1000 grams of solvent. In dilute aqueous solution this is roughly equivalent to the concentration in gram ions per liter.

Example: The E.M.F. of the cell

$$\text{Ag} \mid \text{AgCl}(s) \mid 0.1\ \text{N KCl} \mid \text{Hg}_2\text{Cl}_2(s) \mid \text{Hg}$$

is +0.0455 volt at 25°C; calculate the approximate activity (or concentration) of the Ag^+ ions in the saturated solution of AgCl in 0.1 N KCl.

The E.M.F. is the sum of the oxidation potential of the Ag electrode and the reduction potential of the Hg electrode. The reduction potential of the Hg electrode, i.e., 0.1 N KCl | $Hg_2Cl_2(s)$ | Hg is +0.334; hence, E_{Ag}, the oxidation potential of the Ag electrode, is

$$E_{Ag} = +0.0455 - 0.334 = -0.289 \text{ volt}.$$

For an electrode reversible with respect to Ag^+ ions, n is 1, and $a_{red} = a_{Ag} = 1$; thus equation (48.10) becomes

$$E_{Ag} = E^0_{Ag} - 0.0592 \log a_{Ag^+}.$$

From Table 48.1, E^0_{Ag} for the Ag | Ag^+ electrode is −0.7991 volt; hence

$$-0.289 = -0.7991 - 0.0592 \log a_{Ag^+}$$

$$\log a =_{Ag^+} -8.630 = 0.370 - 9$$

$$a_{Ag^+} = 2.34 \times 10^{-9} \text{ gram ion per 1000 grams of water.}$$

Since the aqueous solution is dilute, the approximate activity or concentration of the silver ions is 2.34×10^{-9} gram ion per liter.

(It may be noted that although the left-hand electrode is generally regarded as being reversible to Cl^- ions, it is treated here as being reversible to Ag^+ ions. This does not affect the results, for both points of view may be used.)

II. Influence of Ionic Concentration on Electrode Potential.—The oxidation potential of an electrode in a system for which $a_{ox} = x$ and $a_{red} = y$ is given by the general equation

$$E_1 = E^0 - \frac{RT}{nF} \ln \frac{x}{y}.$$

If y is held constant and the activity x is decreased to one-tenth of its initial value, that is to say to $0.1x$, the electrode potential becomes

$$E_2 = E^0 - \frac{RT}{nF} \ln \frac{0.1x}{y}.$$

The resulting change of potential is obtained by subtracting E_1 from E_2; thus,

$$E_2 - E_1 = -\frac{RT}{nF}\left(\ln \frac{0.1x}{y} - \ln \frac{x}{y}\right) = \frac{RT}{nF} \ln 10.$$

Inserting the values of R, F and T (for 25°C), and converting the logarithms this becomes

$$E_2 - E_1 = \frac{0.0592}{n} \text{ volt.} \tag{48.11}$$

At 25°C every ten-fold *decrease* in the ratio of the activities or, approximately, in the concentrations, of the *cations* results in the oxidation potential becoming *more positive* by $0.0592/n$ volt, where n is the valence of the ions. For univalent ions, n is 1, and hence the potential changes by 0.0592 volt. For bivalent ions, such as Zn^{+2}, Cd^{+2}, Fe^{+2}, Cu^{+2}, etc., the value of n is 2, and hence the electrode potential changes by 0.0592/2, i.e., 0.0296 volt, for a ten-fold change of ionic activity. For every ten-fold change in activity (or concentration) the same change in electrode potential would occur; hence, for a hundred-fold change the potential change is $2 \times 0.0592/n$ volt, for a thousand-fold change $3 \times 0.0592/n$, and so on. The *alteration of potential* is not determined by the actual ionic concentrations or activities, but by the *ratio* of the two concentrations, that is, by the relative change of concentration. Thus, a change from 1.0 gram ion to 0.1 gram ion per liter produces the same change in potential as a decrease from 10^{-6} to 10^{-7} gram ion per liter; in each case the ratio of the two concentrations is the same, viz., 10 to 1. For reduction potentials, the changes are of the same magnitude as for oxidation potentials, but the signs are reversed in each case.

It will have been noted that the formula of mercurous chloride is written as Hg_2Cl_2, and not HgCl, and that of the mercurous ion is represented by Hg_2^{+2} in Table 48.1. One argument for the use of the double formula is the fact that a ten-fold change in the concentration of mercurous nitrate solution was found to alter the potential by 0.0296 volt at ordinary temperatures. This result indicates that for the mercurous ions n is 2, so that they carry two unit charges per ion; the formula must consequently be Hg_2^{+2} and not Hg^+.

III. Potentiometric Titration.—One of the most interesting applications of electrode potentials is in connection with **potentiometric titration,** or **electrometric titration,** that is, the detection of the end point of a titration in quantitative analysis by measurement of electrode potential. Suppose a standard solution of silver nitrate is titrated by means of a solution of sodium chloride; as the titration proceeds, silver chloride is precipitated, and the concentration of the silver ions remaining in solution decreases steadily. The potential of a silver electrode, which in this case acts as the **indicator electrode,** changes correspondingly. The change of potential is quite small, at first, since a hundredfold decrease of concentration alters the potential by only 0.118 volt. However, when the end point of the titration is approached, the *relative* change of concentration of silver ions for a given amount of sodium chloride added increases rapidly; there is a corresponding rapid change in the silver electrode potential. The end point can thus be found by determining the quantity of titrant added when the rate of change of the electrode potential is a maximum. Hence, a silver electrode can be used as an indicator for the quantitative analysis of chloride solutions, or of solutions of any anion forming an insoluble silver salt, e.g., bromide, iodide, cyanide, thiocyanate and phosphate. Other metal electrodes may be adapted to the analysis of other anion solutions.

The general form of the potentiometric titration curve, showing the variation of the potential of the indicator electrode with the amount of titrant added, is depicted in Fig. 48.3; the sharp change of potential at the end point is evident. In order to determine the position of the end point with some degree of precision, it is necessary to find the point at which the slope of the titration curve is a maximum. The method adopted to find this point is to plot the ratio $\Delta E/\Delta V$ of the change ΔE of electrode potential, for the addition of a definite small volume of titrant solution, to the volume ΔV added. Provided ΔV is not large, $\Delta E/\Delta V$ is a close approximation to the slope of the

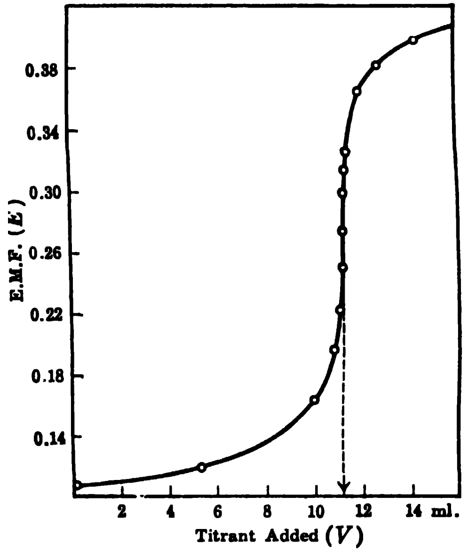

FIG. 48.3. Potentiometric titration

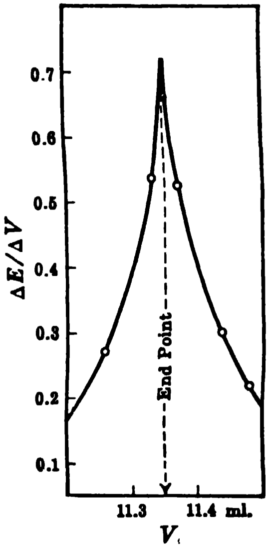

FIG. 48.4. Potentiometric end point

titration curve in Fig. 48.3, and it has a maximum value at the end point, as shown in Fig. 48.4. The height of this maximum, and the accuracy with which the end point can be estimated, are smaller the more dilute the solutions being titrated and the more soluble the precipitated salt.

The principles described above can be used for other forms of titration; for example, in the titration of an acid solution by a base, a suitable hydrogen indicator electrode is used in the same way as a silver electrode was employed in the precipitation titration. Titrations involving conventional oxidizing and reducing agents, e.g., permanganate or dichromate and ferrous ions, can also be followed potentiometrically; here again the potential of the system undergoes a rapid change at the end point, provided the oxidation and reduction reactions go to virtual completion (see § 48g). The indicator electrode employed for this type of titration consists of an unattackable electrode, such as one of platinum.

The potentiometric procedure can be employed with colored solutions, and often in dilutions at which ordinary titrations with colored indicators would be very inaccurate. The general method is to place the indicator electrode in the solution to be titrated and to combine it with a reference electrode of constant potential, e.g., a calomel electrode, thus forming a complete cell. The E.M.F. of this cell is measured, by a suitable potentiometer, as various known amounts of titrant solution are added. The actual potential of the indicator electrode need not be known; since the potential of the reference electrode remains constant, the E.M.F. of the complete cell will undergo the same changes as does the potential of the indicator electrode. The end point of the titration is then the point at which $\Delta E/\Delta V$ is a maximum, where ΔE is given by the changes in the E.M.F. of the cell. Devices are now available which perform titrations and draw the titration curves automatically.

48f. Standard Free Energy Changes and Spontaneous Reactions.— The E.M.F. of a cell and even its sign depend on the activities, or concentrations, of the reactants and products of the reaction taking place in the cell; hence, the value of the free energy change will vary in an analogous manner. For many purposes it is convenient to consider the standard free energy change ΔF^0 associated with the reaction, i.e., when all the substances are in their standard states of unit activity. The appropriate form of equation (47.1) is

$$\Delta F^0 = -nFE^0_{\text{cell}}, \tag{48.12}$$

where E^0_{cell} is the standard E.M.F. of the reversible cell in which the given reaction occurs; the value of E^0_{cell} can be obtained in the usual manner, by adding the standard oxidation potential of the left-hand electrode and the standard reduction potential of the right-hand electrode. The standard free energy change of the cell reaction can then be derived from equation (48.12).

Consider, for example, the particular Daniell cell

$$\text{Zn} \mid \text{ZnSO}_4\ (a_{\text{Zn}^{++}} = 1) \parallel \text{CuSO}_4\ (a_{\text{Cu}^{++}} = 1) \mid \text{Cu}$$

for which the reaction is

$$Zn + Cu^{+2} = Zn^{+2} + Cu$$

for the passage of two faradays. The standard oxidation potential of the left-hand, i.e., Zn | Zn^{+2}, electrode is +0.763 volt (Table 48.1), whereas the standard oxidation potential of the right-hand, i.e., Cu | Cu^{+2}, electrode is −0.337 volt; E^0_{cell} is thus +0.763 − (−0.337) = 1.100 volt at 25°C, and by equation (48.12)

$$\Delta F^0 = -2 \times 96{,}500 \times 1.100 = -212{,}000 \text{ joules}$$

$$= -212{,}000 \times 0.2390 = -50{,}700 \text{ cal, i.e., } -50.7 \text{ kcal, at } 25°\text{C.}$$

Since E^0_{cell}, the standard E.M.F. of the cell, is positive, the standard free energy change ΔF^0 is negative, and the reaction as written is spontaneous; hence, metallic zinc can react spontaneously with cupric ions at unit activity to produce metallic copper and zinc ions also at unit activity.

Suppose it is required to determine whether the reaction

$$Cd + 2H^+ (a = 1) = Cd^{+2} (a = 1) + H_2 \text{ (1 atm)},$$

that is, the displacement of hydrogen ions from solution by metallic cadmium, is possible theoretically, when all the substances are in their standard states. This reaction would occur in the cell

$$Cd \mid Cd^{+2} (a = 1) \parallel H^+ (a = 1) \mid H_2 \text{ (1 atm)} \mid Pt,$$

the standard E.M.F. of which is the same as the oxidation potential of the cadmium electrode, i.e., +0.403 volt at 25°C. Since E^0_{cell} is positive, ΔF^0 is negative, and the reaction should be capable of taking place spontaneously. For the cell reaction as written, $n = 2$ and so, by equation (48.12),

$$\Delta F^0 = -2 \times 96{,}500 \times 0.2390 \times 0.403$$

$$= -18{,}500 \text{ cal} = -18.5 \text{ kcal.}$$

If the cell reaction had been written as

$$\tfrac{1}{2}Cd + H^+ = \tfrac{1}{2}Cd^{+2} + \tfrac{1}{2}H_2,$$

the E.M.F. would be exactly the same as before, i.e., +0.403, but n would now be 1 and ΔF^0 would be half the value calculated above. This result serves to illustrate the statement in § 47a that the E.M.F. of a cell is an intensive property; it is independent of the quantity of material in the cell or the extent of the reaction occurring within it. The free energy change, however, is an extensive property and its value is determined by the extent of the chemical reaction.

An illustration of another kind is provided by the cell

$$Ag \mid AgClO_4 (a = 1) \parallel Fe(ClO_4)_2, Fe(ClO_4)_3 (a = 1) \mid Pt$$

for which the reaction is

$$\mathrm{Ag}(s) + \mathrm{Fe}^{+3} = \mathrm{Ag}^{+} + \mathrm{Fe}^{+2}$$

for the passage of one faraday. The standard oxidation potential of the left-hand ($\mathrm{Ag} \mid \mathrm{Ag}^{+}$) electrode is -0.799 volt, whereas the oxidation potential of the right-hand ($\mathrm{Pt} \mid \mathrm{Fe}^{+2}, \mathrm{Fe}^{+3}$) electrode is -0.771 volt (Table 48.1). Hence, E^0_{cell} is $-0.799 - (-0.771) = -0.028$ volt; since E^0_{cell} is negative, ΔF^0 is positive, and the reaction as written will not occur spontaneously, for the reactants and products in their standard states at 25°C. For the reverse reaction, however, ΔF^0 will be negative, so that the process

$$\mathrm{Fe}^{+2} + \mathrm{Ag}^{+} = \mathrm{Fe}^{+3} + \mathrm{Ag}(s)$$

can be spontaneous if all the substances taking part are at unit activity.

An examination of the foregoing results, or a general consideration of the situation, will reveal the fact that the standard E.M.F. of a cell is positive when the standard oxidation potential of the left-hand electrode is more positive than the standard oxidation potential of the right-hand electrode, that is, when the former lies above the latter in Table 48.1. When this is the case, the cell reaction will be capable of occurring spontaneously, oxidation taking place at the left-hand side and reduction at the right-hand side. It follows, therefore, that any system in Table 48.1 should be able, theoretically, to reduce any system lying below it in the table, while it is itself oxidized, provided all the substances concerned are in their standard states of unit activity. Thus, zinc (higher in the table) reduces cupric ions to copper (lower in the table), while it is itself oxidized to zinc ions; similarly, cadmium reduces hydrogen ions to hydrogen gas, and is itself oxidized to cadmium ions. In general, any metal higher in Table 48.1 will displace from solution, i.e., reduce, the ions of a metal (or of hydrogen) lower in the table of standard oxidation potentials.

It is important to remember that these conclusions are strictly applicable only when the ions are all at unit activity. It follows from equation (47.5), that by changing the activity ratio term Q_a, the sign of the E.M.F. of a cell can be reversed. These changes need not be large if the standard potentials of the electrodes are not far apart and E^0_{cell} is small. The result is that a process which is not spontaneous when the various substances are in their standard states (ΔF^0 is positive) can be made to occur spontaneously (ΔF is negative). For example, copper should be unable to displace hydrogen ions from solution, since the $\mathrm{Cu} \mid \mathrm{Cu}^{+2}$ system has a lower standard oxidation potential than the $\mathrm{H}_2 \mid \mathrm{H}^{+}$ system; this is true in so far as copper does not normally liberate hydrogen from acid solution. However, if the concentration of the cupric ions is decreased very greatly by the formation of complex ions, e.g., with cyanide or bromide, the oxidation potential is increased until it is greater than that of hydrogen against hydrogen ions in the same solution. In these circumstances, the displacement of hydrogen ions by metallic copper, with the evolution of hydrogen gas, becomes possible.

Similar observations have been made in connection with the $\mathrm{Ag} \mid \mathrm{Ag}^{+}$

and Fe^{+2}, Fe^{+3} systems; as seen above, if all the substances are in their standard states of unit activity, the spontaneous reaction should be the reduction of silver ions to metallic silver by ferrous ions, as is actually the case. The standard oxidation potentials of the two systems are not very different, although that of the Fe^{+2}, Fe^{+3} system is the higher. In the presence of thiocyanate ions, which maintain a low concentration of Ag^+ ions by the precipitation of silver thiocyanate, in addition to removing many of the Fe^{+3} ions in the form of a complex, the potentials are reversed, and metallic silver then reduces the ferric compound to the ferrous state.

Although the standard potentials provide some indication, therefore, of the direction in which a particular reaction may be expected to proceed spontaneously, especially if the potentials are appreciably different for the two systems involved, the results may sometimes be misleading. The real criterion, which is always satisfactory, is that *the* E.M.F. *of the actual cell*, i.e., E, with the substances at the given activities, and not necessarily E^0_{cell}, when the activities are all unity, *should be positive for the reaction to be spontaneous.* In other words, the *actual* oxidation potential of the left-hand electrode must be more positive than that of the right-hand electrode if the reaction occurring in the cell is to proceed spontaneously.

Example: According to the data in Table 48.1, metallic Pb cannot displace Sn^{+2} ions from solution to form metallic Sn when the ions are all at unit activity, since E^0_{Pb} is +0.126 and E^0_{Sn} is +0.140 volt; can this displacement occur if Pb is placed in a solution in which the activity of the Sn^{+2} ions is 1.0 g ion per liter and that of the Pb^{+2} ions is 0.1 g ion per liter?

The problem reduces itself to the question of finding whether ΔF for the reaction

$$Pb(s) + Sn^{+2}(a = 1.0) = Pb^{+2}(a = 0.1) + Sn(s)$$

is negative or not. The reaction as written will take place spontaneously in the cell

$$Pb \mid Pb^{+2}(a = 0.1) \parallel Sn^{+2}(a = 1.0) \mid Sn$$

provided its E.M.F. is positive, for then ΔF will be negative. Two procedures, which are ultimately identical, may be employed to determine E and ΔF.

First, the potentials of the two electrodes may be calculated from equation (49.10); for the left-hand electrode, E^0_{Pb} is +0.126 volt, n is 2, and $a_{ox} = a_{Pb^{+2}} = 0.1$; hence at 25°C,

$$E_{Pb} = +0.126 - \frac{0.0592}{2} \log 0.1 = +0.156 \text{ volt.}$$

For the analogous right-hand electrode, E^0_{Sn} is +0.140 volt, n is 2, $a_{red} = a_{Sn^{+2}} = 1.0$, so that

$$E_{Sn} = +0.140 - \frac{0.0592}{2} \log 1.0 = +0.140 \text{ volt.}$$

The E.M.F. of the cell as written is the algebraic sum of the oxidation potential of the lead electrode and the reduction potential of the tin electrode, i.e., $+0.156 - 0.140 = +0.016$ volt. Since E is positive, ΔF, equal to $-2 \times 96{,}500 \times 0.016 = -3090$

joules, is negative. The reaction under consideration will thus take place spontaneously with the specified activities; the change of activities consequently permits the reaction to take place in the direction which is not possible when the activities of both ions are unity.

The second method of calculating E is to make use of the general equation (47.5); in the present case this is

$$E = E^0_{\text{cell}} - \frac{RT}{2F} \ln \frac{a_{\text{Pb}^{+2}} \times a_{\text{Sn}}}{a_{\text{Pb}} \times a_{\text{Sn}^{+2}}},$$

with n equal to 2. The activities of the solid lead and tin are both unity, and hence at 25°C this equation for the E.M.F. of the cell is

$$E = E^0_{\text{cell}} - \frac{0.0592}{2} \log \frac{a_{\text{Pb}^{+2}}}{a_{\text{Sn}^{+2}}}.$$

The value of E^0_{cell} is equal to $E^0_{\text{Pb}} - E^0_{\text{Sn}}$, i.e., $+0.126 - 0.140 = -0.014$ volt; hence,

$$E = -0.014 - \frac{0.0592}{2} \log \frac{0.1}{1.0} = +0.016 \text{ volt},$$

as found above.

48g. Equilibrium Constants.—For many purposes it is more convenient to calculate the equilibrium constant of a reaction, instead of the free energy change; this constant provides the same information from a slightly different viewpoint. The equilibrium constant is related to the standard free energy change by equation (34.1), viz.,

$$\Delta F^0 = -RT \ln K,$$

and since ΔF^0 is equal to $-nFE^0_{\text{cell}}$, by equation (48.12), it follows that

$$E^0_{\text{cell}} = \frac{RT}{nF} \ln K, \qquad (48.13)$$

or at 25C°, with E^0_{cell} in volts,

$$E^0_{\text{cell}} = \frac{0.0592}{n} \log K. \qquad (48.14)$$

By means of these equations the equilibrium constant of any reaction can be readily calculated from the standard E.M.F. of the reversible cell in which the reaction occurs.

The reaction in the Daniell cell, for example, is

$$\text{Zn}(s) + \text{Cu}^{+2} = \text{Zn}^{+2} + \text{Cu}(s)$$

for the passage of two faradays, i.e., $n = 2$, and the equilibrium constant is given by

$$K = \frac{a_{\text{Zn}^{+2}} \times a_{\text{Cu}}}{a_{\text{Cu}^{+2}} \times a_{\text{Zn}}}$$

and setting a_{Cu} and a_{Zn} for the solids equal to unity

$$K = \left(\frac{a_{\mathrm{Zn}^{+2}}}{a_{\mathrm{Cu}^{+2}}}\right)_e, \tag{48.15}$$

where the subscript e is used to show that the activities are the values when the reacting system attains equilibrium. The standard E.M.F. of the cell, as seen above, is equal to $E^0_{\mathrm{Zn}} - E^0_{\mathrm{Cu}}$, i.e., 1.100 volt at 25°C; hence, by equations (48.14) and (48.15),

$$1.100 = \frac{0.0592}{2} \log \left(\frac{a_{\mathrm{Zn}^{+2}}}{a_{\mathrm{Cu}^{+2}}}\right)_e$$

$$\left(\frac{a_{\mathrm{Zn}^{+2}}}{a_{\mathrm{Cu}^{+2}}}\right)_e = 1.7 \times 10^{37}.$$

The ratio of the activities of the zinc and copper ions in the solution at equilibrium will be approximately equal to the ratio of the concentrations under the same conditions; hence, when a system consisting of metallic zinc and copper and their bivalent ions in aqueous solution attains equilibrium, the ratio of the zinc ion to the cupric ion concentration is extremely large. If zinc is placed in a solution of cupric ions, the latter will be displaced to form metallic copper until the $c_{\mathrm{Zn}^{+2}}/c_{\mathrm{Cu}^{+2}}$ ratio in the solution is about 10^{37}. In other words, the zinc will displace the copper from the solution until the quantity of cupric ions remaining is extremely small.

Stannous chloride is frequently employed for the reduction of ferric to ferrous ions, according to the reaction

$$\mathrm{Sn}^{+2} + 2\mathrm{Fe}^{+3} = \mathrm{Sn}^{+4} + 2\mathrm{Fe}^{+2}.$$

This process is made up of the oxidation process

$$\mathrm{Sn}^{+2} = \mathrm{Sn}^{+4} + 2\epsilon,$$

and the reduction

$$2\mathrm{Fe}^{+3} + 2\epsilon = 2\mathrm{Fe}^{+2},$$

so that it can take place for the passage of two faradays in the reversible cell

$$\mathrm{Pt} \mid \mathrm{Sn}^{+2}, \mathrm{Sn}^{+4} \parallel \mathrm{Fe}^{+2}, \mathrm{Fe}^{+3} \mid \mathrm{Pt}.$$

The standard oxidation potentials of the two electrodes are given in Table 48.1 as -0.15 and -0.771 volt, respectively, and so E^0_{cell} is $-0.15 - (-0.771) = +0.62$ volt; hence, at 25°C, by equation (48.14),

$$0.62 = \frac{0.0592}{2} \log K,$$

$$K = \left(\frac{a_{\mathrm{Sn}^{+4}} \times a^2_{\mathrm{Fe}^{+2}}}{a^2_{\mathrm{Fe}^{+3}} \times a_{\mathrm{Sn}^{+2}}}\right)_e = 1.0 \times 10^{21}$$

The high value of the equilibrium constant means that when equilibrium is attained in the ferrous-ferric and stannous-stannic mixture, the concentrations (activities) of stannous and ferric ions must be negligibly small in comparison with those of the stannic and ferrous ions. In other words, when a stannous salt is added to a solution of ferric ions, the latter are reduced virtually completely to ferrous ions.

It is apparent from these calculations that the large equilibrium constants, indicating almost complete reaction from left to right, are due to the high value of the standard E.M.F. of the cell, i.e., E^0_{cell} in which the reaction may be supposed to occur. The farther the standard potentials of the two systems concerned are apart in Table 48.1, the greater will be E^0_{cell}, and hence the more complete will be the reaction as written. This is in general accord with the conclusions reached in § 48f.

If the two standard potentials are not very different, all the substances involved will be present in somewhat similar concentrations at equilibrium, and the reaction will not be complete in either direction. This may be illustrated by reference to the reaction

$$\text{Ag}^+ + \text{Fe}^{+2} = \text{Ag}(s) + \text{Fe}^{+3}$$

for which it is found, from the known Ag | Ag$^+$ and Pt | Fe^{+2}, Fe^{+3} standard potentials, that

$$K = \left(\frac{a_{\text{Fe}^{+3}}}{a_{\text{Ag}^+} \times a_{\text{Fe}^{+2}}}\right)_e = 2.97.$$

This value of the equilibrium constant shows that appreciable concentrations of silver and ferrous ions must be present at equilibrium; the reaction, therefore, does not normally approach completion, and so it could not be used for analytical purposes. It may be recalled that in the presence of thiocyanate ions the reverse reaction, i.e., the reduction of ferric ions by metallic silver, takes place to a considerable extent. This is not due to any change in the equilibrium constant, which must always have the same value at a given temperature, but to the fact that the precipitation of the silver ions as silver thiocyanate makes a_{Ag^+} very small, so that $a_{\text{Fe}^{+3}}$ must be diminished correspondingly in order to maintain the value of the equilibrium constant. The reaction under consideration consequently takes place from right to left.

The equilibrium constant of a process can be obtained in another manner, which is fundamentally identical with that just described, although the approach is somewhat different. When the activities of various substances present in a reversible cell happen to correspond to the equilibrium values, the E.M.F. of the cell will be zero. This statement can be proved in various ways. For example, for a system at equilibrium, at constant temperature and pressure, ΔF is zero (§ 9b); consequently, since ΔF is equal to $-nFE$, the E.M.F. of the cell, i.e., E, containing the equilibrium system must be zero. If the E.M.F. of the cell is zero, it follows that the potentials of the two electrodes must be identical; the activities (or concentrations) for which the two electrodes of a cell have the same (oxidation) potential must consequently be the equilibrium values.

Example: Utilize the fact that two electrodes must have the same potential when equilibrium is attained to calculate K for the familiar reaction $Zn + Cu^{+2} = Zn^{+2} + Cu$.

If $(a_{Zn^{+2}})_e$ and $(a_{Cu^{+2}})_e$ represent the activities of the respective ions when equilibrium is attained, the potentials of the $Zn \mid Zn^{+2}$ and $Cu \mid Cu^{+2}$ electrodes, which must then be equal, are given by

$$E_{Zn} = E^0_{Zn} - \frac{RT}{2F} \ln (a_{Zn^{+2}})_e = +0.763 - 0.0296 \log (a_{Zn^{+2}})_e$$

$$E_{Cu} = E^0_{Cu} - \frac{RT}{2F} \ln (a_{Cu^{+2}})_e = -0.337 - 0.0296 \log (a_{Cu^{+2}})_e.$$

Equating these potentials, it is seen that

$$+0.763 - 0.0296 \log (a_{Zn^{+2}})_e = -0.337 - 0.0296 \log (a_{Cu^{+2}})_e$$

$$\left(\frac{a_{Zn^{+2}}}{a_{Cu^{+2}}}\right)_e = K = 1.7 \times 10^{37},$$

which is identical with the result obtained previously. The two methods of calculation are, of course, the same, although the point of view is somewhat different.

In the foregoing treatment standard electrode potentials have been employed to calculate equilibrium constants; the reverse calculation is equally possible and has, in fact, been used in certain cases. For example, the standard potential of $Sn \mid Sn^{+2}$ given in Table 48.1 was obtained in this manner.

Example: Finely divided metallic lead and tin were shaken with solutions containing stannous and plumbous perchlorates until the equilibrium in the reaction

$$Sn(s) + Pb^{+2} = Sn^{+2} + Pb(s)$$

was reached; the ratio of the concentrations of stannous and plumbous ions at equilibrium, i.e., $(c_{Sn^{+2}}/c_{Pb^{+2}})_e$, was found to be 2.98 at 25°C. Calculate the standard oxidation potential of the $Sn \mid Sn^{+2}$ electrode at 25°C.

If the ratio of the concentrations is equal to the ratio of the activities in terms of molalities, as is probably the case if the solutions are dilute, it follows that

$$K = \left(\frac{a_{Sn^{+2}}}{a_{Pb^{+2}}}\right)_e = 2.98.$$

The reaction under consideration may be separated into the oxidation and reduction processes, viz.,

$$Sn(s) = Sn^{+2} + 2\epsilon \qquad \text{and} \qquad Pb^{+2} + 2\epsilon = Pb(s),$$

so that the complete reaction, as written above, takes place in the reversible cell

$$Sn \mid Sn^{+2} \parallel Pb^{+2} \mid Pb$$

for the passage of two faradays, i.e., n is 2. In this case $E^0_{\text{cell}} = E^0_{\text{Sn}} - E^0_{\text{Pb}}$, where E^0_{Pb} is +0.126 volt at 25°C; hence, by equation (48.14),

$$E^0_{\text{cell}} = E^0_{\text{Sn}} - 0.126 = \frac{0.0592}{2} \log 2.98$$

$$= 0.0140,$$

$$E^0_{\text{Sn}} = +0.140 \text{ volt.}$$

The standard potential of the Sn | Sn^{+2} electrode is thus +0.140 volt at 25°C.

CONCENTRATION CELLS

49a. Concentration Cells with Transference.—Imagine two electrodes of the same metal (or hydrogen), represented by M, in contact with two solutions in which the corresponding M^{+n} ion activities are $(a_+)_1$ and $(a_+)_2$. Suppose the electrodes are combined to form a cell in which the liquid junction potential is assumed to be eliminated; thus,

$$\text{M} \mid \text{M}^{+n}\ (a_+)_1 \parallel \text{M}^{+n}\ (a_+)_2 \mid \text{M}.$$

This is a form of **concentration cell** since its E.M.F. depends on the difference in the concentrations (activities) of two solutions of the same electrolyte. The oxidation potential of the left-hand electrode is

$$E_1 = E^0_{\text{M}} - \frac{RT}{nF} \ln (a_+)_1,$$

and the reduction potential of the right-hand electrode is

$$E_2 = -E^0_{\text{M}} + \frac{RT}{nF} \ln (a_+)_2.$$

The E.M.F. of the cell is equal to $E_1 + E_2$, in the usual manner, so that

$$E = E_1 + E_2 = \frac{RT}{nF} \ln \frac{(a_+)_2}{(a_+)_1}. \qquad (49.1)$$

The E.M.F. of the concentration cell thus depends only on the ratio of the ionic activities in the two solutions; as mentioned earlier, single ion activities do not have precise thermodynamic significance, and so the ratio $(a_+)_2/(a_+)_1$ may be taken as (approximately) equal to the ratio of the *mean activities* (see below) of the ions in the respective solutions.

If the liquid junction potential between the two solutions is not eliminated, the E.M.F. of the concentration cell has a different value from that obtained above. Consider, for example, the cell

$$\text{Pt} \mid \text{H}_2\ (1 \text{ atm}) \mid \text{HCl}(a_1) \mid \text{HCl}(a_2) \mid \text{H}_2\ (1 \text{ atm}) \mid \text{Pt}$$

in which the two solutions of hydrochloric acid are in contact. When this cell operates, the concentration of the electrolyte in the more concentrated solution will decrease while that of the less concentrated solution increases. This is equivalent to the transfer of electrolyte from the more concentrated to the more dilute solution in the cell; it is, therefore, referred to as a **concentration cell with transference.** When one faraday passes through the cell, 1 gram atom of hydrogen gas is oxidized at the left-hand electrode to yield 1 gram ion of hydrogen ions; the same amount of hydrogen ions is reduced to form 1 gram atom of hydrogen gas which is liberated at the right-hand electrode. If t_+ and t_- are the transference numbers of the hydrogen cations and the chloride anions, representing the fractions of the current carried by the respective ions, then during the passage of the one faraday through the cell, t_+ faradays will be carried by t_+ gram ion of hydrogen ions in one direction (from left to right), while t_- faradays will be carried by t_- gram ion of chloride ions in the opposite direction, as shown below.

$$\text{Pt}|\ \text{H}_2\ (1\ \text{atm})\ |\ \text{HCl}(a_1) \qquad | \qquad \text{HCl}(a_2)\ |\ \text{H}_2\ (1\ \text{atm})|\ \text{Pt}$$

$$\tfrac{1}{2}\text{H}_2(g) \rightarrow \text{H}^+\ (\text{soln.}) \qquad \xrightarrow{t_+} \text{H}^+ \qquad \text{H}^+\ (\text{soln.}) \rightarrow \tfrac{1}{2}\text{H}_2(g)$$

$$\text{Cl}^- \xleftarrow[t_-]{}$$

The net result is an increase in the left-hand electrode of $1 - t_+ = t_-$ gram ion of hydrogen ions and of t_- gram ion of chloride ions; at the same time a decrease of $1 - t_+ = t_-$ gram ion of hydrogen ions and of t_- gram ion chloride ions occur in the right-hand electrode. This is equivalent to the transfer of t_- gram ion of hydrogen ions and t_- gram ion of chloride ions from right to left, i.e., from the solution represented by the subscript 2 to that indicated by the subscript 1. (The assumption is made that the transference numbers are the same in both solutions.) Utilizing equation (26.4), it follows that the free energy change accompanying the transfer is given by

$$\Delta F = t_-RT \ln \frac{(a_+)_1}{(a_+)_2} + t_-RT \ln \frac{(a_-)_1}{(a_-)_2}, \tag{49.2}$$

where a_+ and a_- refer to the activities of the hydrogen and chloride ions, respectively, in the indicated solutions. The **mean ionic activity** of an electrolyte is defined as *the geometric mean of the activities of the component ions.* If $(a_\pm)_1$ and $(a_\pm)_2$ are the mean activities of the ions in the two hydrochloric acid solutions, it follows by the definition that

$$(a_\pm)_1^2 = (a_+)_1(a_-)_1 \qquad \text{and} \qquad (a_\pm)_2^2 = (a_+)_2(a_-)_2. \tag{49.3}$$

Utilizing these results, equation (49.2) becomes

$$\Delta F = 2t_-RT \ln \frac{(a_\pm)_1}{(a_\pm)_2}. \tag{49.4}$$

The free energy change, by equation (47.1), is also equal to $-EF$, since n is 1, for the passage of one faraday; hence, from equation (49.4),

$$E = 2t_- \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}. \tag{49.5}$$

An alternative treatment is to consider the cell reaction as the transfer of t_- moles of hydrogen chloride, rather than of t_- gram ions of hydrogen and chloride ions, from the solution in which *the activity of the hydrogen chloride* is a_2 to the one in which it is a_1. The free energy change is then

$$\Delta F = t_- RT \ln \frac{a_1}{a_2}$$

and since $n = 1$ the E.M.F. is

$$E = t_- \frac{RT}{F} \ln \frac{a_2}{a_1}. \tag{49.6}$$

Since the E.M.F. of the cell is the same, irrespective of the method of calculation, comparison of equations (49.5) and (49.6) shows that $a_2/a_1 = [(a_\pm)_2/(a_\pm)_1]^2$ This relationship between the activity of the electrolyte (HCl) and the mean activity of the ions (H^+ and Cl^-) is considered more fully in § 49d.

The E.M.F. of the cell depends on the transference number of the anion as well as on the ratio of the ionic activities. In general, if the electrodes of a concentration cell are reversible with respect to the cation, i.e., the hydrogen ion in the case considered, then the transference number of the anion appears in the equation for the E.M.F. of the cell.

In the cell

$$\mathrm{Ag} \mid \mathrm{AgCl}(s) \mid \mathrm{HCl}(a_1) \mid \mathrm{HCl}(a_2) \mid \mathrm{AgCl}(s) \mid \mathrm{Ag}$$

the electrodes are reversible with respect to the *anion*. The passage of one faraday through the cell is found to result in the transfer of t_+ gram ions of hydrogen ions and of chloride ions (or t_+ moles of hydrogen chloride) from solution 2 to solution 1, and the E.M.F. is consequently

$$E = 2t_+ \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1} = t_+ \frac{RT}{F} \ln \frac{a_2}{a_1} \tag{49.7}$$

and is dependent upon the transference number of the cation.

49b. Liquid Junction Potential.—The equation derived above, for the E.M.F. of the concentration cell with transference, includes the potential at the junction between the two solutions of hydrochloric acid. If this potential could be eliminated entirely, the E.M.F. of the corresponding concentration cell would be given by an expression similar to equation (49.1) with $n = 1$ and a_+ referring to the hydrogen ion. If the assumption is made that the hydrogen and chloride ions have the same activity in a given solution, then a_+ is equal to the mean ionic activity $a_\pm$, in accordance with equation (49.3). The (approximate) E.M.F. of the cell in which the liquid junction is eliminated would then become

$$E = \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}. \tag{49.8}$$

The difference between equations (49.5) and (49.8) thus gives the value of the liquid junction potential E_l, so that

$$E_l = (2t_- - 1)\frac{RT}{F}\ln\frac{(a_\pm)_2}{(a_\pm)_1}. \tag{49.9}$$

Although this expression for the liquid junction potential was developed by considering a cell containing hydrochloric acid solutions, it holds equally for any two solutions of uni-univalent electrolytes with mean ionic activities $(a_\pm)_1$ and $(a_\pm)_2$. Since $t_+ + t_- = 1$ or $t_- - 1 = -t_+$, it follows that $2t_- - 1 = t_- + (t_- - 1) = t_- - t_+$ and making the substitution in equation (49.9) this becomes

$$E_l = (t_- - t_+)\frac{RT}{F}\ln\frac{(a_\pm)_2}{(a_\pm)_1}. \tag{49.10}$$

It is apparent from this result that the sign and magnitude of the liquid junction potential depends on the transference numbers of the anions and cations. In general, the side of the boundary towards the more dilute solution acquires a potential of the same sign as the faster moving ion. If the transference numbers of the two ions of the electrolyte are not very different, the liquid junction potential will be small. This conclusion is of general applicability, and it accounts for the use of concentrated solutions of potassium chloride to minimize liquid junction potentials (§ 48c); the transference numbers of the potassium and chloride ions in this electrolyte are approximately equal, as is evident from the data in Table 44.1.

Example: Calculate the liquid junction potential at 25°C between two solutions of HCl of mean ionic activities 0.1 and 0.01, respectively; the mean value of the cation transference number (t_+) in this range may be taken as 0.828 (Table 44.1).

Since t_+ is 0.828, t_- is 0.172, so that equation (49.10) becomes, at 25°C,

$$E_l = (0.172 - 0.828) \times 0.0592 \log \frac{0.01}{0.1}$$
$$= 0.039 \text{ volt.}$$

(This result gives an indication of the magnitude of liquid junction potentials; the value is increased by increasing the ratio of the concentrations, or activities, of the two solutions. For hydrochloric acid, and other acids, the potentials are exceptionally high, because of the large transference number of the hydrogen ion.)

49c. Concentration Cells without Transference.—For the cell

$$\text{Pt} \mid H_2 \text{ (1 atm)} \mid \text{HCl}(a_1) \mid \text{AgCl}(s) \mid \text{Ag},$$

the reaction is

$$\tfrac{1}{2}H_2 \text{ (1 atm)} + \text{AgCl}(s) = H^+(a_+)_1 + Cl^-(a_-)_1 + \text{Ag}(s),$$

where $(a_+)_1$ and $(a_-)_1$ are the activities of the hydrogen and chloride ions in the hydrochloric acid solution of activity a_1. If the cell is reversed, and the activity of the solution is changed to a_2, viz.,

$$\mathrm{Ag} \mid \mathrm{AgCl}(s) \mid \mathrm{HCl}(a_2) \mid \mathrm{H_2}\ (1\ \mathrm{atm}) \mid \mathrm{Pt}$$

the reaction is

$$\mathrm{H^+}(a_+)_2 + \mathrm{Cl^-}(a_-)_2 + \mathrm{Ag}(s) = \tfrac{1}{2}\mathrm{H_2}\ (1\ \mathrm{atm}) + \mathrm{AgCl}(s).$$

If the two cells as written are joined together to give the combined cell

$$\mathrm{Pt} \mid \mathrm{H_2}\ (1\ \mathrm{atm}) \mid \mathrm{HCl}(a_1) \mid \mathrm{AgCl}(s) \mid \mathrm{Ag} \mid \mathrm{AgCl}(s) \mid \mathrm{HCl}(a_2) \mid \mathrm{H_2}\ (1\ \mathrm{atm}) \mid \mathrm{Pt},$$

the overall reaction, for the passage of one faraday, is obtained by summing the separate reactions in the two component cells; thus,

$$\mathrm{H^+}(a_+)_2 + \mathrm{Cl^-}(a_-)_2 = \mathrm{H^+}(a_+)_1 + \mathrm{Cl^-}(a_-)_1.$$

The cell reaction for the passage of one faraday, i.e., n is 1, is thus a decrease of 1 gram ion of hydrogen ions and 1 gram ion of chloride ions in the solution represented by the subscript 2, and an equal increase in the solution indicated by the subscript 1. This is equivalent to the transfer of 1 gram ion each of hydrogen and chloride ions (or 1 mole of hydrogen chloride) from solution 2 to solution 1. Again, by means of equation (26.4), the free energy accompanying the transfer is

$$\Delta F = RT \ln \frac{(a_+)_1}{(a_+)_2} + RT \ln \frac{(a_-)_1}{(a_-)_2},$$

and since ΔF is also equal to $-EF$, since n is unity, it follows, by exactly the same arguments as in § 49a, that

$$E = \frac{2RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1} = \frac{RT}{F} \ln \frac{a_2}{a_1}, \qquad (49.11)$$

where, as before, $(a_\pm)_1$ and $(a_\pm)_2$ are the mean activities of the ions and a_1 and a_2 are the activities of hydrogen chloride in the two solutions.

A cell of the type described is called a **concentration cell without transference,** for the E.M.F. depends on the relative concentrations (activities) of the two solutions concerned; the operation of the cell is not accompanied by the *direct* transfer of electrolyte from one solution to the other. The transfer occurs indirectly, as shown above, as the result of chemical reactions. A comparison of the concentration cell with transference in § 49a with that for the same solutions without transference shows that the change of type is achieved by introducing an intermediate electrode, $\mathrm{AgCl}(s) \mid \mathrm{Ag} \mid \mathrm{AgCl}(s)$, between the two solutions. In general, any concentration cell with transference, in which the electrodes are reversible with respect to the cation, can be converted into one without transference by separating the two solutions, in the manner indicated above, by means of an electrode that is reversible with respect to the anion of the electrolyte. In the case under consideration, the end electrodes are hydrogen electrodes, and so the intermediate electrode is reversible with respect to the chloride ion. If the end electrodes had been anion electrodes, then a concentration cell without transference would be obtained by using a suitable cation electrode to separate the two solutions.

The E.M.F. of a cell *with transference*, represented by the symbol E_t, is given by equation (49.6) as

$$E_t = t_- \frac{RT}{F} \ln \frac{a_2}{a_1}.$$

The E.M.F. of the same cell, that is, with the same end electrodes and with the same solutions, *without transference*, represented by E, is given by equation (49.11); it is immediately evident that

$$\frac{E_t}{E} = t_-. \qquad (49.12)$$

The ratio of the E.M.F.'s of the two concentration cells, one with transference and the other without transference, is thus equal to the transference number of the anion, in this case. If the end electrodes had been reversible with respect to the anion, then it follows from equations (49.7) and (49.11) that the ratio E_t/E would give the transference number t_+ of the cation. This method for the determination of transference numbers, by measuring the E.M.F.'s of cells with and without transference, has been employed in a number of cases. As with the methods described in Chapter 12, the values obtained are the transference numbers of the ion constituents. A difficulty arises in practice because the transference number varies with the concentration, although in the foregoing treatment the tacit assumption has been made that it is constant. Mathematical methods have been devised to allow for this variation.

49d. Determination of Activities and Activity Coefficients.—The measurement of the E.M.F.'s of concentration cells without transference provides one of the most convenient methods for evaluating the activities and activity coefficients of electrolytes. As seen in § 49c, the concentration cell without transference may be regarded as made up of two similar cells connected in opposite directions; these cells differ only in the activities of the electrolytes contained in them. If E_1 and E_2 are the E.M.F.'s of these partial cells, or half-cells, in which the mean ionic activities are $(a_\pm)_1$ and $(a_\pm)_2$, respectively, the E.M.F. of the whole cell is equal to $E_1 - E_2$; hence, by equation (49.11), for the particular cells described in § 49c,

$$E_1 - E_2 = \frac{2RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}. \qquad (49.13)$$

If in one of the two solutions the mean ionic activity, e.g., $(a_\pm)_2$, is unity, the corresponding E.M.F. of the half-cell containing that solution is the standard E.M.F., i.e., E^0; equation (49.13) then reduces to the form

$$E - E^0 = -\frac{2RT}{F} \ln a_\pm, \qquad (49.14)$$

where E represents the E.M.F. of the half-cell

$$H_2\ (1\ \text{atm}) \mid HCl(m) \mid AgCl(s) \mid Ag,$$

in which m is the molality of the hydrochloric acid solution, and $a_\pm$ is the mean ionic activity; the standard E.M.F. of this cell with $a_\pm$ equal to unity is then E^0. If the quantity $(2RT/F) \ln m$ is added to both sides of equation (49.14) the result is

$$E + \frac{2RT}{F} \ln m - E^0 = -\frac{2RT}{F} \ln \frac{a_\pm}{m}. \qquad (49.15)$$

As seen in § 26d, the ratio of the activity to the molality is equal to the activity coefficient γ; in the present case the ratio $a_\pm/m$ in equation (49.15) is the **mean activity coefficient** $\gamma_\pm$ of the electrolyte (hydrochloric acid) in the solution of molality m. Making this substitution, inserting the values of R, T and F in the usual manner and rearranging, equation (49.15) becomes, at 25°C,

$$E + 0.1183 \log m = E^0 - 0.1183 \log \gamma_\pm. \qquad (49.16)$$

Since the E.M.F. of the half-cell, i.e., E, can be measured for any molality m of the electrolyte, it should be possible to evaluate the corresponding activity coefficient $\gamma_\pm$ from equation (49.16), provided E^0 were known. Several methods, of varying degrees of accuracy, are available for the determination of E^0; one of the simplest will be described here. At infinite dilution the solution behaves ideally, and then a and m are identical, so that $\gamma_\pm$, equal to $a_\pm/m$, is unity; $\log \gamma_\pm$ is then zero, and hence, by equation (49.16), $E + 0.1183 \log m$ gives the value of E^0. The procedure is to plot the experimental values of $E + 0.1183 \log m$, for various molalities m of the electrolyte, against a convenient function of m, and to extrapolate the curve to m equal to zero, i.e., to infinite dilution.* The extrapolated result gives E^0, which is found to be +0.2223 volt at 25°C for the cell depicted above (see § 48c). With E^0 known, it is possible to determine the mean activity coefficient $\gamma_\pm$ of hydrochloric acid at any molality by means of equation (49.16); the product of the molality and the mean activity coefficient gives the corresponding mean ionic activity of the electrolyte.

Concentration cells with transference have also been employed for the evaluation of activity coefficients; the calculations require, in addition, a knowledge of transference numbers over a range of concentrations. The procedure is too involved to be described here. The actual values for the activity coefficients of a number of electrolytes at various molalities will be given in Chapter 14, where the reasons for the difference between the activity and the concentration (or molality), that is, the departure from ideal behavior, will be considered.

49e. Gas Concentration Cells.—An interesting, and theoretically important, type of concentration cell is obtained when the two electrodes consist of a gas at different pressures, p_1 and p_2, in contact with the same solution of the corresponding ions (see § 53c), e.g.,

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*A more accurate extrapolation is possible by plotting $E + 0.1183 \log m - 0.062\sqrt{m}$, derived from the Debye-Hückel theory (§ 51d), against m.

$$\mathrm{Pt} \mid \mathrm{H_2}(p_1) \mid \text{Solution of hydrogen ions} \mid \mathrm{H_2}(p_2) \mid \mathrm{Pt}.$$

The oxidation reaction at the left-hand electrode is

$$\mathrm{H_2}(p_1) = 2\mathrm{H}^+ + 2\epsilon,$$

while the reduction at the right-hand electrode is

$$2\mathrm{H}^+ + 2\epsilon = \mathrm{H_2}(p_2),$$

the hydrogen ions referring to the same solution. The complete cell reaction for the passage of two faradays is thus

$$\mathrm{H_2}(p_1) = \mathrm{H_2}(p_2),$$

that is, the transfer of 1 mole of hydrogen gas from the electrode of pressure p_1 to that of pressure p_2. If these pressures are not too high, and the gas may be supposed to behave ideally, the free energy change accompanying this transfer from p_1 to p_2 is given by equation (9.22) as

$$\Delta F = RT \ln \frac{p_2}{p_1}. \tag{49.17}$$

If E is the E.M.F. of the cell, the free energy change ΔF is also equal to $-2EF$, since n is 2; hence, from equation (49.17),

$$E = \frac{RT}{2F} \ln \frac{p_1}{p_2}. \tag{49.18}$$

This equation has been verified for hydrogen gas pressures from 0.005 to 100 atm. At higher pressures deviations are observed, mainly because of departure of the gas from ideal behavior.

Expressions similar to equation (49.18) can be derived for cells with chlorine or oxygen electrodes; in the latter case, it should be remembered that four faradays must pass through the cell for the transfer of 1 mole of gas from one electrode to the other, i.e., n is equal to 4 for the cell reaction. It will be noted that the E.M.F. of a gas cell of the type considered is independent of the concentration of the electrolyte.

Example: Calculate the E.M.F. at 25°C of a hydrogen gas cell in which the left-hand electrode is at a pressure (p_1) of 0.1 atm and the right-hand electrode (p_2) at 1 atm.

The E.M.F. required is given by equation (49.18); at 25°C, this becomes

$$E = \frac{0.05915}{2} \log \frac{p_1}{p_2} = 0.0296 \log \frac{0.1}{1.0}$$
$$= -0.0296 \text{ volt.}$$

(Since the E.M.F. is negative, the oxidation potential of the left-hand electrode is smaller than that of the right-hand electrode. This is to be expected, since the spontaneous reaction must involve the transfer of gas from the higher pressure, i.e., right-hand, to the lower pressure, i.e., left-hand. Oxidation must therefore occur at the former and reduction at the latter.)

THE DISCHARGE OF IONS

50a. Decomposition Voltage and Discharge Potential.—One of the essential characteristics of a reversible cell is that the reaction occurring in the cell can be reversed by the application of an external E.M.F. just greater than that of the cell itself. For example, the cell

$$\text{Zn} \mid \text{M ZnBr}_2 \text{ solution} \mid \text{Br}_2(l) \mid \text{Pt}$$

will have an E.M.F. of about 1.83 volt, made up of +0.76 volt, for the oxidation potential of the zinc electrode, plus +1.07 volt, for the reduction potential of the bromine electrode (Table 48.1). The reactions at the two electrodes are

$$\text{Zn} = \text{Zn}^{+2} + 2\epsilon \qquad \text{and} \qquad \text{Br}_2 + 2\epsilon = 2\text{Br}^-,$$

so that zinc dissolves at one electrode while bromine passes into solution at the other. If an external E.M.F. just greater than 1.83 volt is applied to a molar solution of zinc bromide, therefore, these processes should be reversed; zinc ions should be discharged to form metallic zinc at one electrode (cathode), while bromide ions should be neutralized to liberate free bromine at the other electrode (anode). The application of an E.M.F. of about 1.8 volt should thus be capable of causing continuous electrolysis of a solution of zinc bromide. The **decomposition voltage** of an electrolyte is defined as *the minimum external* E.M.F. *which must be applied between two electrodes in the electrolyte in order to bring about continuous electrolytic decomposition.* The decomposition voltage of zinc bromide solution should thus be about 1.8 volt, and this has been verified by direct experiment.

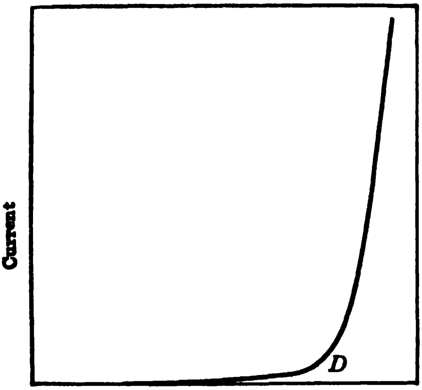

Fig. 50.1. Variation of current with cell voltage

The general method used to determine decomposition voltages is to place two unattackable, e.g., platinum, electrodes in the solution to be studied. These electrodes are connected through a variable resistance to a battery, so that a gradually increasing E.M.F. can be applied. The current passing through the solution is measured by means of a milliammeter and the corresponding applied voltage is determined by a voltmeter connected directly between the electrodes. If the current is plotted against the voltage, the resulting curve is generally of the form in Fig. 50.1. It is seen that only when the applied voltage attains the value D, can appreciable current flow through the solution. At D, therefore, steady electrolysis commences and the E.M.F. applied to the electrodes at this point represents the decomposition voltage of the electrolyte. Because of the shape of the curve, the exact position of D cannot always be determined precisely, but an approximate indication is usually adequate.

From the arguments presented above, it follows that the decomposition voltage of any solution should be approximately equal to the E.M.F. of the galvanic cell consisting of the substances liberated at the two electrodes in contact with the same solution. This agreement is to be expected, of course, only if the electrodes behave reversibly, and it has been confirmed for a number of such cases. It will be seen shortly, however, that certain ions are not discharged reversibly, and then the rule fails to hold. The difference between the observed decomposition voltage and that to be expected for a reversible cell is called the **polarization voltage,** and the electrodes are said to be **polarized.** Some aspects of electrolytic polarization or irreversible behavior in electrolysis will be considered later; for the present, however, reversible behavior will be assumed.

The decomposition voltage may be separated into two parts, representing the potentials which must be applied to each of the electrodes. Thus, in the continuous electrolysis of zinc bromide solution, the potential at the cathode must be just greater than the reversible Zn | $ZnBr_2$ soln. potential, and that at the anode must just exceed the reversible $ZnBr_2$ soln. | Br_2 | Pt, potential. The **discharge potential** or **deposition potential** at any elecrode is defined as *the potential at which the continuous deposition of material* (*or discharge of ions*) *commences at that electrode.* This should be equal to the reversible potential of the deposited material in the same solution, as has been verified in many instances, such as the deposition of zinc, cadmium, copper, silver, mercury, chlorine, bromine and iodine from solutions of their ions. The metals nickel, cobalt and iron behave somewhat abnormally in this connection, for reasons not clearly understood; however, the abnormality disappears as the temperature is raised, and the deposition potentials of these metals approach the ordinary reversible potentials. The method used for determining discharge potentials at the individual electrodes is a modification of that used for decomposition voltages and is described in § 50g.

In certain electrolyses the discharge of anions does not occur readily, but an equivalent electrical process, namely the passage of the anode metal into solution, takes place. An instance of this behavior is found with a silver anode in a solution of silver nitrate; the process occurring at the anode is not the discharge of an anion, but the metallic silver enters the solution as silver ions. In cases of this kind the potential of the anode, again, just exceeds the reversible potential of the metal in the given solution, e.g., silver in silver nitrate.

50b. Consecutive Electrode Processes at the Cathode.—If an electrolyte contains a number of different positive and negative ions then, provided there are no disturbing factors, *each ionic discharge will take place as the appropriate potential is reached.* When the external E.M.F. applied to an electrolytic cell is gradually increased, the potentials of the electrodes change until the discharge potentials of the most easily discharged ions are attained.

The cations that are discharged most readily are those having the largest (algebraic) *reduction potential,* since the free energy of the process

$$M^+ + \epsilon = M$$

will then have its greatest negative value, indicating a considerable tendency for the discharge process to occur. The largest reduction potential corresponds to the smallest oxidation potential; hence, the lower the oxidation potential, the more easily will the metallic ion be discharged. This means that for solutions of approximately equivalent ionic concentrations, *metals lower in Table 48.1 will be deposited before those higher in the table.* Consider, for example, the electrolysis of a solution containing molar zinc and copper sulfates; the oxidation potentials of the respective metals in these solutions are +0.76 and −0.34 volt. It follows, therefore, from the foregoing arguments that the cupric ions will be discharged first and metallic copper will be deposited on the cathode. If the electrolysis is prolonged to such an extent that the copper ions in the solution are almost exhausted, the cathode potential must be increased until that for zinc deposition is attained if electrolysis is to continue. In general, if a solution contains a number of different cations, each will be deposited in turn, starting from the one with the lowest oxidation potential *in the given solution.* In other words, *successive cathodic processes take place in order of increasing oxidation potential* in the solution being electrolyzed. This is the principle used in the separation of metals by electrolysis for analytical and other purposes.

Sometimes two metals have potentials that are not very different in the particular electrolyte; then simultaneous deposition of both metals occurs in the form of an alloy. Such is the case, for example, for copper and zinc in a solution containing their complex cyanides. Although the potentials of these metals differ considerably in sulfate solutions, the ionic concentrations are so changed in the complex cyanide solutions as to bring their respective potentials close together. When these solutions are electrolyzed, an alloy of zinc and copper, i.e., brass, is deposited on the cathode. Other alloys can be obtained in an analogous manner.

It should be pointed out that all aqueous solutions contain hydrogen ions; consequently the discharge of these ions, with the liberation of hydrogen, is a possibility to be taken into consideration. The discharge of certain cations, such as those of tin, nickel, iron, etc., is almost invariably accompanied by the evolution of hydrogen, particularly if the electrolytic solution is appreciably acid.

50c. Processes at the Anode.—The behavior at an anode is, in general, analogous to that at a cathode; the process associated with the largest negative free energy change, whether it be solution of the metallic anode to form cations or the discharge of anions, will take place first. Subsequent anodic processes will follow in order of decreasing negative free energy change. The reaction taking place at the anode is always an oxidation, and so *anodic processes take place in order of decreasing oxidation potential,* since ΔF is equal to

$-nFE$ [equation (47.1)]. For solutions of approximately the same ionic concentration, the order of anodic process, viz., formation of cations or discharge of anions, is that of the potentials in Table 48.1; the higher the process in this table, the more easily does it occur at an anode.

If a copper electrode is placed in an acid solution of M copper sulfate, three anodic processes are possible; these are first, solution of the copper to form cupric ions at a potential of -0.34 volt; second, discharge of hydroxyl ions, which are always present in aqueous solution, at about -1.2 volt ($c_{OH^-} = 10^{-14}$g-ion l^{-1}); and third, discharge of SO_4^{-2} ions, probably at a very high negative potential, e.g., about -2 volts. It is evident, therefore, that when an external E.M.F. is applied to the copper anode, the first process to occur will be that of the anode passing into solution as cupric ions, since the reaction $Cu = Cu^{+2} + 2\epsilon$ has the highest (most positive or least negative) oxidation potential. The next possible process is the discharge of hydroxyl ions, but this will not occur unless for some reason the solution of the anode is prevented. At an unattackable anode, such as platinum, where anion discharge is the only possible process, hydroxyl ions would be discharged and oxygen evolved. The discharge of SO_4^{-2} ions, with a large negative potential, is in any event highly improbable. The same, incidentally, is true of other similar ions, such as NO_3^-, PO_4^{-3}, etc., which do not correspond to stable uncharged molecules; they have high negative oxidation potentials, and their discharge from aqueous solutions does not commonly take place.

The consecutive discharge of anions may be illustrated by reference to the electrolysis of a N solution of neutral potassium iodide; such an electrolyte contains iodide and hydroxyl ions, whose oxidation potentials in the given electrolyte are about -0.54 (Table 48.1) and -0.80 volt ($c_{OH^-} = 10^{-7}$ g-ion l^{-1}), respectively. When this solution is electrolyzed by means of an external E.M.F., using a platinum anode, it is evident that iodide ions will be discharged preferentially. If the supply of these ions is exhausted, the anode potential must be made more negative for electrolysis to continue; hydroxyl ions will discharge and oxygen evolution will occur.

50d. Carriage of Current and Discharge of Ions.—Attention may be called here to an important matter in connection with electrolysis and ionic discharge that was referred to briefly in § 43a. It is essential to distinguish clearly between the ions *carrying the current to the electrode* and those actually *discharged at the electrode.* The carriage of current depends on the concentrations and speeds of the various ionic species present in the solution, whereas the discharge potential is determined essentially by the reversible potential in the given solution of the particular ion discharged. The two aspects of the problem are quite independent and should not be confused. As long as the appropriate quantity of electricity is transferred across the solution and at the electrodes, it is immaterial which ions perform the respective functions. In an acid solution of copper sulfate, for instance, the current is carried toward the anode almost exclusively by sulfate ions, and toward the cathode largely by hydrogen ions and to some extent by cupric ions; nevertheless, cupric ions only are discharged at the cathode, while at an inert, unattackable anode, such as one of platinum, hydroxyl ions are discharged, although they play a negligible part in the carriage of current.

50e. Electrolytic Polarization: Concentration Polarization.—Although many electrodes behave in a reversible manner, as assumed above, when the electrolyzing current is small, there is invariably some polarization, i.e., a departure from the theoretical decomposition voltage or discharge potential, as the current is increased. This is apparent, for example, in Fig. 50.1 from the slope to the right of the applied voltage curve, beyond *D*, with increasing current strength. If there were no polarization at all, the curve would be almost vertical. Polarization is invariably due to the slowness of one or more of the processes involved in bringing an ion up to the electrode and causing it to discharge. With small currents, when the rate of the over-all electrode process is low, the fact that one or the other stage is slow is of little significance. However, as the current strength is increased and the rate of discharge of ions increases correspondingly, the slow stage acts somewhat like a brake. To overcome this and permit electrolysis to continue at the rate required by the current strength, the applied voltage must be increased; the result is that what might be called the "driving force" of the discharge reaction is increased and the rate of the slow stage increases correspondingly.

In the discharge of ions at an electrode in electrolysis, there are two general types of slow stages which may be responsible for the observed polarization, i.e., increase in voltage. The first type, which undoubtedly occurs at all electrodes, is due to the slowness with which ions diffuse up to the electrode to replace those that have been discharged. This is called **concentration polarization** because it is associated with a decrease in concentration of the electrolyte in the immediate vicinity of the electrode. The slight slope to the right of the curve in Fig. 50.1 is largely due to concentration polarization. Any action which helps to bring the discharging ions up to the electrode at a faster rate will tend to decrease the concentration polarization. For a given solution, increase of temperature and, especially, vigorous agitation, have this result. For a given current strength, the concentration polarization is less in a concentrated than in a more dilute solution.

As seen in § 48e, II, every ten-fold change in ionic concentration changes the potential of an electrode by $0.0592/n$ volt at 25°C. Hence, a thousand-fold decrease in concentration, due to slowness of ionic diffusion, will result in a polarization of the order of $3 \times 0.0592/n$, i.e., about $0.18/n$ volt. Thus, concentration polarization is generally not large. However, if the current is increased sufficiently, a point is reached at which the particular ions are being discharged as fast as the maximum rate at which they can diffuse in the given solution. Any further increase in current will be possible only as a result of the discharge of another ion, such as the hydrogen ion, present in the solution. Although the bulk of the solution still contains adequate amounts of the first ion, the electrode behaves just as if this ion were completely exhausted. The electrode potential must then increase, as described above, to permit the discharge of another ion to occur. An important practical application of this phenomenon associated with concentrated polarization will be described in § 50h.

In the foregoing discussion, reference was frequently made to the current strength. The quantity which determines polarization, no matter what its cause, is the **current density**, i.e., *the current per unit area of electrode surface*, usually expressed in amperes (or fractions of an ampere) per sq cm. This is readily seen to be the case in connection with concentration polarization; the total rate at which ions diffuse to the electrode is proportional to its area. Hence, it is the relation between the diffusion rate per unit area and the current per unit area which determines the extent of the concentration change and the polarization.

50f. The Decomposition of Water.—The second type of polarization is due to a slow step in the actual process of discharge of the ion on the electrode. It is especially apparent in the discharge of hydrogen ions to yield hydrogen gas at a cathode and of hydroxyl ions to produce oxygen at an anode. A reversible cell consisting of a hydrogen gas electrode and an oxygen gas electrode, each at 1 atm pressure, has an E.M.F. of about 1.2 volt in any dilute aqueous solution.[*] Consequently, if the discharge of hydrogen and hydroxyl ions occurred reversibly, the decomposition voltage of a solution of acid or base should be 1.2 volt. The experimental results obtained in a number of instances, using the method described in § 50a with platinum for both cathode and anode, are quoted in Table 50.1 (M. Le Blanc, 1893); in each case hydrogen and oxygen gas were liberated at the respective electrodes.

TABLE 50.1. DECOMPOSITION VOLTAGES OF AQUEOUS SOLUTIONS OF ACIDS AND BASES

Acid	Volts	Base	Volts
Phosphoric	1.70	Tetramethylammonium OH	1.74
Nitric	1.69	Ammonia	1.74
Sulfuric	1.67	Sodium hydroxide	1.69
Perchloric	1.65	Potassium hydroxide	1.67

It is evident that the decomposition voltages of the aqueous solutions of acids and bases differ considerably from 1.2 volt, although they are all approximately constant at 1.7 volt. In all cases, therefore, there is a total polarization of about 0.5 volt at the platinum anode and cathode. However, the value depends on the nature of the electrode materials. Thus, with a lead anode and a platinum cathode in dilute sulfuric acid, the decomposition voltage is about 1.6 volt, but if the cathode is lead and the anode is platinum, the value is increased to 2.25 volts. The significance of these results will be examined below (§ 50g).

In most cases, especially if the electrodes are not attacked, the decomposition voltage, for given electrode materials, is the same for a variety of acids

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[*] This result may be derived very simply from the fact that ΔF^0 for the reaction $H_2(g) + \frac{1}{2}O_2(g) = H_2O(l)$, occurring in the hydrogen-oxygen cell for the passage of two faradays, is −56,700 cal at 25°C. Hence, by equation (48.12), since $n = 2$, $E^0 = -(-56{,}700)/2 \times 96{,}500 \times 0.2390 = 1.23$ volt.

and bases as in Table 50.1; this suggests that the electrolytic processes occurring at the anode and the cathode, respectively, are identical in all the solutions. The only process which could be common to all these solutions is the decomposition of water; hydrogen ions are discharged at the cathode, to yield hydrogen gas, and hydroxyl ions are discharged at the anode, leading to the evolution of oxygen, in every case. In a dilute solution of sulfuric acid, for example, the only cations are hydrogen ions, and so these must be discharged at the cathode. The most abundant anions in the solution are the sulfate ions, and these undoubtedly carry the current to the anode, but the hydroxyl ions have the higher oxidation potential, and so they are actually discharged in spite of their extremely low concentration in acid solution. Similarly, in a solution of sodium hydroxide, it is easy to understand that hydroxyl ions are discharged at the anode. At the cathode, however, hydrogen ions are most easily discharged, although their concentration is small in comparison with that of the sodium ions; the discharge of the latter requires a much larger cathode potential.

50g. Overvoltage.—As stated above, the decomposition voltage of a solution, from which hydrogen and oxygen gases are liberated, depends on the nature of the cathode and of the anode. In general, each electrode is polarized and its potential is in excess of the calculated reversible value by an amount that is dependent upon the nature of the metal and upon whether it forms the cathode or the anode. *The difference between the potential of an electrode at which gas evolution occurs and the theoretical reversible potential for the same solution* is called the **overvoltage.** By measuring the separate potentials at cathode and anode, when hydrogen and oxygen, respectively, are being evolved, and subtracting the calculated reversible potentials for the same solution, the cathodic and anodic overvoltages can be determined.

One way in which the measurements can be performed is by means of the apparatus shown in Fig. 50.2. The electrolysis vessel is an H-shaped cell containing the experimental solution with the electrodes A and B in separate units. These are connected, through a variable resistance D, to a battery C.

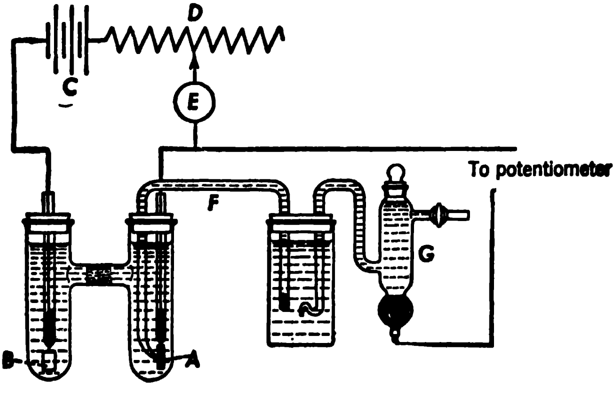

FIG. 50.2. Measurement of anode or cathode potential

The current passing through the cell is indicated on the galvanometer or meter *E*. The potential of the experimental electrode during electrolysis is measured by connecting it through a salt bridge (§ 48c) *F* to a reference, e.g., calomel, electrode *G*. The E.M.F. of the cell consisting of the electrodes *A* and *G* is determined with a potentiometer, and the potential of *A* is then obtained by subtracting the known potential of the reference electrode *G*. By adjusting the resistance *D*, the current through the cell is gradually increased and a number of determinations of the potential of *A*, which may be either anode or cathode, is made at a series of electrode current densities.

As is to be expected, the overvoltage at an electrode increases with the current density. Although there are exceptions, this increase can usually be represented by a logarithmic expression, first proposed by J. Tafel (1908), namely

$$\omega = a + b \log I, \tag{50.1}$$

where ω is the overvoltage at the current density I; the quantities a and b are constant for a given electrode under specified conditions. In many cases of hydrogen evolution, especially, b is approximately 0.12 which is roughly $2 \times 2.303RT/F$, and this is believed to have theoretical significance. However, observed values of b range from 0.02 to 0.3. The magnitude of a is a measure of the overvoltage, at different electrodes, for a given current density; some indication of these is given in Table 50.2. Unfortunately, overvoltage data are not too precise; the results depend on the state of the surface, which frequently changes with continued electrolysis, and are often affected by small traces of impurities. The hydrogen overvoltages recorded in the table were obtained from measurements, made under similar conditions, in N hydrochloric acid at a current density of 1 milliampere per sq cm at ordinary temperatures. An interesting generalization is apparent from Table 50.2: metals of low melting point have high overvoltages and vice versa.

TABLE 50.2. HYDROGEN OVERVOLTAGE IN N HYDROCHLORIC ACID AT 1 MILLIAMPERE PER SQ CM CURRENT DENSITY

Electrode Material	Overvoltage (volts)	Electrode Material	Overvoltage (volts)
Platinum (black)	0.01	Copper	0.54
Gold	0.17	Aluminum	0.58
Platinum (smooth)	0.26	Tin	0.85
Nickel	0.33	Lead	0.88
Iron	0.40	Cadmium	0.99
Silver	0.46	Mercury	1.04

Increasing the effective area of the surface causes a decrease in overvoltage, as is shown by the difference between smooth platinum and an electrode coated with finely divided platinum black. Increase of temperature also decreases overvoltage. In dilute solutions of pure acids, at least, the hydrogen overvoltage is independent of the hydrogen ion concentration of the electrolyte.

Although numerous experimental and theoretical studies of overvoltage have been made, there is no general agreement as to the basic cause of the polarization effect measured as overvoltage in the electrolytic liberation of hydrogen gas. While it is accepted that several steps are involved in the discharge of a hydrogen ion and that one, at least, is relatively slow, there is considerable controversy as to the nature of this slow step. It is probable that no single mechanism will account for the overvoltage at all cathodes and it is, in fact, possible that more than one slow stage may be effective even at a given cathode.

In the conversion of a hydrated hydrogen (H_3O^+) ion in aqueous solution to hydrogen gas at a cathode, there are three processes which might conceivably be slow. There is first, the removal of a proton from the hydrogen ion, its neutralization by an electron and the formation of a hydrogen atom attached to the surface of the cathode metal (M); thus,

$$\text{(I)} \qquad H_3O^+ + M + \epsilon \rightarrow H-M + H_2O.$$

This may be followed by catalytic combination of the hydrogen atoms on the cathode metal surface to form molecular (gaseous) hydrogen, i.e.,

$$\text{(II)} \qquad 2H-M \rightarrow H_2 + 2M,$$

which may be a slow process. As an alternative to this, a further hydrated hydrogen ion may be discharged on (or adjacent to) the hydrogen atom, to form molecular hydrogen by what is called the electrochemical mechanism; thus,

$$\text{(III)} \qquad H_3O^+ + H-M + \epsilon \rightarrow H_2 + M + H_2O.$$

A modification of the step I suggests that, because of the great preponderance of water molecules in an aqueous solution, the proton discharged at the cathode originates in a water molecule. It is postulated that the initial (slow) step is the transfer of a proton from a water molecule in solution to one attached to the cathode metal, i.e.,

$$\text{(I}'\text{)} \qquad H_2O + H_2O-M \rightarrow OH^- + H_3O^+-M,$$

followed by rapid neutralization of the H_3O^+ ion by an electron. This appears to be more plausible than the suggestion that the electrical neutralization process, as in I, is slow.

Arguments have been presented both for and against all these proposals concerning the nature of the slow step in hydrogen ion discharge. An interesting point that has been quoted in favor of process II as the slow stage is that the best catalysts for hydrogenation reactions, e.g., platinum, nickel and copper, which facilitate the reaction $2H \rightleftharpoons H_2$ in both directions, have the lowest overvoltage. However, it is possible that there is no direct cause and effect relationship. Another property, e.g., the high strength of the H—M bond, could be independently responsible for both good hydrogenation catalysis and low overvoltage.

Oxygen overvoltage at anodes are even more difficult to measure accurately than are hydrogen overvoltages. One reason is that the anode metal generally becomes covered with a layer of oxide (or oxides) which may be invisible. The exact nature of the anode surface is therefore in doubt. The results in Table 50.3, obtained at a current density of 0.1 milliampere per sq cm in N potassium hydroxide, give some indication, however, of the magnitude of the oxygen overvoltage at a few anodes. The variation with current density is sometimes represented by the Tafel equation (50.1) with *b* ranging from 0.07 to 0.30, but as a general rule, the logarithmic variation is less definite than for hydrogen overvoltage.

TABLE 50.3. OXYGEN OVERVOLTAGE IN N POTASSIUM HYDROXIDE AT 0.1 MILLIAMPERE PER SQ CM CURRENT DENSITY

Anode Material	Overvoltage (volts)	Anode Material	Overvoltage (volts)
Platinum (black)	0.32	Silver	0.45
Iron	0.37	Copper	0.49
Carbon (graphite)	0.37	Platinum (smooth)	0.80
Nickel	0.45	Gold	0.93

The cause of oxygen overvoltage is even more uncertain than that of hydrogen overvoltage. The slow step has been assigned to the electrical neutralization of the hydroxyl ions, as intermediate state in the formation of oxygen molecules from the resulting radicals, or the transfer of a proton from a water molecule attached to the anode to one in the solution. This last suggestion is seen to be analogous, but opposite, to mechanism (I′) proposed to account for hydrogen overvoltage. For some metals, e.g., platinum, there is a similarity in the anodic and cathodic behavior with current density which lends some support to the proton transfer mechanism. But it is doubtful whether this similarity extends to other electrode materials.

The theoretical interpretation of overvoltage requires precise measurements at exactly known current densities under controlled conditions. For practical purposes, however, a useful quantity is the overvoltage at which visible gas evolution in the form of bubbles commences. This bubble overvoltage has no theoretical significance, but it gives a useful indication of the polarization required at an electrode before gas evolution commences at an observable rate. It corresponds roughly to the situation at which the decomposition voltage in a solution is measured. Some approximate bubble overvoltages of a few common electrodes at ordinary temperatures are given in Table 50.4.

TABLE 50.4. CATHODIC AND ANODIC BUBBLE OVERVOLTAGES

Electrode	Hydrogen	Oxygen
Platinized platinum	~0.00 volt	0.25 volt
Iron	0.08	0.25
Smooth platinum	0.09	0.45
Nickel	0.21	0.06
Cadmium	0.48	0.43
Lead	0.64	0.31
Zinc	0.70	—
Mercury	0.78	—

It is seen that the hydrogen overvoltage at a smooth platinum cathode is 0.09 volt, and the oxygen overvoltage at an anode of this metal is 0.45 volt; the total excess potential is thus 0.54 volt. If this is added to the reversible E.M.F. of the hydrogen-oxygen cell, i.e., 1.2 volt, which is the theoretical decomposition voltage for the simultaneous liberation of hydrogen and oxygen, the result approximates the actual decomposition voltage of 1.7 volt.

Example: An aqueous solution is electrolyzed with a lead anode and a mercury cathode so that oxygen and hydrogen, respectively, are evolved. Calculate the approximate decomposition voltage at ordinary temperatures.

The oxygen overvoltage at a lead anode is 0.31, and the hydrogen overvoltage at a mercury cathode is 0.78 volt; the total overvoltage is thus $0.31 + 0.78 = 1.09$ volt. This must be added to the theoretical decomposition voltage, i.e., 1.2, giving about 2.3 volts for the actual value.

There are several important consequences of overvoltage, but a few only will be mentioned here. Consider a solution containing approximately molar zinc sulfate and sulfuric acid; the reversible oxidation potentials of zinc and hydrogen are +0.76 volt and 0.0 volt, respectively. It is to be expected, therefore, that when such a solution is electrolyzed hydrogen alone, and no zinc, should be liberated at the cathode. In actual practice, however, considerable amounts of zinc are deposited, in addition to hydrogen, in spite of the large difference in the reversible potentials. The explanation for this behavior is to be found in the high overvoltage for hydrogen evolution at a zinc cathode. From the data in Table 50.4, this is seen to be about 0.7 volt, and so the evolution of hydrogen will not take place until a potential of 0.7 volt is attained, instead of about 0.0 volt. The former potential is so close to that for zinc ion discharge (0.76 volt) in the same solution that simultaneous deposition of hydrogen and zinc occurs. The fact that zinc can be deposited on the cathode by the electrolysis of an acid solution of zinc sulfate is thus to be attributed to the high hydrogen overvoltage of zinc. The deposition of other metals lying above hydrogen in the table of electrode potentials (Table 48.1) is also largely due to overvoltage effects.

Overvoltage also plays an important part in the industrial production of sodium hydroxide and chlorine by the electrolysis of sodium chloride solutions. If the discharge of hydroxyl ions were reversible it should occur in preference to that of chloride ions, so that oxygen would be evolved, and not chlorine. Because of the high overvoltage accompanying the evolution of oxygen, and the small, or zero, overvoltage for chlorine, the order of the two anode processes is reversed and chlorine is actually obtained.

Example: In an alkali-chlorine cell a saturated (about 6 N) solution of sodium chloride is electrolyzed, at ordinary temperatures, between a steel cathode (hydrogen overvoltage 0.2) and a graphite anode (oxygen overvoltage 0.6 volt; chlorine overvoltage negligible). Explain the nature of the electrode processes.

Cathode. The cations present in the solution are H^+ and Na^+; the concentrations (approx. activities) are 10^{-7} (for a neutral solution) and 6 g ion per liter, respectively.

The standard oxidation potentials (Table 48.1) are 0.0 and +2.71 volt, respectively; hence, the reversible potentials in the given electrolyte are

$$E_{H} = 0 - 0.059 \log 10^{-7} = +0.41 \text{ volt}$$

$$E_{Na} = +2.71 - 0.059 \log 6 = +2.66 \text{ volt.}$$

Since the hydrogen overvoltage is 0.2, the potential for the discharge of hydrogen ions and the evolution of hydrogen gas is +0.41 + 0.2 = 0.61 volt (note signs!); this is so much below that required for Na^+ ion discharge, that the former process obviously takes place in preference (§ 50b). Only by raising the potential to 2.66 volt, e.g., by a large increase of current, would discharge of Na^+ ions become possible. Incidentally, this is another illustration of the fact that the ions carrying the current are not necessarily those discharged (§ 50d). The removal of H^+ ions by discharge leaves an excess of OH^- ions in the solution, and this accounts for the formation of sodium hydroxide.

Anode. The anions present are OH^- and Cl^-, the concentrations being 10^{-7} and 6 g ion per liter, as for H^+ and Na^+, respectively. The standard oxidation potentials of O_2 and Cl_2 are −0.40 and −1.36, respectively, and hence the reversible potentials in the given electrolyte are

$$E_{O} = -0.40 + 0.059 \log 10^{-7} = -0.81 \text{ volt}$$

$$E_{Cl} = -1.36 + 0.059 \log 6 = -1.31 \text{ volt.}$$

Allowing for the overvoltage (0.6 volt), the oxygen evolution potential resulting from the discharge of OH^- ions, is −0.81 − 0.6 = −1.41 volt (note signs!), and hence discharge of chloride ions, and the formation of chlorine gas, will take place in preference. By increasing the anode potential, however, oxygen evolution would tend to occur.

50h. The Dropping Mercury Cathode.—The dropping mercury cathode is the basis of a highly versatile analytical device known as the **polarograph.** Its use involves both overvoltage and concentration polarization. The apparatus consists, essentially, of an electrolytic cell in which the cathode is of mercury which is being continuously renewed by falling in drops from the end of a capillary tube. The anode is a relatively large pool of mercury at the bottom of the vessel. A dilute solution containing one or more salts for analysis is placed in the cell and an E.M.F. applied between the two mercury electrodes. This E.M.F. is gradually increased and the corresponding value of the current is recorded photographically or in other ways. A drawing of a **polarogram** obtained in this way from a solution containing six cations, each at a concentration of 10^{-4} gram ion per liter, is shown in Fig. 50.3.

In the electrolysis of this solution, copper deposits first on the cathode as this has the lowest oxidation potential. As the current increases, a point is reached at which diffusion of copper ions to the dropping mercury cathode is no longer able to satisfy the requirements of the current. Another process, in this case the discharge of lead ions, must occur in addition. There is thus an increase in potential to that at which lead deposition is possible. Subsequently, discharge of cadmium, zinc, etc., ions take place, at the appropriate potentials. The discharge of each ion species is accompanied by a "wave," represented by an increase of current, and is followed by an increase

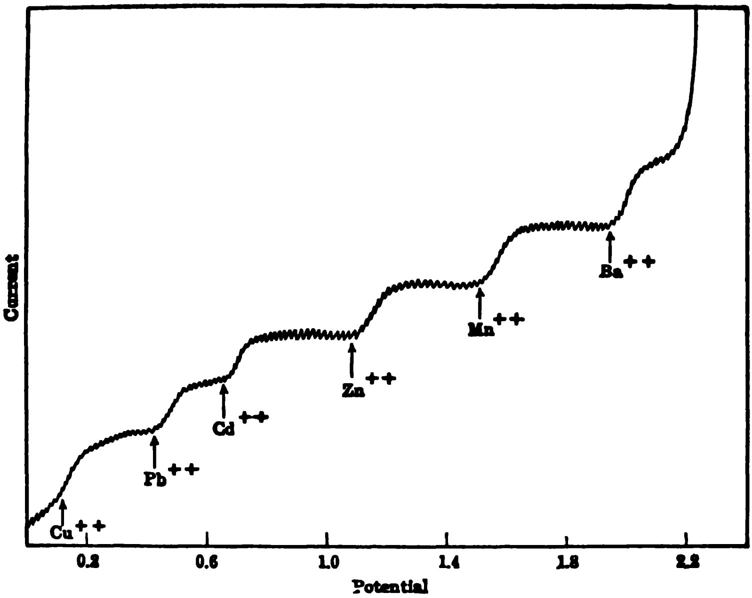

FIG. 50.3. Polarographic waves

of potential, at almost constant current, to the next wave.* The height of a wave, in units of current, is called the **diffusion current** and is proportional to the concentration in the solution of the ion being discharged. The potential at the center of the rising part of the wave, referred to as the **half-wave potential,** serves to identify the ion. This is the basis of the use of the polarograph as an analytical tool.

In addition to being a liquid metal, so that the surface can be continuously renewed in the form of drops, the mercury serves other purposes. The high overvoltage of hydrogen at a mercury cathode (Tables 50.2 and 50.4) makes possible the discharge of cadmium, zinc, and other ions, including sodium, in preference to hydrogen ions. This discharge is facilitated by the fact that many metallic elements dissolve in mercury, and the deposition, e.g., of sodium, in such a solution (or amalgam) occurs more readily than deposition of the pure element. For these reasons, the polarograph can be used for the analysis of ions which would not normally be deposited in electrolysis.

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2. **Hydrogen overpotential.** Bockris, *ibid.*, **43,** 525 (1948).
3. **Silver-silver halide electrodes.** Janz and Tamaguchi, *ibid.*, **53,** 397 (1953).
4. **Concentration cell measurements.** Hoyt, *J. Chem. Ed.*, **14,** 185 (1937).

* The small oscillations in the waves in Fig. 50.3 are caused by the changes in the area of the cathode during growth and detachment of the mercury drops.

5. **Transference numbers by E.M.F.** Masson and Mellon, *ibid.*, 16, 512 (1939); 17, 96 (1940).

6. **Electrode sign conventions.** Anson, *ibid.*, 36, 394 (1959).

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PROBLEMS

1. For the cell Ag(*s*) | AgBr(*s*) | KBr(*aq*) | Hg_2Br_2(*s*) | Hg(*l*), the E.M.F. is independent of the concentration of KBr; the values at several temperatures are

t°C	20	25	30
E.M.F. volts	0.06630	0.06839	0.07048

(*a*) Write the cell reaction for the passage of two faradays. (*b*) Calculate ΔH^0, ΔF^0 and ΔS^0 at 25°C. (*c*) Determine the standard entropy of Hg_2Br_2(*s*) at 25°. The standard entropy of AgBr is 25.60 e.u.; other necessary data will be found in previous chapters.

2. The E.M.F. of the cell H_2(*g*, 1 atm) | HBr(*m*) | AgBr(*s*) | Ag(*s*) at 25°C for several molalities is given as

m	*E*	*m*	*E*
1.262×10^{-4}	0.53300 v	10.994×10^{-4}	0.42280 v
1.775	.51616	18.50	.39667
4.172	.47211	37.19	.36173

(*a*) Evaluate E^0. (*b*) What is the standard electrode potential of the Ag | AgBr electrode? (*c*) Determine the mean activity coefficient of 0.01 *m* HBr for which $E = 0.31262$ v.

3. The standard potential of the electrode Pb(*s*) | $PbSO_4$(*s*) | SO_4^{-2} is 0.355 v at 25°C. Determine the approximate concentration of Pb^{+2} in solution.

4. (*a*) Formulate a cell in which the following reaction could occur: $Fe^{+2} + \frac{1}{2}Br_2 = Fe^{+3} + Br^-$. (*b*) Determine E^0, ΔF^0 and *K* for the reaction at 25°C. (*c*) What would be the corresponding values for the reaction $2Fe^{+2} + Br_2 = 2Fe^{+3} + 2Br^-$?

5. For the cell Pb(*s*) | $PbSO_4$(*s*) | H_2SO_4(*m*) | $PbSO_4$(*s*) | PbO_2(*s*), the E.M.F. is 2.004 v when *m* is 3. At this concentration the activity of the sulfuric acid is 0.303 and the activity of the water in the acid is 0.851. (*a*) Write the cell reaction. (*b*) Determine the standard potential of the $PbSO_4$ | PbO_2 electrode.

6. The equilibrium constant for the reaction $2Cu^+ = Cu^{+2} + Cu(s)$ at 25°C is 1.646×10^6. (*a*) Construct a cell in which the reaction could occur. (*b*) Calculate the standard E.M.F. for the cell. (*c*) Evaluate the standard potential of the Cu | Cu^+ electrode.

7. (*a*) Calculate the potential of the electrode Pt | Ce^{+4}, Ce^{+3} at 25°C when a 0.10 M solution of $Ce(SO_4)_2$ is reduced to the following extent: 25%, 50%, 99%, 99.9%. (*b*) What would be the E.M.F. in each case of a cell composed of the electrode and a saturated calomel electrode?

8. A cell consists of a Pt electrode immersed in the redox system, $A^{+z} = B^{+(z+n)} + ne$ combined with a saturated calomel electrode. From the following data at 30°C, determine the value of *n*.

% in reduced form	24.4	48.8	73.2	85.4
E.M.F. volts	0.101	0.116	0.129	0.139

The oxidation potential of the calomel electrode at 30°C is −0.238 v.

9. Given the metals silver and copper and solutions of silver nitrate and cupric nitrate. (*a*) Construct a cell which will operate spontaneously. (*b*) Write the equation for the reaction. (*c*) Calculate the equilibrium constant for the reaction.

10. (*a*) Calculate the E.M.F. of the amalgam concentration cell

$$\mathrm{Zn(Hg)}(c_1) \mid \mathrm{ZnSO_4}\ (aq) \mid \mathrm{Zn(Hg)}(c_2)$$

at 60.0°C when c_1 and c_2 are 6.08×10^{-5} and 2.28×10^{-3} g atom l^{-1} respectively. The amalgams are sufficiently dilute to be considered ideal. (*b*) Write the equation for the reaction when the cell has delivered one faraday.

11. The E.M.F. of the normal Weston cell at 25°C is 1.0184 v. (*a*) Calculate $\gamma_\pm$ of the cadmium sulfate in the solution. The concentration of the saturated solution is $3.683m$; $E^0_{298} = 0.3517\mathrm{v}$ for $\mathrm{Cd(Hg)} = \mathrm{Cd^{+2}} + 2\epsilon$ and $E^0_{298} = -0.6143\mathrm{v}$ for $2\mathrm{Hg}(l) + \mathrm{SO_4^{-2}} = \mathrm{Hg_2SO_4}(s) + 2\epsilon$. (*b*) Calculate $a_{\mathrm{H_2O}}$. The vapor pressure of the saturated solution is 21.17 mm at 25°.

12. The concentration cell

$$\mathrm{Ag}(s) \mid \mathrm{AgCl}(s) \mid \mathrm{KCl}\ (0.50\ \mathrm{N}) \mid \mathrm{K(Hg)} \mid \mathrm{KCl}\ (0.05\ \mathrm{N}) \mid \mathrm{AgCl}(s) \mid \mathrm{Ag}(s)$$

has an E.M.F. of $-0.10740\mathrm{v}$ at 25°C. (*a*) Formulate the corresponding cell with transference. (*b*) Write the equations for the cell reactions for the passage of 2 faradays. (*c*) The E.M.F. of the cell in (*a*) is $-0.05357\mathrm{v}$. Calculate the transference number of the $\mathrm{Cl^-}$.

13. What is the maximum hydrogen ion concentration permissible in a solution of a nickel salt ($a_{\mathrm{Ni^{+2}}} = 0.10$), so that the reversible deposition of nickel on the cathode during electrolysis could occur without hydrogen evolution at 25°C?

14. A solution containing $\mathrm{Fe^{+2}}$ and $\mathrm{Cd^{+2}}$ at unit activity is electrolyzed at 25°C. What fraction of the cadmium can be deposited before iron starts to plate out, assuming reversible behavior?

14

Equilibria in Electrolytes

ACTIVITY COEFFICIENTS

51a. Ionization Equilibrium Constants.—In a solution of any electrolyte there should be an equilibrium between the free ions, on the one hand, and undissociated molecules, on the other hand; the latter may consist of both true nonionized, covalent molecules, if any are present, and also of ion-pairs held together by electrostatic forces (§ 45f). Writing the equilibrium in the form

$$MA \rightleftharpoons M^+ + A^-,$$

the equilibrium constant is

$$K = \frac{a_{M^+} \times a_{A^-}}{a_{MA}}, \tag{51.1}$$

where, as usual, the a factors are the activities of the indicated species. The activity may be replaced by the product of the concentration c, in gram ions or moles per liter, and the activity coefficient f (§ 26d); hence, equation (51.1) may be written as

$$K = \frac{c_{M^+} \times c_{A^-}}{c_{MA}} \cdot \frac{f_{M^+} \times f_{A^-}}{f_{MA}}. \tag{51.2}$$

Alternatively the activity may be expressed as the product of the molality m and the activity coefficient γ, so that

$$K = \frac{m_{M^+} \times m_{A^-}}{m_{MA}} \cdot \frac{\gamma_{M^+} \times \gamma_{A^-}}{\gamma_{MA}}. \tag{51.3}$$

Although these K's are both constants, they are different because different standard states are involved in expressing the activities.

For weak electrolytes, the ionic concentrations are low and the solutions do not deviate appreciably from ideal behavior. The individual activity coefficients are close to unity and so also is the activity coefficient factor in equations (51.2) and (51.3). Reasonably good values, not very greatly different from the true constant K, can then be obtained by considering only the equilibrium concentration (or molality) terms in the equations. These, as will be seen later (§ 52c), can be derived from conductance measurements.

For strong electrolytes, however, except at extreme dilutions, there is marked departure from ideality; the activity coefficient factor then differs considerably from unity, and also varies with the concentration. It is necessary, therefore, to take into consideration the activity coefficients in evaluating ionization equilibrium constants. The subject of activity coefficients, particularly of strong electrolytes, is therefore of interest.

51b. Mean Activity Coefficients of Strong Electrolytes—It must be emphasized that there is no experimental method whereby the activities (or activity coefficients) of individual ionic species can be determined. It is impossible to prepare a solution containing only one kind of ion and so what is determined is the activity of the electrolyte containing the particular ion. Fortunately, for most purposes it is sufficient to known the mean ionic activity, defined by equation (49.3) for a 1-1 electrolyte.* Consider an electrolyte M_xA_y ionizing in the manner

$$M_xA_y \rightleftharpoons xM^+ + yA^-$$

to form positive M^+ and negative A^- ions. For simplicity, these are indicated with a single + and − respectively, although this is not meant to imply that the ions necessarily have only a single charge. The activity a of the electrolyte solute and the mean ionic activity $a_\pm$ are then defined by

$$a = (a_+)^x(a_-)^y = (a_\pm)^{x+y}. \tag{51.4}$$

This is in harmony with the result obtained in § 49a for a 1-1 electrolyte that $a_2/a_1 = [(a_\pm)_2/(a_\pm)_1]^2$. Determinations of activities by E.M.F. methods give either a or $a_\pm$, depending upon how the equations are written. The freezing point (§ 26e) and vapor pressure (§ 26e) methods, however, yield the activity a of the solute, and $a_\pm$ for the same solution can then be obtained from equation (51.4).

The ionic activities in equation (51.4) may be replaced by the products $m_+\gamma_+$ and $m_-\gamma_-$, so that

$$a = (m_+\gamma_+)^x(m_-\gamma_-)^y = (a_\pm)^{x+y}. \tag{51.5}$$

If m is the molality of the electrolyte solute in the solution, then the ionic molalities m_+ and m_- are xm and ym, respectively; these values may be substituted into equation (51.5) with the result

$$a = (xm\gamma_+)^x(ym\gamma_-)^y = x^xy^y(m\gamma_\pm)^{x+y}, \tag{51.6}$$

where the mean (molal) ionic activity coefficient $\gamma_\pm$ is defined by

$$(\gamma_\pm)^{x+y} = \gamma_+^x\gamma_-^y. \tag{51.7}$$

Hence, if a is determined experimentally, the mean ionic activity coefficient can be easily derived, since x and y are known. For a 1-1 electrolyte, such as NaCl, for example, $x = 1$ and $y = 1$, so that $a = a_\pm^2$ by equation (51.4) and

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* Electrolytes may be classified according to the valence (or charge) of the ions they contain; two numbers are used, the first giving the charge of the positive ion and the second that of the negative ion. For example, KCl is a 1-1 electrolyte, $Ba(NO_3)_2$ is 2-1, Na_2SO_4 is 1-2, etc.

$a = m^2\gamma_\pm^2$. For a 1-2 electrolyte, e.g., Na_2SO_4, $x = 2$, $y = 1$, so that $a = a_\pm^3 = 1^1 \times 2^2 \times (m\gamma_\pm)^3 = 4m^3\gamma_\pm^3$; exactly the same result is obtained for a 2-1 electrolyte such as $Ba(NO_3)_2$.

Three methods have been chiefly employed for the determination of the mean activity coefficients of strong electrolytes; the freezing point and E.M.F. methods have been used for solutions of all kinds, whereas the procedure based on vapor measurements has also been employed for less dilute solutions. The results obtained by these methods, as well as in other ways, are in good agreement with one another and may be accepted as accurate. Mean ionic activity coefficients are usually expressed in terms of molalities, and some of the most reliable data for a number of electrolytes at 25°C are quoted in Table 51.1. By expressing the activity as the product of the concentration c moles per liter and the activity coefficient f, equations exactly analogous to those given above can be derived. However, for dilute aqueous solutions there is little difference between activity coefficients based on molalities and those based on concentrations. For concentrations of 0.01 molar (or molal) the difference is approximately 0.5 per cent and is even less for more dilute solutions. Hence, for these solutions the figures in Table 51.1 may be employed in equations such as (51.2) without serious error.

TABLE 51.1. MEAN MOLAL IONIC ACTIVITY COEFFICIENTS AT 25°C

Molality	HCl	NaCl	KCl	$CaCl_2$	$ZnCl_2$	H_2SO_4	$LaCl_3$	$ZnSO_4$
0.001	0.966	0.966	0.966	0.888	0.881	—	0.853	0.734
0.005	0.930	0.928	0.927	0.789	0.767	0.643	0.716	0.477
0.01	0.906	0.903	0.902	0.732	0.708	0.545	0.637	0.387
0.02	0.878	0.872	0.869	0.669	0.642	0.455	0.552	0.298
0.05	0.833	0.821	0.816	0.584	0.556	0.341	0.417	0.202
0.10	0.798	0.778	0.770	0.524	0.502	0.266	0.356	0.148
0.50	0.769	0.679	0.652	0.510	0.376	0.155	0.303	0.063
1.00	0.811	0.656	0.607	0.725	0.325	0.131	0.387	0.044
2.00	1.011	0.670	0.577	1.554	—	0.125	0.954	0.035
3.00	1.31	0.719	0.572	3.38	—	0.142	—	0.041

An examination of the mean activity coefficients recorded in the table brings to light a number of interesting facts. It will be observed, in the first place, that the values always decrease initially as the concentration is increased, but they generally pass through a minimum and then increase again. This is seen more clearly in Fig. 51.1, where the activity coefficients of a few electrolytes have been plotted against the square root of the corresponding molality. In dilute solutions of strong electrolytes, therefore, the deviations from ideal behavior make the activity, which may be regarded as the effective or ideal concentration, less than the actual concentration; in concentrated solutions, however, the effective concentration is greater than the actual value, since the activity coefficient exceeds unity. It will be seen, further, from Table 51.1, that electrolytes of the same valence type, e.g., sodium and potassium chlorides, etc., or calcium and zinc chlorides, etc., have almost identical activity coefficients at the same concentration, in dilute solution.

Finally, it will be noted that the deviation from ideal behavior, that is, the departure of the activity coefficients from unity, at a given concentration is greater the higher the product of the valences of the two ions constituting the electrolyte.

51c. The Ionic Strength.—In order to represent the variation of activity coefficient with concentration, especially in the presence of added electrolytes, a quantity called the **ionic strength** was introduced (G. N. Lewis and M. Randall, 1921); it is a measure of the intensity of the electrical field due to the ions in a solution. The ionic strength is usually represented by the symbol μ, and is defined as *half the sum of the terms obtained by multiplying the molality (or concentration) of each ion in the solution by the square of its valence.* Thus, if a solution contains a number of different ionic species, indicated by the subscripts 1, 2, 3, etc., so that their respective molalities are m_1, m_2, m_3, etc., in gram ions per 1000 grams of solvent, and z_1, z_2, z_3, etc., are the corresponding valences, i.e., the charges carried by the ions, then the ionic strength is given by

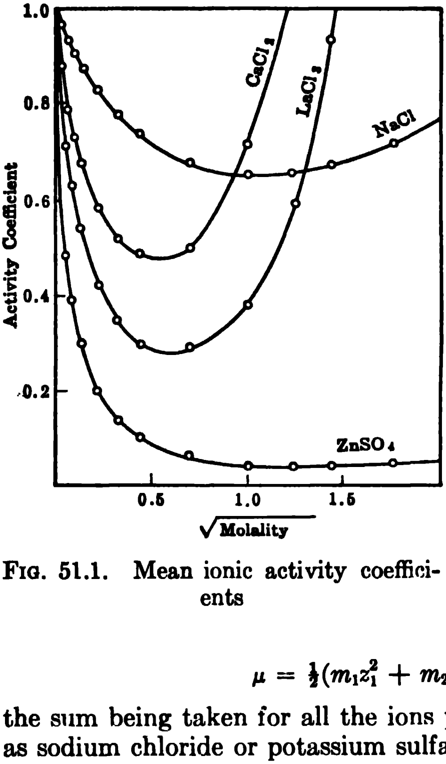

FIG. 51.1. Mean ionic activity coefficients

$$\mu = \tfrac{1}{2}(m_1 z_1^2 + m_2 z_2^2 + m_3 z_3^2 + \cdots), \tag{51.8}$$

the sum being taken for all the ions present. For a single electrolyte, such as sodium chloride or potassium sulfate, the equation reduces to two terms, one for the positive and one for the negative ion, viz.,

$$\mu = \tfrac{1}{2}(m_+ z_+^2 + m_- z_-^2). \tag{51.9}$$

Example: Calculate the ionic strength of (i) 0.1 molal KCl, (ii) 0.2 molal K_2SO_4, (iii) a solution containing 0.1 molal KCl and 0.2 molal K_2SO_4, (iv) 0.2 molal $BaCl_2$.

(i) The molality of each ion in 0.1 molal KCl is 0.1, i.e., $m_+ = 0.1$ and $m_- = 0.1$; also $z_+ = 1$ and $z_- = 1$, so that,

$$\mu = \tfrac{1}{2}(0.1 \times 1^2 + 0.1 \times 1^2) = 0.1.$$

(For any single uni-univalent electrolyte the ionic strength is always equal to the molality of the solution.)

(ii) Since K_2SO_4 produces two K^+ ions and one SO_4^{-2} ion, the molality of the ions in 0.2 molal K_2SO_4 is thus $m_+ = 2 \times 0.2 = 0.4$, and $m_- = 0.2$; $z_+ = 1$, $z_- = 2$; hence,

$$\mu = \tfrac{1}{2}(0.4 \times 1^2 + 0.2 \times 2^2) = 0.6.$$

(iii) In the mixture of 0.1 molal KCl and 0.2 molal K_2SO_4, the total molality m_1 of the K^+ ions = 0.1 + 0.4 = 0.5 and $z_1 = 1$; for the Cl^- ions, $m_2 = 0.1$ and $z_2 = 1$; for the SO_4^{-2} ions, $m_3 = 0.2$ and $z_3 = 2$; hence,

$$\mu = \tfrac{1}{2}(0.5 \times 1^2 + 0.1 \times 1^2 + 0.2 \times 2^2) = 0.7.$$

(It will be noted that the ionic strength of the mixture is the sum of the ionic strengths of the constituents.)

(iv) For the 0.2 molal $BaCl_2$ solution, $m_+ = 0.2$, $z_+ = 2$ and $m_- = 2 \times 0.2 = 0.4$ and $z_- = 1$, so that

$$\mu = \tfrac{1}{2}(0.2 \times 2^2 + 0.4 \times 1^2) = 0.6.$$

(For the same concentration μ is the same for the 2-1 electrolyte as it is for the 1-2 electrolyte in part (ii).)

It has been found from a study of the experimental data that in dilute solutions, more dilute than about 0.1 molal (or molar), *the mean activity coefficient of a given electrolyte is approximately the same in all solutions of a given ionic strength.* The particular ionic strength may be partly due to the presence of other salts; it is the *total* ionic strength, however, which determines the activity coefficient of the electrolyte under consideration. This generalization which, as will be seen shortly, has a theoretical basis, holds only for solutions of relatively low ionic strength; as the concentration is increased, the specific influence of the added salts becomes apparent.

51d. The Debye-Hückel Theory.—The fact that solutions of electrolytes do not behave ideally, and give activity coefficients that differ from unity, has been accounted for quantitatively, at least for dilute solutions; this has been achieved by means of the interionic attraction theory described in connection with conductance in § 45d. When an ideal solution is diluted there is a definite change of free energy which depends only on the initial and final concentrations of the solute. In the case of an ionic solution, however, there is an additional free energy change equivalent to the work done against the electrostatic attraction in removing an ion from its oppositely charged ionic atmosphere. This difference between the actual and ideal free energy of dilution is related to the activity coefficient of the ion in the given solution.

Using equation (26.6) and the alternative symbol $\bar{F}$ for the chemical potential,* the partial molal free energy of an ionic species in solution may be written as

$$\bar{F} = \bar{F}^0 + RT \ln a_i = \bar{F}^0 + RT \ln c_i + RT \ln f_i.$$

In an ideal solution the term $RT \ln f_i$ would be zero, since f_i is unity. Assuming that neutral, i.e., uncharged, particles in solution would behave ideally, $RT \ln f_i$ may then be identified with the excess free energy needed to charge the neutral particles so that they become ions. P. Debye and E. Hückel (1923) showed how the electrical free energy could be calculated by determining the electrostatic potential of an ion due to its oppositely charged ionic atmosphere and then evaluating the work done in charging the neutral

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* This is usually represented by μ, but it is not used here in order to avoid confusion with the ionic strength.

particle to this potential. By equating this free energy to the term $RT \ln f_i$, the result is

$$\log f_i = -1.823 \times 10^6 \frac{z_i^2}{(DT)^{3/2}} \sqrt{\mu} \tag{51.10}$$

for the variation of the activity coefficient f_i of an ion i of valence z_i with the *total* ionic strength μ of the solution; D and T represent the dielectric constant of the solvent and the absolute temperature. For a given solvent and temperature, D and T have definite values which may be inserted; equation (51.10) then takes the general form

$$\log f_i = -A z_i^2 \sqrt{\mu}, \tag{51.11}$$

where A is a constant for the solvent at the specified temperature. For comparison with experiment, equation (51.11) must be converted into an expression for the mean ionic activity coefficient; this is

$$\log f_{\pm} = -A z_+ z_- \sqrt{\mu}, \tag{51.12}$$

where z_+ and z_- are the (numerical) valences of the two ions. For water as solvent at 25°C, the dielectric constant D is 78.54 and T is 298.15°K; the constant A is then 0.509, so that equation (51.12) becomes

$$\log f_{\pm} = -0.509 z_+ z_- \sqrt{\mu}. \tag{51.13}$$

The foregoing equations represent the **Debye-Hückel limiting law**; the term "limiting" is used because the derivation is such that the results are applicable only to very dilute solutions approaching the limit of infinite dilution.

For an ideal solution the activity coefficient $f_{\pm}$ is unity, and hence $\log f_{\pm}$ would be zero; the fact that $\log f_{\pm}$ is negative, according to the Debye-Hückel equations, means that the activity coefficient should be less than unity, as it actually is in dilute solutions of electrolytes. According to equation (51.12) the plot of $\log f_{\pm}$ against $\sqrt{\mu}$ should be a straight line, passing through the origin, with a slope equal to $-A z_+ z_-$. Measurements of activity coefficients of various electrolytes, some of which will be referred to more explicitly in § 51f, in aqueous and nonaqueous solutions, at various temperatures, have established the quantitative accuracy of the Debye-Hückel equation for dilute solutions. The experimental values of $\log f_{\pm}$, for three salts of different valence types in aqueous solution, are plotted against $\sqrt{\mu}$ in Fig. 51.2; the dashed lines show the behavior to be expected from equation (51.12) or (51.13). It is evident that the experimental results tend toward the values required by the Debye-Hückel limiting law as infinite dilution is approached.

It can be readily shown in other ways that the Debye-Hückel theory is in general agreement with conclusions already noted from experimental data. By equation (51.12) or (51.13) the activity coefficient of a given electrolyte, for which z_+ and z_- are constant, should depend only on the ionic strength of the solution; this is identical with the empirical rule of Lewis and Randall

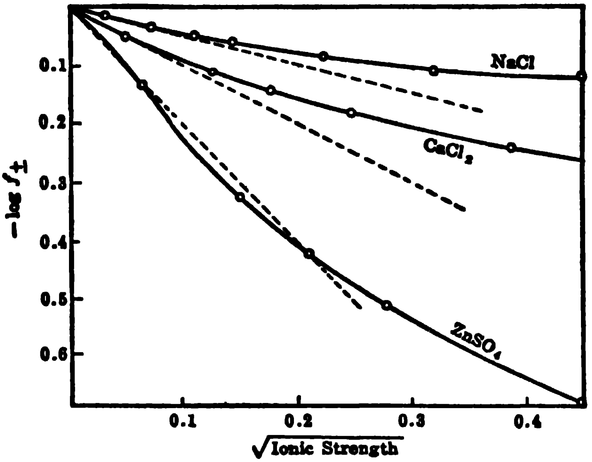

FIG. 51.2. Test of the Debye-Hückel limiting law

mentioned in the preceding section. Further, the Debye-Hückel limiting equation contains no reference to the specific nature of the electrolyte, apart from the valence of the ions; hence, electrolytes of the same valence type should have equal activity coefficients at the same concentration or ionic strength. This is in agreement with experiment, as the data in Table 51.1 show. Finally, the value of $\log f_\pm$, which is a measure of the deviation of the activity coefficient from unity, should be numerically proportional to z_+z_-, the product of the valences of the ions; this derivation from the interionic attraction theory is also supported by the experimental facts (Fig. 51.2).

Example: Calculate the mean activity coefficient of (i) a 1-1 electrolyte, e.g., HCl, NaCl, etc., at a molality of 0.01, and of (ii) a 1-2 or 2-1 electrolyte, e.g., Na_2SO_4, $CaCl_2$, etc., at a molality of 0.001, in aqueous solution at 25°C.

(i) For a 1-1 electrolyte, the ionic strength is equal to the molality; hence $\mu = 0.01$; z_+ and z_- are both unity, and so by equation (51.13), for an aqueous solution at 25°,

$$\log f_\pm = -0.509 \times 1 \times 1 \times \sqrt{0.01} = -0.0509$$

$$f_\pm = 0.889.$$

(The experimental value is about 0.90.)

(ii) For the 0.001 molal 1-2 electrolyte $\mu = \frac{1}{2}(0.002 \times 1^2 + 0.001 \times 2^2) = 0.003$; hence,

$$\log f_\pm = -0.509 \times 1 \times 2 \times \sqrt{0.003} = -0.0558$$

$$f_\pm = 0.879.$$

(The experimental value is about 0.88.)

According to the Debye-Hückel equation (51.10) the mean ionic activity coefficient of an electrolyte in different solvents should be dependent on the dielectric constant; the limiting slopes, at high dilution, of the plot of log $f_\pm$ against $\sqrt{\mu}$ should be inversely proportional to $D^{3/2}$, at constant temperature. The results of a comprehensive investigation in solutions of dielectric constant ranging from 9.53 to 78.6, at 25°C, are shown by the curves in Fig. 51.3.

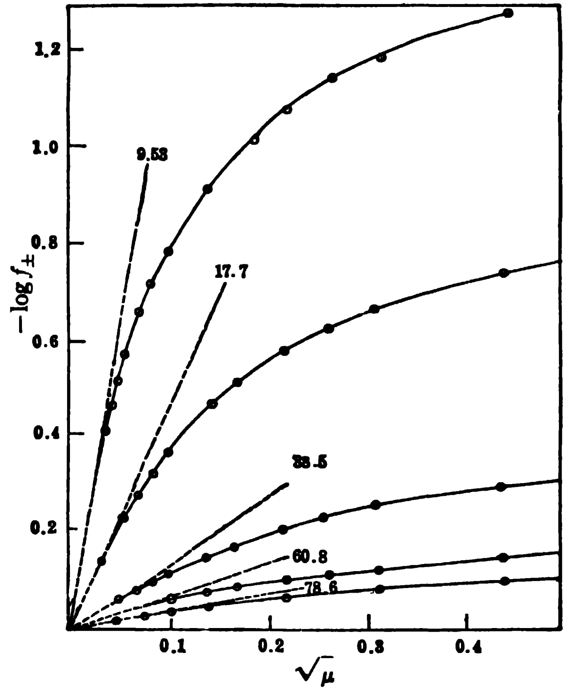

FIG. 51.3. Limiting Debye-Hückel equation for different dielectric constants (Harned, *et al.*)

The limiting slopes, calculated from equation (51.10), are indicated by the dotted lines marked with the values of the appropriate dielectric constants. The agreement with experiment in the dilute solutions is striking.

In general, the Debye-Hückel limiting law holds within the limits of experimental error for ionic strengths up to about 0.01. Beyond this point, the activity coefficient decreases more slowly, passes through a minimum, and then increases as the concentration is increased. Although the valence type is still an important factor, the specific properties of the individual electrolyte now becomes apparent. To account for the variation of activity coefficient with the ionic strength in solutions that are not very dilute, two empirical corrections have been applied to the Debye-Hückel treatment; one makes allowance for the sizes of the ions, and the other for the clustering or orientation of the dipolar water molecules around every ion. The effect of finite ionic size can be included by modifying equation (51.12) to

$$\log f_{\pm} = -\frac{Az_{+}z_{-}\sqrt{\mu}}{1 + aB\sqrt{\mu}}, \tag{51.14}$$

where a is the mean distance of approach of the ions and B is a constant, derived theoretically, for a given solvent and temperature. Since ions in solution are solvated, a is not the interionic distance obtained from X-ray measurements on crystals; it must be derived empirically using experimental measurements of activity coefficients. Since ions are approximately 10^{-8} cm in diameter and B is of the order of 10^{8} cm^{-1}, the product aB is close to unity. Consequently, equation (51.14) in the form

$$\log f_{\pm} = -\frac{Az_{+}z_{-}\sqrt{\mu}}{1 + \sqrt{\mu}} \tag{51.15}$$

may be used as a good approximation. For example, for 1-1 electrolytes, equation (51.15) is satisfactory at concentrations up to about 0.1 M.

The orientation of the solvent molecule dipoles around an ion is equivalent to an increase in the dielectric constant of the medium in the vicinity of the ion. This results in a decrease in the interionic forces and hence a smaller deviation from ideal behavior; the activity coefficient is therefore larger than would have otherwise been the case. Allowance for the orientation effect is made by adding to equation (51.14) a term proportional to μ; thus

$$\log f_{\pm} = -\frac{Az_{+}z_{-}\sqrt{\mu}}{1 + aB\sqrt{\mu}} + C'\mu. \tag{51.16}$$

Upon rearrangement and the neglect of small terms, this becomes

$$\log f_{\pm} = -Az_{+}z_{-}\sqrt{\mu} + C\mu, \tag{51.17}$$

where the empirical constant $C = aAB + C'$, can only be evaluated from experimental data; the value of C depends on the nature of the electrolyte, but no method has yet been devised for its calculation theoretically. For 1-1 electrolytes, equations (51.16) and (51.17) give satisfactory agreement with experiment at concentrations up to about 1 M.

Since equation (51.17) involves two terms, each being a function of the ionic strength, but of opposite sign, it can obviously satisfy the condition that the activity coefficient should have a minimum value at a particular ionic strength. At low concentrations the $-Az_{+}z_{-}\sqrt{\mu}$ term predominates, but as the concentration increases the $C\mu$ term becomes more important; hence, the activity coefficient will decrease with increasing ionic strength in dilute solutions, but it will increase in more concentrated solutions. It was seen above that the activity coefficient can be greater than unity, so that the activity exceeds the concentration; the physical interpretation of this fact is that the attraction between the ions and the solvent (dipole) molecules results in such a segregation of the latter that the *effective* concentration of the solution, relative to the *free* solvent molecules, becomes greater than the actual concentration. This decrease in the quantity of free solvent accounts for the familiar salting-out effect used in organic chemistry whereby the addition of an electrolyte decreases the solubility of a nonelectrolyte in water.

51e. Solubility Equilibria: The Solubility Product.—When a solution is saturated with a salt there is an equilibrium between the excess solid and the ions in solution. To consider a simple case, such as that of the sparingly soluble salt silver chloride in contact with its saturated solution, the equilibrium may be represented by

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-,$$

where Ag^+ and Cl^- refer, as usual, to the hydrated ions in solution. The corresponding equilibrium constant is given in the familiar manner as

$$K = \frac{a_{Ag^+} \times a_{Cl^-}}{a_{AgCl}}. \tag{51.18}$$

Since the silver chloride is present in the solid state, its activity is taken as unity, in accordance with convention (§ 33a); equation (51.18) then reduces to

$$K_s = a_{Ag^+} \times a_{Cl^-},$$

where the constant K_s is known as the **solubility product constant** of the silver chloride. In general, for any electrolyte having the general formula M_xA_y, in contact with its saturated solution, the equilibrium between the solid and the ions in solution is

$$M_xA_y(s) \rightleftharpoons xM^+ + yA^-,$$

and the solubility product constant is given by

$$K_s = a^x_{M^+} \times a^y_{A^-}. \tag{51.19}$$

This expression is the basis of the solubility product principle which states that *when a solution is saturated with a given salt, the product of the activities (or concentrations) of its constituent ions, raised to the appropriate powers, must be constant,* irrespective of the nature of the other electrolytes present in the solution.

If the activity of each ion is written as the product of its concentration in gram ions per liter and the corresponding activity coefficient, as in § 51a, the expression for the solubility product of M_xA_y becomes

$$K_s = (c^x_{M^+} \times c^y_{A^-})(f^x_{M^+} \times f^y_{A^-}), \tag{51.20}$$

and by a relationship analogous to equation (51.7) involving f instead of γ

$$K_s = (c^x_{M^+} \times c^y_{A^-})f^{x+y}_{\pm}, \tag{51.21}$$

where $f_{\pm}$ is the mean ionic activity coefficient of the M^+ and A^- ions in the solution. If the solid is sparingly soluble, as is the case with silver chloride, and the solution does not contain added electrolyte, the ionic strength of the medium will be low and the activity coefficients will not differ greatly from unity. In these circumstances, equation (51.21) may be reduced to the approximate expression

$$K'_s = c^x_{\mathrm{M}^+} \times c^y_{\mathrm{A}^-}, \tag{51.22}$$

so that equation (51.21) may be written as

$$K_s = K'_s f_{\pm}^{x+y}.$$

Unlike K_s, which is a constant at any given temperature, K'_s, called the concentration solubility product, will vary with the activity coefficient of M^+ and A^- in the solution, i.e., with the ionic strength of the solution. At low ionic strengths, where the activity coefficients approach unity, K_s and K'_s are not greatly different, so that K'_s defined by equation (51.22) is approximately constant.. This is the form in which the solubility product principle is frequently employed. However, at ionic strengths above 0.01, K'_s varies appreciably with the total concentration of the solution, and assuming it to be constant can lead to approximate results only.

The solubility product can be related to the observed solubility of the substance in pure water. Let S_0 mole per liter be the solubility of the substance $\mathrm{M}_x\mathrm{A}_y$; then since ionization may be assumed to be complete in the dilute solution, $c_{\mathrm{M}^+} = xS_0$ and $c_{\mathrm{A}^-} = yS_0$ g ions per liter. Hence, by equation (51.21)

$$K_s = (S_0 f_{\pm})^{x+y} x^x y^y \tag{51.23}$$

or, more approximately,

$$K'_s = S_0^{x+y} x^x y^y.$$

For a sparingly soluble 1-1 electrolyte, like silver chloride, $x = 1$ and $y = 1$, so that

$$K'_s = c_{\mathrm{Ag}^+} \times c_{\mathrm{Cl}^-} = S_0^2. \tag{51.24}$$

The solubility of silver chloride in pure water, as derived from conductance measurements, is 1.31×10^{-5} mole per liter at 25°C; the value of K'_s is consequently $(1.31 \times 10^{-5})^2$, i.e., 1.72×10^{-10}. At this low concentration, the mean activity coefficient may be calculated readily from equation (51.13) with $z_+ = 1$, $z_- = 1$ and $\mu = 1.31 \times 10^{-5}$; the value of $f_{\pm}$ is found to be 0.996. Consequently, it is reasonably justifiable to assume both complete dissociation and an activity coefficient of unity for the silver chloride solution in pure water, as was done in the foregoing calculations.

Another method for determining solubility products is based on the evaluation of ionic activities by measurements of electrode potential; this procedure may also be illustrated by reference to silver chloride. A solution of 0.1 N potassium chloride is saturated with silver chloride, and the silver ion activity a_{Ag^+} is determined by means of a silver electrode; the value, as shown by the example in § 48e,I, is found to be 2.34×10^{-9} gram ion per 1000 grams of water or, with sufficient accuracy, 2.34×10^{-9} gram ion per liter at 25°C. The chloride ion activity a_{Cl^-} in the solution may be taken as equal to the mean activity of the 0.1 N potassium chloride, in which the silver chloride is dissolved; this is equal to the product of the concentration, i.e., 0.1, and the mean activity coefficient 0.77 (Table 51.1), so that a_{Cl^-} is 0.077. The solubility product is then given by

$$K_s = a_{Ag^+} \times a_{Cl^-} = 2.34 \times 10^{-9} \times 0.077$$
$$= 1.80 \times 10^{-10},$$

a result in satisfactory agreement with K'_s obtained above by a different procedure.

Example: The silver ion activity in a saturated solution of Ag_2CrO_4 in 0.1 M K_2CrO_4 was found to be 6.4×10^{-6} g ion per liter at 25°C; assuming the mean activity coefficient of the K_2CrO_4 to be equal to that of another 1-2 electrolyte at the same concentration, calculate the solubility of Ag_2CrO_4 in pure water at 25°C.

From Table 51.1, the mean activity coefficient of a 1-2 electrolyte at 0.1 M is about 0.50; hence, the activity of the CrO_4^{-2} ions in 0.1 M K_2CrO_4 may be taken as $0.10 \times 0.50 = 0.050$. The solubility product constant of Ag_2CrO_4 is then

$$K_s = a^2_{Ag^+} \times a_{CrO_4^{-2}} = (6.4 \times 10^{-6})^2 \times 0.050$$
$$= 2.05 \times 10^{-12}.$$

If s mole per liter is the solubility of Ag_2CrO_4 in water, and the salt is assumed to be completely dissociated, c_{Ag^+} is equal to $2s$ and $c_{CrO_4^{-2}}$ is s g ion per liter; the solubility product is then $(2s)^2 \times s = 4s^3$, so that

$$4s^3 = 2.05 \times 10^{-12}$$
$$s = 8.0 \times 10^{-5} \text{ mole per liter.}$$

51f. Solubility and Activity Coefficient.—Since the activity coefficients vary with the ionic strength of the solution, it is apparent from equation (51.13) that the solubility of a sparingly soluble salt will not be the same in the presence of other electrolytes as it is in pure water. The relationship derived below is quite general, but for simplicity it will be assumed that the sparingly soluble substance is the 1-1 electrolyte silver chloride. Then equation (51.23) may be written as

$$K_s = S_0^2 f_0^2. \qquad (51.25)^*$$

If S is the solubility in any aqueous solution containing added electrolytes, *other than silver salts or chlorides*, and $f_\pm$ is the mean activity coefficient of the silver and chloride ions in this solution, then

$$K_s = S^2 f_\pm^2. \qquad (51.26)$$

Combination of this result with equation (51.25) gives

$$S_0 f_0 = S f_\pm,$$

and upon taking logarithms and rearranging, the result is

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* To simplify the representation, the subscript ± has been omitted from f_0; it should not be forgotten, however, that it is the *mean* ionic activity coefficient.

$$\log \frac{S}{S_0} = \log f_0 - \log f_{\pm}. \tag{51.27}$$

Although this equation has been derived for a 1-1 electrolyte, viz., silver chloride, it holds for a sparingly soluble substance of any valence type.

Equation (51.27) can be used to test the Debye-Hückel limiting law equation (51.12); thus, writing $-Az_+z_-\sqrt{\mu}$ for $\log f_{\pm}$, the result is

$$\log \frac{S}{S_0} = Az_+z_-(\sqrt{\mu} - \sqrt{\mu_0}), \tag{51.28}$$

where μ_0 is the ionic strength of the solution containing the sparingly soluble salt alone. A plot of $\log S/S_0$ against $\sqrt{\mu} - \sqrt{\mu_0}$ should thus be a straight line of slope Az_+z_-, where z_+ and z_- are the numerical valences of the ions of the sparingly soluble substance. The results of solubility measurements on a number of salts of different valence types in the presence of various added electrolytes at a number of ionic strengths are given in Fig. 51.4. The experimental data are indicated by the small circles. The full lines show the theoretical slopes to be expected from the Debye-Hückel theory; the agreement is seen to be excellent in dilute solutions.

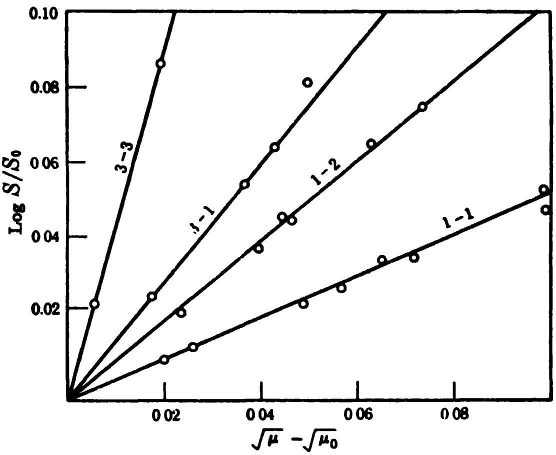

Fig. 51.4. Solubility and the Debye-Hückel theory

It is evident from Fig. 51.4 that in the presence of neutral salts, not containing a common ion, the solubility of a sparingly soluble salt increases with increasing ionic strength, that is, with increasing concentration of the neutral salts. The reason for this will be apparent from equation (51.26); as the ionic strength of the medium is increased, the activity coefficient $f_{\pm}$ decreases, and hence the solubility S must increase in order that the solubility product K_s may remain constant. However, if the ionic strength is made sufficiently large, the activity coefficient will pass through a minimum and then increase; the solubility of the sparingly soluble salt should thus attain a maximum value and then decrease, as the ionic strength of the solution is increased by the addition of neutral salts. This behavior was observed many years ago, but it could not be explained until the concept of activity and activity coefficients was developed. It should be noted that the concentration solubility product K'_s, defined by equation (51.22), gives no indication of the change in solubility; according to the equation the solubility should remain constant regardless of changes in the ionic strength of the solution.

The mean ionic activity coefficient of a sparingly soluble salt in solutions of various ionic strengths can be obtained from solubility determinations with the aid of equation (51.26) for a 1-1 salt or the analogous equation for salts of other types. Rearrangement of the equation gives

$$f_{\pm} = \frac{\sqrt{K_s}}{S}, \tag{51.29}$$

and since the solubility S can be measured, the problem is reduced to the evaluation of the solubility product constant. At infinite dilution, $f_{\pm} = 1$ and so, in these circumstances, equation (51.29) shows that $\sqrt{K_s} = S$. Solubility measurements at infinite dilution are, of course, impossible but determinations can be made on a series of solutions over a range of ionic strengths, obtained by adding various amounts of neutral electrolytes. The results are then plotted against a function of the ionic strength, generally $\sqrt{\mu}$, and extrapolated to infinite dilution. The extrapolated solubility is substituted for $\sqrt{K_s}$ in equation (51.29) and the mean ionic activity coefficient of the sparingly soluble salt in any other solution can then be determined from its solubility in that solution. For example, the solubility of thallous chloride in aqueous solutions at 25°C extrapolated to infinite dilution is 0.0142 mole per liter; this is then the value of $\sqrt{K_s}$. In a 0.1 M solution of potassium nitrate the observed solubility S was 0.0196 mole per liter. The value of $f_{\pm}$ for thallous chloride in this solution is then 0.0142/0.0196 = 0.724.

51g. Influence of Common Ion on Solubility.—If the solution contains a salt having an ion which is the same as one of the ions produced by the sparingly soluble salt, this must be taken into consideration in the application of the solubility product principle. For instance, if a solution which is being saturated with silver chloride already contains chloride ion, then the term c_{Cl^-} in equation (51.24) must represent the *total* concentration of chloride ion in the solution. Since this is greater than that in a solution containing no excess of chloride ion, the value of c_{Ag^+} according to equation (51.24) will be less in the former case, in order that the product of c_{Ag^+} and c_{Cl^-} may remain constant. The silver chloride may be regarded as completely dissociated in solution; hence, the silver ion concentration is a measure of the solubility of the salt. It follows, therefore, that silver chloride is less soluble in the presence of an excess of chloride ions than it is in pure water. The same conclusion may be reached with reference to a solution containing excess of silver ions, instead of chloride ions. In general, *if there is no formation of complex* *ions to disturb the equilibrium, the solubility of any salt is less in a solution containing a common ion than in water alone;* this effect, called the **common ion effect,** finds frequent application in analytical chemistry.

The solubility of a salt in the presence of a common ion may be calculated in the following manner; for simplicity, the saturating salt will be assumed to be silver chloride and the common ion to be the chloride ion. Suppose the addition of x mole per liter of potassium chloride reduces the solubility of silver chloride from S_0 to S mole per liter. The concentration c_{Ag^+} of silver ions in the solution, assuming the silver chloride to be completely dissociated, will then be S gram ion per liter, and that of the chloride ions, c_{Cl^-}, will be $S + x$, the potassium chloride being also taken to be completely dissociated. It follows, therefore, that

$$K'_s = c_{\text{Ag}^+} \times c_{\text{Cl}^-} = S(S + x). \tag{51.30}$$

Since K'_s is also equal to S_0^2, by equation (51.24),

$$S(S + x) = S_0^2, \tag{51.31}$$

$$S = -\tfrac{1}{2}x + \sqrt{\tfrac{1}{4}x^2 + S_0^2}. \tag{51.32}$$

The solubility S of the salt in the presence of x mole per liter of added common ion can thus be calculated, if the solubility S_0 in water is known. In the event that the solubility S is small, so that it may be neglected in comparison with x, equation (51.31) reduces to $S = S_0^2/x$; on the other hand, if x is small in comparison with S_0, equation (51.32) gives

$$S = -\tfrac{1}{2}x + S_0. \tag{51.33}$$

Example: The solubility of silver nitrite in pure water is 0.0269 mole per liter; what is the solubility in the presence of 0.0118 mole per liter of silver nitrate, assuming the salts to be completely dissociated and the activity coefficients to be unity?

Since S_0 is 0.0269 and x is 0.0118 mole per liter, equation (51.32) gives

$$S = -0.0059 + \sqrt{\tfrac{1}{4}(0.0118)^2 + (0.0269)^2} = 0.0216 \text{ mole per liter.}$$

If x is treated as small in comparison with S_0, equation (51.33) would give S as 0.0210 mole per liter. (The same results would be obtained if 0.0118 mole per liter of potassium nitrite were substituted for the silver nitrate.)

Solubilities, in the presence of a common ion, calculated by equation (51.32) will be lower than the observed values because of the neglect of the activity coefficients.* The exact form of equation (51.31) is

$$S(S + x)f_\pm^2 = S_0^2 f_0^2,$$

where, as before, f_0 is the mean ionic activity coefficient of the sparingly soluble salt in its saturated solution in pure water. Upon solving for S, the result is

$$S = -\tfrac{1}{2}x + \sqrt{\tfrac{1}{4}x^2 + (S_0 f_0/f_\pm)^2} \tag{51.34}$$

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* At very high ionic strengths of solutions containing polyvalent ions, the activity coefficient may exceed unity and then the reverse will be true.

instead of equation (51.32). To utilize this equation to calculate S, the mean ionic activity coefficients f_0 and $f_\pm$ can be derived from the Debye-Hückel equation. The corresponding ionic strengths, assuming all 1-1 electrolytes, are S_0 and $S + x$, respectively. Since S is not known, an approximate value is first obtained from equation (51.32); from this, a preliminary value of $f_\pm$ is obtained and then a better estimate of S is made from equation (51.34). By successive approximations, a satisfactory solution can be obtained.

Example: Recalculate the data in the preceding example taking into account the ionic activity coefficient.

For the solution in pure water, $\mu = S_0 = 0.0269$ and by equation (51.13)

$$\log f_0 = -0.509\sqrt{0.0269} = -0.0835,$$

so that $f_0 = 0.825$. The approximate value of S obtained from the preceding example is 0.0216, so that $\mu = S + x = 0.0216 + 0.0118 = 0.0334$; hence, for a preliminary value,

$$\log f_\pm = -0.509\sqrt{0.0334} = -0.0930$$

and $f_\pm = 0.807$. Upon substituting these values of f_0 and $f_\pm$ in equation (51.34), with $x = 0.0118$ and $S_0 = 0.0269$,

$$S = -0.0059 + \sqrt{\tfrac{1}{4}(0.0118)^2 + (0.0269 \times 0.825/0.807)^2}$$

$$= 0.0222 \text{ mole per liter.}$$

With this value of S, it is found that $f_\pm = 0.806$ and from equation (51.34) S is now found to be 0.0223 mole per liter. Further approximation leaves the result unchanged. (The experimental value of the solubility is 0.0224 mole per liter).

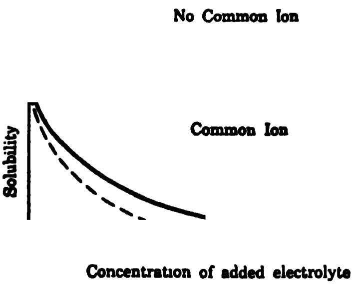

FIG. 51.5. Variation of solubility of a slightly soluble salt with electrolyte content of its solution.

The general trend of the solubilities in the presence of added salts, as predicted by the concentration solubility product and by the use of the activity solubility product, is shown in Fig. 51.5. The full lines represent the experimental behavior and that determined by the use of K_s, whereas the dotted lines indicate the results of calculations based on the approximation of taking K'_s to be constant, i.e., by assuming all activity coefficients to be unity.

51h. Complex Ions.—In certain cases excess of a common ion brings about a marked increase, instead of a decrease, in the solubility of a sparingly soluble salt. Instances of this type of behavior are to be found in the solubility of silver cyanide and several other insoluble cyanides in alkali cyanide solutions, and of mercuric iodide in iodide solutions. The results, however, do not violate the solubility product principle. The increase of solubility is due to the removal of the simple ions by the formation of complex ions; for example, the silver ions produced by silver cyanide when it dissolves are removed by the formation of the complex $Ag(CN)_2^-$ ions in the presence of excess cyanide ions. As a result, the silver cyanide must continue to dissolve in order to increase the concentration of free silver ions to the point that the solubility product $a_{Ag^+} \times a_{CN^-}$ is attained. When this condition is reached considerable amounts of silver will be in the solution, although almost the whole will be in the form of $Ag(CN)_2^-$ ions. It is of interest to mention that the solubility product of silver sulfide is so very low, viz., about 10^{-50}, that it can be precipitated from a cyanide solution of silver; even the small concentration of free silver ions in the presence of excess of cyanide ions is sufficient to enable the solubility product of the sulfide to be readily exceeded. Complex ion formation is more profitably studied in connection with qualitative and quantitative analysis, and so further discussion of the subject will not be undertaken here.

ACIDS AND BASES

52a. The Proton Transfer Theory.—Acids and bases have been defined in a number of different ways, but a point of view that has proved useful in several aspects of physical chemistry is that associated with the names of J. N. Brønsted (1923) and T. M. Lowry (1923).* As a result of various studies, particularly on the catalytic influence of nonionized molecules of acids and bases and of certain ions (§ 60b), a concept of acids and bases has been developed which has proved useful in the study of equilibria in solutions. *An acid is defined as a substance with a tendency to lose a proton, and a base is a substance with a tendency to gain a proton.* The "strength" of an acid is a measure of its tendency to lose a proton, and the "strength" of a base is similarly a measure of its tendency to take up a proton.

According to the foregoing definitions there must be a relationship between an acid and a base; when an acid loses a proton the residue will have some tendency to regain the proton, and hence it will be a base. It is thus possible to write the general expression

$$\underset{\text{acid}}{A} \rightleftharpoons \underset{\text{proton}}{H^+} + \underset{\text{base}}{B}.$$

The acid and base which differ by a proton, in accordance with this relationship, are said to form a **conjugate pair;** every acid must have its conjugate base, and every base its conjugate acid. According to this general concept, NH_4^+, HCl and HCO_3^- are all acids and their conjugate bases would be NH_3, Cl^- and CO_3^{-2}, respectively. Thus, acids and bases may be ions or mole-

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* In its widest sense, a base has been defined as a substance capable of furnishing a pair of electrons to a bond, while an acid is able to accept a pair of electrons (G. N. Lewis, 1938). The Brønsted-Lowry acids and bases are thus a more or less limited group in a larger field.

cules, but at least one of the members of a conjugate pair must be ionic in character.

In order that an acid may exhibit its acidic properties it is necessary that a substance capable of accepting a proton, i.e., a base of some kind, should be present. In a solution of hydrogen chloride in benzene there are no molecules that are able to take up the proton from the hydrogen chloride; however, if a base, such as ammonia or an amine, is added to the solution, the proton can be transferred to the base. Many solvents, such as water and alcohols, are themselves bases because the molecules are able to take up protons; in fact, the ionization of acids in water and similar solvents is probably to be ascribed to the transfer of a proton from the acid to the solvent molecule. The ionization equilibrium of hydrochloric acid in water, for example, may be written as

$$\underset{\text{acid}}{\mathrm{HCl}} + \underset{\substack{\text{base}\\(\text{solvent})}}{\mathrm{H_2O}} \rightleftharpoons \underset{\text{acid}}{\mathrm{H_3O^+}} + \underset{\text{base}}{\mathrm{Cl^-}},$$

and other acids ionize in an analogous manner.

An examination of this equation will reveal a number of interesting points. First, it implies that the hydrogen ion in aqueous solution is not H^+, i.e., a proton, but it consists of at least one water molecule in addition; its *minimum formula* is thus that of the **hydronium ion** H_3O^+, although there are probably several other, less firmly bound, molecules of water associated with this unit, as is the case with other ions in aqueous solution. Since the formation of H_3O^+ ions occurs in the ionization of acids, the acidity of an aqueous solution is attributed to this ion.

Another important general result is that interaction between an acid (HCl) and a base (H_2O) leads to the formation of another acid (H_3O^+) conjugate to the base, and of another base (Cl^-) conjugate to the acid. Actually, all types of acid-base reactions can be represented as an equilibrium between two acid-base systems, viz.,

$$\text{Acid 1} + \text{Base 2} \rightleftharpoons \text{Acid 2} + \text{Base 1}, \tag{52.1}$$

where Acid 1 and Base 1 are the conjugate acid and base of one system, and Acid 2 and Base 2 are those of the other system, e.g., the solvent. The forward reaction involves the transfer of a proton from Acid 1 to Base 2, while the reverse reaction is the transfer of a proton from Acid 2 to Base 1.

The general expression for the ionization equilibrium of an acid HA in water is represented by

$$\underset{\text{acid 1}}{\mathrm{HA}} + \underset{\text{base 2}}{\mathrm{H_2O}} \rightleftharpoons \underset{\text{acid 2}}{\mathrm{H_3O^+}} + \underset{\text{base 1}}{\mathrm{A^-}},$$

and the position of equilibrium, i.e., to the right or left of the equation, depends on the "strengths" of the acids and bases concerned. If the acid HA is a strong acid, e.g., HCl, it will tend to give up its proton readily, and even if the base H_2O is fairly weak, the equilibrium will lie considerably to the right; the extent of ionization will then be large. In this case, the reverse reaction, that is, the transfer of a proton from the acid H_3O^+ to the base A^- will occur to a small extent only. In other words, if the acid HA is a strong acid, its conjugate base A^- will be a very weak base. Since hydrochloric acid is a strong acid, its conjugate base, the chloride ion, is very weak. On the other hand, if HA is a very weak acid, such as phenol, the equilibrium lies well to the left, and the anion A^- of the very weak acid, the phenoxide ion, will be a moderately strong base. Hence, ionization occurs to a small extent only and an aqueous solution of a weak acid is consequently a weak electrolyte (§ 45c).

The reciprocal relationship between the strength of an acid and that of its conjugate base is applicable to acids of all types, irrespective of whether they consist of neutral molecules or of ions. The reverse is, of course, also true; the weaker the base the stronger will be its conjugate acid. Water, for example, is a very weak base, and its conjugate acid H_3O^+ is a strong acid.*

Just as the ionization of an acid requires a solvent that can act as a base, so the ionization of a base requires a solvent having acid character. It happens that water and related solvents actually possess both acidic and basic properties; hence, bases, as well as acids, can ionize in water. With the base ammonia, for example, the ionization equilibrium is

$$\underset{\text{base 1}}{NH_3} + \underset{\substack{\text{acid 2}\\ \text{(solvent)}}}{H_2O} \rightleftharpoons \underset{\text{acid 1}}{NH_4^+} + \underset{\text{base 2}}{OH^-},$$

the NH_4^+ ion being the acid conjugate to the base NH_3, and OH^- is the base conjugate to the acid H_2O. Since NH_3 is a weak base, NH_4^+ is a moderately strong acid; on the other hand, H_2O is a very weak acid and so OH^- is a strong base. Further, because neither NH_3 nor H_2O is strong, the ionization equilibrium in this case lies to the left; an aqueous solution of ammonia is thus a weak electrolyte. The ionizations of other weak bases, which are generally amines, i.e., substituted ammonias, are similar to that given above for ammonia; the corresponding ammonium ions are the conjugate acids, and the solutions are slightly ionized.

Although strong acids, such as HCl, HNO_3 and $HClO_4$, consist of covalent molecules that are not appreciably ionized in the pure state, the so-called strong bases, such as the alkali or alkaline-earth hydroxides, are invariably ionic in character even in the solid state. The basic character of these strong bases is due to the OH^- ions which are always present and interaction with the solvent is not an essential preliminary. Strictly speaking, therefore, such substances as NaOH and $Ca(OH)_2$, like sodium acetate, are to be regarded as "salts" rather than as bases, for it is the OH^- that is the real base.

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* It is possible for both the acid and base of a conjugate pair to be weak. It will be shown later (§ 52f) that the reciprocal relationship can be expressed by the equation $K_aK_b = K_i$, where K_a is the acid ionization constant, K_b the base ionization constant, and K_i a constant characteristic of the solvent; for water K_i is approximately 10^{-14}. Thus, if K_a is 10^{-6}, K_b will be 10^{-8}; thus, although the acid is stronger than the base, both are weak.

52b. Influence of Solvent.—In view of the general equilibrium represented by equation (52.1), viz.,

$$\text{Acid 1} + \text{Base 2} \rightleftharpoons \text{Acid 2} + \text{Base 1},$$

the ionization of any Acid 1 will depend to some extent on the basic strength of the solvent acting as Base 2. The situation is, in fact, very similar to that encountered in the study of oxidation-reduction equilibria; the higher the standard oxidation potential of one system compared with that of the other, the further will the reaction proceed to completion (§ 48g). Similarly, in the case of acid-base equilibria, the greater the tendency of Acid 1 to lose a proton, i.e., the greater its strength, compared with that of Acid 2, the further will the ionization process occur. If Acid 2 is very weak, i.e., the solvent is a moderately strong base, the equilibrium will lie well to the right; on the other hand, if Acid 2 is fairly strong, i.e., the solvent is a very weak base, the equilibrium will lie to the left. The behavior of a particular acid must therefore depend on the proton accepting tendency, that is, the basic strength, of the solvent.

These conclusions may be illustrated by reference to three solvents of increasing basic character, viz., glacial acetic acid, water and liquid ammonia. In spite of the fact that acetic acid normally behaves as an acid, it is nevertheless able to take up a proton to a small extent, thus acting as a very weak base. The ionization of an acid HA in glacial acetic acid as solvent is thus represented by

$$\underset{\text{acid}}{HA} + \underset{\substack{\text{base}\\(\text{solvent})}}{CH_3COOH} \rightleftharpoons \underset{\text{acid}}{CH_3COOH_2^+} + \underset{\text{base}}{A^-},$$

but the equilibrium cannot lie far to the right, so that even strong acids, such as hydrochloric acid, can only be slightly ionized in this solvent. By means of conductance measurements, the relative ionizations of a number of acids, which are strong acids in aqueous solution, have been determined, using glacial acetic acid as solvent (Fig. 52.1). The order of their ionization, as indicated by the values of the equivalent conductance at a given concentration, and hence of their tendency to lose a proton, is found to be as follows:

$$HClO_4 > HBr > H_2SO_4 > HCl > HNO_3.$$

This gives the correct order of the strengths of these acids although they appear to be equally strong in aqueous solution.

Water is a stronger base than acetic acid, and so the ionization equilibria for these strong acids in aqueous solution lie well to the right; it is consequently not possible to distinguish between their relative strengths, except perhaps in concentrated solutions. Water is thus said to exert a "leveling" effect on the strengths of these acids. For weak acids, like formic, lactic, acetic, propionic, phosphoric acids, etc., the equilibria do not proceed so far, and it is possible to determine the order of their strengths in aqueous solution, as will be seen in § 52c.

With liquid ammonia as solvent, the proton-accepting tendency of the base is so great that even with an acid as weak as acetic acid, the ionization equilibrium, viz.,

$$\underset{\text{acid}}{CH_3COOH} + \underset{\substack{\text{base}\\\text{(solvent)}}}{NH_3} \rightleftharpoons \underset{\text{acid}}{NH_4^+} + \underset{\text{base}}{CH_3COO^-},$$

lies so far to the right that the acid behaves like a strong acid. In fact, all acids stronger than acetic acid appear to be about equally strong in liquid ammonia as solvent; acetic and hydrochloric acids, for example, behave as if they had almost the same strength.

The influence of the solvent on the ionization and apparent strength of bases, other than hydroxides, is similar in nature. In water it is possible to distinguish between the strengths of various weak bases, because water is a relatively weak acid. If the solvent has stronger acid character, this distinction is no longer possible. In pure acetic acid as solvent all bases stronger than aniline, which is a very weak base in water, behave as strong bases. This fact is made use of in the analytical titration, by means of acid, of bases which are too weak to be titrated satisfactorily in aqueous solution.

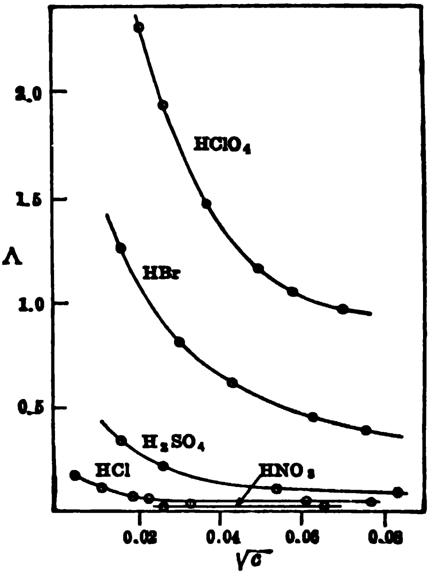

FIG. 52.1. Conductance of acids in glacial acetic acid (Kolthoff and Willman)

An extreme type of solvent effect occurs when the solvent has only acidic and no basic properties, as is the case with liquid hydrogen fluoride. Not even the strongest acid can ionize *as an acid* when dissolved in this solvent, but it may ionize *as a base*. As mentioned previously, acetic acid has some slight tendency to accept a proton, and when it is dissolved in liquid hydrogen fluoride it ionizes as a base; thus,

$$\underset{\text{base}}{CH_3COOH} + \underset{\substack{\text{acid}\\\text{(solvent)}}}{HF} \rightleftharpoons \underset{\text{acid}}{CH_3COOH_2^+} + \underset{\text{base}}{F^-}.$$

The behavior may again be compared with that in oxidation-reduction processes; a particular system may behave as an oxidizing agent to one having a higher oxidation potential, but it will be a reducing agent to a system with a lower potential. So the acidic or basic character of a substance, such as acetic acid, will depend on the tendency of the solvent to gain or lose protons, respectively. A substance such as hydrogen chloride has virtually no basic character, and so it will not ionize when dissolved in hydrogen fluoride, although acetic, nitric, sulfuric and other acids, which contain an oxygen atom, and can take up protons to some extent, will give conducting systems. Even acetone, which is a nonconductor in aqueous solution, becomes conducting when dissolved in liquid hydrogen fluoride.

52c. Ionization Constants.—The comparison of the strengths of acids or bases, other than the strongest, in a given solvent, such as water, is conveniently made by utilizing the ionization equilibrium constant of the acid or base (§ 51a).

I. Acids.—For any acid HA dissolved in water, the ionization equilibrium is

$$\mathrm{HA} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{A^-},$$

and the equilibrium constant in terms of activities is

$$K = \frac{a_{\mathrm{H_3O^+}} \times a_{\mathrm{A^-}}}{a_{\mathrm{HA}} \times a_{\mathrm{H_2O}}}. \tag{52.2}$$

If the concentration of dissolved substances in the water is not too large, the activity $a_{\mathrm{H_2O}}$ of the water molecules is approximately equal to that in pure water, and this, by convention, is taken as unity. The equilibrium constant in equation (52.2) may now be represented as K_a, given by

$$K_a = \frac{a_{\mathrm{H_3O^+}} \times a_{\mathrm{A^-}}}{a_{\mathrm{HA}}}, \tag{52.3}$$

which is exactly analogous to equation (51.1); this is the general expression for the true **ionization constant** of the acid HA. The formula $\mathrm{H_3O^+}$ is used for the hydrogen ion in aqueous solution to show that the proton is associated with one strongly bound molecule of water; however, for simplicity of representation it is adequate to use the symbol $\mathrm{H^+}$, *provided it is clearly understood that this does not refer to a proton, but to the hydrogen ion as it exists in solution.* With this simplification, equation (52.3) for the ionization constant K_a of the acid may be written as

$$K_a = \frac{a_{\mathrm{H^+}} \times a_{\mathrm{A^-}}}{a_{\mathrm{HA}}}. \tag{52.4}$$

As in § 51a, each activity term may be replaced by the product of the corresponding concentration and activity coefficient, so that

$$K_a = \frac{c_{\mathrm{H^+}} \times c_{\mathrm{A^-}}}{c_{\mathrm{HA}}} \cdot \frac{f_{\mathrm{H^+}} \times f_{\mathrm{A^-}}}{f_{\mathrm{HA}}}. \tag{52.5}$$

If α is the degree of ionization of the acid HA in the aqueous solution of total concentration c mole per liter; $c_{\mathrm{H^+}}$ and $c_{\mathrm{A^-}}$ are then both equal to αc, whereas c_{HA}, the concentration of the nonionized portion, is given by $(1 - \alpha)c$, and equation (52.5) becomes

$$K_a \quad \frac{\alpha^2 c}{1 - \quad} \cdot \frac{f_{H^+} \times f_{A^-}}{f_{HA}} \tag{52.6}$$

If the solution of the acid HA behaves ideally, the activity coefficient factor in equation (52.6) would be equal to unity, and the first factor on the right-hand side would be equal to the ionization constant. Although this is not the case for actual solutions, nevertheless for a weak electrolyte, it is useful to write

$$K'_a = \frac{c_{H^+} \times c_{A^-}}{c_{HA}} = \frac{\alpha^2 c}{1 - \alpha}, \tag{52.7}$$

where K'_a, which may be called the **ionization concentration quotient,** is approximately constant; it becomes equal to the ionization constant K_a at infinite dilution when the activity coefficients are all unity.

The degree of ionization α can be derived from conductance measurements by equation (45.12), but if the approximation is made of neglecting the variation of ionic speeds with concentration, α may be identified with the conductance ratio Λ/Λ_0, [equation (45.13)].* The equivalent conductances Λ at 25°C of acetic acid solutions at various concentrations are recorded in Table 52.1; from these, together with the limiting conductance Λ_0 of 390.7 ohms^{-1} cm^2, obtained in § 45h, the values of Λ/Λ_0 in the third column have been calculated. They have been corrected for the variation in ionic speeds, by means of equation (45.12) as shown in the example in § 45e. The results are given in the fourth column of Table 52.1; these are seen to be only slightly larger than the conductance ratios in the third column. The next column gives K'_a obtained from equation (52.7), using the corrected degrees of ionization.

TABLE 52.1. IONIZATION CONSTANT OF ACETIC ACID

$c \times 10^3$	Λ	Λ/Λ_0	α	K'_a	K_a
0.02801	210.38	0.5384	0.5393	1.768×10^{-5}	1.752×10^{-5}
0.11135	127.75	0.3270	0.3277	1.779	1.754
0.21844	96.49	0.2470	0.2477	1.781	1.751
1.02831	48.15	0.1232	0.1238	1.797	1.751
2.41400	32.22	0.08247	0.08290	1.809	1.750
5.91153	20.96	0.05364	0.05401	1.823	1.748
9.8421	16.37	0.04189	0.04222	1.832	1.747
20.000	11.57	0.02961	0.02987	1.840	1.737
52.303	7.202	0.01843	0.01865	1.854	1.722

In order to obtain the true ionization constant K_a, it is necessary to extrapolate K'_a to infinite dilution; this can be very conveniently done with the aid

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* Strictly speaking, these equations give the degree of dissociation, as defined in § 45e, but for weak electrolytes, such as considered here, this is virtually identical with the degree of ionization.

of the Debye-Hückel limiting law. By combining equations (52.6) and (52.7) it is seen that

$$K_a = K'_a \frac{f_{\mathrm{H}^+} \times f_{\mathrm{A}^-}}{f_{\mathrm{HA}}}. \tag{52.8}$$

Provided the ionic strength of the medium is not too high, the activity coefficient of the nonionized molecules HA does not differ greatly from unity; hence, equation (52.8) may be written as

$$K_a = K'_a(f_{\mathrm{H}^+} \times f_{\mathrm{A}^-}) = K'_a f_{\pm}^2, \tag{52.9}$$

where $f_{\pm}$ is the mean activity coefficient of the ions. According to the Debye-Hückel limiting equation (51.12)

$$\log f_{\pm} = -A\sqrt{\mu}, \tag{52.10}$$

since both ions are univalent, and z_+ and z_- are equal to unity. The ionic strength μ of the solution is equal to the ionic concentration αc, as is true for all 1-1 electrolytes; hence, taking logarithms of equation (52.9) and substituting equation (52.10), the result, after rearrangement, is

$$\log K'_a = \log K_a + 2A\sqrt{\alpha c}. \tag{52.11}$$

The plot of $\log K'_a$ against $\sqrt{\alpha c}$, the values of which can be obtained from the data in Table 52.1, should thus be a straight line of slope $2A$; for water at 25°C, A is 0.509, and so the slope should be 1.018. Further, according to equation (52.11), the intercept on the $\log K'_a$ axis, for $\sqrt{\alpha c}$ equal to zero, should give $\log K_a$; this is actually the extrapolated value of $\log K'_a$ at infinite dilution. The results for acetic acid are shown in Fig. 52.2; the theoretical

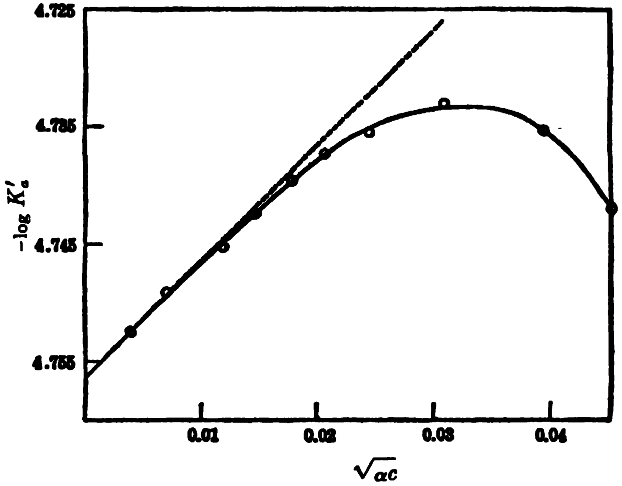

FIG. 52.2. Ionization constant of acetic acid (MacInnes and Shedlovsky)

limiting slope, according to equation (52.11), is indicated by the dashed line. The experimental and theoretical slopes are seen to approach one another in dilute solution, thus providing support for the Debye-Hückel limiting equation. The extrapolated value of log K_a', which is equal to log K_a, is -4.7564, so that K_a for acetic acid at 25°C is 1.752×10^{-5}.

An alternative method of using the data in Table 52.1 is to substitute 0.509 for A in equation (52.11) and then to calculate K_a at various concentrations using the K_a' values in the fifth column and α and c from the fourth and first columns, respectively. The results so obtained are given in the last column of the table. The essentially constant value in dilute solutions is in agreement with that derived from Fig. 52.2.

The treatment just described, utilizing conductance data appropriately corrected, provides one of the most accurate devices for the evaluation of the ionization constants of acids that are not too weak. Another highly accurate method, which can be used for very weak acids in addition, is based on E.M.F. measurements of special galvanic cells free from liquid junctions. A somewhat more approximate procedure involves the determination of hydrogen ion concentrations (activities) in solutions containing a mixture of known amounts of the acid and its salt; the equation required for this purpose is derived in § 53a.

II. Bases.—The ionization of a base B in aqueous solution may be represented as

$$\mathrm{B} + \mathrm{H_2O} \rightleftharpoons \mathrm{BH^+} + \mathrm{OH^-},$$

so that the ionization constant K_b of the base is given by

$$K_b = \frac{a_{\mathrm{BH^+}} \times a_{\mathrm{OH^-}}}{a_{\mathrm{B}}}, \tag{52.12}$$

the activity $a_{\mathrm{H_2O}}$ of the water being taken as unity. The nonionized base is represented by B, whereas $\mathrm{BH^+}$ is the ionized portion; hence, if α is the degree of ionization, the concentrations of $\mathrm{BH^+}$, $\mathrm{OH^-}$ and B are given by αc, αc and $(1 - \alpha)c$, respectively. It can thus be readily seen that equation (52.12) can be reduced to a form exactly analogous to equation (52.6), viz.,

$$K_b = \frac{\alpha^2 c}{1 - \alpha} \cdot \frac{f_{\mathrm{BH^+}} \times f_{\mathrm{OH^-}}}{f_{\mathrm{B}}}. \tag{52.13}$$

It is thus possible to obtain K_b for a moderately weak base by utilizing conductance data in a manner exactly analogous to that described above for acetic acid. Methods based on E.M.F. measurements and on hydrogen ion determinations have also been used. One of the difficulties experienced in making accurate measurements on certain bases, such as ammonia and the lower amines, is their volatility; in addition, many amines are unstable when exposed to air, especially in the presence of light. For these reasons there are not many accurate data for the ionization constants of bases.

III. Polyprotic Acids.—A diprotic acid, such as carbonic or oxalic acid, has two protons which can be lost from the molecule; similarly, a tripotic acid, such as phosphoric or citric acid, can lose three protons. These protons are detached from the acid molecule in turn, so that there are a number of stages of ionization corresponding to the number of protons available. The three ionization stages of phosphoric acid, for example, are as follows:

$$\begin{aligned} &\text{1st stage:} && H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^- \\ &\text{2nd stage:} && H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{-2} \\ &\text{3rd stage:} && HPO_4^{-2} + H_2O \rightleftharpoons H_3O^+ + PO_4^{-3}. \end{aligned}$$

The corresponding ionization constants for the three stages are given by

$$K_1 = \frac{a_{H^+} \times a_{H_2PO_4^-}}{a_{H_3PO_4}}$$

$$K_2 = \frac{a_{H^+} \times a_{HPO_4^{-2}}}{a_{H_2PO_4^-}}$$

$$K_3 = \frac{a_{H^+} \times a_{PO_4^{-3}}}{a_{HPO_4^{-2}}}.$$

Conductance methods have been used for evaluating the ionization constants of polyprotic acids, but the results are not accurate because of approximations that must be made in the calculations. It is therefore the general practice to employ E.M.F. methods. The values of the dissociation constants of successive stages of a polyprotic acid always decrease steadily; thus, for phosphoric acid K_1 is 7.52×10^{-3}, K_2 is 6.22×10^{-8} and K_3 is 4.8×10^{-13} at 25°C. The reason for this decreasing tendency for the proton to be lost in successive ionizations is that in the first stage the positively charged proton is detached from an uncharged molecule, e.g., H_3PO_4, but in the later stages it must be removed from an ion of increasingly negative charge, e.g., $H_2PO_4^-$ and HPO_4^{-2}. On account of the electrostatic attraction, the removal of the proton becomes increasingly difficult in successive stages, and so the ionization constants decrease correspondingly. This conclusion is applicable to polyprotic acids of all types.

Attention may be called to a matter of general interest; in the first stage of ionization of phosphoric acid, $H_2PO_4^-$ is the base conjugate to the acid H_3PO_4, but in the second stage $H_2PO_4^-$ functions as an acid. Similarly, HPO_4^{-2} is the conjugate base in the second stage of ionization, but is the acid in the third stage. In general, the intermediate ion (or ions) of a polyprotic acid will possess both acidic and basic character; such ions are therefore said to be "amphiprotic" or "amphoteric" (Greek: amphi, *both*).

IV. Results.—The ionization constants at 25°C of a number of acids and bases are recorded in Table 52.2;* as a general rule, change of temperature

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* The ionization constants of acids and bases are sometimes referred to as "acidity constants" and "basicity constants," respectively.

TABLE 52.2. IONIZATION CONSTANTS OF ACIDS AND BASES AT 25°C

Monoprotic Acids

Acid	K_a	Acid	K_a
Formic	1.774×10^{-4}	Lactic	1.37×10^{-4}
Acetic	1.752×10^{-5}	Glycolic	1.48×10^{-4}
Benzoic	6.31×10^{-5}	Phenol	1.20×10^{-10}
Chloroacetic	1.33×10^{-3}	Hydrogen cyanide	7.24×10^{-10}
Phenylacetic	4.90×10^{-5}	Boric	5.75×10^{-10}

Polyprotic Acids

Acid	K_1	K_2	K_3
Oxalic	5.02×10^{-2}	5.18×10^{-5}	—
Phthalic	1.29×10^{-3}	3.80×10^{-6}	—
Carbonic	4.47×10^{-7}	5.62×10^{-11}	—
Hydrogen sulfide	6.3×10^{-8}	1.3×10^{-12}	—
Citric	8.7×10^{-4}	1.8×10^{-5}	4.0×10^{-6}
Phosphoric	7.52×10^{-3}	6.22×10^{-8}	4.8×10^{-13}

Bases

Base	K_b	Base	K_b
Ammonia	1.74×10^{-5}	Aniline	4.1×10^{-10}
Methylamine	5.0×10^{-4}	Diphenylamine	6.9×10^{-14}
Dimethylamine	7.4×10^{-4}	Pyridine	1.6×10^{-9}
Trimethylamine	7.4×10^{-5}	Quinoline	3.5×10^{-10}

has a relatively small effect on the ionization constant. An acid having an ionization constant of about 10^{-2} to 10^{-3} is regarded as "moderately strong"; if the value is 10^{-4} to 10^{-7}, the acid is referred to as "weak"; if it is in the region of 10^{-8} to 10^{-11} the acid may be described as "very weak," while an "extremely weak" acid would have an ionization constant of 10^{-12} or less. This classification is, of course, very rough, although it is useful for some purposes.

52d. The Ionic Product of Water.—Since water behaves as both an acid and a base, that is to say, a molecule of water is capable of losing as well as gaining a proton, there must exist *in all aqueous solutions*, as well as in pure water, the proton transfer equilibrium represented by

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-.$$

The equilibrium constant is then

$$K = \frac{a_{H_3O^+} \times a_{OH^-}}{a_{H_2O}^2},$$

and if, as in other cases, the solution is so dilute that the activity of the water may be taken as unity (see § 48b, footnote), the result is

$$K_w = a_{H_3O^+} \times a_{OH^-} \ (\text{or } a_{H^+} \times a_{OH^-}), \tag{52.14}$$

where the constant K_w is known as the **ionic product** of water. This means that *in pure water or in any dilute aqueous solution, the product of the activities* *of the hydrogen and hydroxyl ions is constant*, at a given temperature. For moderately dilute solutions the activities may be replaced by the corresponding concentrations, so that K'_w defined by

$$K'_w = c_{H^+} \times c_{OH^-}, \tag{52.15}$$

is approximately constant.

Several methods have been used to determine the ionic product of water; those described below are based on conductance and E.M.F. measurements, respectively.

I. Conductance Method.—Because of the equilibrium under consideration, even the purest water will contain a certain amount of hydrogen and hydroxyl ions, and hence it will possess a definite, although very small, electrical conductance. It has been estimated from accurate measurements that the specific conductance, that is, the conductance of a 1 cm cube, of perfectly pure water is 5.54×10^{-8} ohm^{-1} cm^{-1} at 25°C. The equivalent conductances of hydrogen and hydroxyl ions at the very small concentrations existing in pure water may be taken as equal to the values at infinite dilution, i.e., 349.8 and 198.6 ohms^{-1} cm^2, respectively (Table 45.2). The total conductance of 1 gram equiv. of hydrogen and hydroxyl ions in very dilute solution would thus be $349.8 + 198.6 = 548.4$ ohms^{-1} cm^2; it follows, therefore, that a 1 cm cube, that is, 1 cc, of pure water contains

$$\frac{5.54 \times 10^{-8}}{548.4} = 1.01 \times 10^{-10} \text{ gram equiv. per cc}$$

of hydrogen and hydroxyl ions. Since the ions are univalent, gram equiv. and gram ions are identical, and so the concentration of hydrogen ions and of hydroxyl ions is 1.01×10^{-7} gram ion per 1000 cc, i.e., per liter; thus, in pure water, where the hydrogen and hydroxyl ions are present at the same concentration,

$$c_{H^+} = c_{OH^-} = 1.01 \times 10^{-7} \text{ gram ion per liter.}$$

By equation (52.15), therefore,

$$K'_w = c_{H^+} \times c_{OH^-} = 1.02 \times 10^{-14} \text{ at } 25°\text{C.}$$

Since the ionic concentrations in pure water are very small, the activity coefficients are virtually unity, and so 1.02×10^{-14} may be taken as the value of K_w.

II. E.M.F. Methods.—The simplest, although approximate, E.M.F. method for determining the ionic product of water employs a galvanic cell,

$$\text{Pt} \mid \text{H}_2 \text{ (1 atm)} \mid \text{KOH (0.01 N)} \parallel \text{HCl (0.01 N)} \mid \text{H}_2 \text{ (1 atm)} \mid \text{Pt},$$

with a salt bridge to minimize the liquid junction potential. The E.M.F. of this cell, according to equation (49.1), is

$$E = \frac{RT}{F} \ln \frac{a'_{H^+}}{a_{H^+}}, \tag{52.16}$$

where a'_{H^+} and a_{H^+} represent the hydrogen ion activities in the right-hand and left-hand solutions, i.e., in 0.01 N hydrochloric acid and 0.01 N potassium hydroxide, respectively. If a_{OH^-} is the hydroxyl ion activity in the latter solution, then by the ionic product principle,

$$a_{H^+} \times a_{OH^-} = K_w,$$

$$a_{H^+} = K_w/a_{OH^-},$$

and substitution of this value for a_{H^+} in equation (53.16) gives

$$E = \frac{RT}{F} \ln \frac{a'_{H^+} \times a_{OH^-}}{K_w}$$

$$= 0.05915 \log \frac{a'_{H^+} \times a_{OH^-}}{K_w} \qquad (52.17)$$

at 25°C. The value of a'_{H^+} is equal to the product of the concentration of the hydrogen ions in 0.010 N HCl, i.e., 0.010 gram ion per liter, and the activity coefficient in the solution; from the data in Table 51.1, as well as by means of the Debye-Hückel equation, this activity coefficient is found to be about 0.90, so that a'_{H^+} is 0.010 × 0.90, i.e., 0.0090 gram ion per liter. Similarly, a_{OH^-} is the hydroxyl ion activity in 0.010 N KOH; this is, likewise, approximately 0.0090 gram ion per liter. The E.M.F. of the cell was found to be 0.5874 volt at 25°C, so that by equation (52.17),

$$0.5874 = 0.05912 \log \frac{0.0090 \times 0.0090}{K_w}$$

$$K_w = 0.95 \times 10^{-14} \text{ at } 25°\text{C}.$$

This result obtained by an entirely different procedure is very close to that given by the conductance method.

The most accurate values of the ionic product of water have been derived from measurements with galvanic cells free from liquid junctions. The reaction in the cell

$$\text{Pt} \mid H_2 \text{ (1 atm)} \mid \text{KOH } (m_1) \text{ KCl } (m_2) \mid \text{AgCl } (s) \mid \text{Ag}$$

consisting of hydrogen and silver-silver chloride electrodes immersed in a solution containing potassium hydroxide (m_1) and potassium chloride (m_2) is

$$\tfrac{1}{2}H_2 \text{ (1 atm)} + \text{AgCl } (s) = \text{Ag } (s) + H^+ + Cl^-$$

for the passage of one faraday. The E.M.F. is thus

$$E = E^0 - \frac{RT}{F} \ln (a_{H^+} \times a_{Cl^-}),$$

where a_{H^+} and a_{Cl^-} are the activities of the indicated ions in the solution. Replacing a_{H^+} by K_w/a_{OH^-}, in accordance with equation (52.14), writing the activities as the product of the molalities and the respective activity coefficients, and rearranging, the result is

$$E - E^0 + \frac{RT}{F}\ln\frac{m_{\text{Cl}^-}}{m_{\text{OH}^-}} = -\frac{RT}{F}\ln K_w - \frac{RT}{F}\ln\frac{\gamma_{\text{Cl}^-}}{\gamma_{\text{OH}^-}}.$$

At infinite dilution, the last term on the right of this equation becomes zero, since the activity coefficients are unity; the left side of the equation is then equal to $-(RT/F)\ln K_w$. Hence, if the values of the left side, for various concentrations of hydroxide and chloride, are plotted against a suitable function of the concentration, e.g., the ionic strength, and the results extrapolated to infinite dilution, the value of K_w can be determined.

The results obtained at a number of temperatures are summarized in Table 52.3. It will be seen that K_w increases rapidly with increasing temperature. The concentration of hydrogen and hydroxyl ions in pure water at any temperature are equal; expressed in gram ion per liter, these are given by the square root of the concentration ionic product [see equation (52.15)]; i.e.,

TABLE 52.3. IONIC PRODUCT OF WATER

Temperature	0°	10°	20°	25°	30°	40°	50°c
K_w	0.113	0.292	0.681	1.008	1.468	2.917	5.474×10^{-14}

$$c_{\text{H}^+} = c_{\text{OH}^-} = \sqrt{K'_w}. \tag{52.18}$$

At ordinary temperatures K'_w is very close to 10^{-14}, and so the concentration of hydrogen and hydroxyl ions in pure water may be taken, for most purposes, as 10^{-7} gram ion per liter.

52e. Heat of Neutralization.—In a dilute solution of a strong acid in water the ionization reaction

$$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$$

may be regarded as being virtually complete; a dilute solution of hydrochloric or nitric acid thus behaves as if the acid were entirely in the form of H_3O^+ ions. Similarly, a strong base, such as sodium hydroxide, in dilute solution is probably completely dissociated; the basic character of the solution is due to OH^- ions. According to these arguments, the neutralization of any *strong acid by a strong base in dilute solution* may be represented by the proton transfer process

$$\text{H}_3\text{O}^+ + \text{OH}^- = \text{H}_2\text{O} + \text{H}_2\text{O},$$

which is independent of the nature of the strong acid or base. This result explains the observation that the enthalpy change ΔH accompanying the neutralization of a strong acid by a strong base in dilute solution has the constant value of -13.69 kcal at 20°C. The observed enthalpy change is, in every case, that for a reaction between hydrogen and hydroxyl ions, and hence it is a constant, independent of the nature of the acid and base, provided they are both strong and the solution is dilute.

It will be observed that the reaction depicted above is exactly the reverse of that given in § 52d for the self-ionization of water. It should be possible to calculate the heat of reaction in the latter case from the variation with temperature of the equilibrium constant, i.e., the ionic product, by means of the integrated form of the van't Hoff equation (§ 34a),

$$\log \frac{(K_w)_2}{(K_w)_1} = \frac{\Delta H}{4.576}\left(\frac{T_2 - T_1}{T_1 T_2}\right).$$

According to Table 52.3, the value of K_w is 0.681×10^{-14} at 20°C, i.e., 293.2°K, and 1.468×10^{-14} at 30°C, i.e., 303.2°K; hence,

$$\log \frac{1.468}{0.681} = \frac{\Delta H}{4.576} \times \frac{10}{293.2 \times 303.2}$$

$$\Delta H = 13.56 \text{ kcal.}$$

The mean value of ΔH between 20° and 30°C for the ionic dissociation of water is thus 13.56 kcal, which is very close, but of opposite sign, to that for the neutralization of a strong acid by a strong base in dilute solution. The agreement supports the view that this neutralization is effectively the combination of a hydrogen and a hydroxyl ion. The acidity of a strong acid in dilute solution may thus be attributed to the H_3O^+ ion, and the alkalinity of a strong base is due to the OH^- ion.

With an aqueous solution of a weak acid, such as acetic acid, the acidity is due partly to H_3O^+ ions, but mainly to the nonionized CH_3COOH molecules; the neutralization by a strong base is thus represented almost entirely by the reaction

$$CH_3COOH + OH^- = CH_3COO^- + H_2O.$$

The change of enthalpy of the reaction would not necessarily be the same as for the neutralization of a strong acid; the values observed are actually different and depend on the nature of the weak acid. However, if the results obtained at a number of concentrations are extrapolated to infinite dilution, when ionization of the weak acid to form H_3O^+ ions, or of the weak base to yield OH^- ions, would be complete, the value of ΔH is found to be the same as for a strong acid and a strong base.

52f. Incomplete Neutralization.—The term **neutralization** is generally applied to the reaction of one equivalent of an acid with one equivalent of a base; if the terms "acid" and "base" are employed in the sense defined in § 52a, the products are not necessarily a salt and water. They are, however, always the conjugate base and acid, respectively, of the reacting acid and base, in accordance with equation (52.1). The following reactions, for example, are all to be described as neutralizations:

$$\begin{array}{llcllcll}
H_3O^+ & + & OH^- & = H_2O & + & H_2O & & \\
CH_3COOH & + & (Na^+)OH^- & = H_2O & + & (Na^+)CH_3COO^- & & \\
HCl & + & NH_3 & = NH_4^+ & + & Cl^- & & \\
HCl & + & (Na^+)CH_3COO^- & = CH_3COOH & + & (Na)^+Cl^- & & \\
NH_4^+(Cl^-) & + & (Na^+)OH^- & = H_2O & + & NH_3 & & + (Na^+Cl^-) \\
\text{Acid 1} & & \text{Base 2} & \text{Acid 2} & & \text{Base 1} & &
\end{array}$$

The last two reactions are of special interest, since they belong to the category usually known as "displacement reactions." In the first of these, a strong acid displaces a weak acid, acetic acid, from its salt; in the second, a weak base, ammonia, is displaced from its hydrochloride by a strong base. A much better understanding of these processes can be obtained by treating them as neutralizations that are not fundamentally different from other acid-base reactions.

When equivalent amounts of strong acid and strong base are mixed, the reaction goes to virtual completion, leaving a very small concentration of free acid and base, viz., 10^{-7} gram ion per liter of H_3O^+ and of OH^- ions. If the acid or base, or both, are weak, the neutralization process is incomplete in aqueous, and similar, solutions. Suppose an acid HA reacts with a base B; the neutralization reaction is represented by

$$\underset{\text{acid}}{HA} + \underset{\text{base}}{B} \rightleftharpoons \underset{\text{acid}}{BH^+} + \underset{\text{base}}{A^-}. \tag{52.19}$$

Since BH^+ is an acid and A^- is a base, a proton transfer equilibrium can be established with the solvent, e.g., water, acting as a base or acid, respectively; thus,

$$\underset{\text{acid}}{BH^+} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{acid}}{H_3O^+} + \underset{\text{base}}{B} \tag{52.20}$$

$$\underset{\text{base}}{A^-} + \underset{\text{acid}}{H_2O} \rightleftharpoons \underset{\text{base}}{OH^-} + \underset{\text{acid}}{HA}. \tag{52.21}$$

In the first of these reactions the free base B is regenerated, while in the second the free acid HA is re-formed, so that they tend to oppose the neutralization. *This partial reversal of neutralization, or the prevention of complete neutralization, due to the action of the solvent water* is referred to as **hydrolysis.** In general, for any solvent capable of acting as an acid or base, or both, the phenomenon is known as **lyolysis** or **solvolysis.**

The conditions for hydrolysis to be appreciable can be readily derived from information already gained concerning the relative strengths of conjugate acids and bases. If the hydrolysis reaction indicated by equation (52.20) is to take place to any considerable extent, that is, if the equilibrium is to lie to the right-hand side, the acid BH^+ must be strong or moderately strong. Since there is a reciprocal relationship between the strengths of a conjugate pair (§ 52a), it is evident that the conjugate base B must be relatively weak. It follows, therefore, that the neutralization reaction in equation (52.19) will be incomplete, and hydrolysis of the type of equation (52.20) will take place, if B is a weak base. It can be seen in an exactly analogous manner that if the hydrolytic reaction in equation (52.21) is to be appreciable, the base A^- must be strong, and hence the conjugate acid HA should be weak. The conclusion to be drawn, then, is that *neutralization is incomplete and hydrolysis occurs when the acid or base, or both, are weak.* Consideration will show that the phenomenon of lyolysis, in general, also depends on the acidic or basic character of the solvent, since this plays a part in the reactions which reverse the neutralization.

It has been the common practice in the past to refer to the equilibrium constant of equation (52.20), which is established in a solution of the salt, e.g., NH_4Cl, of a weak base, NH_3, as the hydrolysis constant of the salt. The same term has been applied to the equilibrium constant of equation (52.21) for a salt, e.g., NaAc, of a weak acid HAc, where Ac represents the acetate ion. However, what is called the hydrolysis constant is really the ionization constant of the acid (NH_4^+) conjugate to the weak base (NH_3) in the former case, and of the base (Ac^-) conjugate to the weak acid (HAc) in the latter.

A relationship between the ionization constants of the acid and base in a conjugate pair can be readily derived. The ionization constants of the base B [equation (52.12)] and of its conjugate acid BH^+ [equation (52.20)] are given by

$$K_b = \frac{a_{BH^+} \times a_{OH^-}}{a_B} \quad \text{and} \quad K_a = \frac{a_{H^+} \times a_B}{a_{BH^+}},$$

respectively. If these are multiplied, it follows that

$$K_aK_b = a_{H^+} \times a_{OH^-} = K_w \tag{52.22}$$

or, in general,

$$K_aK_b = K_s,$$

where K_s is the ionic product of the solvent. Exactly the same result is obtained by considering an acid HA and its conjugate base A^-. These equations not only express quantitatively the familiar inverse relationship between the strength of an acid and its conjugate base, they also show that the acid-base ionization of the solvent is an important factor.

Since the hydrolysis constant of a salt such as BHCl, e.g., NH_4Cl, is K_a for the acid BH^+, it is equal, according to equation (52.22) to K_w/K_b, where K_b is the ionization constant of the weak base B. Similarly, the hydrolysis constant of the salt NaA, e.g., NaAc, is equal to K_w/K_a, where K_a is the ionization constant of the weak acid HA.

It follows from equation (52.20) that, as a consequence of hydrolysis, a solution of a salt of a weak acid has an acid reaction due to the formation of H_3O^+ ions. Similarly, by equation (52.21), a solution of a salt of a weak base will be alkaline because of the OH^- ions. The hydrogen (or hydroxyl) ion concentrations of the salt solutions may be obtained by using exactly the same equations as are employed for acids and bases in general. These are derived and their application described below.

52g. Amino Acids.—The amino acids are **amphiprotic electrolytes** or **ampholytes,** *possessing both acidic and basic groups;* they are consequently capable of being neutralized by a base or an acid, respectively. If an acid is added the amino acid exercises its basic function, while the addition of a base causes the acidic property of the ampholyte to be apparent. The aliphatic amino acids are usually represented by the general formula NH_2RCOOH; the simplest of these substances, i.e., glycine or aminoacetic acid, is NH_2CH_2COOH. There are, however, many excellent reasons for stating that in aqueous solution these substances exist in the form of **dual ions,**[*] having the structure $^+NH_3RCOO^-$.

For example, the ionization constants of an amino acid are in better agreement with those to be expected for the acidic $^+NH_3$— and basic —COO^- groups than for the basic NH_2— and acidic —$COOH$ groups. The Raman spectrum (§ 29f) of neutral solutions of amino acids do not exhibit the lines which are characteristic of the NH_2— and —$COOH$ groups, although they do appear when alkali or acid, respectively, is added. The alkali converts the $^+NH_3$— into NH_2—, and the acid changes —COO^- into —$COOH$. The high melting point, relatively high solubility in water but low solubility in organic solvents and increased solubility in water in the presence of neutral salts, all of which are properties associated with ionized substances, favor the dual ion structure of amino acids. Although these ions have a net electric charge of zero, their properties are quite different from those to be expected from the truly uncharged, neutral molecules, NH_2RCOOH.

The acidic ionization of an amino acid is represented by

$$^+NH_3RCOO^- + H_2O \rightleftharpoons H_3O^+ + NH_2RCOO^-,$$

and the basic ionization by

$$^+NH_3RCOO^- + H_2O \rightleftharpoons {}^+NH_3RCOOH + OH^-.$$

However, an amino acid is now generally treated as an intermediate stage in the ionization of a diprotic acid, $^+NH_3RCOOH$, with two different sources of protons, namely the $^+NH_3$— and —$COOH$ groups, the latter being the stronger acid. The two stages of ionization are written

$$^+NH_3RCOOH + H_2O \overset{K_1}{\rightleftharpoons} {}^+NH_3RCOO^- + H_3O^+$$

and

$$^+NH_3RCOO^- + H_2O \overset{K_2}{\rightleftharpoons} NH_2RCOO^- + H_3O^+,$$

where K_1 and K_2 are the respective ionization constants. The acidic ionization constant of $^+NH_3RCOO^-$ is thus equal to K_2 and the basic constant to K_w/K_1. The $^+NH_3RCOOH$ ion is the main form in which the amino acid would exist in acidic solution; this also represents the formula of the cation in the crystals of a salt such as the hydrochloride. On the other hand, the

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[*] Such ions are also referred to as "zwitterions" (hybrid ions), ampholyte ions or dipolar ions.

NH_2RCOO^- ion would be the main form in alkaline solutions and is the anion in the sodium salt.

Since the ionic component of an amino acid solution ranges from $^+NH_3RCOOH$ at high hydrogen ion concentrations to NH_2RCOO^- at very low hydrogen ion concentrations, there should be an intermediate condition at which the two amino-acid ions are present in equivalent amounts. This is referred to as an **isoelectric solution** or as the **isoelectric point** of the solution. At this point, the hydrogen ion concentration has a definite value which is characteristic of the amino acid at the existing temperature. The physical properties, e.g., viscosity, solubility, etc., of an amino acid are frequently a maximum or a minimum at the isoelectric point; for example, the solubility of an ampholyte is generally a minimum.

Attention may be called to the fact that aromatic amino-sulfonic acids e.g., sulfanilic acid, probably exist in the dual-ion form in solution, but the aromatic amino-carboxylic acids, e.g., the aminobenzoic acids, are present mainly as uncharged molecules, viz., $NH_2C_6H_4COOH$, and not as dual ions.

HYDROGEN ION CONCENTRATIONS

53a. Calculation of Hydrogen Ion Concentration.—Provided the solutions are not too concentrated, a strong acid, such as hydrochloric acid, may be regarded as being completely ionized in aqueous solution; the hydrogen ion concentration is then equal to the total acid concentration. Thus, if the concentration of a solution of hydrochloric acid is 0.1 mole per liter, the hydrogen ion concentration c_{H^+} will be 0.1 gram ion per liter. Further, the addition of the salt of the strong acid will have little effect on the hydrogen ion concentration, although it may affect the activity to some extent. The value of c_{H^+} in a solution of 0.1 mole of hydrochloric acid and 0.1 mole of sodium chloride per liter may thus be taken as remaining at 0.1 gram ion per liter.

With weak acids the situation is quite different, because ionization is far from complete, even in the most dilute solutions that are generally encountered. In order to calculate the hydrogen ion concentration, it is necessary to consider the various ionization equilibria, including that of the solvent. The following treatment of a solution of an acid and its conjugate base is completely general. However, it is easier to understand the argument if the case is considered of an acid HA and its conjugate base A^- in the form of the completely ionized salt NaA. Suppose the solution has an overall (or stoichiometric) composition of a moles of acid HA and b moles of the conjugate base A^-, as the salt NaA, per liter, then

$$a + b = c_{HA} + c_{A^-}, \tag{53.1}$$

where part of the c_{A^-} arises from ionization of the HA. In addition to H^+, Na^+ and A^- ions, resulting from the ionization of the acid and the salt, the solution will contain OH^- ions from the ionization of the water. Electrical neutrality requires that the sum of all the positive charges be equal to the sum of all the negative charges, so that

$$c_{\mathrm{H^+}} + c_{\mathrm{Na^+}} = c_{\mathrm{A^-}} + c_{\mathrm{OH^-}}. \tag{53.2}$$

Since the salt NaA is assumed to be completely ionized, $c_{\mathrm{Na^+}}$ is equal to b, and hence

$$c_{\mathrm{H^+}} + b = c_{\mathrm{A^-}} + c_{\mathrm{OH^-}}. \tag{53.3}$$

By means of equations (53.1) and (53.3) it is possible to eliminate $c_{\mathrm{A^-}}$ and c_{HA} from equation (52.5) defining K_a, the ionization constant of the acid HA; the result, after rearrangement is

$$c_{\mathrm{H^+}} = K_a \frac{a - c_{\mathrm{H^+}} + c_{\mathrm{OH^-}}}{b + c_{\mathrm{H^+}} - c_{\mathrm{OH^-}}} \cdot \frac{f_{\mathrm{HA}}}{f_{\mathrm{H^+}} f_{\mathrm{A^-}}}. \tag{53.4}$$

In principle, this equation can give the hydrogen ion concentration in any solution containing the acid alone ($b = 0$), the conjugate base alone ($a = 0$) or a mixture of the acid and base. These cases will be considered in turn.

I. Solution of Weak Acid. In equation (53.4) b is now zero, and taking the activity coefficient factor as approximately unity,

$$c_{\mathrm{H^+}} \approx K_a \frac{a - c_{\mathrm{H^+}} + c_{\mathrm{OH^-}}}{c_{\mathrm{H^+}} - c_{\mathrm{OH^-}}}. \tag{53.5}$$

Except possibly in dilute solutions of very weak acids, the hydroxyl ion concentration is negligible in comparison with that of the hydrogen ion, so that, neglecting the $c_{\mathrm{OH^-}}$ terms, equation (53.5) becomes

$$c_{\mathrm{H^+}} \approx K_a \frac{a - c_{\mathrm{H^+}}}{c_{\mathrm{H^+}}}.$$

This quadratic equation in $c_{\mathrm{H^+}}$ can be readily solved to give

$$c_{\mathrm{H^+}} \approx -\tfrac{1}{2}K_a + \sqrt{\tfrac{1}{4}K_a^2 + aK_a}, \tag{53.6}$$

where a is the concentration of the acid solution. In most cases of interest, $\frac{1}{4}K_a^2$ is negligible in comparison with aK_a, so that

$$c_{\mathrm{H^+}} \approx -\tfrac{1}{2}K_a + \sqrt{aK_a}. \tag{53.7}$$

Except at very high dilutions, a further simplification is possible by neglecting the term $-\frac{1}{2}K_a$; the result is

$$c_{\mathrm{H^+}} \approx \sqrt{aK_a}. \tag{53.8}$$

The hydrogen ion concentration in a solution of a weak acid is thus approximately proportional to the square root of its ionization constant, at a given acid concentration.

Example: Calculate the hydrogen ion concentration in a precisely 0.1 M solution of acetic acid using equations (53.7) and (53.8).

Since K_a is 1.75×10^{-5} and $a = 0.100$, it follows from equation (53.7) that

$$c_{H^+} = -(\tfrac{1}{2} \times 1.75 \times 10^{-5}) + \sqrt{0.100 \times 1.75 \times 10^{-5}} = 1.32 \times 10^{-3} \text{ g ion per liter.}$$

From equation (53.8) on the other hand

$$c_{H^+} = \sqrt{0.100 \times 1.75 \times 10^{-5}} = 1.32 \times 10^{-3} \text{ g ion per liter.}$$

Then, to three significant figures, which are all that can be justified in view of the neglect of activity coefficients, the two values are identical. Further, it is seen that no detectable difference would result if equation (53.6) were used.

In view of the neglect of the activity coefficient factor, the equation derived above should, strictly speaking, use K'_a in place of K_a. Hence, if the value of K'_a at the given acid concentration were available, the calculated c_{H^+} would be closer to the experimental value.

Example: From conductance measurements, K'_a for exactly 0.1 M acetic acid is 1.846×10^{-5}. Calculate the hydrogen ion concentration in this solution.

By equation (53.7)

$$c_{H^+} = -(\tfrac{1}{2} \times 1.846 \times 10^{-5}) + \sqrt{0.1000 \times 1.846 \times 10^{-5}} = 1.349 \times 10^{-3} \text{ g ion per liter.}$$

This is more accurate than 1.32×10^{-3} g ion per liter obtained above.

The foregoing equations apply to weak acids of all types. If the acid is a cation, e.g., NH_4^+, the acid solution will actually be a solution of an ammonium salt. Thus, equations (53.7) and (53.8) can be used to determine the hydrogen ion concentration in the solution of a salt of a weak base and strong acid. In this case, a in the equation represents the salt concentration and K_a is the strength of the acid conjugate to the weak base, so that by equation (52.22) it is equal to K_w/K_b, where K_b is the ionization constant of the weak base.

II. Solution of Base. In this case, a in equation (53.4) is zero, so that

$$c_{H^+} \approx K_a \frac{c_{OH^-} - c_{H^+}}{b + c_{H^+} - c_{OH^-}}, \tag{53.9}$$

where b is the concentration of base in the solution; K_a is the ionization constant of the acid conjugate to the base. Unless this base is exceptionally weak, the solution will be moderately alkaline, at least, so that $c_{OH^-} > c_{H^+}$. If c_{H^+} is neglected in comparison with c_{OH^-}, equation (53.9) becomes

$$c_{H^+} \approx K_a \frac{c_{OH^-}}{b - c_{OH^-}} \approx K_a \frac{c_{OH^-}}{b}, \tag{53.10}$$

since at reasonable concentrations $b \gg c_{OH^-}$. Replacing c_{OH^-} by K_w/c_{H^+} and solving for c_{H^+}, the result is

$$c_{H^+} \approx \sqrt{\frac{K_a K_w}{b}}. \tag{53.11}$$

Alternatively, replacing K_a by K_w/K_b

$$c_{H^+} \approx \frac{K_w}{\sqrt{bK_b}}. \tag{53.12}$$

These equations may be used to determine the hydrogen ion concentration in a solution of a weak nonionic base, such as NH_3, or of an anionic base, e.g., acetate, in the form of a salt of the conjugate acid and strong base, e.g., sodium acetate.

III. Solution of Conjugate Acid and Base. Unless the solution contains a large excess of one or other of the conjugate acid or base, c_{H^+} and c_{OH^-} are not very different, so that $c_{H^+} - c_{OH^-}$ can be neglected in equation (53.4); the result is

$$c_{H^+} \approx K_a \frac{a}{b} \tag{53.13}$$

or, more exactly,

$$c_{H^+} = K'_a \frac{a}{b}. \tag{53.14}$$

A solution of a weak acid and its highly ionized salt, e.g., acetic acid and sodium acetate, or of a weak base and its salt, e.g., ammonia and ammonium chloride, is a mixture of conjugate acid and base to which equations (53.13) and (53.14) are applicable. In the former case, a is equal to the stoichiometric concentration of acid and b is that of the salt in the solution. The equations may then be written in the form

$$c_{H^+} = K'_a \frac{[\text{acid}]}{[\text{salt}]} \approx K_a \frac{[\text{acid}]}{[\text{salt}]}. \tag{53.15}$$

It is evident from equation (53.15) that increasing the proportion of salt to acid in the solution, e.g., of an acid HA and its salt NaA, will decrease the hydrogen ion concentration. This is to be expected, since the addition of the common ion A^- will decrease the ionization of the acid HA, which is almost entirely responsible for the hydrogen ions in the solution.

Example: Calculate the hydrogen ion concentration of a solution containing 0.1 M acetic acid and 0.05 M sodium acetate.

In this case, [acid] = 0.100 and [salt] = 0.0500; K_a is 1.75×10^{-5}, and consequently, by equation (53.15)

$$c_{H^+} = 1.75 \times 10^{-5} \times \frac{0.100}{0.0500} = 3.50 \times 10^{-5} \text{ g ion per liter.}$$

(This may be compared with 1.32×10^{-3} g ion per liter for 0.1 molar acetic acid in the absence of sodium acetate, as found in a preceding example.)

When a solution contains a weak acid and its salt in equimolar amounts, so that [salt] = [acid], the value of c_{H^+} is equal to K'_a by equation (53.15). A determination of the hydrogen ion concentration in such a solution, e.g., by means of a hydrogen electrode (§ 53c), constitutes one of the simplest methods for determining K'_a for an acid. For mixtures containing other proportions of acid and salt, equation (53.15) may be used to determine K'_a if c_{H^+} has been measured.

53b. The pH Scale and Buffer Solutions.—Hydrogen ion concentrations can cover a wide range, from about 1 gram ion (or more) per liter in acid solutions to 10^{-14} gram ion (or less) per liter in alkaline solutions. To avoid the use of negative exponents, S. P. L. Sørensen (1909) introduced a convenient scale for expressing hydrogen ion concentrations that has been widely adopted. In its original form, *the negative logarithm of the hydrogen ion concentration was called the* pH of the solution; thus

$$\text{pH} = -\log c_{H^+}.$$

In more recent times, with the realization of the thermodynamic significance of the activity, this definition has been modified to

$$\text{pH} = -\log a_{H^+}, \tag{53.16}$$

although the more approximate form is commonly used.

The logarithmic representation has been extended to hydroxyl ions, so that

$$\text{pOH} = -\log a_{OH^-}.$$

In addition, ionization constants of acids and bases and the ionic product of water are frequently expressed in a similar manner; thus

$$\text{p}K_a = -\log K_a \qquad \text{and} \qquad \text{p}K_w = -\log K_w,$$

where $\text{p}K_a$ and $\text{p}K_w$ are called the ionization exponents of the acid and of water, respectively.

Aqueous solutions of a salt of a strong acid and strong base, e.g., sodium chloride, and of ammonium acetate have a pH of about 7, but the addition of 1 ml of 0.1 molar hydrochloric acid to 1 liter alters the pH to 4 in the former solution, although it hardly affects the pH of the latter. The addition of an equivalent quantity of sodium hydroxide would likewise change the pH of sodium chloride solution from 7 to 10, but it would not appreciably alter that of the ammonium acetate solution. The solution of ammonium acetate thus has the property of resisting change of pH when acid or alkali is added, and this property is known as **buffer action.** In general, a **buffer solution** is *one which is resistant to change of* pH *upon the addition of acid or alkali.* Such solutions usually consist of a mixture of a weak acid and its salt (conjugate base) or of a weak base and its salt (conjugate acid); a salt of a weak acid and a weak base, such as ammonium acetate, also has some buffer action, as indicated above.

The buffer action of a solution of a weak acid HA and its highly ionized salt is explained by the "neutralization" of added hydrogen ions by the anions A^- acting as a base; thus the reaction

$$H_3O^+ + A^- = H_2O + HA$$

takes place to a considerable extent. If hydroxyl ions are added, they are removed by reaction with the HA in the solution,

$$OH^- + HA = H_2O + A^-.$$

If the buffer mixture consists of a weak base B and its salt, which provides BH^+ ions, the corresponding equations for the removal of hydrogen and hydroxyl ions by the constituents of the solution are

$$H_3O^+ + B = H_2O + BH^+ \qquad \text{and} \qquad OH^- + BH^+ = H_2O + B.$$

In view of these reactions it can be understood why a buffer solution of the type described resists change of pH when acid (H_3O^+ ions) or alkali (OH^- ions) are added.

Buffer solutions of definitely known pH are of great value in various aspects of chemistry, and the problem of preparing such solutions is of interest. The hydrogen ion concentration of a buffer solution, consisting of a weak acid and its salt, is given with fair approximation, in the pH range of 4 to 10, by equation (53.15), i.e.,

$$c_{H^+} \approx K_a \frac{[\text{acid}]}{[\text{salt}]}.$$

Strictly speaking K'_a should be used rather than K_a, but since great accuracy is not expected, it is preferable to use a tabulated constant (Table 52.2). Upon taking logarithms, and changing the signs throughout, this equation becomes

$$-\log c_{H^+} \approx -\log K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{pH} \approx \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}. \qquad (53.17)$$

By means of equation (53.17), known as the Henderson-Hasselbalch equation, it is possible to calculate the pH of a buffer solution of known concentration; alternatively, it may be employed to prepare a buffer solution of definite pH.

In general, the resistance to change in the [salt]/[acid] ratio, and hence in the pH of the solution, upon the addition of acid or alkali, is greatest when the ratio is unity. The **buffer capacity** is therefore a maximum in a solution containing equivalent amounts of a weak acid and its salt; it falls off as the ratio of salt to acid changes in either direction. Although it is difficult to give an exact limit, it is generally accepted that a solution has useful buffer capacity provided the value of [salt]/[acid] lies within the range of 10 to 0.1, i.e., ten parts of salt to one of acid, at one extreme, to one part of salt to ten of acid, at the other extreme. It follows, therefore, from equation (53.17) that a particular acid can be employed for making useful buffer solutions of pH lying within the range of $\text{p}K_a - 1$ to $\text{p}K_a + 1$. Acetic acid, for example, has a $\text{p}K_a$ of 4.76 at 25°C; hence, mixtures of sodium acetate and acetic acid can be used for preparing buffer solutions whose pH's are roughly in the range of 3.75 to 5.75. Outside this range the buffer capacity of the sodium acetate-acetic acid system is too small to be of practical value.

Any given weak acid can be used for the preparation of buffer solutions over a limited range of pH only; hence, a number of different acids, and their salts, are required to cover the useful range of pH from about 2 to 12. Some of the recommended mixtures and their effective ranges are given in Table 53.1; the pH values have been obtained by experimental determinations with the hydrogen electrode (§ 53c). By following the directions given in the literature a solution of any desired pH value can be prepared with rapidity and precision.

TABLE 53.1. BUFFER MIXTURES

Constituents	pH Range
Glycine and Glycine hydrochloride	1.0-3.7
Phthalic acid and Potassium acid phthalate	2.2-3.8
Acetic acid and Sodium acetate	3.7-5.6
Disodium citrate and Trisodium citrate	5.0-6.3
Monosodium phosphate and Disodium phosphate	5.8-8.0
Boric acid and Borax	6.8-9.2
Borax and Sodium hydroxide	9.2-11.0
Disodium phosphate and Trisodium phosphate	11.0-12.0

Provided there is no chemical action, other than the establishment of acid-base equilibria, a mixture of two different buffer solutions will be effective over the pH ranges of both solutions separately. A simple and ingenious combination of this kind consists of citric acid and disodium hydrogen phosphate in various proportions; this is equivalent to a system of five acids, viz., three stages of citric acid and the first two stages of phosphoric acid. This system, with the constituents in various proportions, can be used for preparing buffer solutions having definite pH values between 2.2 and 8.0. The inclusion of diethylbarbituric acid (veronal) and boric acid extends the range to pH 12.

According to equation (53.17) the pH of a buffer solution is determined by the *ratio* of the concentrations of salt and acid, and not by their amounts; nevertheless, the buffer capacity at a given pH does depend on the actual concentrations. The more concentrated the solution the greater will be the resistance to change of pH upon the addition of an acid or a base. This can be readily proved by means of equation (53.17), using two hypothetical cases in which the salt and acid concentrations are different but the ratio is the same. In practice the solutions employed are usually about 0.1 to 0.2 molar, because the use of more concentrated solutions introduces so-called "salt effects"; the ionic strength is then so high that it produces marked deviations from unity in the activity coefficients.

53c. Experimental Determination of pH: The Hydrogen Gas Electrode.—To establish the pH scale and to make possible the determination of pH values of solutions in general, it is necessary to measure the hydrogen ion concentration (or activity) of a conveniently reproducible solution. For this purpose, a hydrogen gas electrode and a suitable reference electrode are inserted into the solution and the E.M.F. of the resulting cell is measured. This cell may be represented by

$$\text{Pt} \mid \text{H}_2 \text{ (1 atm)} \mid \text{Solution} \mid \text{Sat. KCl solution} \mid \text{Reference electrode}$$

with a salt bridge of saturated potassium chloride solution between the solution and the reference electrode. The potential of the hydrogen electrode is given by equation (48.3) as

$$E_{\text{H}} = E^0 - \frac{RT}{nF} \ln \frac{a_{\text{H}^+}}{a_{\text{H}_2}}.$$

If the gas is at 1 atm pressure, $a_{\text{H}_2} = 1$ and since E^0 is zero and $n = 1$ this reduces to

$$E_{\text{H}} = -\frac{RT}{F} \ln a_{\text{H}^+}. \tag{53.18}$$

Converting the logarithms in equation (53.18), and taking the temperature to be 25°C, this becomes

$$E_{\text{H}} = -0.0592 \log a_{\text{H}^+}. \tag{53.19}$$

Utilizing the definition of $\text{pH} = -\log a_{\text{H}^+}$, this takes the form

$$E_{\text{H}} = 0.0592 \text{ pH}. \tag{53.20}$$

If the oxidation potential of the reference electrode is represented by E_{ref}, the measured E.M.F. of the cell, E, is equal to $E_{\text{H}} - E_{\text{ref}}$; hence,

$$E = E_{\text{H}} - E_{\text{ref}} = 0.0592 \text{ pH} - E_{\text{ref}}$$

$$\text{pH} = \frac{E + E_{\text{ref}}}{0.0592}. \tag{53.21}$$

This equation provides, in principle, a direct method for measuring the pH of any solution.

Two sources of uncertainty arise, however, in the application of equation (53.21); one is concerned with the two liquid junction potentials in the cell and the other with the exact significance of pH. In the first place, in spite of the use of a salt bridge, there is no certainty that the liquid junction potential has been eliminated. It may have a small, but appreciable, value which is included in the measured E.M.F. Second, the interpretation of the pH is somewhat indefinite. When the pH scale was first introduced, c_{H^+} in a solution of a weak acid was expressed, quite correctly, as αc, but the assumption made that $\alpha = \Lambda/\Lambda_0$ is now known to be an approximation. If the definition $\text{pH} = -\log a_{\text{H}^+}$ is adopted, as in equation (53.16), a knowledge of single ion activities is implied and this is impossible to obtain experimentally. Consequently, equation (53.21) must be regarded as a semiempirical equation for calculating a useful number, the pH of a solution, related approximately to c_{H^+} and a_{H^+}.

If the potential of the reference electrode, as given in § 48c. is substituted in equation (53.21), the pH obtained for solutions of weak acids, for example, will differ from those calculated from the ionization constants of the acids. In order to eliminate this discrepancy, as far as possible, an empirical value for E_{ref} is chosen such that its use in equation (53.21) will give results, for a number of buffer solutions, in agreement with those calculated from the known ionization constants of the acids. For the calomel electrode in 0.1 N potassium chloride the value of E_{ref} obtained in this manner is -0.3358 volt at 25°C. Consequently, if E is the E.M.F. of a cell, consisting of a hydrogen electrode in a given solution, a salt bridge and this calomel electrode, the pH of the solution at 25°C is determined by equation (53.21) in the form

$$\text{pH} = \frac{E - 0.3358}{0.0592}. \tag{53.22}$$

This equation thus establishes the scale for the experimental determination of pH values, based on the use of the hydrogen electrode.

Various forms of the hydrogen electrode were depicted in Fig. 48.1 and described in § 48c. Some of the drawbacks associated with the use of this electrode were mentioned. Gas of high purity is required and its partial pressure should be known, after making allowance for the aqueous vapor pressure of the solution. If this is appreciably different from 1 atm (760 mm of mercury), a correction must be applied by using equation (49.17).

The hydrogen gas electrode cannot be employed in solutions of oxidizing agents, such as nitrates, permanganates, ferric salts, etc., or other substances capable of reduction by hydrogen in the presence of finely divided platinum. The electrode does not behave satisfactorily in solutions containing ions of metals lying below hydrogen in the table of standard potentials, e.g., gold, silver, mercury and copper. In addition, traces of compounds of mercury, sulfur and arsenic "poison" the electrode, so that it will not function even in other solutions. In spite of these limitations, the hydrogen gas electrode has been extensively employed for precise measurements in cells with or without liquid junctions, and for the standardization of buffer solutions.

53d. Other Hydrogen Ion Electrodes.—The hydrogen gas electrode is the ultimate standard of reference for all pH measurements, but owing to the limitations and experimental difficulties associated with its use, other electrodes have been devised which are reversible with respect to hydrogen ions. The most important of these will be described below.

I. The Quinhydrone Electrode.—According to equation (48.8) the potential of the quinone-hydroquinone system is

$$E = E^{0}_{\text{el.}} - \frac{RT}{2F} \ln \frac{a_{\text{Q}}}{a_{\text{H}_2\text{Q}}} - \frac{RT}{F} \ln a_{\text{H}^+}, \tag{53.23}$$

where a_{Q} and $a_{\text{H}_2\text{Q}}$ refer to the activities of the quinone and hydroquinone, respectively; the potential is evidently dependent on the hydrogen ion activity of the solution, and hence it offers possibilities for the determination of the latter. For this purpose a small quantity of the compound quinhydrone, which consists of equimolar amounts of quinone and hydroquinone, is dissolved in the solution. The ratio of the concentrations of these two substances is thus equal to unity, and if the ratio of the activities is taken as equal to the ratio of the concentrations, a_Q/a_{H_2Q} is also equal to unity. The second term on the right-hand side of equation (53.23) is then zero, and so the potential of the **quinhydrone electrode** is given by

$$E_Q = E_Q^0 - \frac{RT}{F} \ln a_{H^+} = E_Q^0 + 0.0592\,\text{pH at } 25°\text{C}. \qquad (53.24)$$

By measurement of the quinhydrone electrode potential in buffer solutions of known pH's, the value of E_Q^0 is found to be -0.6994 volt at 25°C. For practical purposes the electrode is best combined with a calomel electrode in 0.1 N potassium chloride and a salt bridge, as in § 53c; the potential of the calomel electrode is taken as -0.3358 volt, so that E, the E.M.F. of the resulting cell, is equal to $E_Q + 0.3358$. Consequently, by equation (53.24), using -0.6994 for E_Q^0,

$$E = E_Q + 0.3358 = -0.6994 + 0.0592\,\text{pH} + 0.3358$$

$$\text{pH} = \frac{E + 0.3636}{0.0592}. \qquad (53.25)$$

The quinhydrone electrode is easily set up by adding a small amount of the sparingly soluble solid quinhydrone to the experimental solution, and then inserting an indicator electrode of clean gold or platinum. The electrode gives accurate results in solutions of pH less than 8; in more alkaline solutions errors arise, first, because of oxidation of the hydroquinone by oxygen of the air, and second, on account of the ionization of the hydroquinone as an acid. The quinhydrone electrode can be used in the presence of the ions of many metals which have a harmful effect on the hydrogen gas electrode. The potential of the electrode is affected, however, by neutral electrolytes which increase the ionic strength of the solution; under these conditions the ratio of the activities a_Q/a_{H_2Q} is not equal to unity, as was assumed in deriving equation (53.24). Because of its simplicity and the accuracy of which it is capable, the quinhydrone electrode has been widely used for pH measurements.

II. The Glass Electrode.—At the interface between glass and a solution with which it is in contact there is a difference of potential which has been found by experiment to be dependent upon the pH of the solution; this dependence corresponds to the usual type of equation for a reversible hydrogen electrode, viz.,

$$E_G = E_G^0 - 0.0592 \log a_{H^+} = E_G^0 + 0.0592\,\text{pH at } 25°\text{C}, \qquad (53.26)$$

where E_G^0 is a constant for the given electrode. In its simplest form the glass electrode consists of a glass tube terminating in a thin-walled bulb, as shown at *A* in Fig. 53.1; a special glass of relatively low melting point and high electrical conductance is used for the purpose. The bulb contains a solution of constant hydrogen ion concentration and an electrode of definite potential; an Ag|AgCl(*s*) electrode in 0.1 molar hydrochloric acid, or a platinum wire inserted in a pH 4.00 buffer solution containing a small quantity of quinhydrone, is usually employed. The bulb is inserted in the experimental solution *B*, and the resulting glass electrode is combined through a salt bridge with a reference electrode, e.g., a calomel electrode *C*, to form the cell

Ag | AgCl(*s*) | 0.1 N HCl | glass | experimental solution || calomel electrode.

The E.M.F. is the algebraic sum of $E_{\text{Ag}} + E_G + E_{\text{cal}}$ and since E_{Ag} and E_{cal} are constant, the E.M.F. will vary as E_G. Because of the high resistance of the glass, viz., 10 to 100 million ohms, special vacuum-tube potentiometers are used to determine the E.M.F. Several commercial forms of apparatus are now available, by means of which the glass electrode potential can be measured with an accuracy of about 0.0005 volt or 0.01 pH unit. The constant E_G^0 in equation (53.26) is evaluated by standardizing the particular electrode in a number of buffer solutions of definitely known pH values.

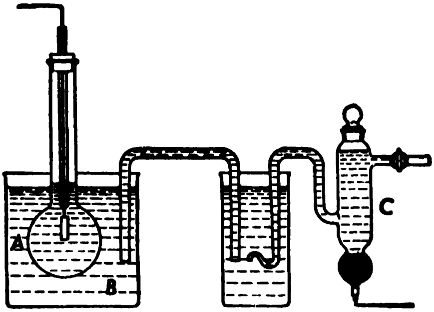

FIG. 53.1. Glass electrode cell

The glass electrode can be employed in aqueous solutions of almost any kind, provided the pH lies within the range of 1 to 9; for higher pH's, up to 12, special glass should be used. Because of its very wide applicability, its indifference to oxidizing agents, metallic ions, poisons, etc., and the simplicity of its operation, the glass electrode has been extensively adopted for pH determination in chemical and biological laboratories and for industrial control purposes.

The theory of the glass electrode has not yet been completely worked out, but its action appears to be related to the transfer of hydrogen ions through the glass. A potential is set up at the glass-solution interface which is analogous to that at a junction between two solutions containing hydrogen ions; the value of such a potential is given by equation (49.10), but in this case only the hydrogen ions can move across the boundary, so that t_- is zero while t_+ is unity. The potential at the interface is then given by the expression

$$E_G = -\frac{RT}{F} \ln \frac{a_2}{a_1}, \tag{53.27}$$

where a_1 and a_2 are the hydrogen ion activities on the two sides of the glass wall. One of these solutions, e.g., a_1, inside the glass bulb, is constant in nature, and so equation (53.27) reduces to

$$E_G = \text{constant} - \frac{RT}{F} \ln a_2,$$

which is identical in form with the experimental equation (53.26).

53e. Hydrogen Ion (Acid-Base) Indicators.—An acid-base or hydrogen ion **indicator** is a substance which, within certain limits, *varies its color according to the hydrogen ion concentration* (*or activity*) *of its environment.* It is thus possible to determine the pH of a solution by observing the color of a suitable indicator when placed in that solution. An acid-base indicator is invariably a weak acid HIn which differs in color from its conjugate base In^-; the equilibrium between the two forms may be represented by

$$\text{HIn} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{In}^-.$$

As with any other weak acid, the ionization constant of the indicator acid may be related to the hydrogen ion concentration of the solution by means of equation (52.6) or (52.7); the result is

$$c_{\text{H}^+} \approx K_{\text{In}} \frac{c_{\text{HIn}}}{c_{\text{In}^-}}, \tag{53.28}$$

where K_{In} is known as the **indicator constant.** Although this equation is approximate, since it assumes the activity coefficient fraction to be unity, it is well within the limits of accuracy of most work with indicators.

The hydrogen ion concentration in equation (53.28) is that of the solution containing the indicator, irrespective of whether it is due to the indicator alone or to other substances that may be present. Hence the ratio of the concentrations of HIn and In^- present at equilibrium depends on the hydrogen ion concentration of the solution in which the indicator is present. Since the species HIn and In^- have different colors, the actual color exhibited by the indicator will depend on the hydrogen ion concentration of the medium. In an acidic solution, that is, one containing excess of H_3O^+ ions, the equilibrium will be displaced to the left; the indicator will thus consist predominantly of HIn, and it will exhibit the color of the acid form. On the other hand, if the solution is alkaline, containing OH^- ions which combine with the H_3O^+ ions and reduce their concentration, the equilibrium point will lie to the right, and the indicator will be largely in the In^- form; in alkaline solution the indicator will consequently have the color of the conjugate base.

53f. Indicator Exponent and Useful Range.—By taking logarithms of equation (53.28) and changing signs throughout, it follows that

$$\text{pH} = \text{p}K_{\text{In}} + \log \frac{[\text{In}^-]}{[\text{HIn}]}, \tag{53.29}$$

where $\text{p}K_{\text{In}} = -\log K_{\text{In}}$ is called the **indicator exponent;** $[\text{In}^-]/[\text{HIn}]$ represents the ratio of the amounts (or colors) of the conjugate base to acid of the indicator present in the solution of given pH. Color changes can usually be detected as the relative amounts of HIn and In^- vary roughly from

90% HIn and 10% In^-, i.e., $[In^-]/[HIn] = 0.9$, to 10% HIn and 90% In^-, i.e., $[In^-]/[HIn] = 9$. It follows, therefore, according to equation (53.29), that the minimum pH at which the indicator is effective is given by

$$\mathrm{pH} = \mathrm{p}K_{\mathrm{In}} + \log \tfrac{1}{9} \approx \mathrm{p}K_{\mathrm{In}} - 1$$

and the maximum pH by

$$\mathrm{pH} = \mathrm{p}K_{\mathrm{In}} + \log 9 \approx \mathrm{p}K_{\mathrm{In}} + 1.$$

It is seen from these results that the **useful range** of an indicator is approximately one unit of pH on each side of the $\mathrm{p}K_{\mathrm{In}}$ of the particular indicator. Since the useful range of an indicator is restricted to about two units of pH, it is evident that a number of indicators are required to cover the range of pH from zero to 14, i.e., from completely acid to completely alkaline solutions. A selection of useful indicators is given in Table 53.2 together with the values of their exponents and their acidic and alkaline colors; the effective range, as determined by experiment, is given in each case. In addition to these individual indicators, mixtures of indicators, known as **universal indicators,** have been found useful for approximate pH determinations. A convenient and simple form of universal indicator, covering the range of pH from 4 to 11, is made from methyl red, α-naphtholphthalein, thymolphthalein, phenolphthalein and bromthymol blue; the colors at different pH values are given below.

TABLE 53.2. SOME USEFUL INDICATORS

	Color			
Indicator	Acid	Alkaline	$\mathrm{p}K_{\mathrm{In}}$	pH range
Thymol blue	Red	Yellow	1.51	1.2-2.8
Methyl orange	Red	Yellow	3.7	3.1-4.4
Bromphenol blue	Yellow	Blue	3.98	3.0-4.6
Methyl red	Red	Yellow	5.1	4.2-6.3
Chlorphenol red	Yellow	Red	5.98	4.8-6.4
Bromcresol purple	Yellow	Purple	6.3	5.2-6.8
Bromthymol blue	Yellow	Blue	7.0	6.0-7.6
Phenol red	Yellow	Red	7.9	6.8-8.4
Cresol red	Yellow	Red	8.3	7.2-8.8
Thymol blue (2nd range)	Yellow	Purple	8.9	8.0-9.6
Phenolphthalein	Colorless	Red	9.4	8.3-10.0
Thymolphthalein	Colorless	Blue	9.4	9.2-10.6

pH	4	5	6	7	8	9	10	11
Color	Red	Orange-red	Yellow	Green-yellow	Green	Blue-green	Blue-violet	Red-violet

53g. Determination of pH by Indicators: I. With Buffer Solutions.—If a number of buffer solutions of known pH are available, the estimation of the unknown pH of an experimental solution is a relatively simple matter.

The pH is first determined approximately by means of a universal indicator; this permits the best indicator to be chosen from Table 53.2. A definite quantity of this indicator is then added to a certain volume of the test solution; the color produced is compared with those obtained, with the same concentration of indicator, in a series of buffer solutions of known pH. By matching the colors, the pH of the unknown solution may be estimated within 0.05 pH unit.

II. Without Buffer Solutions.—Provided the exponent of an appropriate indicator is known, the pH of an unknown solution can be obtained without the use of buffer solutions, by means of equation (53.29). The practical problem is the determination of the ratio of the intensities of the two colors of the indicator when the latter is placed in the experimental solution. Absorption spectra and colorimeter methods have been employed for accurate work; for approximate purposes, a number of simple devices have been used.

In the "wedge method" of N. Bjerrum (1914), a rectangular box is divided by a diagonal glass sheet into two wedge-shaped compartments, as shown in plan in Fig. 53.2. A solution of the indicator which has been made definitely acid (color A) is placed in one wedge, and an alkaline solution (color B) is placed in the other. By viewing the combination from the front, a gradation of color, from pure A to pure B, can be seen as a result of the superposition of steadily varying proportions of the two individual colors. The test solution is placed in a narrow glass cell C of the same thickness as the combined wedges, and the indicator is added so that its concentration is the same as in the wedges. A position is then found at which the color of the test solution matches that of the superimposed acidic and basic colors in the wedges. The ratio of the depths of the wedge solutions at this point gives the ratio $[\mathrm{In}^-]/[\mathrm{HIn}]$ required for equation (53.29).

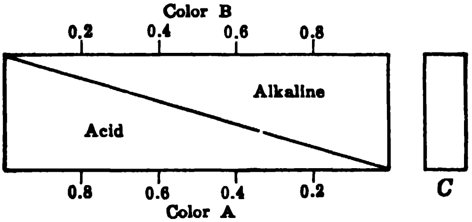

FIG. 53.2. Bjerrum wedge for pH determination

Example: With bromphenol blue as indicator, a given solution shows the best color match in a Bjerrum wedge at a point where the thickness of the alkaline wedge is 0.85 of the total. What is the pH of the solution?

The thickness of the alkaline wedge (color B) is 0.85, and so that of the acid wedge (color A) must be 0.15; hence the ratio of color B to color A is 0.85/0.15. The pK_{In} of bromphenol blue is 3.98 (Table 53.2); the required pH is thus given by equation (53.29) as

$$\mathrm{pH} = 3.98 + \log\frac{0.85}{0.15} = 4.7.$$

Another simple procedure for determining the color ratio is the "drop ratio" method of L. J. Gillespie (1920). A set of pairs, generally nine pairs, of test tubes is prepared, one tube of each pair contains acid and the other alkali. Various numbers of drops of indicator, increasing from one to nine, are placed in the tubes containing acid, and a corresponding decreasing number of drops of indicator, from nine to one, are placed in the tubes containing alkali. Each pair of tubes thus contains a total of ten drops of indicator, but the color as seen through the combination of both tubes varies regularly from one extreme to the other. A quantity of the experimental solution, equal in volume to that in the tubes, is placed in a similar tube, and ten drops of the same indicator are added. The color of this solution is then matched against the pairs of tubes. The ratio of the numbers of drops of alkaline form (color B) to the number of drops of acidic form (color A) of the indicator, in the pair giving the best match, is then equal to the ratio $[\mathrm{In}^-]/[\mathrm{HIn}]$ in the test solution.

Example: With bromthymol blue as indicator, a given solution exhibits the best color match with a pair of tubes containing 3 drops of alkaline color and 7 drops of the acidic color; what is the pH of the solution?

The ratio of color B to color A is $\frac{3}{7}$; $\mathrm{p}K_{\mathrm{In}}$ for bromthymol blue is 7.0, and so by equation (53.29),

$$\mathrm{pH} = 7.0 + \log \tfrac{3}{7} = 6.6.$$

It should be remembered that the equations derived above are approximate, since they are based on the use of concentrations instead of activities. However, the errors introduced in this manner are not serious, provided the experimental solutions do not contain relatively large amounts of electrolytes, i.e., the ionic strength is low. The presence of neutral salts in appreciable quantities may produce color changes of an indicator which are not due to changes of pH but to alterations in the activities; this is known as the **salt effect** of the indicator. Erroneous results are also frequently obtained in the presence of proteins, and indicator methods are not satisfactory in solutions containing these substances.

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PROBLEMS

1. Determine the correction in mv which should be applied to the reading of a hydrogen electrode at 25°C, if the gas bubbles through the solution at a barometric pressure of 740 mm. The vapor pressure of the solution may be taken as essentially that of water at 25°, i.e., 23.7 mm.

2. By suitably combining the potentials for the electrodes $Ag(s) \mid AgCl(s) \mid Cl^-$, $E^0_{298} = -0.2223$v, and $Ag(s) \mid Ag^+$, it is possible to determine the potential corresponding to the reaction $AgCl(s) = Ag^+ + Cl^-$. Determine the equilibrium constant, i.e., the solubility product, of AgCl at 25°C.

3. Determine K_a at 25°C for α-crotonic acid from the following data for the variation of the equivalent conductance with concentration and Λ_0 383.01:

$c \times 10^3$	Λ	$c \times 10^3$	Λ
0.9583	51.632	4.9736	23.677
1.0750	39.473	7.1422	19.861
3.2327	29.083	14.511	14.053

4. The ion product constant for D_2O varies with temperature as follows: 15°, 8.32×10^{-16}; 25°, 1.95×10^{-15}; 35°C, 4.27×10^{-15}. Evaluate the mean heat of ionization.

5. Determine the pD and pOD at 25°C of (*a*) a 0.01 N DCl solution in D_2O, (*b*) 0.01 N NaOD in D_2O, and (*c*) pure D_2O.

6. The E.M.F. of the cell

$$H_2(1\text{ atm}) \mid NaOH(m)\ NaCl(m) \mid AgCl(s) \mid Ag,$$

with the NaOH and NaCl at equal molalities, approaches the limiting value 1.0508v at 25°C as the solutions are diluted. Calculate the ion product of water.

7. (*a*) On mixing 10.00 ml of 0.200 N acetic acid and 4.00 ml of 0.200 N sodium hydroxide, the pH was found to be 4.33. Determine pK'_a and pK_a. Repeat the calculation for a mixture (*b*) of 10.00 ml of acid and 5.00 ml of base, pH 4.49, and (*c*) 6.00 ml of base and 10.00 ml of acid, pH 4.65.

8. The complex cobaltammine salt $[Co(NH_3)_4C_2O_4]_2S_2O_6$, a 1-2 salt, has a water solubility at 15°C of 1.545×10^{-4} mole l^{-1}. Calculate its mean activity coefficient in (*a*) 0.0050 N K_2SO_4 and (*b*) 0.0050 N $K_3Co(CN)_6$. (*c*) Determine its solubility in 0.0050 N KNO_3. (The Debye-Hückel constant *A* has the value 0.500 at 15°C.)

9. The solubility of $AgIO_3$ in water is 1.761×10^{-4} mole l^{-1} at 25°C. Calculate the solubility in (*a*) 0.010 M KNO_3, (*b*) 0.010 M $AgNO_3$. (*c*) Determine the thermodynamic solubility at $\mu = 0$.

10. The solubility product of $BaSO_4$ is 1.08×10^{-10} at 25°C. Calculate (*a*) the solubility in pure water, (*b*) in 0.01 M $BaCl_2$ (*c*) at $\mu = 0$.

11. The solubility of $La(IO_3)_3$ in water at 25°C is 8.901×10^{-4} mole l^{-1}. Calculate (*a*) the mean activity coefficient, (*b*) the solubility and mean activity coefficient in 0.0010 M potassium chloride.

12. For the amino acid alanine, $pK_1 = 2.34$ and $pK_2 = 9.87$. Calculate the approximate pH of 0.10 M solutions of (*a*) alanine hydrochloride, (*b*) the free amino acid and (*c*) sodium alaninate.

13. Determine the approximate pH of the following solutions: (*a*) 0.05 M lactic acid, (*b*) 0.02 M phosphoric acid, (*c*) 0.10 M potassium oxalate, (*d*) 0.01 M pyridine nitrate.

14. A solution has a pH of 5.8. If a saturated calomel electrode is placed in the solution, what will be the E.M.F. at 25°C of the resulting cell when the second electrode is (*a*) hydrogen gas at 1 atm, (*b*) quinhydrone?

15. The E.M.F. of the cell

$$\text{Hg} \mid \text{HgCl}(s) \mid \text{KCl satd.} \mid \text{phenylacetic acid, 0.050 M} \mid \text{Quinhydrone} \mid \text{Pt}$$

is 0.292v at 25°C. Determine (*a*) pK_a', (*b*) the mean activity coefficient for the 0.050 M solution, (*c*) pK_a.

15

Surface Chemistry and Colloids

ADSORPTION

54a. Adsorption and Adsorbents.—An important property of surfaces is that known as **adsorption**; this term is used to describe *the existence of a higher concentration of any particular substance at the surface of a liquid or solid than is present in the bulk of the medium.* It is necessary to distinguish between "adsorption" and "absorption" as applied to solids; while the former refers to an excess concentration at the surface, the latter implies a more or less uniform penetration of the solid by a given substance. It is probable that adsorption occurs at all surfaces, but for the purpose of studying the phenomena of adsorption it is convenient to employ porous substances which have a large effective area for a given mass. Among the best known of these is charcoal, made by burning some form of wood, e.g., coconut shells, in a limited supply of air. It has long been known that charcoal can take up relatively large volumes of gases, and also that it can remove dyestuffs and other substances from solution, e.g., in the purification of sugar and other organic compounds. These are examples of adsorption of gases and from solution, respectively. Silica gel, made by partially drying gelatinous silicic acid, and alumina, obtained by heating aluminum hydroxide, are important adsorbing materials, i.e., **adsorbents.** The substances adsorbed are called **adsorbates.** Other oxides, particularly chromium sesquioxide (Cr_2O_3) and zinc oxide, are used for adsorbing gases. Certain metals, such as platinum palladium, copper and nickel, when prepared in a suitable manner are also able to adsorb gases, particularly hydrogen, in appreciable amounts. It should be clearly understood that although the large surface is of importance in determining the adsorbing properties of a given material, the extent and firmness of adsorption are dependent to a great extent on the nature of the adsorbent and the substance adsorbed. A given metal may adsorb one gas but not another; thus, nickel adsorbs hydrogen strongly, but the adsorption of nitrogen is quite small. For the further consideration of the phenomena of adsorption it is convenient to treat adsorption of gases and adsorption from solution separately.

54b. Adsorption of Gases.—*Increase of pressure and decrease of temperature increase the extent of the adsorption of a gas by a solid;* the curves in Fig. 54.1 show the quantities of nitrogen gas adsorbed by 1 gram of charcoal at various temperatures and pressures. Each of the curves is called an **adsorption isotherm,** since it gives the extent of adsorption, over a range of pressures,

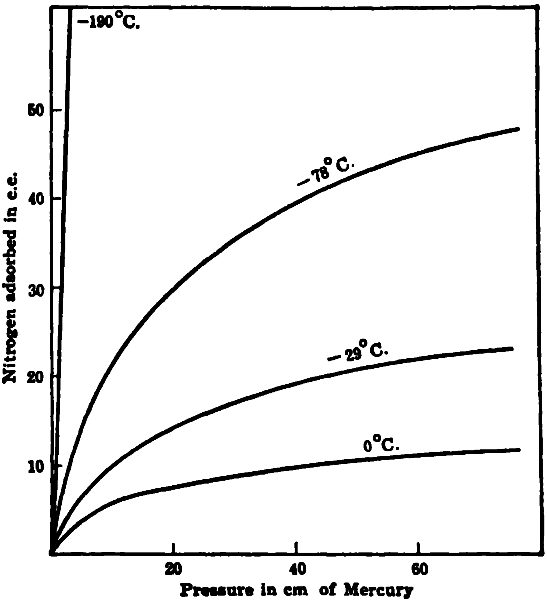

FIG. 54.1. Adsorption isotherms of nitrogen by charcoal

at a specified temperature. It will be observed that, particularly at low temperatures, the adsorption of gas increases very rapidly as the pressure is raised; at higher temperatures this increase is less marked. Diminution of temperature, at a given pressure, is associated with a marked increase of the adsorption of gases. This fact is utilized in the production of high vacua; the partly evacuated apparatus is connected to a vessel containing charcoal cooled in liquid air. Under these conditions the adsorptive capacity of the charcoal is so high that it is able to take up a large proportion of the gas remaining in the apparatus, and so it brings about a considerable reduction of pressure. The fact that adsorption decreases with increasing temperature means, according to the Le Chatelier principle (§ 30f), that the adsorption of a gas is accompanied by a decrease of enthalpy, i.e., an evolution of heat; this is known as the **heat of adsorption.** For every gas and solid there is a more or less definite heat of adsorption, although the actual value depends to some extent on the amount of gas already adsorbed by the solid.

The variation of gas adsorption with pressure at constant temperature can often be represented, over a limited range of pressure, by an empirical equation, commonly known as the Freundlich adsorption isotherm.* It is

$$a = kp^n \tag{54.1}$$

where a is the amount of gas adsorbed by unit mass, e.g., 1 gram, of adsorbent

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* Named for H. Freundlich (1910) who did not originate it but used it extensively, especially in the form applicable to adsorption from solutions (§ 54e).

at the pressure p; k and n are constants for the given adsorbate and adsorbent at the particular temperature. The value of n in equation (54.1) is less than 1 for a wide variety of adsorbents and adsorbates, especially at moderate and high temperatures, and so the quantity of gas adsorbed increases less rapidly than the pressure, as is evident from the curves in Fig. 54.1. With decreasing temperature, n approaches unity, and the adsorption becomes more nearly proportional to the pressure, at least at low pressures. Upon taking logarithms, equation (54.1) gives

$$\log a = \log k + n \log p, \tag{54.2}$$

so that the plot of log a against log p should be a straight line. The actual plots show a slight curvature, especially at low temperatures, so that the adsorption isotherm equation (54.1) can be regarded as approximate only, although it is convenient to use over a short range of pressure.

54c. Types of Adsorption.—An examination of the phenomena associated with the adsorption of gases shows that there are probably at least two different types of adsorption. The first type, known as **van der Waals adsorption** or **physical adsorption,** is exhibited by all substances, particularly at low and moderately low temperatures; *it is characterized, chiefly, by relatively low heats of adsorption,* namely about 5 to 10 kcal per mole of gas. These heat changes are of the same order as heats of condensation of gas to liquid; it appears, therefore, that the forces by which the adsorbed gas molecules are held to the surface of the solid are similar to the forces of cohesion of molecules in the liquid state. In other words, the molecules are adsorbed by van der Waals forces, or dispersion forces (§ 4f); it is for this reason that the term van der Waals adsorption is used for this type of adsorption.

Another characteristic of van der Waals (or physical) adsorption is that for a given adsorbent *the extent of adsorption, under given conditions, is roughly related to the ease of liquefaction of the gas;* this is to be expected if the forces concerned are similar to those operative in liquids. The volumes of various gases adsorbed by 1 gram of charcoal at 15°C and 1 atm pressure are given in Table 54.1, together with the respective boiling points of the liquefied gases.

TABLE 54.1. VAN DER WAALS ADSORPTION OF GASES BY CHARCOAL

Gas	Volume Adsorbed	Boiling Point	Gas	Volume Adsorbed	Boiling Point
Sulfur dioxide	380 ml	263.1°K	Carbon dioxide	48 ml	— °K
Chlorine	235	238.5°	Methane	16.2	111.7°
Ammonia	181	239.7°	Carbon monoxide	9.3	81.6°
Hydrogen sulfide	99	213.5°	Oxygen	8.2	90.2°
Hydrogen chloride	72	188.1°	Nitrogen	8.0	77.3°
Nitrous oxide	54	183.7°	Hydrogen	4.7	20.3°

It is seen that there is a distinct parallelism between the extent of adsorption of a gas and the boiling point; the most easily liquefiable gases, that is, with the largest van der Waals forces of cohesion, are those which are most strongly adsorbed. Physical adsorption is reversible, so that if the pressure is reduced, desorption of gas usually follows the same isotherm as adsorption.

The second type of adsorption is referred to as **activated adsorption** or **chemisorption**; *the heats of adsorption are much higher than for van der Waals adsorption*, the values being 10 to 100 kcal per mole. Chemisorption occurs in limited cases only, and it is generally observed at moderately high temperatures. *As the temperature is raised the van der Waals adsorption, for an appropriate gas and solid, may pass over into chemisorption*. As the name implies. chemisorption probably involves forces of interaction between the adsorbent and the gas that are chemical in nature, as distinct from the physical forces responsible for van der Waals adsorption. This explains the larger heat changes associated with the former type of adsorption. It also accounts for the fact that chemisorption is not reversible; it is necessary to raise the temperature, often considerably, to remove the adsorbed gas.

Chemisorption or activated adsorption is highly specific in character, depending on the chemical properties of the gas and adsorbent. Consequently, many gas-solid systems do not exhibit chemisorption at any temperature. The adsorption of oxygen or of carbon monoxide on tungsten is chemical in nature, as is evident from the fact that tungsten oxide or tungsten carbonyl, respectively, can be distilled from the surface. Similarly, when oxygen is chemisorbed on charcoal, carbon monoxide and dioxide are obtained by raising the temperature and pumping off the adsorbed gas. Chemisorption also occurs with hydrogen and carbon monoxide on zinc oxide-chromium sesquioxide mixtures, and with hydrogen on nickel and copper. It is probable that in the activated adsorption of hydrogen the molecules are partly, or completely, dissociated into hydrogen atoms which are held to the surface atoms by forces of a chemical nature, that is, by electron sharing. Although the word "activated" was not intended to imply any particular activity of the adsorbed substance, the adsorbed hydrogen is nevertheless more active chemically than free hydrogen gas, presumably because it is almost in the state of free atoms.* It is for this reason that chemisorption is important in relation to catalytic action on surfaces (§ 60d).

54d. The Langmuir Adsorption Isotherm.—Since chemical forces fall off very rapidly with distance, it is probable that chemisorption does not extend beyond a single layer of gas molecules on the surface of the solid. It is to be anticipated, therefore, as first pointed out by I. Langmuir (1916), that chemisorbed gas layers are in general only one molecule in thickness. Although direct experimental evidence is difficult to obtain, because of the uncertainty concerning the area of the surface, it seems to have been definitely established in a number of cases that there is a single layer of adsorbed molecules. When van der Waals adsorption occurs, the forces can extend from one layer of molecules to another, and so it is possible, in fact probable, that the gas adsorbed on the surface is several molecular layers in thickness, especially at relatively low temperatures and moderately high pressures. How-

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* The term "activated" arises from the fact that, as with most chemical reactions, this adsorption process is associated with an appreciable "energy of activation" (§ 58a).

ever, when the temperatures are sufficiently high for chemisorption to be evident, the van der Waals adsorption is usually negligibly small.

By supposing that a unimolecular layer only of gas can be adsorbed on the surface of a solid, Langmuir was able to derive an adsorption isotherm relating the pressure of the gas to the extent of adsorption. Consider an adsorbing surface exposed to a gas; molecules of gas will strike the surface and will adhere for an appreciable time, while other gas molecules will tend to evaporate from the surface. When a state of adsorption equilibrium is attained, the rate at which the gas molecules strike the surface and are held there, i.e., the rate of adsorption, will be equal to the rate of evaporation under the given conditions. According to the kinetic theory of gases, at constant temperature gas molecules strike a surface at a rate proportional to the pressure p of the gas (§ 3a). If at any instant a fraction θ of the adsorbing surface is already covered with gas molecules, the fraction $1 - \theta$ of the surface will be bare. Since only a single layer of molecules is to be adsorbed, it follows that only those molecules striking the bare parts of the surface can be retained, i.e., adsorbed; hence,

$$\text{Rate of adsorption of gas molecules} = kp(1 - \theta), \tag{54.3}$$

where k is a proportionality constant. The rate at which gas molecules evaporate from the surface will be proportional to the extent θ to which it is covered with these molecules; consequently,

$$\text{Rate of evaporation of gas molecules} = k'\theta. \tag{54.4}$$

At equilibrium the rates of adsorption and evaporation (or desorption), as given by equations (54.3) and (54.4), will be equal, so that

$$kp(1 - \theta) = k'\theta$$

$$\tag{54.5}$$

If the surface can become covered with a uniform layer of gas, one molecule in thickness, the amount of gas a adsorbed per unit mass of adsorbent is directly proportional to the fraction θ of the surface covered, i.e., $a = k''\theta$. Inserting the value of θ given by equation (54.5), and dividing through numerator and denominator by k', the result is

$$a = \frac{(kk''/k')p}{(k/k')p + 1}$$

$$\tag{54.6}$$

$$k_2p + 1$$

where $k_1 = kk''/k'$ and $k_2 = k/k'$.

It is seen that equation (54.6) relates the extent of adsorption to the pressure of the gas, at constant temperature; it is consequently known as the **Langmuir adsorption isotherm.** In order to test this isotherm by means of experimental data, equation (54.6) is rearranged so as to give

$$\frac{p}{a} = \frac{1}{k_1} + \frac{k_2}{k_1}p.$$

Hence, if p/a is plotted against the pressure p, a straight line should be obtained; that this is so is shown by the results in Fig. 54.2 for the adsorption of ethylene gas on charcoal. Numerous instances of adsorption have been found to satisfy the Langmuir isotherm; where deviations arise they are often due to the simultaneous occurrence of physical and chemisorption. It should be understood that equation (54.6) can be expected to apply only when there is adsorption of a single uniform layer of molecules. It is, therefore, particularly applicable to chemisorption, since this condition is then usually satisfied.

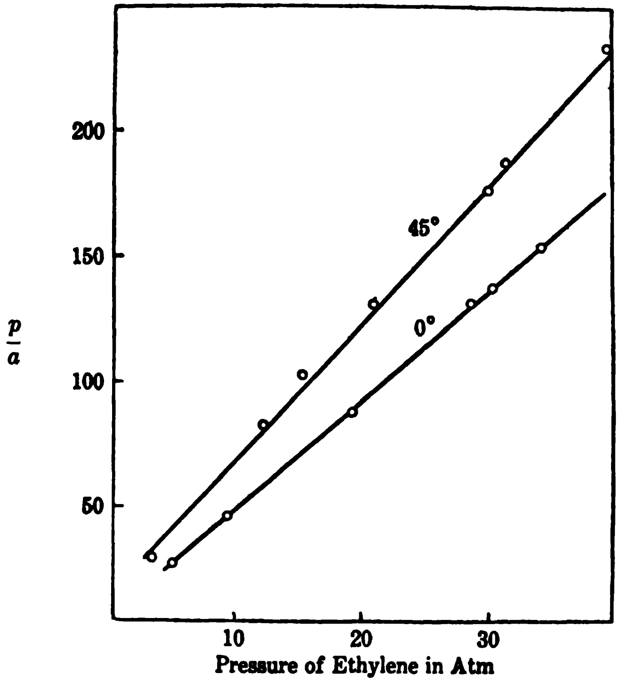

FIG. 54.2. Langmuir adsorption isotherms

Two special cases of the Langmuir isotherm are of interest. If the gas pressure is very low, it is possible to neglect k_2p in comparison with unity in the denominator of equation (54.6); under these conditions this becomes

$$k_1p. \qquad (54.7)$$

The extent of adsorption should then be directly proportional to the pressure; it can be readily seen from Fig. 54.1 that this is the case at very low pressures.

On the other hand, at high pressures, unity may be neglected in comparison with k_2p; equation (54.6) then reduces to

$$a = \frac{k_1}{k_2}. \qquad (54.8)$$

According to this result, the amount of gas adsorbed at any temperature should reach a constant limiting value at high pressures as is apparent from the curves for the higher temperatures in Fig. 54.1. This condition arises when the surface is completely covered by a unimolecular layer of gas molecules. At intermediate pressures an expression of the type

$$a = kp^n,$$

where n lies between zero and unity, may be expected to hold. This result is, of course, identical with the adsorption isotherm of equation (54.1).

54e. Physical Adsorption Isotherms.—Physical adsorption of gases is generally not in agreement with the Langmuir isotherm. Five different types of adsorption isotherms have been distinguished, as shown in Fig. 54.3; the pressure p_0 represents the pressure required to condense the gas to liquid, i.e., the vapor pressure, at the experimental temperature. Type I corresponds to the formation of a unimolecular layer, the volume of gas adsorbed reaching a limiting amount as the gas pressure is increased. The shapes of the curves in Types II and III have been explained by postulating the formation of several physically adsorbed layers of gas molecules. This multilayer type of adsorption is to be expected especially as the gas pressure is increased, since the van der Waals forces of the gas molecules in the first layer will tend to hold a second layer, and so on. In some cases, actual condensation of the gas may occur in the small pores and capillaries of the adsorbent, even at pressures below p_0; adsorption isotherms of Types IV and V are then to be expected. Although no single combination of adsorbent and adsorbate shows all types of behavior,

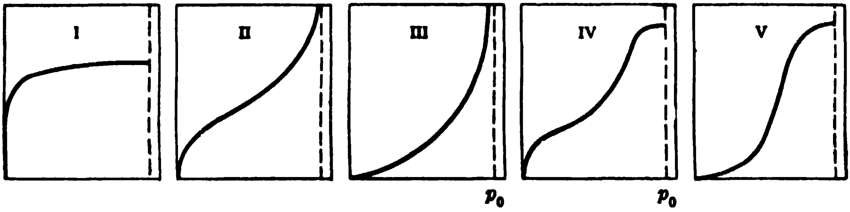

FIG. 54.3. Five types of van der Waals (or physical) adsorption isotherms

Type I. Nitrogen on charcoal at −183°C
Type II. Nitrogen on an iron catalyst at −195°C
Type III. Bromine on silica gel at 79°C
Type IV. Benzene on ferric oxide gel at 50°C
Type V. Water vapor on charcoal at 100°C

there is a tendency for the isotherms to change gradually from Type I to Type V as the temperature is lowered.

By applying the Langmuir treatment to the concept of multilayer physical adsorption of gas molecules, S. H. Brunauer, P. H. Emmett and E. Teller (1938) derived the B-E-T equation

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c}\frac{p}{p_0},$$

where v is the volume of gas adsorbed at the pressure p, and v_m is the volume adsorbed when the surface of the adsorbent is covered with a single layer of molecules; c is a constant, approximately equal to $e^{(E_1 - E_L)/RT}$ where E_1 is the heat evolved in the adsorption of the first layer of gas molecules and E_L is the heat of condensation of the gas to liquid. The B-E-T equation gives an adsorption curve of Type II if $E_1 > E_L$ so that $c > 1$, but if $E_1 < E_L$ so that $c < 1$, the curve is of Type III.

The B-E-T equation requires that a plot of $p/v(p_0 - p)$ against p/p_0 should be a straight line with slope $(c - 1)/v_m c$ and intercept $1/v_m c$. Some examples of such linear plots, for three gases adsorbed on silica gel, are shown in Fig. 54.4. From the slope and the intercept, the value of v_m, i.e., the volume of gas required to form a single molecular layer on the adsorbent, can be obtained. From the known molecular diameter and assuming close packing in the unimolecular layer, the surface area of the adsorbent can be calculated. For example, from the data in Fig. 54.4, the surface area of silica gel is found to be about 450 sq. meters per gram, irrespective of the nature of the adsorbate.

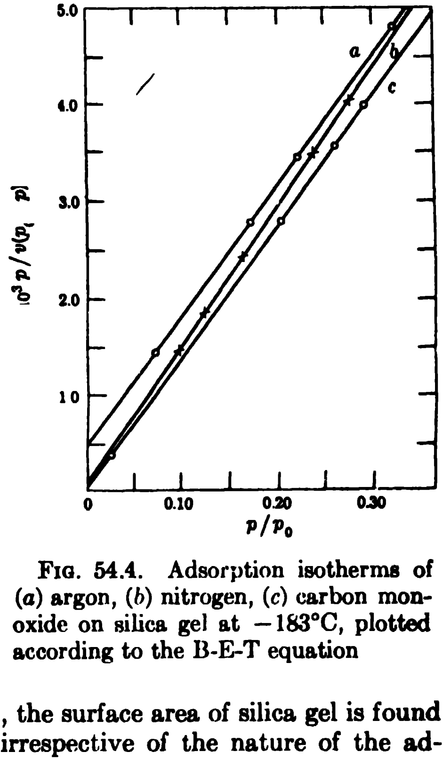

FIG. 54.4. Adsorption isotherms of (*a*) argon, (*b*) nitrogen, (*c*) carbon monoxide on silica gel at −183°C, plotted according to the B-E-T equation

A thermodynamic approach to the problem of physical adsorption, based on the Gibbs equation described in the next section, has been made by W. D. Harkins and G. Jura (1944). The adsorption isotherm derived is of the form

$$\log p = B - \frac{S}{v^2},$$

where v is the quantity of gas adsorbed and B and S are constants; thus the plot of $\log p$ against $1/v^2$ should be a straight line with slope $-S$. The treatment indicates that the surface area of the adsorbent is proportional to $\sqrt{S}$, the proportionality constant depending only on the nature of the adsorbate. Hence, if this constant is determined with a particular gas and an adsorbent of known surface area, the areas of other adsorbents can be calculated if S is known. The values obtained in this manner generally agree well with those given by the B-E-T method.

54f. Adsorption from Solutions: The Gibbs Equation.—It was pointed out by J. Willard Gibbs (1878) that the concentration of a solute at the surface of a liquid could be greater than in the bulk of the solution. The thermodynamic relationship expressing this behavior is usually referred to as the **Gibbs adsorption equation.** For a dilute solution of concentration c this equation is

$$S = -\frac{c}{RT} \cdot \frac{d\gamma}{dc}, \qquad (54.9)$$

where S is the *excess concentration* of solute per sq cm of surface, as compared with that in the bulk of the solution; $d\gamma/dc$ is the rate of increase of the surface tension of the solution with the concentration of the solute; R is the familiar gas constant, and T is the absolute temperature. According to equation (54.9), any solute which causes the surface tension of the solvent to decrease, i.e., $d\gamma/dc$ is negative, will have a higher concentration in the surface than in the bulk of the solution, since S will be positive. In other words, *a substance which decreases the tension at an interface will concentrate at that interface.* If $d\gamma/dc$ is positive, the dissolved substance raising the surface tension, then S will have a negative value; the concentration of the solute will thus be lower in the surface than in the body of the solution. This behavior, known as **negative adsorption,** has been observed with some electrolytes.

When a finely powdered porous substance, such as charcoal or silica gel, is added to a solution, the area of the interface is very large, and the possible extent of adsorption is considerable. In this case the Gibbs adsorption equation applies to the surface of contact between the solid and the solution; hence, $d\gamma/dc$ refers, strictly, to the influence of concentration on the solid-liquid interfacial tension. Very little information is available concerning such interfacial tensions, but as an approximation it is assumed that the influence of concentration is the same as on the corresponding air-liquid surface tension. It may be supposed, therefore, as a rough general rule, that a particular substance will be adsorbed from solution by a solid adsorbent if that substance reduces the surface tension of the solvent.

Water has a high surface tension, and most solutes reduce its value; hence, the great majority of substances are positively adsorbed from aqueous solution by such an adsorbent as charcoal. The surface tension of ethanol (Table 12.1) is much lower than that of water; consequently most solutes will decrease the surface tension of ethanol less than they do that of water. It is to be expected, therefore, that a given solute will generally be more readily adsorbed from aqueous than from alcoholic solution. This anticipation has been confirmed in many cases, although exceptions are known.

There is evidence that in some instances adsorption from solution leads to the formation of a single layer of solute molecules on the surface of the solid, analogous to that in the chemisorption of a gas. In this event, an equation similar to the Langmuir isotherm will be applicable to the effect of concentration on the extent of adsorption from solution; the appropriate isotherm is obtained by replacing the pressure p in equation (54.6) by the concentration. For most purposes, however, the empirical Freundlich isotherm, now taking the form

$$a = kc^n, \tag{54.10}$$

is found to be adequate for adsorption from solution over a considerable range of concentrations. As before, a is the amount of solute adsorbed by unit mass of adsorbent from a solution of concentration c; k and n are constants for the given adsorbent and absorbate. Taking logarithms of equation (54.10)

$$\log a = \log k + n \log c, \tag{54.11}$$

so that log a against log c should give a linear plot. In Fig. 54.5, data for the adsorption of acetic acid from aqueous solution at 25°C are plotted according to equations (54.10) and (54.11); curve I is the plot of a against c, whereas II shows the variation of log a with log c.

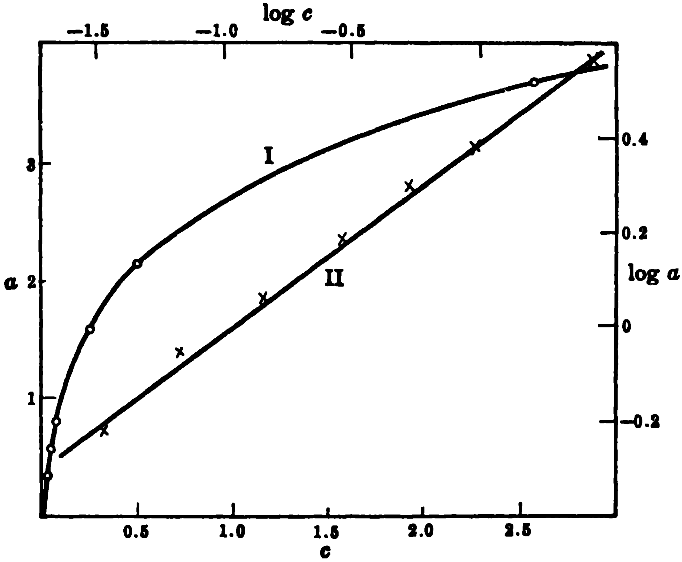

Fig. 54.5. Adsorption of acetic acid by charcoal

54g. Unimolecular Insoluble Films.—An interesting surface phenomenon which is related, at least theoretically, to adsorption is observed in connection with the spreading of films of certain insoluble substances on the surface of water. If a small amount of a hydrocarbon oil is placed on water it does not spread, but forms a lens-like drop; if, however, the molecules of the oil possess a polar group, e.g., —CH_2OH or —COOH, the oil will spread on the surface to form a uniform film. Examples of such spreading oils are the long-chain fatty acids and alcohols; many of these are really solids at ordinary temperatures, but they can be made to spread as thin films on a water surface by pouring a small quantity of a solution in benzene on to the water and allowing the benzene to evaporate. Since these films are insoluble, they remain on the surface of the water and they can be confined between glass barriers; in this way many interesting studies of their properties have been made. It appears that the oil films consist of a single layer of molecules, frequently referred to as a **monolayer**; by gradually diminishing the area covered by the film until it resists further compression, it is possible to determine the area occupied by a single molecule in the closely packed monolayer.

Example: When 5.19×10^{-5} g of palmitic acid ($C_{15}H_{31}COOH$), in the form of a dilute solution in benzene, was spread on the surface of water, it could be compressed to an area of 265 sq cm before the resisting force increased sharply. Calculate the area occupied by a single molecule in the closely packed layer.

The molecular weight of palmitic acid is 256, and hence the 5.19×10^{-5} g contain $5.19 \times 10^{-5}/256$ moles, or $6.02 \times 10^{23} \times 5.19 \times 10^{-5}/256$ individual molecules, since there are 6.02×10^{23}, i.e., the Avogadro number, molecules per mole of any substance. The area occupied by these molecules in the closely packed monolayer is 265 sq cm; hence,

$$\text{Area per single molecule} = \frac{265 \times 256}{6.02 \times 10^{23} \times 5.19 \times 10^{-5}} = 21.7 \times 10^{-16} \text{ sq cm.}$$

It is a very striking fact that the area of surface per single molecule was found to be almost constant, namely, about 21 sq A, i.e., 21×10^{-16} sq cm, for a series of long-chain compounds with polar end-groups, such as fatty acids, alcohols, methyl ketones and amides, independent of their chain length. The simplest interpretation of these results is that *the oil films consist of a single layer in which the molecules are arranged almost vertically;* the polar end-groups are attracted by, and hence are "dissolved" in, the water, while the long, insoluble hydrocarbon chains project from the surface, as indicated diagrammatically in Fig. 54.6. If the film consists of an oriented monolayer, as suggested, it is evident that the area per molecule in the close-packed film should be equal to the cross-sectional area of the hydrocarbon chain. The value will thus be independent of the chain length, and also largely of the nature of the polar end-group, as found experimentally. By the foregoing arguments the area of cross section of a hydrocarbon chain should thus be about 21 sq A; this has been confirmed

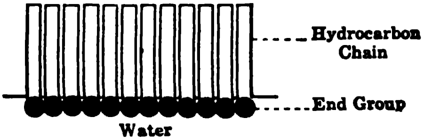

FIG. 54.6. Monolayer on the surface of water

by X-ray diffraction studies of crystals of long-chain compounds. Many results of interest have been obtained in the study of monolayers, but it is not possible to discuss them here.

54h. Chromatographic Adsorption.—An application of adsorption which has found wide use for separation, purification and analysis of substances of various kinds, is that generally referred to as **chromatography.***[*] Chromatographic analysis is based on the fact that a given adsorbent will adsorb to varying extents the constituents of a mixture present in solution. If such a solution is poured down a column filled with a powdered adsorbent, the material retained in the upper layers will consist mainly of the solute that is most readily adsorbed, together with lesser amounts of the others. The latter will be gradually adsorbed as they pass farther down the column, so that a partial separation of the constituents of the mixtures has been achieved.

The separation can be improved in various ways. One is to allow some of the pure solvent to flow slowly through the column. The less easily adsorbed solutes present in the upper parts pass into solution and are readsorbed at lower levels. The result is the formation of a series of almost distinct layers containing individual solutes, in order of decreasing ease of adsorption down the column. If sufficient solvent is used, the solutes may be extracted, i.e., eluted, or separated, the least easily adsorbed coming off first. Another method of separation is to pour a solution of a very highly adsorbable substance through the column. The solute displaces those already adsorbed, and they move downward and form separate zones just as when the solvent is used.

Although the adsorbent is frequently a fine powder, e.g., alumina, magnesium oxide, charcoal, or even sucrose, contained in a vertical tube, paper chromatography utilizes filter paper as the medium. The processes involved, however, are not strictly adsorption and desorption. A solution of the mixture to be separated is spread along a narrow band parallel with and close to one edge of a sheet of filter paper. The paper is then dried and a second solvent is used to separate the constituents of the mixture by spreading them in a direction at right angles to the original band. A form of chromatography has also been applied to the analysis of mixtures of gases.

54i. Ion Exchange Separations.—It has long been known that soils and certain minerals, e.g., zeolites, have the ability to exchange some of the cations they contain for others in solution. The same property of cation exchange is possessed by synthetic resins, consisting of organic polymers containing acidic groups, such as —COOH, —SO_3H or —OH. If the polymer contains basic groups, e.g., —NR_2 or =NR, then the solid resin is capable of exchanging anions with those in solution. As prepared, a cation exchange resin may be regarded as possessing a number of exchangeable hydrogen ions which are attached to the resin by some kind of adsorption. When placed in a solution of salt, some of the hydrogen ions of the resin enter the solution and an electrically equivalent quantity of the cations of the salt become adsorbed on the

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[*] The name chromatography, which implies color, was given to the technique because some of its earliest uses were in connection with the separation of materials having different colors.

resin. The **ion exchange** process is chemically reversible; in the case of exchange with sodium ions the reaction is

$$\mathrm{H}_n\mathrm{R}\ (\text{resin}) + n\ \mathrm{Na}^+\ (\text{soln}) \rightleftharpoons \mathrm{Na}_n\mathrm{R}\ (\text{resin}) + n\ \mathrm{H}^+\ (\text{soln}),$$

so that an equilibrium is attained. The sodium-containing resin can exchange with other ions, e.g., with calcium ions, thus

$$2\mathrm{Na}_n\mathrm{R} + n\ \mathrm{Ca}^{+2} \rightleftharpoons \mathrm{Ca}_n\mathrm{R}_2 + 2n\ \mathrm{Na}^+,$$

the number of calcium ions adsorbed on the resin being half that of sodium ions displaced, in order to maintain electrical neutrality.

The ability of a resin to adsorb different cations is determined by their charge and by the size of the hydrated ions in solution. Under equivalent conditions, adsorption increases with the charge on the ion and decreases with increasing size. It appears that the adsorption is electrostatic in character, but the size of the spaces between the atoms in the solid resin exerts an effect in determining the ease of adsorption.

Since 1943, extensive use has been made of ion exchange procedures. One is for the separation of elements, such as those of the rare earth series, which are difficult to separate in other ways. The general procedure is very similar to that employed in chromatography, the essential difference being that for ion exchange the adsorption and desorption processes can be described in terms of a chemical equilibrium. The solution containing a mixture of salts is first poured through a column filled with particles of the ion exchange resin. The cations in solution then exchange with the hydrogen (or other) ions on the resin; the most strongly adsorbed ions are near the top and the other farther down the column. An eluting solution containing a strongly adsorbable cation, e.g., hydrogen ion in hydrochloric acid, is allowed to percolate through the column, gradually displacing the other cations. The eluate, i.e., the liquid emerging from the bottom of the column, contains first one, and then another of the adsorbed ions, in order of increasing strength of adsorption. For the separation of ions which are very similar, e.g., those of the rare earth elements, elution with acid is not very efficient. Much better results are obtained with a citrate solution, the results being dependent on the varying stability of the complex anions formed between the various cations and the citrate ions. The ions forming the most stable complexes are the easiest to desorb from the resin.

THE COLLOIDAL STATE

55a. General Properties of Colloidal Systems.—In a true solution, such as one of sugar or a salt in water, the particles of solute distributed in the solvent consist essentially of single molecules or ions. On the other hand, a suspension contains particles that are large enough to be seen by the naked eye or, at least, in the microscope. Between these two extremes are to be found the **colloidal dispersions**; the important characteristic of the colloidal state is *the presence of particles which are larger than molecules but not large enough to be seen in the microscope.* It is obviously impossible to draw a distinct line between true (molecular) solutions and colloidal dispersions, at one extreme, and between colloidal dispersions and suspensions, at the other extreme. There is a gradual transition from one type of system to the other; nevertheless, colloidal systems have certain properties which, as a general rule, place them in a more or less separate category.

The upper limit of size of particles in the colloidal state may be taken as approximately the lower limit of microscopic visibility, i.e., 2×10^{-5} cm or 0.2μ,* whereas the lower limit is roughly 5×10^{-7} cm or 5 $m\mu$. The latter figure is about the same as the diameters of certain complex molecules of high molecular weight, e.g., proteins, starch, rubber and other polymers. Solutions of these substances exhibit colloidal behavior although the particles are single molecules.

The essential properties of colloidal dispersions can be ascribed to the fact that the ratio of surface area to volume of the particles is very large. In a true solution the system consists of one phase only, and there is no true surface of separation between the molecular particles of solute and solvent. Colloidal dispersions, however, are two-phase systems, and for each particle there is a definite surface of separation between it and the liquid medium. At this interface characteristic properties, such as adsorption and electrical potential, are evident. When the total surface area is relatively small, as with suspensions, where the particles are relatively large, the effect of these properties is not marked, but in colloidal systems the surface area, for a given quantity of material, is so large that they play an important part. For example, the total surface area of 1 cc of solid in the form of a cube of 1 cm edge is 6 sq cm; when divided into cubes of 10^{-6} cm edge, which approximates to the dimensions of the particles in many colloidal systems, the total area of the same volume of material is increased a million fold, i.e., to 6×10^{6} sq cm. It is to be expected, therefore, that surface phenomena will influence the behavior of colloidal dispersions.

The two phases involved in a colloidal or dispersed system may be distinguished by the terms **disperse phase,** for *the phase forming the particles,* and **dispersion medium** for *the medium in which the particles are dispersed.* So far it has been assumed that the dispersion medium is a liquid; such colloidal systems are called **sols.** In other cases the medium may be solid or even gaseous; similarly, the disperse phase may be solid, liquid or gaseous, thus leading to a number of possible types of colloidal systems. **Smokes** and **dusts,** for example, consist of solid particles dispersed in a gaseous medium, whereas in **fog, mist** and **cloud** the disperse phase is liquid and the dispersion medium is a gas. Many minerals contain gas, liquid or solid dispersed in a solid medium, and ruby glass consists of fine particles of gold dispersed in glass. A **foam** is a two-phase system of gas dispersed in a liquid. If, in a liquid medium, the disperse phase is solid and the particles are relatively

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* The symbol μ is used to represent a *micron,* which is 10^{-6} meter or 10^{-4} cm; a millimicron, represented by $m\mu$, is equal to 10^{-3} μ or 10^{-7} cm.

large, a **suspension** is obtained, but if the disperse phase is a liquid the result is an **emulsion.** In these systems the particles of disperse phase are somewhat larger than in true colloidal solutions, but they possess certain properties analogous to those of the latter. Although many of the systems referred to in this paragraph are of considerable interest, they will not all be discussed; most attention will be paid to those in which the dispersion medium is a liquid, e.g., sols and emulsions.

Sols may be divided roughly into two categories, referred to as **lyophobic** (Greek: *liquid hating*) and **lyophilic** (*liquid loving*) sols. If water is the dispersion medium, as it is in most of the systems to be considered in this chapter, the terms **hydrophobic** and **hydrophilic,** respectively, are sometimes employed. As the names imply, lyophobic sols are relatively unstable compared with lyophilic sols; in the former type, small quantities of electrolytes are able to cause the coagulation and precipitation of the dispersed particles, but the latter are not affected unless large amounts of electrolyte are added. Upon evaporation or cooling of lyophobic systems, solids are obtained which cannot be reconverted into sols by reversing the physical change, i.e., by adding solvent or by warming, respectively. Lyophilic sols, however, are generally reversible in this respect, and consequently they behave like true solutions to some extent. This is in agreement with the view that in many lyophilic sols, e.g., of proteins, the dispersed particles are actually large single molecules. Typical examples of lyophobic sols are those of metals, sulfur, sulfides and silver halides; on the other hand, sols of gums, starches and proteins provide instances of lyophilic systems. As in most cases of colloidal behavior, it is not possible to draw a sharp line of demarcation between lyophobic and lyophilic sols; colloidal dispersions of a number of metallic oxides, for instance, possess intermediate properties.

55b. Preparation of Colloidal Dispersions.—Many solid substances form colloidal dispersions when they are brought into contact or warmed with a suitable dispersion medium, e.g., gelatin and starch in water, and rubber in benzene; substances of this type form what are called **intrinsic colloids.** They are either compounds having large molecules, called **macromolecules,** of colloidal dimensions, such as those mentioned above, or the molecules consist of long chains, with a polar end group, which tend to aggregate and form "micelles" of colloidal size, e.g., soaps. Intrinsic colloids usually have lyophilic character. On the other hand, the **extrinsic colloids** are dispersions of small particles of insoluble materials of low molecular weight. Such colloidal dispersions are almost invariably lyophobic sols and they have to be prepared by special methods which yield particles of the appropriate size; various procedures have been used, and these may be considered under the headings of "condensation methods" and "dispersion methods."

I. Condensation Methods.—The essential principle of these methods is that the materials from which the sol is prepared are originally present in true solution, as ions or molecules; as a result of a chemical reaction between them, insoluble particles of colloidal size are obtained. The experimental conditions, particularly as regards the concentrations of electrolytes, must be closely controlled in order to prevent the growth and consequent precipitation of the small particles. Chemical reactions of various types have been used for the preparation of colloidal solutions by the condensation method. Metal sols have been obtained by the *reduction* of solutions of their soluble salts or oxides; the reducing agents employed for this purpose are nonelectrolytes, e.g., hydrogen, carbon monoxide, formaldehyde, hydrazine and hydroxylamine. Sols of gold, silver, platinum, iridium and palladium have been prepared in this manner. The presence of a small amount of gum arabic acts as a stabilizing agent (§ 55f). *Oxidation* has also been used to prepare colloidal dispersions; for example, an aqueous solution of hydrogen sulfide can be oxidized by oxygen or by sulfur dioxide to yield a sulfur sol. Selenium sols have been obtained in a similar manner from hydrogen selenide solution.

Sols of the hydrous oxides* of weakly electropositive metals, such as iron, aluminum, chromium, tin, thorium, zirconium, etc., have been obtained by *hydrolysis* of their salts in aqueous solution. The bases corresponding to these metals are all weak, and hence the salts are considerably hydrolyzed in solution. By suitable adjustment of the conditions, the hydrous oxides are not precipitated but remain in a state of colloidal dispersion. The hydrolytic reaction is a type of double decomposition (or metathesis), and other double decomposition reactions have been employed for the production of colloidal dispersions. The passage of hydrogen sulfide through solutions of mercuric cyanide or arsenious oxide leads to the formation of colloidal mercuric or arsenious sulfide, respectively. In each case the other product is a very weak electrolyte; a strong electrolyte would have caused the sulfide particles to coagulate. Silver halide sols can be obtained by mixing dilute solutions of an alkali halide and a silver salt, one or other being present in very slight excess. One of the best known inorganic sols, that of silicic acid, is generally prepared by a double decomposition reaction between dilute solutions of sodium silicate and hydrochloric acid.

II. Dispersion Methods.—In these methods the starting material consists of the substance in the massive form; by means of suitable devices it is then disintegrated into particles of colloidal dimensions which remain for some time in the dispersed state. In this connection the principle of **peptization** is frequently used; this term refers to the direct disintegration (or dispersion) of a substance into particles of colloidal size by an added agent, the latter being known as a **peptizing agent.** In the preparation of lyophilic sols, such as those of gelatin or starch, the dispersion medium, i.e., water, is itself the peptizing agent. Incompletely nitrated cellulose is peptized by various organic solvents, e.g., mixtures of ethanol and ether; in this case the product is the familiar "collodion" sol. In other cases, however, a peptizing agent must be present in addition; freshly precipitated substances, such as the hydrous oxides of metals, can frequently be peptized to the colloidal state by dilute solutions of alkali hydroxides. In general, the presence of a common

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* These are often, but erroneously, called "hydroxides"; however, X-ray diffraction has shown that they consist of small particles of the oxides and molecules of water.

ion encourages peptization, provided the total concentration of electrolyte is not too great; thus, alkali hydroxides peptize oxides, hydrogen sulfide peptizes sulfides, and the chloride ion can peptize freshly precipitated silver chloride.

Many substances can be reduced to colloidal size in a *colloid mill*, consisting of a series of closely spaced discs, each rotating at a very high speed in a direction opposite to that of its immediate neighbors. The dispersion medium, together with the substance to be dispersed, and a stabilizing agent are passed through the mill; after a time a dispersion results.

A process which involves both dispersion and condensation makes use of *electrical disintegration;* a direct current electric arc is struck between wires of platinum, gold or silver immersed in water, and a sol of the metal is obtained. The high temperature of the arc causes the metal to vaporize, and the vapor is then condensed by the water to form colloidal particles. Traces of electrolytes are usually necessary for stability. The electrical method of preparing sols has been modified so that it can be used for nonmetals as well as for metals. The electrodes are of iron or aluminum, which do not disintegrate, and the material to be dispersed is suspended, in the form of granules or foil, in the liquid through which the arc is passed. Sols in organic dispersion media have been prepared in this manner.

55c. Purification of Colloidal Dispersions.—Two main procedures have been applied to the removal from sols of substances in true solution; both methods depend on the relatively large size of the colloidal dispersed particles. The process known as **dialysis** (T. Graham, 1861) utilizes the fact that the great majority of *substances in true solution can pass through a membrane while colloidal particles are retained.* It should be noted that the dialyzing membrane does not act merely as a sieve, retaining the larger particles; this sieve action is, no doubt, partly responsible for dialysis, but the difference in the relative rates of diffusion of the particles is probably the most important factor. Colloidal particles diffuse very slowly, chiefly because of their relatively large dimensions, while the small molecules and ions in true solution diffuse much more rapidly.

Various forms of dialyzers and a variety of dialyzing materials have been used for the purification of colloidal dispersions. In addition to parchment, membranes of Cellophane, cellulose nitrate and cellulose acetate have been found satisfactory; these may be in the form of an elongated tube, or of a bag or thimble. The colloidal dispersion is placed inside the tube or bag, and this is suspended in a vessel containing water; the latter is changed either periodically or continuously, as the dissolved molecules pass out from the interior of the dialyzer into the surrounding water.

In **electrodialysis** the removal of electrolytes is facilitated by means of an electric field. The colloidal dispersion containing the unwanted electrolyte is placed between two dialyzing membranes, with pure water in a compartment on each side. By means of electrodes placed in these compartments an E.M.F. is applied which causes the ions to migrate out of the colloidal dispersion into the water; the latter is replaced continuously or as required.

The second important method for purifying sols is known as **ultrafiltration**

(H. Bechhold, 1907). The pores of even the best filter papers permit the passage of colloidal particles, but membranes with pores sufficiently small to hold back such particles can be made from collodion or a regenerated cellulose, such as Cellophane or Visking. Membranes can be prepared with pores of different sizes; with their aid a colloidal dispersion may not only be purified from dissolved material, but it may be separated into fractions containing particles of different size. Since ultrafiltration membranes are fragile, they are often supported on wire screens, especially if liquid is being forced through them under pressure. Collodion membranes may be deposited in filter paper or in porous porcelain for increased strength.

55d. Optical Properties of Sols.—Colloidal particles are too small to be seen in the microscope; nevertheless, their presence can be made evident by optical means. If a strong beam of light is passed through a medium which is "optically clear," that is, it contains no particles larger than about 10^{-7} cm, the path of the light cannot be easily detected. If particles of larger, e.g., colloidal, size are present, however, they will scatter the light, and as a result the beam is rendered visible. Most true solutions are optically clear, but colloidal dispersions scatter light, producing what is known as the **Tyndall effect.** The path of the light through the sol, which is rendered visible as a result of the scattering, is called the **Tyndall beam.**

In the instrument known as the **ultramicroscope,** invented by H. Siedentopf and R. Zsigmondy (1903), the scattered light in the Tyndall beam is observed in a microscope. In this way the presence of individual particles in a colloidal dispersion becomes apparent as flashes of scattered light. Although the particles themselves are actually too small to be visible in the microscope, the light scattered by them can be seen in the ultramicroscope; particles as small as 5 to 10 mμ diameter can be detected in this manner.

In the slit ultramicroscope a narrow, powerful beam of parallel or slightly convergent light, from an arc lamp, is passed horizontally through a cell on the stage of a microscope. If the solution in the cell is optically clear, the microscopic field will appear completely dark. On the other hand, if it contains a colloidal dispersion, the particles scatter the light, some of which passes vertically into the microscope; each particle thus appears as a small disc of light on a black background. Other forms of ultramicroscope have been designed, but the one just described is the most satisfactory.

The size of the luminous reflections seen in the ultramicroscope bears no relation to the actual size of the particles, it is possible, nevertheless, to utilize the ultramicroscope to determine the dimensions of colloidal particles. If the total weight of material dispersed in a given volume of sol is known, and the density of the particles is assumed to be the same as in the macroscopic (massive) state, the total volume of the dispersed phase can be calculated. To determine the volume or size of each particle it is required to find the number of particles in a given quantity of the sol. The counting is carried out by diluting the sol to a definite extent, if necessary, and noting the number of particles visible in the ultramicroscope; the observations are repeated many times and the average taken. From a knowledge of the volume of sol in the field of the ultramicroscope, the number of particles in a given volume can be calculated. All the information is thus available for determining the dimensions of the particles, which are generally assumed to be spherical.

When observed in the ultramicroscope colloidal particles are seen to be undergoing continuous and rapid motion in all directions; in other words, the particles exhibit Brownian movement (§ 3k). The vertical distribution of colloidal particles under the influence of gravity, when equilibrium is attained, should be given by an expression identical with equation (3.31). By determining the numbers of particles at different levels in a gold sol, by means of the ultramicroscope, a value of the Avogadro number has been obtained which is in excellent agreement with that derived in other ways.

55e. Hydrophobic Sols: Electrical Properties.—In considering the electrical properties of aqueous sols, it is convenient to treat lyophobic (hydrophobic) sols separately from those possessing lyophilic character. When a hydrophobic sol is placed in an electric field the particles move definitely in one direction or another; this means that *colloidal particles are electrically charged with respect to the dispersion medium.* The phenomenon of *the migration of colloidal particles under the influence of an electrical potential* is called **electrophoresis.** The movement of particles in an electric field can be observed in the ultramicroscope, but a more convenient method is to use a U-tube containing the sol covered by the pure dispersion medium, e.g., water, into which dip platinum electrodes connected to a source of E.M.F. If the boundary between the sol and the pure water is sharp and visible, its rate of motion, which is equal to the speed of electrophoresis of the dispersed particles, can be determined. The potential gradient in volts per cm can be derived from the applied E.M.F. and the dimensions of the apparatus; hence, the velocity of the particles under a fall of potential of 1 volt per cm, i.e., the **electrophoretic mobility,** may be calculated. The sign of the charge carried by the particles can, of course, be determined by observing the direction in which the boundary moves.

Sols of basic dyestuffs and of hydrous oxides of metals usually contain positively charged particles, whereas in sols of metals, sulfur, metallic sulfides, acidic hydroxides and acidic dyestuffs the particles carry negative charges. In some cases the sign of the electrical charge depends on the method of preparing the colloidal solution, but one particular type is usually more stable than the other. In spite of the varying nature of the dispersed particles, the electrophoretic mobilities for aqueous sols almost always lie within the range of 2 to 4×10^{-4} cm per sec. It is of interest to note that the mobilities of ordinary ions, with the exception of hydrogen and hydroxyl ions, are about 4 to 8×10^{-4} cm per sec, under the same potential gradient of 1 volt per cm. Since colloidal particles migrate with a velocity comparable to that of electrolytic ions, sols might be expected to possess appreciable electrical conductance; however, this is not the case, because the number of particles in a colloidal solution is very small in comparison with an electrolytic solution of the same weight concentration.

The electrical charge carried by colloidal particles is of fundamental importance, because without it lyophobic sols would be extremely unstable. The question of the origin of the charge is therefore of some interest. It has been frequently observed that small quantities of electrolytes are associated with colloidal systems; if they are removed by persistent dialysis, or in other ways, the sol becomes unstable, and the dispersed particles grow in size and are eventually precipitated. It appears, therefore, that traces of ions present in the sol are responsible for both the charge and stability of the colloidal system. Further, if a dilute solution of a silver salt is added to a slight excess of dilute sodium iodide solution, a negatively charged sol of silver iodide is obtained; however, if the dilute iodide solution is added to excess of the silver nitrate, a positively charged sol results. If the two solutions are mixed in exactly equivalent amounts, the silver iodide sol is unstable, and complete precipitation occurs.

In the light of these experimental facts, the stability and charge of the negative silver iodide sol formed in the presence of an excess of iodide (negative) ions may be attributed to the adsorption of these ions by the particles of silver iodide; the positive sols are similarly stabilized by the adsorption of silver (positive) ions, since the latter are in excess in the solution. As a general rule, ionic solids, such as silver halides, oxides and sulfides, preferentially adsorb ions which are common to them; thus a colloidal silver halide will tend to adsorb either silver or halide ions, and a metallic oxide will adsorb ions of the metal or hydroxyl ions in preference to others. Such behavior is not unreasonable, for it indicates a natural tendency for the ionic crystal to extend its own space lattice, which already consists of ions (§ 18b).

The two oppositely charged silver iodide sols are represented in Fig. 55.1.

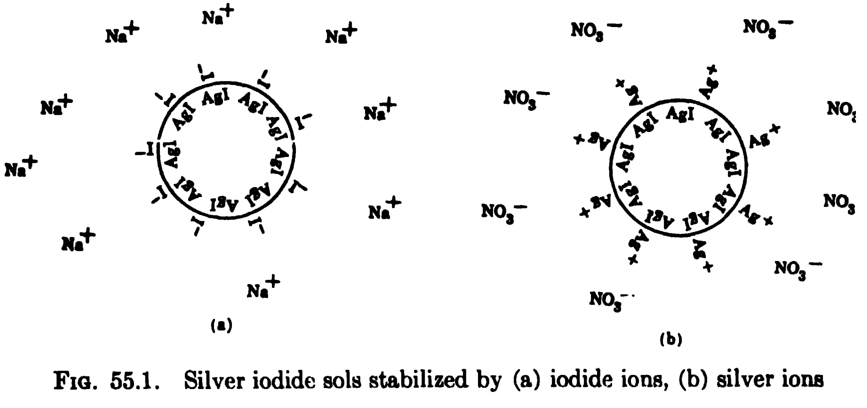

FIG. 55.1. Silver iodide sols stabilized by (a) iodide ions, (b) silver ions

At the left, the silver iodide particle has adsorbed iodide ions, giving a negative charge, whereas at the right, silver ions are adsorbed and the particle has a positive charge. In both cases the ions of the opposite sign, viz., Na^+ and NO_3^-, respectively, will remain in solution; these will be mainly in proximity to the colloidal particle because of the electrostatic attraction.

Hydrous ferric oxide sols have been prepared both positively and negatively charged; the particles of the former, obtained in the presence of excess of ferric ions, are stabilized by these ions, viz., $[Fe_2O_3 \cdot xH_2O]Fe^{+3}$, whereas in the latter, which is formed when hydroxyl ions are in excess, the particles may be represented by $[Fe_2O_3 \cdot xH_2O]OH^-$. In each case, oppositely charged ions, e.g., Cl^- and Na^+, respectively, remain on the solution side of the particle. Similarly, the stability of negatively charged sulfide sols in the presence of hydrogen sulfide is due to the adsorption of sulfide ions, e.g., $[As_2S_3]S^{-2}$. In general, therefore, it appears that *the electrical charge of lyophobic colloidal particles in an aqueous sol is the result of the preferential adsorption of a particular ion.* The stability of the sol is then due to the electrostatic repulsion of the similarly charged particles. In view of this conclusion it can be understood why the complete removal of all electrolytes often leads to instability of a colloidal system.

55f. Precipitation by Electrolytes.—Although traces of electrolyte are apparently essential to the stability of lyophobic sols, at least in water, somewhat larger amounts cause the particles to aggregate and form a visible precipitate; the phenomenon is known as **precipitation** or **coagulation.** Many experiments have been made on the precipitating effects of various electrolytes on different sols; the results depend on the conditions, to some extent, but two definite conclusions have been drawn. First, *the ion which is effective in causing precipitation of a sol is the one whose charge is of opposite sign to that of the colloidal particles;* and second, *the precipitating effect increases markedly with increasing valence of the ion.* These statements concerning the influence of sign and valence on the precipitation of a colloidal solution are included under the title of the **Hardy-Schulze rule** (H. Schulze, 1882; W. B. Hardy, 1900).

The data in Table 55.1 show the minimum concentrations, in millimoles per liter, of various electrolytes required to cause precipitation of a positively charged ferric oxide sol and of a negatively charged arsenious sulfide sol. In each case it is evident that the result of increasing the valence of the ion of opposite sign to that of the charged particles is to bring about a very marked decrease in the quantity of electrolyte required to cause precipitation; the precipitating effect thus increases with increasing valence of the ion. A

TABLE 55.1. MINIMUM ELECTROLYTE CONCENTRATIONS FOR PRECIPITATION

Ferric Oxide Sol (Positive)			Arsenious Sulfide Sol (Negative)		
Electrolyte	Anion Valence	Min. Conc.	Electrolyte	Cation Valence	Min. Conc.
KCl	1	103	NaCl	1	51
KBr	1	138	KNO_3	1	50
KNO_3	1	131	$\frac{1}{2}K_2SO_4$	1	63
K_2CrO_4	2	0.325	$MgSO_4$	2	0.81
K_2SO_4	2	0.219	$BaCl_2$	2	0.69
$K_3Fe(CN)_6$	3	0.096	$AlCl_3$	3	0.093

change in the valence of the ion of the same sign as the colloidal particle has only a relatively small influence, as is evident from the results for the precipitation of the arsenious sulfide sol.

The addition of a lyophilic substance to a lyophobic sol frequently renders the latter less sensitive to the precipitating effect of electrolytes; this is an illustration of the phenomenon of **protective action,** the lyophilic substance being a **protective colloid.** It appears that the protective (lyophilic) colloid, such as gelatin, albumin, gums, etc., confers upon the lyophobic sol its own stability to electrolytes. Gelatin is a very good protective colloid; egg albumin and gum arabic are less effective, while potato starch has relatively little protective action. The best protective action is thus shown by those lyophilic substances which normally carry electrical charges. It is probable that they are adsorbed on the surface of the colloidal particle by electrostatic forces or sometimes by chemical interaction, thus converting the lyophobic sol into one with more lyophilic character.

55g. Electrokinetic Phenomena.—The electrical properties of colloids, and other related phenomena, can be most clearly understood by a more detailed consideration of the electrical condition of a surface. It was suggested by H. von Helmholtz (1879) that an **electrical double layer,** of positive and negative charges, is generally formed at the surface of separation between two phases. According to modern views, at a solid-liquid interface, this double layer is made up of a layer of ions, in aqueous solution, which are firmly held to the solid, and a more diffuse mobile layer, extending into the solution. The resultant (net) charge of the diffuse layer is equal in magnitude but of opposite sign to that of the firmly held, or fixed, layer. A simplified schematic representation of the structure of the double layer is shown in Fig. 55.2; in one case it is supposed that the fixed part of the double layer is positively charged, while in the other case it is negatively charged. Because of the electrical charges, there is a difference of potential between the dotted line, representing the separation of fixed and diffuse double layers, and the bulk of the solution. This has been called the **electrokinetic potential;** it is often referred to by the noncommittal name of **zeta potential,** because it is represented by the Greek letter *zeta*, ζ.

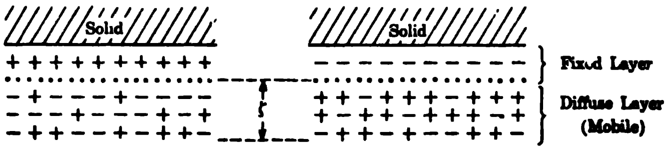

FIG. 55.2. Representation of electrical double layer

The electrical double layer described above presumably exists at all solid-liquid interfaces, and it is undoubtedly formed at the surface of a colloidal particle. The fixed part of the layer then corresponds to the ions adsorbed by the particle and to which it owes its charge; the diffuse portion is represented by the oppositely charged ions in the solution, as described in § 55e. It is probably the presence of electrical double layers surrounding all the particles that accounts for the stability of a colloidal system; the mutual repulsion of these layers prevents the particles from approaching sufficiently closely for them to coalesce. When an ion of opposite charge to that of the colloidal particle is adsorbed, the double layer (electrokinetic) potential is decreased. As a result, the mutual repulsion of the particles is diminished and coalescence, with consequent precipitation, becomes possible. A multicharged ion would be expected to decrease the potential at the double layer more than a singly charged ion; hence, its precipitating effect will be greater in equal concentration.

When an E.M.F. is applied to an electrical double layer there will be a displacement of the oppositely charged layers relative to one another; the actual movement will presumably take place somewhere in the region of the dotted line in Fig. 55.2, since this represents the separation between the two charged layers. In the case of a sol, the colloidal particle and its attached layer move in an electrical field, thus producing the phenomenon of electrophoresis, described above. It is to be expected that there should be a connection between the velocity of electrophoresis and the zeta potential acting at the surface of the colloidal particle. By treating the double layer as a simple electrical capacitor, the relationship

$$\zeta = \frac{4\pi\eta u}{D}$$

has been derived; ζ is the electrokinetic (zeta) potential, u is the electrophoretic mobility of the particle, i.e., under a potential of 1 volt per cm, and η and D are the viscosity and dielectric constant, respectively, of the dispersion medium. Utilizing the electrophoretic mobilities already determined, viz., 2 to 4×10^{-4} cm per sec for most colloidal particles, the corresponding electrokinetic potentials are found to be from 0.03 to 0.06 volt when water is the dispersion medium. Experiments have shown that when this potential falls below about 0.02 volt, as a result of the addition of electrolytes, the repulsion between colloidal particles is reduced to such an extent that coagulation can occur.

If the solid cannot move, the fixed part of the double layer also is unable to move; the application of an E.M.F. will, however, result in movement of the diffuse (mobile) layer ions and liquid. This is the basis of the phenomenon of **electroosmosis**, i.e., *the passage of liquid through a porous diaphragm under the influence of an applied electric field.* If two portions of a liquid, e.g., water, are separated by a porous diaphragm, and an E.M.F. is applied between electrodes placed on each side of the diaphragm, there will be a flow of liquid from one side to the other. A porous diaphragm is actually a mass of small capillaries, and the same type of electroosmotic flow has been observed through glass capillary tubes. In each case, the charged layer attached to the solid cannot move, and so the diffuse layer in the liquid phase, together with the liquid, moves when an electric field is applied. The direction of the electroosmotic flow depends on the charge of the diffuse part of the double layer; in moderately pure water most solids acquire a negative charge, so that the diffuse layer has a resultant positive charge. The flow of water is thus generally toward the cathode. The presence of electrolytes, however, can influence the rate and even the direction of flow. As in the case of precipitation by electrolytes, the most effective ions are those of sign opposite to that carried by the solid, and their influence increases markedly with increasing valence.

It is possible to calculate the value of the zeta potential from a study of electroosmosis, but a more convenient method is to make use of another electrokinetic phenomenon, namely, the **streaming potential**; this is *the production of a potential difference when a liquid is forced through a porous membrane or capillary tube.* The separation of the oppositely charged layers of the electrical double layer, due to the forcible passage of liquid, results in a difference of potential between the two sides of the membrane or the ends of the capillary tube. The streaming potential effect may thus be regarded as the reverse of electroosmosis, for in the latter the application of a potential difference, i.e., an E.M.F., causes a flow of liquid, while in the former the flow of liquid produces a potential difference. The streaming potential can be readily measured by placing identical reversible, e.g., calomel, electrodes (§ 48c) at each end of a capillary tube, and determining the difference of potential that results when water or an aqueous solution is forced through the tube.

By considering the electrical double layer as a simple capacitor, as before, it has been found that the streaming potential S is related to the electrokinetic (zeta) potential ζ by

$$\zeta = \frac{4\pi\eta\kappa S}{PD},$$

where P is the pressure applied to the streaming liquid, whose specific conductance is κ (§ 45a); η and D are the viscosity and dielectric constant, respectively, of the liquid. The values of the electrokinetic potential obtained by means of this equation, from measurements of the streaming potential, are of the order of 0.02 to 0.05 volt, which is similar to that found for colloidal particles. If electrolytes are added to the water the streaming potentials, and hence the zeta potentials, are changed. In agreement with the conclusions already drawn, ions of high valence, with a charge of opposite sign to that carried by the solid material of the tube through which the liquid streams, have a very marked effect in reducing, and eventually reversing the sign of, the electrokinetic potential.

In the foregoing discussion the interface has been treated as one between a solid and a liquid; however, it is probable that a similar electrical double layer exists at a liquid-liquid interface. It would be difficult to observe electroosmosis and the streaming potential under these conditions, since it would not be easy to prepare a fairly rigid porous diaphragm made of liquid. However, electrophoresis can be readily observed when very small droplets of one liquid are suspended in another; the application of an E.M.F. results in the movement of the droplets in one direction or another. A particular case of this type occurs with a mercury sol; the particles are undoubtedly very minute drops of liquid mercury dispersed in water. It will be seen shortly (§ 55m) that emulsions also fall into the category of liquid-liquid systems, and these exhibit the electrophoretic effect.

55h. Properties of Lyophilic Sols: Viscosity and Electrophoresis.—The chief lyophilic substances, e.g., starch, proteins, etc., are naturally occurring, and their colloidal properties are of biological importance. One of the most striking differences between lyophobic and lyophilic sols is the high viscosity of the latter; this is attributed to the extensive solvation (hydration) of the lyophilic particles. The relatively large size of the particles and the decrease in the number of free water molecules result in an increase of viscosity. It is perhaps significant in connection with the idea that lyophilic particles are solvated that solid gelatin and agar, which form lyophilic sols readily in water, are able to take up large quantities of water to form jelly-like masses (§ 55j); rubber takes up benzene in a similar manner.

Particles of lyophilic sols exhibit electrophoretic migration in an electric field; with proteins and related substances, the direction of movement is very sensitive to changes in the hydrogen ion concentration of the medium. Proteins are complex amino acids, and hence are amphiprotic in nature (§ 52g). The charge carried by a protein particle will thus depend on the pH of the sol; in an acid medium it will be positively charged and migrate to the cathode, and in an alkaline solution the charge will be negative and the particles will migrate to the anode. At some intermediate pH, i.e., at the isoelectric point of the particular protein (see § 52g), *the sol will exhibit no electrophoretic movement*. The isoelectric point varies with the nature of the substance; thus, it is at a pH of 2.6 for lecithin, 4.7 for gelatin, 7.0 for hemoglobin and 4.9 for horse serum albumin. The effect of pH on the electrophoretic mobility of protein particles is brought out clearly by the results in Fig. 55.3, which have been obtained by different methods with horse serum albumin at various pH's; the isoelectric point is seen to occur at pH 4.9.

The fact that different proteins have different electrophoretic mobilities at a given pH has been utilized by A. Tiselius (1937) to design a special apparatus which uses the same principle as, but is a considerable refinement over, the U-tube form described in § 55e. It is known as the **Tiselius apparatus**, and it permits the identification and even the separation of proteins present in a mixture, such as in the lyophilic sol blood plasma.

The principle of the method may be illustrated by the sectional drawing of the apparatus in Fig. 55.4. The U-tube portion is in three parts, *A*, *B* and *C*, which can slide horizontally with respect to one another. The lower parts *A* and *B* are filled with a buffer solution of known pH in which the proteins are dispersed. The part *C*, which has been pushed aside, is then filled with the buffer solution alone and slid over *B* to complete the U-tube and establish a sharp boundary in each limb. Each of the large vessels *D* contains a silver-silver chloride electrode *E*. In the immediate vicinity of the electrode material is a concentrated solution of alkali chloride, but the remainder of each

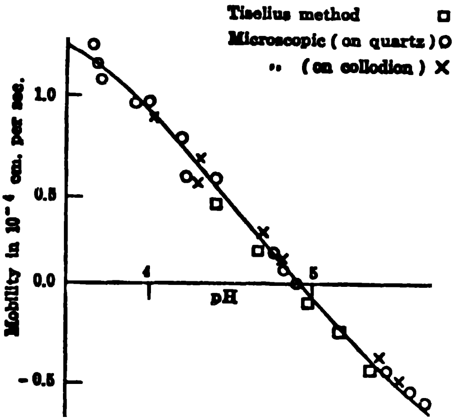

Fig. 55.3. Mobility of horse serum albumin (Abramson, Gorin and Moyer)

of the vessels is filled with the same buffer solutions as in the U-tube, so this is continuous through the apparatus. A source of E.M.F. is then applied to the electrodes and electrophoresis commences; separate boundaries are formed due to the different speeds of the different protein molecules at the pH of the medium. By keeping the temperature at about 3°C, the point of maximum density of the buffer solution, convection effects at the boundaries due to heating by the current are minimized.

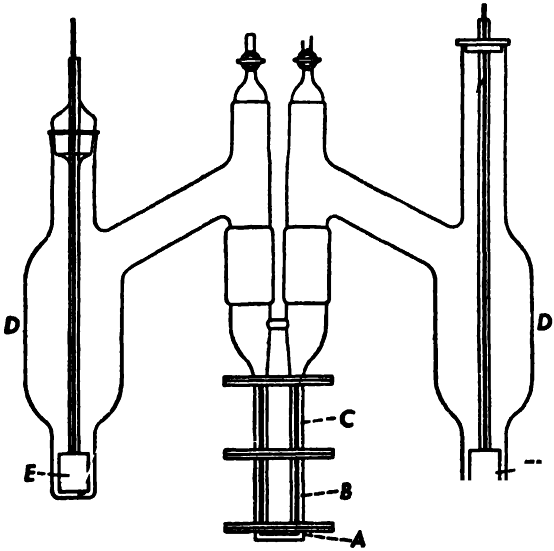

Fig. 55.4. Tiselius apparatus

The positions of the boundaries are generally observed by an optical technique known as the "schlieren" (streak) method. It utilizes the effect on a beam of light of the refractive index gradients in the sol, which are themselves dependent on the variations in the concentrations of the protein particles. The sharp change at a boundary becomes apparent as a peak in the schlieren pattern, and each boundary produces such a peak, as shown in Fig. 55.5. From the position of each peak, which is determined by the electrophoretic mobility, the nature of the protein can be identified; further, the area under the peak is a measure of the amount present in the sol. One difficulty inherent in the Tiselius procedure is the fact that two proteins having the same mobility at the given pH will be indistinguishable and will produce one boundary only. It is sometimes possible to effect a separation by changing the pH, provided denaturation of the protein does not occur.

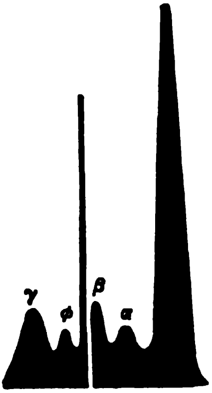

Fig. 55.5. Separation of proteins in blood plasma (Longsworth, Shedlovsky and MacInnes)

55i. Stability of Lyophilic Sols.—Small amounts of electrolytes have no coagulating effect on lyophilic sols, even though the zeta potentials are altered; some sols are actually stable at their isoelectric points, when the electrokinetic potential is zero. It is evident that some factor, in addition to the charge, i.e., the double layer potential, must play a part in determining the stability of lyophilic sols; this factor is believed to be the solvation of the particles, referred to in § 55h as the cause of the high viscosity of lyophilic sols. If alcohol or acetone is added to a lyophilic sol in water, the system becomes sensitive to electrolytes, thus behaving like a lyophobic sol. This action is attributed to the removal of the stabilizing layer of water molecules by the alcohol or acetone; the stability of the resulting unhydrated "bare" particles is now dependent upon the zeta potential, and hence electrolytes can bring about coagulation.

The stability of a hydrophilic sol is therefore determined by two factors, viz., the layer of water molecules, i.e., hydration, and the electric charge. If the hydration is decreased, the sol becomes sensitive to electrolytes. On the other hand, when the electric charge is neutralized, as at the isoelectric point, precipitation can be brought about by dehydrating agents such as alcohol. In some sols, e.g., gelatin, both stabilizing factors are effective and can operate more or less independently.

The addition of *large* amounts of electrolyte to lyophilic sols results in a precipitation of the dispersed substance. The effect, called "salting out," by analogy with the influence of electrolytes on solutions, such as those of ethyl ether, ethyl acetate and aniline in water, is due to dehydration of the dispersed particles by the ions of the added salt. The salting out of soluble organic substances, such as those mentioned above, is attributed to a somewhat similar effect. If the electrolyte is removed from the coagulated lyophilic sol by dialysis, the substance returns to the colloidal state; such is not the case with lyophobic sols.

The coagulating effect of a given salt depends on the nature of its ions, and the salts of a given metal, for instance, can be arranged in order of their decreasing ability to cause precipitation of lyophilic substances from colloidal dispersion. The resulting arrangement is called the **Hofmeister series** (F. Hofmeister, 1891) or the **lyotropic series**; the order of anions, for a given cation, is

$$SO_4^{-2} > C_2H_3O_2^- > Cl^- > NO_3^- > ClO_3^- > I^- > CNS^-,$$

while that of cations, which have a smaller influence than anions, is

$$Mg^{+2} > Ca^{+2} > Sr^{+2} > Ba^{+2} > Li^+ > Na^+ > K^+.$$

It is of interest to note that these series are very similar to those observed for the influence of ions on the salting out of soluble organic substances.

55j. **The Properties of Gels.**—Under certain conditions it is possible to coagulate a sol, particularly a lyophilic sol, in such a manner as to yield *a semi-rigid, jelly-like mass which includes the whole of the liquid present in the sol;* this product is known as a **gel.** The properties of gels divide them into two types, namely, **elastic gels** and **nonelastic gels.** A typical elastic gel is that of gelatin, obtained by cooling the lyophilic sol that results when this substance is warmed with water. Other lyophilic sols, provided they are not too dilute, yield elastic gels upon cooling; examples are agar, starch and pectin sols in water. Such familiar food products as gelatin jellies, fruit jams and jellies, and cornstarch puddings are gels of this type. Solutions of soaps, which form a special group of colloidal substances possessing appreciable electrical conductance, also set to elastic gels.

The best known example of a nonelastic gel is that of silicic acid, usually known as silica gel; this is obtained by mixing solutions of sodium silicate and hydrochloric acid at appropriate concentrations. Under some conditions the whole system sets to a gel immediately, but in other cases the setting process takes a little time. Similar gels of other hydrous oxides, e.g., ferric oxide, have been prepared. The familiar gelatinous precipitates of the hydrous oxides of metals, such as those of iron, aluminum, chromium, tin and lead, are probably related to the nonelastic gels; these precipitates are, however, not true gels because they do not include the whole of the water present.

The elastic and nonelastic gels are distinguished primarily by their behavior upon dehydration and rehydration. Partial dehydration of an elastic (gelatin) gel leads to the formation of an elastic solid from which the original sol may be readily regenerated by the addition of water, and warming if necessary. A nonelastic (silica) gel, on the other hand, becomes glassy or falls to a powder, and loses its elasticity on drying. When a gelatin gel is dehydrated, the vapor pressure decreases continuously, and rehydration by exposure to water vapor takes place almost reversibly over the whole range from completely dry to wet gel. Dehydration of a silica gel is quite different; the vapor pressure exhibits discontinuities, and upon rehydration there is reversibility only for the almost dry gel.

After an elastic gel has taken up as much liquid, e.g., water, as possible from the vapor phase, it can still imbibe considerable amounts when actually placed in the liquid. The phenomenon is referred to as **imbibition or swelling,** because of the marked increase in the dimensions of the gel. The swelling of gels is influenced by electrolytes, the effect of various ions corresponding exactly with the lyotropic or Hofmeister series, referred to in § 55i. If ions are arranged in order of their ability to inhibit swelling, the order will be identical with that given previously. When swelling is considerable, as in solutions of iodides and thiocyanates, the gel often disperses to form a sol spontaneously; in other cases, the sol is formed by warming the gel. The Hofmeister series may thus be taken as giving the order of temperature to which a swollen gel must be heated, in the presence of various ions, before it is transformed into a sol. Similarly, the same series, in reverse, gives the order of temperatures to which the sol must be cooled before it sets to a gel.

Nonelastic gels do not exhibit the phenomenon of swelling, although when moderately dry they are capable of taking up appreciable quantities of liquid without undergoing any marked volume change. The liquid evidently enters the pores of the gel, and since the walls are rigid, as noted above, the volume of the gel does not alter. Another characteristic difference between elastic and nonelastic gels arises in connection with the imbibition of liquid; in the former case the imbibition is selective, but in the latter it is more general. Thus, a gelatin gel will take up water but not alcohol, whereas silica gel will absorb both; in general, a nonelastic gel will take up any liquid by which it is wetted (§ 12b).

There is ample evidence that the transition from sol to gel, and the reverse, takes place gradually, at least with elastic gels; this suggests that there is no essential difference in the structure of sol and gel. The view widely accepted at the present time is that in the course of gelation, i.e., formation of the gel, the particles in the sol gradually unite to form short chains or threads; these become interlocked, so that the viscosity of the system increases, and eventually a semi-solid form is acquired. Part of the dispersion medium may exist as water of hydration of the chains of particles, but the major portion is believed to be held by capillary forces between the threads. This theory of the formation of gel from sol gives a satisfactory picture of the structure of a gel. The same type of structure, of *interlocking solvated threads enclosing the liquid dispersion medium,* is probably applicable to both elastic and nonelastic gels; the difference between them depends on the physical and chemical nature of the material constituting the disperse phase, i.e., the particles of the sol, which forms the threads.

55k. Emulsions.—An **emulsion** consists of *small drops of one liquid dispersed in another liquid;* the globules or droplets of dispersed liquid are from 0.1 to 1 μ in diameter, and hence are larger than those found in sols. Common examples of emulsions are milk and mayonnaise, which consist of small drops of liquid fat dispersed in an aqueous medium; in cod-liver oil emulsions used in pharmacy globules of water are dispersed in the oil. If a hydrocarbon oil is shaken with water, or if a liquid which is immiscible or partially miscible with water, e.g., aniline or nitrobenzene, is distilled in steam, or if a solution of the organic liquid in alcohol or acetone is poured into an excess of water, a faintly milky system is often obtained; this is an emulsion of the **oil in water** type. In these emulsions the disperse phase consists of small drops of oil dispersed in water. The term "oil" is used in connection with emulsions to represent the organic substance insoluble in water, since this is frequently, but not necessarily, a hydrocarbon oil, a vegetable oil, or other liquid fat. In some emulsions the water is in the form of droplets dispersed in a continuous medium of oil; these are known as the **water in oil** type of emulsions.

Several methods are available for distinguishing between emulsions of the two types; the simplest is to place a small quantity of the emulsion under a microscope and to stir into it a drop of either oil or water. If the emulsion is the oil in water type, the water will mix readily but not the oil, since the former is the continuous medium. On the other hand, a water in oil emulsion mixes freely with oil but not with water.

Emulsions are generally unstable unless a third substance, known as an **emulsifying** (or **stabilizing**) **agent,** is present; such an agent makes possible the preparation of emulsions containing relatively large proportions of disperse phase. The most frequently employed emulsifying agents fall into three categories: first, certain long-chain compounds with polar groups, such as the soaps and long-chain sulfonic acids and sulfates, which are now classified under the general heading of **detergents.** It may be noted that the cleansing action of these detergents is ascribed to their emulsifying properties; by breaking up grease and oil into minute droplets they facilitate their removal together with the accompanying dirt. The second group of stabilizing agents are lyophilic substances, such as proteins, gums and agar; in milk, for example, the emulsifying agent is the protein casein, while in mayonnaise the stability of the emulsion is largely due to the presence of egg albumin. The third category of emulsifiers consists of certain insoluble powders, e.g., basic sulfates of iron, copper or nickel, lead sulfate, ferric oxide, clay, calcium carbonate and powdered glass, which stabilize oil in water emulsions, and carbon black which stabilizes water in oil emulsions.

The soaps of alkali metals favor the formation of oil in water emulsions, but soaps of higher valence metals, such as the alkaline earth metals, zinc, iron and aluminum, yield water in oil emulsions. It is for this reason that an emulsion of hydrocarbon oil in water, with a sodium or potassium soap as emulsifier, may be converted into a water in oil emulsion by the addition of a salt of a bi- or tri-valent metal. The latter substance reacts with the alkali metal soap, producing a soap of the higher valence metal which stabilizes the water in oil type of emulsion.

551. Stability of Emulsions.—Because of the forces of surface tension at an interface, the latter tends to become as small as possible; in an emulsion, however, the area of separation between the droplets of disperse phase and the dispersion medium is very large. This means that the interfacial tension is small, and it seems to be the function of the stabilizing agent to decrease the tension at the oil-water interface. In general, droplets of the disperse phase are coated with a film of the stabilizing agent. Which will be the disperse phase, oil or water, depends upon the preferential wetting of the stabilizing agent by the oil or the water; this in turn is dependent upon the effect of the agent on the surface tension of the oil or water. There are two interfaces to consider, viz., one between the oil and stabilizing agent (I), and the other between stabilizing agent and the water (II). If the interfacial tension at the former, i.e., $\gamma_{\rm I}$, is greater than that of the latter, i.e., $\gamma_{\rm II}$, the oil-agent interface (I) will tend to have a smaller area than the agent-water interface, as shown in Fig. 55.6A. This condition can be realized if the water

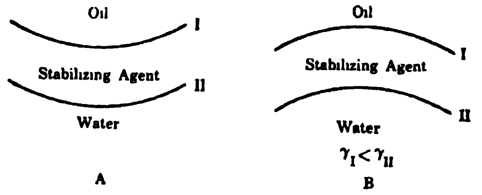

FIG. 55.6. The stability of emulsions

surrounds the oil, and hence an oil in water type of emulsion will be stabilized. If the relative values of the two interfacial tensions are reversed, as in Fig. 55.6B, a water in oil type of emulsion will have preferred stability.

The foregoing considerations provide a basis for the interpretation of the behavior of different soaps or detergents, in general, in stabilizing emulsions of different types. The detergent usually consists of a hydrocarbon chain and a polar group; when added to an oil and water system, the hydrocarbon chain will attach itself to the oil while the polar group will be attracted to the water (§ 54g). If the soap is preferentially adsorbed, or wetted, by the water, or, in more general terms, has a greater attraction for the water than for the oil, the water-soap interfacial tension $\gamma_{\rm II}$ will be reduced, in accordance with the requirement of the Gibbs equation (54.9); an oil in water emulsion will then be stable. The soaps of the alkali metals are of this type, and so their influence in stabilizing oil in water emulsions can be understood. On the other hand, it is an experimental fact that the soaps of calcium, magnesium and other high valence metals, have a greater attraction for oil than for water; in this event, the oil-soap interfacial tension $\gamma_{\rm I}$ is diminished, and the water in oil type of emulsion will be preferred. In the case of solid stabilizing agents, both liquids must be able to wet the powder. The one which wets it most readily becomes the dispersion (or continuous) phase, provided the contact angle is not 0°, 90° or 180°. In these latter cases no stabilization occurs; the solid goes completely into one of the liquids or shows no preference. The particles of solid coat the droplets of the dispersed phase with a film which prevents them from coalescing.

Such "dilute" emulsions as are obtained in the absence of a stabilizing agent possess properties similar to those of lyophobic sols. The globules show Brownian movement, provided they are not too large; they carry a negative electrical charge, and can be "coagulated" by electrolytes, particularly by positive ions of high valence. The droplets exhibit electrophoresis, and the mobility is of the same order as for colloidal particles, viz., about 4×10^{-4} cm per sec for a potential gradient of 1 volt per cm. The electrokinetic potential at the oil-water interface, calculated from the electrophoretic mobility, is about 0.05 volt. It is probable that these "dilute" emulsions owe their stability to the existence of this potential at the interface.

Stabilized emulsions resemble lyophilic, rather than lyophobic, sols; the stabilized emulsion acquires the properties of a sol of the stabilizing agent. Such emulsions can be obtained with relatively high concentrations, have a high viscosity, and are not greatly affected by electrolytes, unless the latter react chemically with the emulsifier. An excess of electrolyte may "salt out" the stabilizing agent, and so cause the emulsion to become unstable.

Emulsions may be "broken," that is, converted into two separate liquid layers, in several ways; the process is sometimes referred to as **demulsification.** Chemical destruction of the emulsifying agent is effective in this respect; for example, the addition of an acid converts a soap into the corresponding fatty acid which is not an emulsifier. Physical methods, such as heating, freezing and centrifuging, are often employed for breaking emulsions. The conversion of cream into butter by churning is an example of the breaking of an emulsion of fat in water; in the separation of cream from milk use is made of centrifuging to bring about demulsification.

MOLECULAR WEIGHTS OF MACROMOLECULAR SUBSTANCES

56a. Osmotic Pressure Method.—Lyophilic sols are essentially solutions of substances of high molecular weight, greater than about 10,000, in suitable solvents, e.g., proteins and starch in water, rubber and polystyrene in benzene, and polyvinyl chloride in dioxane. In principle, it should be possible to determine the molecular weight of a macromolecular substance by utilizing its colligative properties, i.e., lowering of vapor pressure, boiling point elevation, freezing point depression or osmotic pressure, as described in Chapter 8 for small molecules. However, for solutions of a given mass concentration, the number of solute molecules of high molecular weight present is very much less than for a solute of low molecular weight. Consequently, the various colligative effects are correspondingly smaller. For example, a solution of 1.00 gram of solute of molecular weight 100 in 100 grams of water will depress the freezing point by 0.186°C, but if the molecular weight is 10,000 the depression, for the same weight composition, will be only 0.00186°C; this is too small to measure easily. The rise of boiling point, besides being more difficult to determine accurately, is even smaller and the lowering of the vapor pressure of the macromolecular solution is less than the experimental error of the measurements. For the determination of molecular weights in the range from 10,000 to 1,000,000 the osmotic pressure is the only colligative property which can be used, although the accuracy is poor at the upper limit.

Many macromolecular substances consist of long flexible chains of atoms coiled in a random manner. As a result, in solution each molecular coil may encompass a large number of small molecules of the solvent which are thus essentially removed from the solution. The free volume of solvent is therefore greatly decreased and the effective concentration and intermolecular interaction are increased. Hence, such solutions exhibit marked deviations from ideal behavior even at low concentration. To obtain results corresponding to ideal conditions, such as are required for molecular weight determinations, it is therefore necessary to make a series of osmotic pressure measurements at a number of concentrations and to extrapolate the data to infinite dilution. For this purpose, the van't Hoff equation (25.3) is treated as a limiting law and it is expressed as

$$\lim_{c \to 0} \left(\frac{\Pi}{c}\right) = \frac{RT}{M}, \tag{56.1}$$

where Π is the osmotic pressure of a macromolecular solution containing c grams of dispersed material in a given volume of sol. This equation states that the limiting value of Π/c, at infinite dilution, i.e., when $c = 0$, is equal to RT/M, where M is the required molecular weight. A plot of Π/c against c is approximately linear and can easily be extrapolated to $c = 0$. From the extrapolated value, the molecular weight is determined by equation (56.1).

Osmotic pressure measurements of macromolecular substances are frequently made in an apparatus similar to that in Fig. 56.1. A thin sheet of Cellophane is often used as the semipermeable membrane; it may be supported in some manner to provide additional mechanical strength. The narrow tube, in which the liquid rises, has a small internal diameter to minimize dilution of the sol by entering solvent. For measurements in nonaqueous solutions, the Cellophane is "conditioned" by replacing the water it contains with acetone, and the acetone with the required solvent. A 1 per cent by weight solution in water of a substance of molecular weight 100,000 should ideally give an osmotic pressure of roughly 25.2 mm of water. Because of departure from ideal behavior, the actual osmotic pressures are larger and such values can be measured with fair accuracy.

In some macromolecular solutions, e.g., of certain proteins, all (or nearly all) the dispersed particles have the same molecular weight; they are said to be **monodisperse.** Most high molecular weight materials, however, especially those of synthetic linear polymers are **polydisperse**; they are mixtures of molecules of different molecular weights, and the value of M obtained from equation (56.1) is then an average. Since the osmotic pressure depends on the *number* of solute particles in the solution and not on their size, this average is called the **number average molecular weight, $\overline{M}_n$.** It is the total mass of dispersed material divided by the number of molecules present; thus,

$$\bar{M}_n = \frac{n_1M_1 + n_2M_2 + \cdots}{n_1 + n_2 +} = \frac{\Sigma n_iM_i}{\Sigma n_i}$$

where n_i is the number of moles of species i and M_i is its molecular weight. Since large and small molecules contribute equally to the osmotic pressure, a given weight of small molecules will affect $\bar{M}_n$ more than the same weight of large molecules. The presence of 1 per cent by weight of material of molecular weight 1000 in a polymer of molecular weight 100,000 will give a value of $\bar{M}_n$ of 50,000, whereas 1 per cent of molecular weight 1,000,000 will raise $\bar{M}_n$ to 101,000 only.

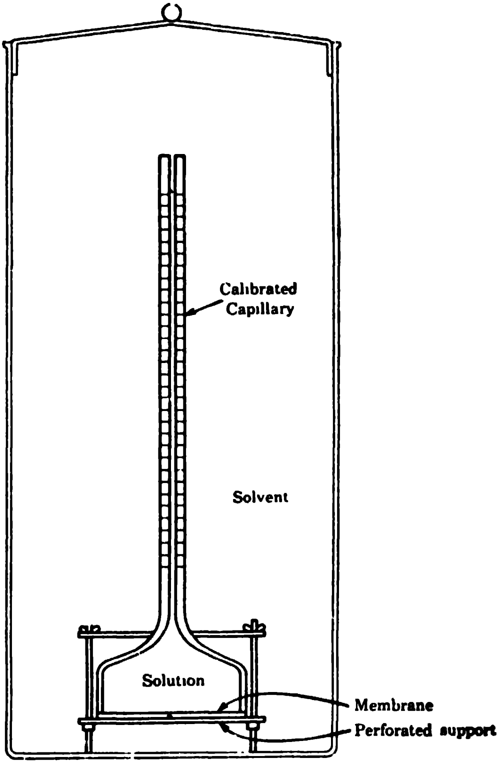

FIG. 56.1. Osmometer

56b. The Donnan Equilibrium.—The determination of the osmotic pressure of an electrically charged macromolecular substance, such as a protein, may be affected by the **Donnan equilibrium** (F. G. Donnan, 1911), which arises when a large, nondiffusible ion, e.g., a protein ion, is separated by a diffusion membrane from a diffusible salt. Suppose a solution of sodium chloride of concentration c_1 is separated by a membrane from a solution of a salt NaR of concentration c_2, where R^- is a nondiffusible ion.

At equilibrium, a certain amount x of sodium and chloride ions will have passed through the membrane, so that the final state will be as represented below.

Equilibrium State

$$\begin{array}{cc:ccc} \mathrm{Na}^+ & \mathrm{Cl}^- & \mathrm{Na}^+ & \mathrm{R}^- & \mathrm{Cl}^- \\ c_1 - x & c_1 - x & c_2 + x & c_2 & x \end{array}$$

The condition of electrical neutrality must apply on both sides of the membrane, and so the total concentration of positive ions is equal to that of the negative ions in each solution. At equilibrium the chemical potential of any substance which is present on both sides of the membrane must be the same on each side; consequently, according to equation (26.6)

$$\mu^0 + RT \ln (a_{\mathrm{NaCl}})_1 = \mu^0 + RT \ln (a_{\mathrm{NaCl}})_2,$$

where a_{NaCl} represents the activity of the sodium chloride, and the subscripts 1 and 2 refer to the solutions at the left and right side of the membrane, respectively. Since, by equation (51.4) $a_{\mathrm{NaCl}} = a_{\mathrm{Na}^+} \times a_{\mathrm{Cl}^-}$, it follows that at equilibrium

$$(a_{\mathrm{Na}^+})_1 \times (a_{\mathrm{Cl}^-})_1 = (a_{\mathrm{Na}^+})_2 \times (a_{\mathrm{Cl}^-})_2. \tag{56.2}$$

If the solutions are dilute, the ionic activities may be replaced by the corresponding concentrations, so that equation (56.2) becomes

$$(c_1 - x)(c_1 - x) = (c_2 + x)x,$$

$$\frac{x}{c_1} = \frac{c_1}{c_2 + 2c_1}. \tag{56.3}$$

This equation shows that the presence of the nondiffusible ion R^- influences the extent of diffusion of the sodium chloride. The fraction x/c_1 represents the proportion of sodium chloride initially present on one side of the membrane which has diffused through to the other side when equilibrium is attained; this is seen to be smaller the larger the concentration c_2 of the nondiffusible ion. As c_2 becomes smaller in comparison with the salt concentration c_1, x/c_1 approaches $\frac{1}{2}$, so that the sodium chloride is almost equally distributed on both sides of the membrane. If the behavior of the solution is assumed to be ideal, the osmotic pressure across the membrane may be calculated from the van't Hoff relationship $\Pi = RTc$ where, in the present case, c is the difference in the molar concentrations on the two sides of the membrane; hence, for the equilibrium state represented above,

$$\begin{aligned} \Pi &= RT\{[(c_2 + x) + c_2 + x] - [(c_1 - x) + (c_1 - x)]\} \\ &= 2RT(c_2 - c_1 + 2x). \end{aligned}$$

If the sodium chloride had been equally distributed on both sides of the membrane, i.e., $c_1 = 2x$, or if there had been no electrolyte, i.e., $c_1 = 0$ and $x = 0$, the osmotic pressure would have been $2RTc_2$. As seen above, if the salt concentration c_1 is large in comparison with the concentration c_2 of the nondiffusible ion, x/c_1 becomes equal to $\frac{1}{2}$, i.e., $2x$ is equal to c_1. Consequently, the effect of the Donnan equilibrium on the osmotic pressure can be largely eliminated by a fairly high salt concentration in the solution. This is the condition frequently used for the determination of the molecular weight of a protein from osmotic pressure measurement. Ideally, such measurements should be made at the isoelectric point where the presence of equal amounts of positive and negative nondiffusible ions makes the net electrolyte effect a minimum. However, osmotic pressure measurements at this point are not reliable and so they are usually made at a pH of about one unit from the isoelectric point.

In these calculations it has been assumed for the sake of simplicity that the diffusible salt has an ion in common, viz., the Na^+ ion, with the substance NaR. A Donnan equilibrium will apply, however, even if this is not the case, e.g., if the electrolyte is potassium chloride, although the situation will now be complicated by the diffusion of Na^+, K^+ and Cl^- ions.

56c. Applications of the Ultracentrifuge.—It was shown in § 3h that by studying the distribution under the influence of gravity of suspended particles undergoing Brownian movement, it was possible to determine the Avogadro number, e.g., by equation (3.30) or (3.31). For this purpose it was necessary to know the actual mass m of the particles, and this was derived from the radius and density. Since the Avogadro number N is now known with considerable accuracy, it is possible to reverse the calculations, and thus to determine the "molecular weight," i.e., the value of Nm, of the dispersed macromolecular particles in a lyophilic sol.

Although, in principle, distribution (or sedimentation) of the macromolecules under the influence of gravity could be used for molecular weight determinations, the results would not be satisfactory for a number of reasons. By means of the **ultracentrifuge**, designed by T. Svedberg (1925), a considerable improvement is possible. In outline, the apparatus (Fig. 56.2) consists of a rotor A, revolving at high speed about the axis BB; a cell C contains the experimental solution through which a beam of light can pass and then fall on a photographic plate P. By rapidly rotating the colloidal solution in this manner a force approaching a half-million times gravity can be applied to the particles. When equilibrium is attained, between the rate of sedimentation and the rate at which the molecules diffuse back because of thermal motion, the distribution of macromolecules at various levels is given by an expression exactly analogous to equation (3.30), with the exception that the gravitational factor $g(h_2 - h_1)$ is replaced by the corresponding centrifugal term $\frac{1}{2}\omega^2(x_1^2 - x_2^2)$, where ω is the angular velocity of rotation of the sol, i.e., 2π times the number of rotations per sec, and x_1 and x_2 are the respective distances of the two levels from the axis of rotation. The condition of **sedimentation equilibrium** is then given by

$$\ln\frac{n_1}{n_2} = \frac{M\omega^2(x_1^2 - x_2^2)}{2RT}\left(1 - \frac{d'}{d}\right), \tag{56.5}$$

where mN has been replaced by the molecular weight M; d and d' are the densities of the dispersed material and of the medium, respectively.

If the amount of light absorbed at any level of the solution is proportional to the number of molecules at that level, the ratio n_1/n_2 can be estimated at two depths x_1 and x_2 from the blackening of the photographic plate P, upon which the beam of light passing through the cell C impinges (Fig. 56.2).* From a knowledge of the speed of rotation of the ultracentrifuge, ω can be derived, and hence all the information is available for the calculation of the molecular weight M by means of equation (56.5).

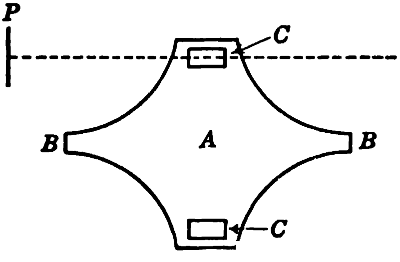

FIG. 56.2. Principle of the ultracentrifuge

In a polydisperse system, sedimentation in the ultracentrifuge distributes the molecules in a nonuniform pattern, according to their respective masses. The average molecular weight derived from equation (56.5) is thus different from that obtained by the osmotic pressure method for then the distribution is uniform. The sedimentation procedure gives the **weight average molecular weight,** $\bar{M}_w$, i.e.,

$$\bar{M}_w = \frac{m_1M_1 + m_2M_2 + \cdots}{m_1 + m_2 + \cdots} = \frac{\Sigma n_i M_i^2}{\Sigma n_i M_i},$$

where the mass m_i of any particular molecular species is equal to n_iM_i. Except for a monodisperse system, where $\bar{M}_n$ and $\bar{M}_w$ are equal, $\bar{M}_w$ is always greater than $\bar{M}_n$. Further, the effect of small molecules on $\bar{M}_w$ is much less than on $\bar{M}_n$, but larger molecules have a greater effect. For example, 1 per cent by weight of material of molecular weight 1000 in a polymer of molecular weight 100,000 changes $\bar{M}_w$ to 99,000, whereas with 1 per cent of molecular weight 1,000,000 the value of $\bar{M}_w$ becomes 109,000.

For sedimentation equilibrium measurements in the ultracentrifuge relatively low centrifugal forces, e.g., 1000 to 100,000 times gravity, are generally used. It may then require several days for equilibrium to be attained. A more rapid procedure, known as the **sedimentation velocity method,** requires only a few hours to complete a series of measurements. This is accomplished by using higher centrifugal forces, up to 500,000 times gravity, and measuring the rate of sedimentation. The equation used for this purpose is

$$\ln \frac{x}{x'} = \frac{2\omega^2 r^2 (d - d')}{9\eta} (t - t'), \qquad (56.6)$$

where x and x' are as the distances of the boundary of the dispersed macromolecules from the axis of rotation at the times t and t'; η is the viscosity of

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* In modern forms of the apparatus, methods other than light absorption are used.

the medium, and r is the radius of the particles in the sol; ω, d and d' have the same significance as before. The position of the boundary after various time intervals is indicated by means of the schlieren technique mentioned in § 55h. It is thus possible to calculate the molecular radius r from equation (56.6), and then $\frac{4}{3}\pi r^3$ gives the volume, assuming the macromolecule to be spherical. Knowing the density d of the material and the Avogadro number N, the molecular weight of the dispersed material, which is equal to $\frac{4}{3}\pi r^3 dN$, can then be evaluated.

The sedimentation equilibrium and osmotic pressure methods are not affected by the shape of the macromolecules since measurements are made at equilibrium. Sedimentation velocity, however, is markedly dependent on shape; an elongated particle, for example, offers more resistance to motion through a liquid than does a spherical one of the same mass. Hence, an elongated macromolecule will have a smaller sedimentation velocity than a spherical molecule of the same molecular weight. When the molecular weight obtained from sedimentation equilibrium and sedimentation velocity measurements agree, the molecules are probably spherical or approximately so; this is the case for many protein molecules.

By combining sedimentation velocity data with the results of diffusion measurements, the effect of molecular shape can be eliminated. Upon rearranging equation (56.6) to

$$\frac{1}{\omega^2(t - t')} \ln \frac{x}{x'} = \frac{2r^2(d - d')}{9\eta},$$

the right side, which is seen to be constant for the given dispersed material and dispersion medium, is called the **sedimentation constant,** s. A particle diffusing through a liquid is subject to the same frictional forces as a sedimenting particle; hence, the two processes, diffusion and sedimentation, will be affected similarly by the shape of the molecules. Diffusion measurements yield a characteristic constant, the **diffusion constant,** D; it is defined as the mass of material diffusing across unit area in unit time under a concentration gradient of unity. Both s and D are found to vary with the concentration of the sol, so that the measurements must be extrapolated to infinite dilution, e.g., by plotting $1/s$ and D, respectively, against the concentration, to give s_0 and D_0. The molecular weight of the dispersed substance is then obtained from the equation

$$M = \frac{RTs_0}{D_0(1 - d'/d)}$$

Some results obtained by these methods with protein solutions are recorded in Table 56.1; molecular weights varying from a minimum of about 20,000 to over 6,000,000 have been observed. It should be remembered that these are true molecular weights only if the particles in the sol consist of a single molecular species; otherwise they are weight averages.

56d. Light Scattering Method.—Because of the thermal motion of the

TABLE 56.1. MOLECULAR WEIGHTS OF PROTEIN PARTICI

Protein	Molecular Weight
Egg albumin	40,000
Insulin	41,000
Hemoglobin (human)	63,000
Serum albumin (horse)	70,000
Serum globulin (human)	176,000
Edestin	310,000
Thyroglobulin	630,000
Hemocyanins	4×10^5 to 6×10^6

molecules of a liquid, the number of molecules in any small volume element varies with time. Over an extended period, the average number of molecules in all volume elements will be the same, but at any instant the molecular distribution will not be uniform. The resultant density fluctuations produce refractive index variations, as a result of which a beam of light passing through the liquid will undergo some scattering. If a solute is present, additional scattering is produced by local concentration fluctuations. It is this effect, in particular, which is the cause of the turbid appearance of many sols. The fraction of light scattered per cm of liquid path is called the **turbidity**, τ, and the turbidity due to concentration fluctuations is the difference between the turbidity of the solution (or sol) and that of the pure solvent. In principle, τ can be determined by measuring either the decrease in intensity of a transmitted beam of light or the intensity of the light scattered at 90° to the beam. The latter method is preferred because the change in the transmitted beam is too small for accurate measurement.

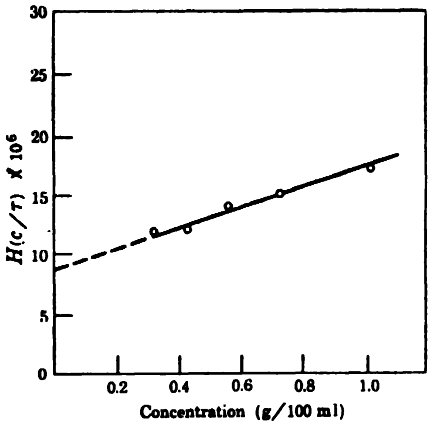

FIG. 56.3. Light scattering of a cellulose acetate preparation

The relationship between the turbidity and the molecular weight of the macromolecules in a sol was derived by P. Debye (1944); it is given by

$$\lim_{c \to 0} H \frac{c}{\tau} = \frac{1}{M}, \tag{56.7}$$

where H, a constant for a specified dispersed material and dispersion medium, is a function of the variation of the index of refraction with concentration and the wave length of the light. Determination of molecular weight thus requires measurement of turbidity and refractive index at various concentrations, followed by extrapolation of $H(c/\tau)$ to infinite dilution (Fig. 56.3). For a macromolecular substance which is a mixture of several components of different molecular weights, the value obtained from equation (56.7) is the weight average, $\overline{M}_w$.

The turbidity of a solution having a given weight concentration increases with increasing molecular weight, in general agreement with equation (56.7). Hence, the accuracy of the method increases with the molecular weight. The light scattering method is especially useful in the range where the osmotic pressure method becomes inaccurate, i.e., for molecular weights above about 1,000,000.

As the size of the macromolecules increases and approaches the wave length of the light used, destructive interference occurs of the light scattered by different parts of the large molecule. This produces a decrease in the overall intensity of the scattered light and a dissymmetry in the angular distribution of the scattering; there is more at angles less than 90° than at larger angles.* The angular variation of the scattered light depends on the shape of the macromolecules; by assuming various geometric shapes, the angular distribution of the light scattering can be calculated and compared with that observed. In this way it has been shown, for example, that amylose (a constituent of starch) and fibrinogen are rod shaped, gelatin and polystyrene form random coils, and serum albumin is spherical. Light scattering studies provide the most reliable method for determining the shapes of large molecules.

56e. Viscosity Method.—The methods described above for molecular weight determinations are too time consuming and complicated to be suitable for routine characterization of macromolecules, especially of industrial polymers. It was noted by H. Staudinger (1930) that the viscosity of a dilute solution of a polymer in a suitable solvent varies in a regular manner with the molecular weight of the polymer. The higher the molecular weight in a homologous series of linear polymers, the greater is the increase in viscosity for a given weight concentration of polymer. Originally derived empirically, the relationship between viscosity and molecular weight has been shown to have a theoretical basis (W. Kuhn, 1932; M. L. Huggins, 1938).

The presence of large molecules in a liquid medium introduces inhomogeneities which increase the resistance to flow of the molecules of liquid and thus increases the viscosity. If η_0 and η are the viscosities of the solvent and solution, respectively, η/η_0 is called the **relative viscosity,** η_r, of the solution; the **specific viscosity,** η_{sp}, which is the relative increase in viscosity, is then equal to $\eta_r - 1$, so that

$$\frac{\eta - \eta_0}{\eta_0} = \frac{\eta}{\eta_0} - 1 = \eta_r - 1 = \eta_{sp}.$$

It is the ratio η_{sp}/c, i.e., the relative increase in viscosity per unit concentration of polymer, which is a function of the molecular weight. Since this

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* For molecules of length less than $\lambda/20$, where λ is the wave length of the light, the angular scattering distribution is uniform.

ratio varies with the concentration, it is necessary to extrapolate a plot of η_{sp}/c against c to infinite dilution; the value thus obtained is called the **intrinsic viscosity**, $[\eta]$, so that

$$[\eta] = \lim_{c \to 0} \left(\frac{\eta_{sp}}{c} \right).$$

Since η_{sp} is dimensionless, $[\eta]$ has the units of a reciprocal concentration and since c is usually expressed in grams per 100 ml of solution, $[\eta]$ is given in deciliters per gram. The relationship between the intrinsic viscosity and the molecular weight of the dispersed polymer is

$$[\eta] = KM^a, \tag{56.8}$$

where K is a constant for a given polymer-solvent system, M is the molecular weight of the polymer and a depends on the shape of the molecules. Theory predicts that a should be zero for large rigid spheres, 0.5 to 0.8 for randomly coiled (flexible) linear chains, and 2 for rigid rods. The highest value found for a is 1.5 for amylose which has been shown by light scattering measurements to be rod shaped.

To obtain molecular weights from viscosity data, K and a in equation (56.8) must be known. However, they can be determined only if molecular weights of samples of the given polymeric material have been obtained in other ways, e.g., by osmotic pressure, sedimentation or light scattering measurements. According to equation (56.8) a plot of log $[\eta]$ against log M will give a straight line of slope a and intercept log K. It is thus seen that the viscosity method is a secondary (or dependent) method for determining molecular weights, in contrast to the other methods which are absolute and yield M directly from measurable quantities. However, once K and a are known for a given type of polymer and solvent, the viscosity method becomes one of the most convenient for the subsequent evaluation of molecular weights, e.g., during the course of a polymerization process. The value obtained is an average which differs slightly from the weight average molecular weight.

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PROBLEMS

1. The adsorption of carbon monoxide on mica at 90°K gave the following results:

Pressure, mm Hg × 10^2	1.05	4.53	5.45	7.91	10.59
Vol adsorbed, $cm^3 \times 10^2$ at S.T.P.	13.0	16.3	16.8	17.8	18.3

(*a*) Show that the data fit the Langmuir adsorption isotherm. (*b*) Evaluate the constants k_1 and k_2. (*c*) Determine the volume adsorbed at saturation. (*d*) The surface area of the mica was 6.239×10^2 cm²; calculate the area covered by one molecule of CO and the radius of the molecule.

2. The adsorption of nitrogen on $ZrSiO_4$ at liquid nitrogen temperature, hence $p_0 = 1$ atm, fits the B-E-T equation. The data are

p, mm Hg	Vol adsorbed, cc at S.T.P.	*p*, mm Hg	Vol adsorbed, cc at S.T.P.
10.4	8.16	190.3	13.73
20.8	8.96	256.0	15.10
76.0	11.04	391.2	18.02
112.0	12.16	471.2	20.32
157.6	13.09	576.0	23.84

Determine (*a*) the volume of nitrogen necessary to form a monolayer on the powdered sample and (*b*) the area per gram of powder if the sample weighs 17.52 g and one molecule of nitrogen occupies 16.2 A².

3. For a 0.050 M solution of phenol in water at 20°C, the rate at which the surface tension varies with concentration, $-d\gamma/dc$, is 165 erg cm^{-2} $mole^{-1}$ l. (*a*) Determine how much phenol, in moles per sq cm, is adsorbed at the surface of the solution. (*b*) How many molecules are there per sq cm, (*c*) per A²? (*d*) When the surface layer was removed with a microtome blade, it was found that an area of 310 cm² contained an average weight of 6.9×10^{-6} g phenol more than the bulk of the solution. Determine the excess concentration of phenol in moles cm^{-2}.

4. A film containing 5.14×10^{-5} g of hexadecyl alcohol spread on water was compressed into a monomolecular layer occupying an area 15.0 × 17.9 cm. The density of the alcohol is 0.818 g cm^{-3}. Calculate (*a*) the cross section of the molecule and (*b*) its length.

5. The osmotic pressures of a sample of polyisobutylene in cyclohexane at 25°C at several concentrations, expressed as the height of liquid multiplied by its density, are as follows:

c, g/100 ml	2.00	1.50	1.00	0.75	0.50	0.25
Π, g cm^{-2}	12.10	6.80	3.12	1.79	0.94	0.36

Determine the number average molecular weight of the sample.

6. By a suitable plot of the following data for solutions in cyclohexane at 25°C, of polyisobutylene fractions of known molecular weight, determine the constants of the equation $[\eta] = KM^a$.

$[\eta]$	$\overline{M}_n$	$[\eta]$	$\overline{M}_n$
1.12	304,000	0.460	73,300
0.830	193,000	0.209	22,900
0.551	98,800	0.152	13,370
0.522	87,500	0.113	8,540

7. The following viscosity data were obtained for a sample of cellulose acetate in acetone at 25°C:

c, g/100 ml	0	0.114	0.351	0.703
η, millipoise	3.16	4.06	6.64	13.02

For this solute-solvent system $K = 1.87 \times 10^{-5}$ and $a = 1.03$. Determine the molecular weight of the sample.

8. Calculate $\overline{M}_n$ and $\overline{M}_w$ for the polydisperse polymer composed of the following mixture of particles:

Weight % of total	20	30	50
Molecular weight	50,000	100,000	200,000

9. From the following light scattering data for solutions of polystyrene in methylethylketone, determine the molecular weight of the polymer:

c, g/100 ml	0.105	0.215	0.315	0.435
$Hc/\tau \times 10^6$	6.21	6.95	7.62	8.34

16

Kinetics of Chemical Reactions

ORDER OF REACTION

57a. Chemical Kinetics.—Every chemical reaction takes place at a definite rate depending on the experimental conditions; the most important of these are the concentrations (or pressures) of the reacting substances, temperature, the presence of a catalyst, and radiation, e.g., light of suitable wave length. Some reactions are so rapid that they appear to be instantaneous, e.g., the neutralization of an acid by a base in aqueous solution, while others are so slow at ordinary temperatures, e.g., the combination of hydrogen and oxygen in the absence of a catalyst, that no detectable change would be observed in many years. Between these two extremes there are many processes, involving both inorganic and organic compounds, taking place with measurable velocities at temperatures that are easily accessible in the laboratory. Many reactions involving gases are extremely slow at ordinary temperatures, but occur with appreciable velocities when the temperature is raised. It is the study of the rates of chemical reactions and of the influence of conditions on these rates that constitute the experimental basis of the subject of **reaction kinetics.**

Based on the early work of L. Wilhelmy (1850), who studied the rate of inversion of sucrose, and of others, it is known that the rate of a chemical reaction is proportional to the concentrations (or pressures) of the reacting substances; since the latter are being continuously consumed in the course of the reaction, their concentrations (or pressures) must be decreasing steadily. It follows, therefore, that the reaction rate must vary with time, somewhat in the manner of Fig. 57.1, the process becoming slower and slower as the reactants are used up.

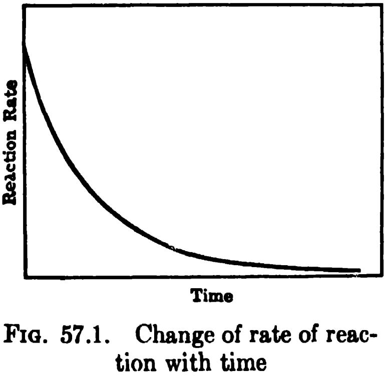


FIG. 57.1. Change of rate of reaction with time

From the standpoint of the quantitative consideration of reaction rates, processes are classified by the **order of the reaction,** that is, by *the number of atoms or molecules whose concentrations (or pressures) determine the rate* *of the reaction.* As will be seen presently, the rate of thermal decomposition of nitrogen pentoxide is directly proportional to its concentration; the reaction is therefore said to be of the **first order.** The hydrolysis of an ester in dilute aqueous solution is also a first order reaction, although the reaction involves a molecule of ester and one of water; the reason is that the concentration of water, which is one of the reactants, does not change appreciably because it is present in large excess. The rate of the reaction is then determined by the concentration of one molecule only, viz., that of the ester.

The dissociation of hydrogen iodide is a **second order** reaction; experiments have shown that the reaction rate is proportional to the *square* of the hydrogen iodide concentration, indicating that the concentrations of two molecules are involved. The reaction between nitric oxide and oxygen is **third order,** the rate being dependent on the concentration of oxygen molecules and the square of the concentration of nitric oxide.

In general, *if it is found experimentally* that the rate of a chemical reaction is proportional to the n_1th power of the concentration c_1 of reactant 1, to the n_2th power of the concentration c_2 of reactant 2, and so on, i.e.,

$$\text{Rate} = kc_1^{n_1}c_2^{n_2}c_3^{n_3} \ldots,$$

then the reaction is said to be of overall order n, where

$$n = n_1 + n_2 + n_3 + \ldots,$$

and of order n_1 in reactant 1, n_2 in reactant 2, etc. Although it might appear, at first sight, that reactions of high order are possible, it is doubtful whether n ever exceeds 3. That is, no reactions are higher than third order.

Another manner of classifying chemical reactions is according to their **molecularity;** this is *the number of atoms or molecules taking part in each act leading to chemical reaction.* If one molecule only is involved, the reaction is said to be **unimolecular;** an illustration of this type of process is the decomposition of nitrogen pentoxide, either in the gas phase or in solution, viz.,

$$N_2O_5 = N_2O_4 + \tfrac{1}{2}O_2.$$

The dissociation of gaseous hydrogen iodide has been shown to be a **bimolecular** reaction, since two molecules take part, thus

$$2HI = H_2 + I_2,$$

and *not* $HI = \tfrac{1}{2}H_2 + \tfrac{1}{2}I_2$. Another type of bimolecular reaction is the hydrolysis of an ester, e.g.,

$$CH_3COOC_2H_5 + H_2O = CH_3COOH + C_2H_5OH.$$

If three molecules are involved in each chemical act, the over-all process is said to be **termolecular;** a possible example of this type is the reaction

$$2NO + O_2 = 2NO_2.$$

For relatively simple reactions occurring in one stage, the molecularity is equal to the number of molecules of reactants appearing in the stoichiometric chemical equation representing the overall reaction. However, many reactions occur in two or more steps, sometimes referred to as **elementary processes.** A molecularity can then be assigned to each individual step, indicating the number of molecules, atoms or ions taking part in that particular process. However, this assignment is possible only if the detailed mechanism of the reaction, i.e., the nature of the elementary processes, is known.

In contrast to the molecularity, the order of a reaction merely expresses the experimentally determined dependence of the reaction rate on the concentrations of the reactants. In some instances the order and molecularity are the same; this has been found to be true for the decomposition of nitrogen pentoxide and of hydrogen iodide. But in most cases they are different. This is almost invariably so in any reaction in which one of the reactants is present in excess, e.g., hydrolysis of an ester in dilute aqueous solutions. Reactions are known to have zero order and, in some circumstances, the decomposition of gaseous acetaldehyde has been found to have an order of $\frac{3}{2}$. The molecularity, on the other hand, must always be an integer and never zero. In spite of the frequent difference between the order and molecularity, the two are not completely independent, for measurements of order are often used to confirm or contradict a proposed mechanism for the reaction.

Although chemical processes are not always simple, it will be convenient, however, to consider in the first place what have been called **isolated reactions,** which are free from secondary effects; the influence of disturbing factors will be referred to later. Further, it is desirable to distinguish clearly between **homogeneous reactions,** which take place entirely in one phase, either gas or solution, and **heterogeneous reactions,** involving two phases, e.g., gas and solid, or solution and solid. The treatment will be restricted first to homogeneous reactions. As already indicated, temperature alters the rate of a reaction, and so it will be assumed that the temperature remains constant while a particular reaction is being studied; subsequently the influence of temperature will be examined in some detail.

Various procedures have been used for following the rates of chemical reactions; both physical and chemical methods have been applied to determine the quantities of the reacting substances still remaining, or of the products that have been formed, after a series of time intervals. The particular procedure adopted depends on the nature of the reactants and the products, and also on the temperature.

In general, if the conditions permit, a physical method, e.g., measurement of pressure of a gas, conductance of an electrolyte, light absorption or rotation of polarized light, is to be preferred, since the reaction can be followed continuously without removal of samples for analysis. A chemical method requires that such samples be taken from time to time, stopping the reaction and then analyzing the sample. Illustrations of some of the methods used in chemical reaction kinetics are given below.

57b. Reactions of the First Order.—In a first order reaction the rate is directly proportional to the concentration of one reactant; this condition can be expressed mathematically by

$$\frac{-dc}{dt} \quad kc, \tag{57.1}$$

where c is the concentration of the reactant at time t, and k is a proportionality constant; the negative sign indicates that c decreases while t increases. The proportionality constant k is called the **velocity constant** or **rate constant** or, more generally, the **specific reaction rate.** The reason for the latter title can be readily seen in the following manner. The left-hand side of equation (57.1) represents the reaction rate; hence, k is equal to the reaction rate for unit concentration, that is, when c on the right-hand side is unity. The specific reaction rate is a constant for the given reaction at a definite temperature; it is evident from equation (57.1) that the reaction rate at any instant is obtained upon multiplying this constant by the concentration of the reactant at that instant.

For practical use, equation (57.1) is rearranged to $-dc/c = k\,dt$ and integrated; thus, if c_0 is the initial concentration of the reactant at time $t = 0$ when the reaction commences and c is the concentration at any subsequent time t,

$$-\int_{c_0}^{c} \frac{dc}{c} = k \int_0^t dt.$$

Since the integral of dc/c is $\ln c$, the result is

$$\ln \frac{c_0}{c} = kt$$

or

$$k = \frac{1}{t} \ln \frac{c_0}{c}. \tag{57.2}$$

A more common form of equation (57.2) is obtained by supposing that a moles of reactant are initially present in unit volume of the reacting system and that x is the number of moles in unit volume that have reacted after time t, leaving $a - x$ unreacted. Then c_0 is proportional to a and c to $a - x$, so that equation (57.2) becomes

$$k = \frac{1}{t} \ln \frac{a}{a - x} = \frac{2.303}{t} \log \frac{a}{a - x}. \tag{57.3}$$

This is known as the **kinetic equation** for a reaction of the first order; it provides a means for calculating the specific reaction rate of the given process at a definite temperature.

Before proceeding to consider examples of first order reactions it is of interest to examine some general consequences of equation (57.3). In the first place, the quantity $a/(a - x)$ is a *ratio* of concentrations, and so its value will be independent of the units used to express these concentrations, provided the same units are used for a and x. This fact makes the evaluation of the first order velocity constant particularly simple, for the values of a and $a - x$

can be given in moles per liter, as ml of a volumetric reagent, as the partial pressure of a gas, or in other ways. Further, since $a/(a - x)$ is a number, independent of the concentration units, it follows from equation (57.3) that the specific reaction rate k has the dimensions of reciprocal time, i.e., t^{-1}; if the time t is given in seconds, as is generally the case, k is expressed in $\sec^{-1}$ units.

Another important characteristic of first order reactions can be derived from equation (57.3) by evaluating the time taken to complete a definite fraction of the reaction; for example, let $t_{0.5}$ be the time required for the concentration of the reacting substance to be reduced to half its initial value, i.e., for x to be equal to $\frac{1}{2}a$. Upon insertion of this value for x into equation (57.3) it follows that

$$t_{0.5} = \frac{2.303}{k} \log 2 = \frac{0.693}{k}. \qquad (57.4)$$

For any given first order reaction $t_{0.5}$ is thus a constant, independent of the initial concentration. Consequently, it will take the same time to reduce the the amount of reactant from 1 mole to 0.5 mole, in a given volume, as is required to decrease the amount from 0.001 to 0.0005 mole, in the same volume. In general, *the time to complete any definite fraction of the reaction is independent of the initial concentration;* this is one of the most striking properties of a first order reaction.

57c. Examples of First Order Reactions.—The application of equation (57.3) may be illustrated by reference to one of the best known first order reactions, namely the decomposition of nitrogen pentoxide. In the gaseous reaction the over-all process may be represented by

$$N_2O_5(g) = N_2O_4(g) + \tfrac{1}{2}O_2(g),$$

intermediate steps being ignored; for every mole of pentoxide decomposed there is a net increase of one-half mole in the reacting system. The partial pressure of the nitrogen pentoxide decomposed, equivalent to x, should thus be equal to double the increase of gas pressure at constant volume, as the reaction proceeds. Unfortunately, the situation is complicated somewhat by the dissociation of the N_2O_4 into $2NO_2$, which causes a further increase of pressure; from a knowledge of the equilibrium constant of this reaction, however, the necessary allowance can be made. It is thus possible from measurements of the total pressure at various times t to determine the partial pressure x of the nitrogen pentoxide decomposed. The initial pressure, expressed in the same units, gives the corresponding value of a, and hence it is possible to calculate the specific rate k by means of equation (57.3). The results obtained in this manner at 35°C are given in Table 57.1 (F. Daniels and E. H. Johnston, 1921); the approximate constancy of the k values for various time intervals indicates that the reaction is of the first order.

The decomposition of nitrogen pentoxide has also been studied in solution; by choosing a suitable solvent, the N_2O_4 and NO_2 can be retained in the solution while the oxygen is evolved and its volume measured. As seen from the

TABLE 57.1. DECOMPOSITION OF GASEOUS NITROGEN PENTOXIDE AT 35°C

Initial Pressure $a = 308.2$ mm

t	x	k sec^{-1}	t	x	k sec^{-1}
1200 sec	53.8 mm	1.60×10^{-4}	3600 sec	121.4 mm	1.39×10^{-4}
1800	72.7	1.49	6000	171.0	1.33
2400	90.0	1.43	8400	206.8	1.33
3000	106.0	1.40	12000	244.6	1.30

equation for the reaction, every mole of oxygen produced means two moles of pentoxide decomposed; hence, the extent of decomposition x at any time t can be obtained. The value of a, in the same units, is derived from the final volume of oxygen when the nitrogen pentoxide has been completely decomposed.

Instead of calculating the individual values of k from the data at each time interval, a graphical method may be employed to cover the whole of the reaction period. By rearrangement, equation (57.3) becomes

$$t = \frac{2.303}{k} \log a - \frac{2.303}{k} \log (a - x). \tag{57.5}$$

This is a linear equation of the slope-intercept type, so that the plot of t against $\log (a - x)$ should be linear if the reaction is first order; the slope of the straight line will be equal to $-2.303/k$, thus enabling the rate constant k to be evaluated. The data in Table 57.1 are plotted in this manner in Fig. 57.2; the points are seen to fall close to a straight line. The slope of this line is -1.706×10^4, and consequently k is 1.35×10^{-4}, in agreement with the mean value from Table 57.1. It is always preferable to plot the experimental results as in Fig. 57.2, to obtain the best value for k. In this manner all the data are taken into consideration and experimental errors become apparent by deviations from the expected linear behavior. When using equation (57.3), as was done for the results in Table 57.1, only two experimental values, the initial concentration and that at time t, are used for each calculation of k.

A different type of first order reaction, as noted earlier, is the hydrolysis of an ester in aqueous solution. Frequently the reaction is too slow to be studied, but the rate is measurable in the presence of a small amount of mineral acid, acting as a catalyst; it does not appear in the equation for the reaction, e.g., the hydrolysis of methyl acetate,

$$CH_3COOCH_3 + H_2O = CH_3COOH + CH_3OH,$$

and its concentration remains unchanged throughout the reaction. Further, the water is present in such large excess that the concentration of this substance is virtually constant. The kinetics of the reaction are then determined solely by the concentration of the ester; hence, the process is of the first order, and equation (57.3) should be applicable. In order to follow the course of the reaction, a definite volume of the reacting solution, consisting

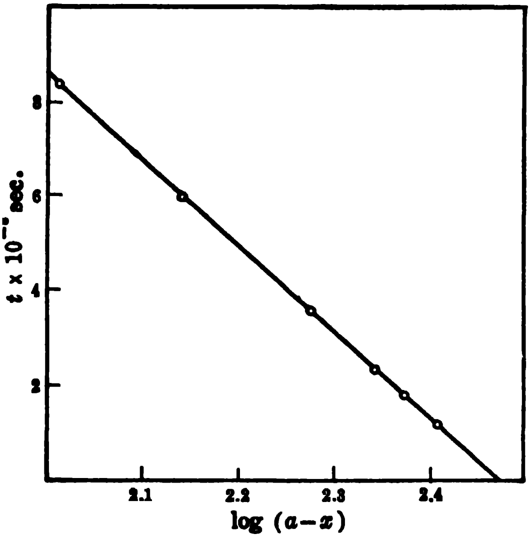


FIG. 57.2. Decomposition of gaseous nitrogen pentoxide

of the ester dissolved in water containing the catalyst, e.g., 0.05 N hydrochloric acid, is withdrawn and titrated with standard alkali. The volume of alkali solution used is equivalent to the total of the hydrochloric acid and the acetic acid produced in the hydrolytic reaction. The titration T_0 at the commencement is equivalent to the catalyst alone, and if T_t is the titration after time t, the difference $T_t - T_0$ is a measure of the acetic acid formed, and hence of the ester decomposed; consequently, $T_t - T_0$ may be identified with x in equation (57.3). After the lapse of sufficient time, when the reaction is complete, the titration T_∞ is equivalent to the catalyst and the acetic acid formed by the hydrolysis of the whole of ester; the difference $T_\infty - T_0$ is thus equivalent to a, the initial concentration of ester. Substitution of these values for a and x in equation (57.3) then gives for the first order reaction

$$k = \frac{2.303}{t} \log \frac{T_\infty - T_0}{T_\infty - T_t}.$$

The results of an actual experiment on the hydrolysis of methyl acetate at 25°C, using 0.05 N hydrochloric acid as catalyst, are recorded in Table 57.2;

t sec	T ml	k sec^{-1}
0	$24.36 = T_0$	—
1200	25.85	5.62×10^{-5}
4500	29.32	5.46
7140	31.72	5.44
∞	$47.15 = T_\infty$	—

in accordance with what has been already stated, the value of k is independent of the units employed for expressing a and x, and so the concentration of the alkali used for the titration is immaterial. The approximate constancy of the results in the last column supports the view that the reaction is first order, in spite of the fact that two molecules of reactant, apart from the catalyst, are involved. The value of k obtained in any particular case does, however, depend on the concentration of the acid catalyst and on that of the water.

Another reaction of the same type is the hydrolysis or "inversion" of sucrose, viz.,

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{dextrose}}{C_6H_{12}O_6} + \underset{\text{levulose}}{C_6H_{12}O_6},$$

which is also catalyzed by acids. The course of the reaction can be followed by measuring, in a polarimeter, the angle of rotation of polarized light; sucrose rotates the plane of polarization to the right, whereas the mixture of dextrose and levulose produced upon hydrolysis has a rotation in the opposite direction. If α_0 and α_∞ are the angles of rotation, including the correct signs, at the beginning and when the reaction is complete, respectively, and α_t is the value after time t, then $\alpha_0 - \alpha_\infty$ is proportional to the initial amount a of sucrose, and $\alpha_t - \alpha_\infty$ is equivalent to $a - x$, the amount still remaining after the time t. It follows then from equation (57.3) that

$$k = \frac{2.303}{t} \log \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty},$$

and it has been verified that the experimental values of k calculated from this expression are constant over the whole period of the inversion process. Here again k varies with the concentrations of acid and of water in the solution.

57d. Reactions of the Second Order.—The rate of a second order reaction depends on two concentration terms; these may both refer to the same reactant, as in the dissociation of gaseous hydrogen iodide, or to two different reactants. If the two reacting molecules are the same, the general reaction would be written as

$$2A \rightarrow \text{products},$$

and the rate would be given by the expression

$$\frac{-dc_A}{dt} = kc_A^2, \tag{57.6}$$

where c_A is the concentration of the reactant A at any time t. Before integration, this equation may be generalized to the case of a reaction of the nth order involving a single reactant; thus,

$$\frac{-dc}{dt} = kc^n \quad \text{or} \quad \frac{-dc}{c^n} = k\,dt. \tag{57.7}$$

Upon integration between the limits of t from 0 to t and of c from c_0 to c, the result is

$$k = \frac{1}{(n-1)t}\left(\frac{1}{c^{n-1}} - \frac{1}{c_0^{n-1}}\right). \tag{57.8}$$

For a second order reaction, with $n = 2$, this becomes

$$k = \frac{1}{t}\left(\frac{1}{c} - \frac{1}{c_0}\right),$$

or writing a for c_0 the initial concentration of reactant and $a - x$ for the concentration at time t, it follows that

$$k = \frac{1}{t}\left(\frac{1}{a-x} - \frac{1}{a}\right) = \frac{1}{t} \cdot \frac{x}{a(a-x)}. \tag{57.9}$$

A second order reaction involving one molecule of each of two different reacting substances A and B may be represented by

$$\mathrm{A} + \mathrm{B} \rightarrow \text{products},$$

so that the reaction rate is given by

$$\frac{-dc_{\mathrm{A}}}{dt} = \frac{-dc_{\mathrm{B}}}{dt} = kc_{\mathrm{A}}c_{\mathrm{B}} \tag{57.10}$$

in place of equation (57.6). If a and b represent the initial molar amounts of A and B, respectively, in a given volume, and x is the amount of each that has reacted after time t, the concentrations c_{A} and c_{B} will be $a - x$ and $b - x$, respectively; equation (57.10) then becomes

$$\frac{dx}{dt} = k(a-x)(b-x). \tag{57.11}$$

When A and B are present in equimolar amounts, i.e., $a = b$, equation (57.11) reduces to

$$\frac{dx}{dt} = k(a-x)^2 = k(b-x)^2$$

and then k can be obtained from equation (57.9). In the general case, however, when a and b are different, integration of equation (57.11) by the method of partial fractions yields

$$k = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)} = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}. \tag{57.12}$$

An examination of equations (57.9) and (57.12) shows that the second order rate constant differs from that for a first order reaction in being dependent on the units employed to express the concentrations. It can be seen that there is one more concentration term in the denominator than in the numerator, and so the specific reaction rate is expressed in conc^{-1} time^{-1}

units. If the time is in seconds, and the concentrations in moles per liter, the specific rate will be in (moles/liter)$^{-1}$ sec^{-1} or liters mole^{-1} sec^{-1}.

The time taken for the initial concentration of the reactants in a bimolecular reaction to be reduced by a definite fraction may be readily calculated; the time $t_{0.5}$ for the concentration, which is taken as being the same for A and B, to be reduced to one-half of its initial value, is given by substituting $\frac{1}{2}a$ for x in equation (57.9). The result is

$$t_{0.5} = \frac{1}{ka}, \tag{57.13}$$

so that the time is inversely proportional to the initial concentration of the reactants; hence, the greater the initial concentration the smaller the time required to reduce it to one-half. The same relationship applies for the completion of any other definite fraction of the reaction. The difference in this respect between first and second order reactions is very striking, and permits them to be distinguished from one another.

57e. Examples of Second Order Reactions.—Although the dissociation of hydrogen iodide is a second order process, its study is rendered somewhat complicated by the fact that the reaction is reversible, and so requires special treatment (§ 57i). There are relatively few gas reactions that are definitely of the second order, free from secondary effects; among these, mention may be made of the combination of hydrogen and ethylene to yield ethane, i.e.,

$$H_2 + C_2H_4 = C_2H_6.$$

The reaction rate in this case may be followed by measurement of the decrease of pressure.

There are, however, a large number of processes taking place in solution that are kinetically of the second order; one of the most familiar of these is the alkaline hydrolysis, or saponification, of an ester, e.g.,

$$CH_3COOC_2H_5 + OH^- = CH_3COO^- + C_2H_5OH.$$

This differs from the hydrolysis in acid solution considered in § 57c, because the two reactants are present in more or less similar amounts; the concentrations of both change appreciably during the reaction, and hence affect the reaction rate. The course of the reaction has been followed in several different ways. One method makes use of the fact that the removal of the hydroxyl ions and their replacement by acetate ions is accompanied by a decrease in the conductance of the reacting system. From this decrease, the extent of the reaction can be calculated. In the second method, definite quantities of the reacting solution are withdrawn from time to time, and the amount of alkali $b - x$ that remains is determined by titration. If the initial concentrations of ester and hydroxide, i.e., a and b, are known, the value of $a - x$ may be obtained, and hence the specific rate k can be calculated from equation (57.12). Some experimental data for the reaction between ethyl acetate (A) and sodium hydroxide (B) at 15.8°C are recorded in Table 57.3; the

TABLE 57.3. ALKALINE HYDROLYSIS OF ETHYL ACETATE AT 15.8°C

a = 0.01211 mole ester per liter
b = 0.02578 mole hydroxide per liter

t sec	$a - b$ mole liter^{-1}	$b - x$ mole liter^{-1}	k liter mole^{-1} sec^{-1}
224	0.00889	0.02256	5.74×10^{-2}
377	0.00734	0.02101	5.74
629	0.00554	0.01921	5.68
816	0.00454	0.01821	5.68

results in the final column are seen to be constant, within the limits of experimental error.

The measurements of second order reactions may also be treated in a graphical manner; thus, if equation (57.12) is written in the form

$$t = \frac{2.303}{k(a-b)} \log \frac{b}{a} + \frac{2.303}{k(a-b)} \log \frac{a-x}{b-x},$$

it is seen that, since a and b are constants, the plot of t against $\log [(a - x)/(b - x)]$ should be a straight line of slope equal to $2.303/k(a - b)$. The results of Table 57.3 are plotted in Fig. 57.3; the slope of the line is −2970, and

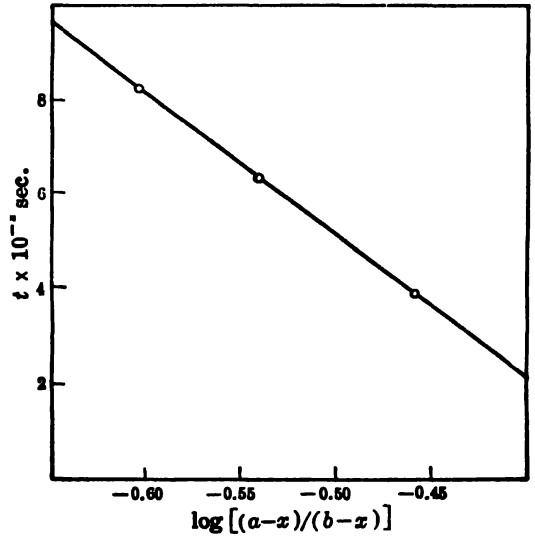


FIG. 57.3. Alkaline hydrolysis of ethyl acetate

hence the over-all value of k is found to be 5.68×10^{-2}, in agreement with the figures in the table.

Other second order reactions taking place in solution are the interaction of alkyl halides with tertiary amines, e.g.,

$$C_2H_5I + C_6H_5N(CH_3)_2 = C_6H_5N(CH_3)_2(C_2H_5)^+ + I^-,$$

and of alkyl iodides with sodium phenoxide, e.g.,

$$RI + C_6H_5ONa = C_6H_5OR + Na^+ + I^-,$$

where R varies from CH_3 to C_8H_{17}. The progress of both these types of processes can be followed by titration, with silver nitrate, of the iodide ions produced in the reaction.

57f. Reactions of the Third Order.—A third order reaction may involve three molecules, e.g., A + B + C, whose concentrations are changing in the course of the reaction, or there may be two molecules of one substance and one of another, e.g., 2A + B, or three molecules of a single substance, e.g., 3A, may be concerned. In the most general case, i.e.,

$$A + B + C \rightarrow \text{products},$$

the reaction rate at any instant is given by

$$\frac{-dc_A}{dt} = \frac{-dc_B}{dt} = \frac{-dc_C}{dt} = kc_Ac_Bc_C. \tag{57.14}$$

In the special case in which there is only one reactant or when there are two or three reactants at the same concentration, this becomes

$$\frac{-dc}{dt} = kc^3,$$

where c refers to any of the reactants. From the general equation (57.8) the result of integration is

$$k = \frac{1}{2t}\left(\frac{1}{c^2} - \frac{1}{c_0^2}\right) \tag{57.15}$$

and replacing c_0 by a and c by $a - x$, as before,

$$k = \frac{1}{2t}\left(\frac{1}{(a-x)^2} - \frac{1}{a^2}\right). \tag{57.16}$$

It is apparent from equation (57.16) that the value of the rate constant depends on the units employed for the concentration terms; since there are always two more such terms in the denominator than in the numerator, k will have the dimensions of $\text{conc}^{-2}\ \text{time}^{-1}$. In general, for a reaction of order n, the units of k are $\text{conc}^{n-1}\ \text{time}^{-1}$.

If it is assumed that the concentrations are all equal, so that equation (57.16) holds, the time to complete a definite fraction of the reaction can be calculated in the usual manner. Thus, when half the reaction is completed, x is equal to $\frac{1}{2}a$, and the corresponding time $t_{0.5}$ is given by equation (57.16) as

$$t_{0.5} = \frac{3}{2ka^2}. \tag{57.17}$$

The time to complete one-half or, in fact, any definite fraction, of the reaction is thus inversely proportional to the square of the initial concentration of the reactants.

Only five homogeneous gas reactions are definitely known to be of the third order; these are all termolecular reactions involving two molecules of nitric oxide, the other reactant being a molecule of hydrogen, deuterium, oxygen, chlorine or bromine. The reaction with chlorine, for example, is

$$2\text{NO} + \text{Cl}_2 = 2\text{NOCl},$$

so that the rate is proportional to the square of the nitric oxide concentration (or pressure) and to the first power of the concentration (or pressure) of the chlorine gas. It may be remarked, incidentally, that for gas reactions in general, concentrations may be replaced by pressures if the deviations from ideal behavior are not large.

The third order reaction of type

$$2\text{A} + \text{B} \rightarrow \text{products}$$

is of interest because it occurs in reactions of nitric oxide (A) with oxygen, hydrogen or halogens (B). In this case

$$\frac{dx}{dt} = k(a - 2x)^2(b - x),$$

where x is the amount of B that has reacted at time t. This also can be integrated by the method of partial fractions and the result is

$$k = \frac{1}{t(2b - a)^2}\left[\frac{(2b - a)2x}{a(a - 2x)} + \ln\frac{b(a - 2x)}{a(b - x)}\right].$$

A number of third order reactions in solution have been described, but the results are somewhat in doubt. For example, the interaction of stannous and ferric salts was at one time thought to be of the third order; it appears, however, that it is more probably of the second order, the presence of the ions introducing a complicating effect. Similar considerations apply to other reactions which are apparently third order.

57g. Reactions Occurring in Stages.—It is generally accepted at the present time that reactions of the third order are uncommon, and that processes of still higher order are either extremely rare or do not occur at all. For a reaction to be of the third order it would be necessary for three of the proper molecules to come together at one instant, and for the arrangement to be suitable for the reaction to take place (§ 58c); this occurrence is evidently rare, as is apparent from the scarcity of third order processes. The fact that the only known third order gas reactions involve two molecules of nitric oxide is commonly attributed to the formation of an intermediate double molecule $(\text{NO})_2$ which has an appreciable life; the reaction will then require an encounter between one of these molecules and a molecule of the other reactant, e.g., oxygen, chlorine, etc. The reaction would then really be bimolecular, thus

$$(NO)_2 + Cl_2 = 2NOCl,$$

although it would still be kinetically of the third order, since the rate will depend on the square of the NO concentration.

It would appear, therefore, that except in very unusual circumstances, *a reaction of the fourth or higher order is improbable, and even those of the third order are not of frequent occurrence.* An exception to this general statement arises for reactions in solution when the solvent is itself one of the reactants; since the solvent molecules are relatively close together, it is possible for two such molecules to be involved in a simultaneous encounter with one or two molecules of another reactant. However, although such reactions between four molecules might take place in solution, the order would probably be not more than second, because the solvent would not appear in the expression for the reaction rate.

In view of the foregoing considerations, it is evident that many reactions, for which the balanced stoichiometric equation involves three or more molecules, must occur in stages. A simple case in point is the reaction between nitric oxide and hydrogen which is kinetically of the third order; the rate is proportional to the square of the pressure of nitric oxide and to the first power of that of the hydrogen. The complete reaction, however, requires two molecules of hydrogen, viz.,

$$2NO + 2H_2 = N_2 + 2H_2O,$$

and so the reaction probably takes place in two stages,* the first being

$$2NO + H_2 \rightarrow N_2 + H_2O_2 \text{ (slow)}$$

followed by

$$H_2O_2 + H_2 \rightarrow 2H_2O \text{ (fast)}.$$

The exact nature of the stages is not known with certainty, but from the reaction kinetics it can be concluded definitely that one of them involves $2NO + H_2$, and the reactions given above appear to be reasonable.

Another illustration of similar behavior is provided by the reaction between hydrogen peroxide and hydrogen iodide in aqueous solution; the over-all process is

$$H_2O_2 + 2H_3O^+ + 2I^- = 4H_2O + I_2,$$

but kinetic measurements indicate that the reaction is of the second order, the rate being directly proportional to the concentrations of hydrogen peroxide and of the iodide ions. The process evidently occurs in stages, and the following have been suggested; first,

$$H_2O_2 + I^- \rightarrow H_2O + IO^- \text{ (slow)},$$

---

* The convention in this book is to use an "equals" sign when writing a complete (or over-all) stoichiometric reaction, and an arrow sign for an intermediate stage.

followed by the establishment of the equilibrium of the weak hypoiodous acid,

$$IO^- + H_3O^+ \rightleftharpoons HIO + H_2O \text{ (fast),}$$

and finally by the reaction

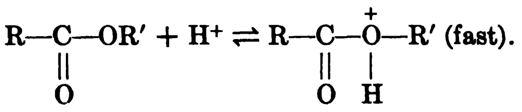
$$HIO + H_3O^+ + I^- \rightarrow 2H_2O + I_2 \text{ (fast),}$$

which may well take place in stages. In every case, addition of the equations for the stages representing the postulated mechanism must give the stoichiometric equation for the reaction.

When a reaction occurs in stages, *the rate is determined by the slowest of these stages*, provided the others are relatively rapid. In this event, *the kinetics and order of the reaction are really those of the slowest stage;* this is frequently called the **rate-determining stage** of the complete reaction. Thus, in the reaction between nitric oxide and hydrogen, the rate-determining stage is known from the kinetics to involve $2NO + H_2$; similarly, in the interaction of hydrogen peroxide and hydrogen iodide in solution, the rate-determining reaction occurs between a molecule of peroxide and an iodide ion. It happens in these two instances that the slow stage which determines the reaction kinetics is the first one, but this is not necessarily always the case; it may be any one of the stages of the complete process. It will be seen, therefore, that a study of reaction kinetics has led to the conclusion that even moderately complex reactions occur in stages, and the order of the reaction gives an indication of the nature of the slowest, or rate-determining, stage.

Since the stoichiometric equation for a reaction seldom indicates the true reacting species, it is of interest to consider how a probable mechanism is deduced in a particular case. Experiments show that the hydrolysis of an ester in a dilute acid medium is first order in both the ester and acid catalyst. The fact that, for strong acids, the reaction rate is essentially independent of the anion indicates that the hydrogen ion is the actual catalyst. The first step in the reaction is thus probably

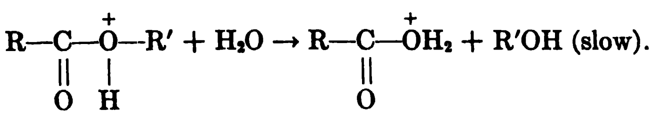
(I)



$$R-\underset{\underset{O}{\|}}{C}-OR' + H^+ \rightleftharpoons R-\underset{\underset{O}{\|}}{C}-\overset{+}{\underset{\underset{H}{|}}{O}}-R' \text{ (fast).}$$

Since at any given acidity the overall reaction rate is found to depend on the ester concentration alone, it is apparent that the equilibrium lies well to the left, otherwise the acidity would decrease. The positive ion formed in reaction (I) then reacts with water, thus,

(II)

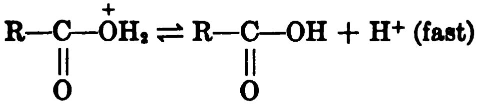


$$R-\underset{\underset{O}{\|}}{C}-\overset{+}{\underset{\underset{H}{|}}{O}}-R' + H_2O \rightarrow R-\underset{\underset{O}{\|}}{C}-\overset{+}{O}H_2 + R'OH \text{ (slow).}$$

This reaction involves the breaking of a covalent (O—R′) bond and experience with organic reactions indicates that such reactions are invariably slow.

Finally, hydrogen ion must be regenerated, since this is a catalyst and is not consumed in the reaction, by the final stage,

(III)



$$\mathrm{R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}\overset{+}{O}H_2 \rightleftharpoons R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}OH + H^+}\ \text{(fast)}$$

which goes practically to completion. Reaction II is thus the rate determining stage in the process; it is bimolecular but first order, since the concentration of water molecules, in this case, remains essentially constant.

It still remains to be shown that the mechanism proposed above is in agreement with the observed kinetics of the reaction. For this purpose use is made of the **stationary** (or **steady**) **state** concept which has been employed extensively in interpreting the rates of reactions occurring in stages. In such reactions there is often produced an unstable species, the concentration of which is never large. According to the stationary state concept, the concentration of this species rises at the very beginning of the reaction, but it soon reaches a constant (or steady) value which persists until the end of the reaction. In the steady state, the unstable species is being removed by subsequent reactions just as fast as it is formed in the earlier stages.

In ester hydrolysis, the ion $\mathrm{RCO\overset{+}{O}HR'}$ formed in stage I satisfies the requirements of the steady state concept; it is unstable and is present in small amounts only, since the equilibrium I lies well to the left. This ion is formed in reaction I and is removed by reaction II, the rates being equal, so that

$$k_1(\mathrm{RCOOR'})(\mathrm{H^+}) = k_2(\mathrm{RCO\overset{+}{O}HR'})(\mathrm{H_2O}), \tag{57.18}$$

where the parentheses are used to indicate concentrations. Since reaction II is the rate-determining stage, its rate is essentially that of the overall reaction. Thus, the right side of equation (57.18) gives the overall reaction rate. But this is equal to $k_1(\mathrm{RCOOR'})(\mathrm{H^+})$, and so the rate should be first order with respect to both the ester RCOOR′ and the hydrogen ions, in agreement with experiment.

57h. Determination of Order of Reaction.—It is opportune, at this point, to review the chief methods for determining the order of a reaction.

I. Method of Trial.—The most obvious method is to determine the amount of reactant decomposed after various intervals of time and to insert the data in the equations for first, second and third order reactions. The equation giving the most constant value for the specific reaction rate for a series of time intervals is the one corresponding most closely to the correct order of the reaction.

A modification of this procedure is to use a graphical method based on the respective rate equations, such as is depicted in Figs. 57.2 and 57.3. In general, if the reactants are all present at the same molar concentration, equation (57.1) will apply when $n = 1$ so that, upon rearrangement and integration,

$$t = \text{constant} - \frac{2.303}{k}\log c, \qquad (57.19)$$

and equation (57.7) applies when $n = 2$ or more, so that

$$t = \text{constant} + \frac{1}{k(n-1)} \cdot \frac{1}{c^{n-1}}. \qquad (57.20)$$

According to equation (57.19), the plot of t against $\log c$ will be a straight line for a first order reaction; this is, of course, equivalent to the result of equation (57.5), since $a - x$ is the same as the concentration c of reactant at any instant. For reactions of higher order, on the other hand, the plot of t against $1/c^{n-1}$ will be linear, where n is the order of the reaction; this result follows directly from equation (57.20), since $k(n-1)$ is a constant for each reaction. For a second order ($n = 2$) process, therefore, a straight line will be obtained if $1/c$ is plotted against the time; for a third order ($n = 3$) reaction, the plot of $1/c^2$ against time will be linear.

II. Time to Complete a Definite Fraction of the Reaction.—A general expression for the time to complete half the reaction is obtained by setting c in equation (57.8) equal to $\frac{1}{2}c_0$; upon rearranging, it is found that

$$t_{0.5} = \text{constant} \times \frac{1}{c_0^{n-1}}.$$

When $n = 1$, then $t_{0.5}$ is constant and independent of the initial concentration c_0, in agreement with equation (57.4). For a reaction of the nth order, $t_{0.5}$ is inversely proportional to c_0^{n-1} and the product of c_0^{n-1} and $t_{0.5}$ should be constant. By varying the initial concentrations of the reactants, and measuring the time taken to decompose the same fraction, e.g., one-half, of the amounts initially present, it is possible to derive the order of the reaction.

Example: In the decomposition of gaseous acetaldehyde at 518°C, the time taken to decompose half the material was found to be 410 sec when the initial pressure was 363 mm, and 880 sec for an initial pressure of 169 mm. What is the apparent order of the reaction?

Since the time $t_{0.5}$ is not constant, the reaction is obviously not of the first order. If the reaction were of the second order ($n = 2$), then the product of the initial concentration (or pressure), i.e., $a^{2-1} = a$, and $t_{0.5}$ should be constant; in the present case the products are 148,830 and 148,720. The values are sufficiently alike to indicate that the reaction is of the second order.

III. The Differential Method.—For two different concentrations c_1 and c_2 of the reactants, equation (57.7) becomes

$$\frac{-dc_1}{dt} = kc_1^n \quad \text{and} \quad \frac{-dc_2}{dt} = kc_2^n,$$

and by taking logarithms, and subtracting, it is found that

$$n = \frac{\log(-dc_1/dt) - \log(-dc_2/dt)}{\log c_1 - \log c_2}. \tag{57.21}$$

The values of dc_1/dt and dc_2/dt are best obtained by plotting the variation of concentration c of the reactants with time and determining the slopes, i.e., dc/dt, of the curve for different values of the concentration. The slope of the linear plot of log $(-dc/dt)$ against c then gives the required n. Alternatively, n may be derived from equation (57.21) by utilizing values of $-dc/dt$ at two concentrations c_1 and c_2. The result obtained is independent of the units used to express the concentration (or pressure), provided, of course, that the same units are used throughout.

If the reaction involves more than one substance it is not necessary that they should all have the same initial concentration. Suppose there are two reactants, A and B, whose concentrations affect the reaction rate. In one set of experiments, c_A is varied while c_B is kept constant; application of equation (57.21) then gives the order n_A with respect to A. In a second set of experiments, c_A is maintained constant while c_B is varied, and hence n_B can be evaluated; the sum of n_A and n_B gives the order of the reaction.

Example: In the reaction between NO and H_2, the value of $-dp/dt$ was found to be 1.50 mm sec^{-1} for a pressure of 359 mm of NO, and 0.25 mm sec^{-1} for a pressure of 152 mm, the pressure of H_2 being constant. On the other hand, when the pressure of NO was kept constant, $-dp/dt$ was 1.60 mm sec^{-1} for a H_2 pressure of 289 mm, and 0.79 mm sec^{-1} for a pressure of 147 mm. Determine the order of the reaction.

The concentrations are expressed in terms of partial pressures, and hence the $-dc/dt$ and c terms in equation (57.21) may be replaced by $-dp/dt$ and p, respectively. The order n_A of the reaction with respect to NO is then obtained from the first set of data, viz.,

$$n_A = \frac{\log 1.50 - \log 0.25}{\log 359 - \log 152} = 2.$$

The second set of data give the order n of the reaction with respect to H_2; thus,

$$n_B = \frac{\log 1.60 - \log 0.79}{\log 289 - \log 147} \approx 1.$$

The reaction is then of the second order with respect to NO, and of the first order with respect to H_2; the whole process is thus of the third order.

57i. Opposing Reactions.—As mentioned at the outset, the treatment so far has been applied to simple or isolated reactions; some reference will now be made to certain of the complications that frequently arise. In the first case, the process may be reversible, in the chemical sense, so that forward and reverse reactions occur simultaneously. The simplest form of this type of process is that in which both reactions are of the first order; thus,

$$A \underset{k'}{\overset{k}{\rightleftharpoons}} B,$$

where k and k' are the specific rates of the forward and reverse reactions, respectively. As stated in § 30b, the ratio k/k' is equal to the equilibrium constant for the given system. If a is the concentration of A at the commencement of the experiment, and there is initially no B present, then after the lapse of time t, the concentrations of A and B will be $a - x$ and x, respectively; the *net rate of reaction* in the forward direction will be given by

$$\frac{dx}{dt} = k(a - x) - k'x, \tag{57.22}$$

where $k(a - x)$ is the actual rate in the forward direction and $k'x$ is that of the reverse reaction. When the system reaches equilibrium the rates of the two reactions are equal (§ 30b), so that

$$k(a - x_e) = k'x_e, \tag{57.23}$$

where x_e is the amount of B formed, or of A decomposed, at equilibrium. Substituting the value of k' derived from equation (57.23) into (57.22), the result is

$$\frac{dx}{dt} = k(a - x) - \frac{kx}{x_e}(a - x_e) = \frac{ka}{x_e}(x_e - x). \tag{57.24}$$

Upon integration, recalling that $x = 0$ when $t = 0$, and $x = x$ when $t = t$, it is found that

$$\frac{ka}{x_e} = \frac{1}{t}\ln\frac{x_e}{x_e - x}. \tag{57.25}$$

By means of equation (57.25) it is possible to derive the specific rate k of the forward reaction, by following the course of the reaction in a suitable manner; the amount of B formed at equilibrium, i.e., x_e, must be determined by allowing sufficient time to elapse. From equation (57.23) it follows that ka/x_e is equal to $k + k'$; the latter quantity is therefore also given by (57.25). This equation thus provides a means for evaluating both k and k', the specific rates of the forward and reverse reactions, respectively, from the experimental data.

Methods similar to that just described have been used for the treatment of more complicated reactions; one of these, to which reference may be made, is the dissociation of gaseous hydrogen iodide, viz.,

$$2\text{HI}(g) \underset{k'}{\overset{k}{\rightleftharpoons}} \text{H}_2(g) + \text{I}_2(g).$$

If the initial concentration of the hydrogen iodide is a, and x is the extent of decomposition after time t has elapsed, the concentration of hydrogen iodide at this time will be $a - x$; the concentrations of hydrogen and iodine will both be $\frac{1}{2}x$, since two moles of hydrogen iodide produce one mole of hydrogen and one of iodine upon decomposition. It is found, therefore, that the net rate of the forward reaction is given by

$$\frac{dx}{dt} = k(a - x)^2 - k'(\tfrac{1}{2}x)^2, \tag{57.26}$$

where k and k' are the specific rates of forward and reverse reactions. At equilibrium the rates of the opposing reactions are equal, so that

$$k(a - x_e)^2 = k'(\tfrac{1}{2}x_e)^2, \tag{57.27}$$

and if the value of k' derived from this expression is inserted in equation (57.26), the result can be integrated to give

$$k = \frac{x_e}{2a(a - x_e)t} \ln \frac{x(a - 2x_e) + ax_e}{a(x_e - x)} \tag{57.28}$$

for the specific rate of the forward reaction. By the use of equations (57.27) and (57.28) it is thus possible to evaluate both k and k' from the experimental measurements. Because the dissociation of hydrogen iodide is not accompanied by a change of volume (or pressure), the course of the reaction is followed by rapidly cooling the reaction system and analyzing the mixture.

57j. Equilibrium Constant and Specific Reaction Rate.—For any reversible reaction, the equilibrium constant K is equal to the ratio of the specific rates of forward and reverse reactions; that is,

$$K = \frac{k}{k'}, \tag{57.29}$$

as already mentioned. This relationship is actually implied in equations (57.23) and (57.27), and hence the values of k and k' derived above cannot be used to verify equation (57.29). However, for some reactions it has been found possible to obtain k and k' separately by studying the forward and reverse reactions in the early stages, when the extent of the opposing reaction is negligible. The values derived in this way, therefore, do not involve any reference to equilibrium. If the equilibrium constant is subsequently determined by analysis of the reacting system when equilibrium is attained, it is possible to verify equation (57.29) by comparison with the ratio k/k'.

The necessary information for this purpose has been obtained for the esterification of acetic acid by ethanol, and the reverse reaction, i.e., the hydrolysis of ethyl acetate, viz.,

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O,$$

in the presence of hydrochloric acid as catalyst. Thus, from observations on the early stages of the direct reaction k was found to be 2.38×10^{-4}, while for the reverse reaction k' was 8.15×10^{-5}, the opposing process being ignored in each case. It follows, therefore, that

$$K = \frac{k}{k'} = \frac{2.38 \times 10^{-4}}{8.15 \times 10^{-5}} = 2.92.$$

The equilibrium constant derived from analysis of the system at equilibrium, in the presence of the same concentration of hydrochloric acid, was found to be 2.84. The agreement is as good as could be expected, the difference being probably due to the fact that the solutions do not behave ideally. It will be noted that the equilibrium constant given here is appreciably lower than that in § 32a; this is to be attributed to the change in the medium resulting from the presence of the hydrochloric acid.

57k. Consecutive Reactions.—In accordance with the statements in § 57g, the great majority of reactions involving three or more molecules actually take place in a series of successive stages. If one of the stages is relatively slow and rate-determining, the kinetics of the reaction can often be treated by means of the steady state concept described above. It is of interest, however, to examine the subject of consecutive reactions when the different stages have specific rates of similar magnitude. The simplest case arises when there are two successive stages of the first order, viz.,

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C},$$

where k_1 and k_2 are the two rate constants. If a is the initial concentration of the reactant A, and c_A, c_B and c_C represent the concentrations of A, B and C, respectively, after the lapse of time t from the commencement of the reaction, it follows that

$$a = c_A + c_B + c_C. \tag{57.30}$$

The decomposition of A is a first order process, and hence the rate of its disappearance at any instant is given by

$$\frac{-dc_A}{dt} = k_1 c_A. \tag{57.31}$$

Utilizing the fact that c_A is equal to a when t is zero, and equal to c_A when t is equal to t, integration of equation (57.31) gives the result

$$c_A = ae^{-k_1 t}, \tag{57.32}$$

which is really another form of equation (57.3). The rate at which the concentration of B increases, i.e., dc_B/dt, is equal to the difference between the rate of its formation from A, by equation (57.31), i.e., $k_1 c_A$, and the rate of its decomposition into C, which is $k_2 c_B$; hence

$$\frac{dc_B}{dt} = k_1 c_A - k_2 c_B. \tag{57.33}$$

Introduction of the result of equation (57.32) and subsequent integration leads to the expression

$$c_B = a \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}). \tag{57.34}$$

The equations (57.32) and (57.34) thus give the values of c_A and c_B at any instant; from these results together with equation (57.30), the corresponding concentration c_C is obtained. The general manner in which the concentrations of A, B and C vary with time is shown by the curves in Fig. 57.4. In order to determine k_1 and k_2 it is necessary to know any two of the concentrations; thus, if c_A and c_B are found by experiment at any time t, the values of k_1 and k_2 can be readily derived from equations (57.32) and (57.34).

A simple case of consecutive reactions is the acid hydrolysis of an ester of a dibasic acid, e.g., diethyl succinate or diethyl tartrate; the two ester groups are hydrolyzed in turn, thus providing two successive first order reactions. The values of k_1 and k_2 can here be determined independently, as well as by using the equations given above. By making measurements on the diethyl ester in the early stages of the acid hydrolysis, before an appreciable amount of the intermediate monoethyl ester has formed, it is possible to obtain satisfactory values of k_1; the method used is similar to that described in § 57c in connection with the acid hydrolysis of ethyl acetate. A separate set of experiments, with the same acid catalyst, are now made with the monoethyl ester; this is free from complications, and the specific rate k_2 can be calculated from the results.

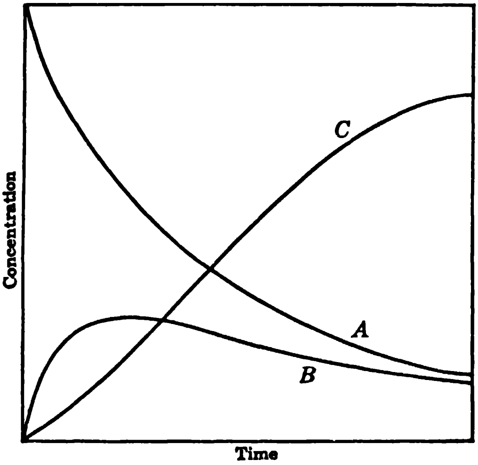


FIG. 57 4. Consecutive reactions A → B → C

57l. Chain Reactions.—A special type of successive reaction phenomenon is encountered in connection with what are known as chain reactions. If a mixture of hydrogen and chlorine gases is exposed to light, the chlorine molecules are dissociated into atoms (§ 62d) and then two successive rapid reactions apparently take place, viz.,

$$Cl + H_2 \rightarrow HCl + H,$$

followed by reaction of the hydrogen atom produced in this manner with the chlorine molecules,

$$H + Cl_2 \rightarrow HCl + Cl.$$

As a result of these two reactions a molecule of hydrogen and one of chlorine have been combined to yield two molecules of hydrogen chloride, but a chlorine atom has been regenerated, and this can set off the combination of further hydrogen and chlorine molecules. The introduction of a few chlorine atoms can thus initiate a chain of consecutive reactions, the two stages depicted above repeating themselves until the reactants are used up. The series of successive processes is referred to as a **chain reaction.** Although it might appear that a chain has unlimited length, ending only when the hydrogen and chlorine have reacted completely, there are always factors operative which tend to terminate or "break" the chains. In the reaction under consideration, for example, removal of the **chain carriers,** that is, the hydrogen and chlorine *atoms*, by any of the processes

$$2H \rightarrow H_2, \qquad 2Cl \rightarrow Cl_2, \qquad \text{and} \qquad H + Cl \rightarrow HCl,$$

will result in the termination of a chain.

All chain reactions are characterized by a mechanism involving the three stages of (1) initiation, (2) propagation and (3) termination. The carriers which propagate the chain are atoms or free radicals and termination occurs most readily by their destruction at the walls of the containing vessel, or, in fact, at any solid surface. The solid acts as a catalyst for the combination of adjacent adsorbed pairs of chain carriers. In addition, the wall dissipates the energy liberated in the combination process. Consequently, the introduction of powdered glass or silica into the reaction vessel is often found to decrease the rate of the reaction, because greater facilities are available for chain breaking. In general, if an increase in the ratio of the surface area to the volume of the vessel decreases the rate of a process, a chain reaction is probably taking place, with the chains being broken at the surface. In some chain reactions, however, the chain termination is brought about mainly by some process taking place within the gas; in cases of this kind, increase of pressure, by increasing the frequency of collisions, often has the effect of decreasing the reaction rate.

Another test for chain reactions, especially those in the gas phase, is based on the observation that traces of certain substances, e.g., nitric oxide and propylene, are able to reduce the rate of a chain process to a few per cent of the original value. The function of these **inhibitors** is apparently to remove the atoms or radicals that would normally act as chain carriers. The phenomenon of "knocking" in the internal combustion engine is associated with a special type of chain which occurs in the reaction between hydrocarbons and oxygen at certain pressures. The presence of small amounts of lead tetraethyl results in the formation of compounds which are able to break the chains, thus permitting a normal type of explosion to take place.

Chain reactions play an important part in many oxidation processes, e.g., of hydrocarbons, carbon monoxide, hydrogen, hydrogen sulfide, phosphine, phosphorus vapor and methanol. It is a remarkable fact that such an apparently simple reaction as the combination of hydrogen and oxygen to form water at 500° to 600°C, is actually a complex process involving reaction chains with hydrogen and oxygen atoms and hydroxyl radicals as chain carriers.

In the decomposition by heat of the vapors of many organic compounds, free radicals frequently act as chain carriers. A fairly simple example is the thermal decomposition of acetaldehyde according to the reaction

$$CH_3CHO = CH_4 + CO,$$

in which free methyl ($CH_3\cdot$) radicals are the chain carriers. The reaction must normally be carried out at temperatures of 500°C or higher, so that sufficient methyl radicals are produced to propagate the reaction chain. However, if azomethane is present, the acetaldehyde decomposition will occur as low as 300°C. At this temperature the azomethane decomposes readily to produce methyl radicals which act as catalysts for the acetaldehyde reaction.

The first (or initiation) step of the thermal decomposition of acetaldehyde is believed to be

$$\text{(I)} \qquad CH_3CHO \rightarrow CH_3\cdot + \cdot CHO \text{ (initiation)}.$$

The $\cdot CHO$ radical probably decomposes rapidly into H and CO and plays a minor part, but the free methyl radical acts as chain carrier according to the reactions

$$\left.\begin{aligned} &\text{(II)} \qquad CH_3\cdot + CH_3CHO \rightarrow CH_4 + CH_3CO\cdot \\ &\text{(III)} \qquad CH_3CO\cdot \rightarrow CO + CH_3\cdot \end{aligned}\right\}\text{(propagation)}$$

by which the methyl radical is regenerated after decomposing a molecule of acetaldehyde. The chains are terminated by the combination of two methyl radicals; thus

$$\text{(IV)} \qquad CH_3\cdot + CH_3\cdot \rightarrow C_2H_6 \text{ (termination)}.$$

The kinetic equation, based on this mechanism, can be readily derived by applying the steady state treatment to the methyl radicals. These are produced in reaction I and removed in IV, so that in the steady state, when the rates of formation and of destruction are equal,

$$k_1(CH_3CHO) = k_4(CH_3\cdot)^2.$$

Reactions II and III can be ignored, since they do not result in any net gain or loss of methyl radicals. The overall rate of reaction, as determined by the production of CH_4, depends on the rate of stage II; so that

$$\text{Reaction rate} = k_2(CH_3\cdot)(CH_3CHO).$$

Upon eliminating the ($CH_3\cdot$) term from these two equations, the result is

$$\text{Reaction rate} = k(CH_3CHO)^{3/2},$$

where $k = k_2(k_1/k_4)^{1/2}$. The reaction is thus of the $\frac{3}{2}$ order, in general agreement with experiment.

It is seen that by applying well established methods of chemical kinetics to the series of reactions involved in the initiation, propagation and termination of reaction chains, it is possible to derive equations expressing the over-all reaction rate in terms of the concentration of the reactants and the specific rate constants of the various stages. In certain cases these expressions reduce to remarkably simple forms in spite of the complexity of the actual reactions. It is possible, for example, for a chain reaction to appear to be kinetically of the first order; consequently, it is necessary to exercise caution in the interpretation of results of reaction kinetics, especially if there are reasons for believing that chains are involved.

It is of interest to mention that the polymerization of many unsaturated compounds, such as ethylene, styrene and vinyl compounds, to produce materials of industrial importance, is a free radical chain process. Polymerization is readily initiated by the introduction of substances which can produce free radicals, e.g., acetone or acetaldehyde exposed to ultraviolet light or benzoyl peroxide. Suppose the unsaturated molecule is $RCH{=}CH_2$ and the initiator is the $CH_3\cdot$ radical; the first reaction is

$$CH_3\cdot + RCH{=}CH_2 \rightarrow R(CH_3)CH{-}CH_2\cdot$$

leading to the formation of another free radical which reacts in turn with $RCH{=}CH_2$ to produce a dimer free radical. This represents the chain propagation, every step involving the production of a radical with an additional $RCH{=}CH_2$. In this respect the polymerization chain propagation differs from most other free radical chains, e.g., decomposition of acetaldehyde where the same radical is regenerated. The process terminates when two free radicals meet and combine to form a molecule. The largely random nature of the chain terminating process accounts for the fact that the polymers contain molecules having different molecular weights.

Direct evidence of the formation of free radicals in chemical reactions has been obtained in various ways. For example, they have been detected by their electronic and other spectra, and also in some cases they have been identified by means of the mass spectrometer.

An interesting procedure for the detection of free radicals, especially the simpler organic radicals, is by means of the mirror technique (F. Paneth, 1929). A film (or mirror) of a metal or metalloid, such as lead, zinc, arsenic, antimony, or tellurium, is deposited on the interior walls of a glass or quartz tube. When a gas containing free, e.g., methyl, radicals is passed through the tube, the radicals will react with the mirror material, which gradually disappears. In the condensate of the effluent gas, the resulting organometallic compound of known composition, e.g., $Pb(CH_3)_4$, $Sb(CH_3)_3$, or $Zn(CH_3)_2$, can be identified.

57m. Branching Chain Reactions.—In the chain reactions considered above, one chain carrier is produced in the propagation phase for each one consumed. This is referred to as a *stationary chain*. In some reactions, however, each propagation cycle serves to increase the number of chain carriers. The result is a **nonstationary** (or **branching**) **chain**, in which the number of carriers increases with great rapidity. Thus if two carriers are produced in each cycle for each one removed, then each of these two will produce two more, and so on. As a result, the rate of production of carriers increases very rapidly and so, correspondingly, does the rate of the overall reaction.

One of the consequences of the formation of branching chains is the phenomenon of explosion limits, discovered independently by N. Semenoff (1927) and C. N. Hinshelwood (1928). It is exhibited by a number of oxidation reactions, e.g., of hydrogen, carbon monoxide, carbon disulfide and phosphine. At a given temperature, lying within a particular range, e.g., about 400° to 600°C for the hydrogen-oxygen reaction, increase of pressure is at first accompanied by a steady increase in reaction rate, as is to be expected. At a certain pressure, however, the reaction suddenly becomes explosive. This means that it is taking place extremely rapidly. The explosive reaction persists with further increase of pressure, but then it suddenly ceases to be explosive and the reaction rate is normal. However, if the pressure is increased still more a condition is once again reached at which the reaction is so rapid as to cause an explosion (Fig. 57.5). These explosion limits may be explained by postulating a branching chain mechanism for the reactions concerned. At low pressures the carriers readily reach the walls of the vessel where they are removed, thus terminating the chains. The rate of reaction is, therefore, not excessive. At a certain pressure, however, the rate of formation of carriers exceeds their rate of destruction at the walls; the reaction rate then becomes so fast that explosion occurs. This represents the condition of the first pressure limit. Further increase of pressure favors termination of the chains by collisions of the carriers in the interior of the gas. Eventually, therefore, the second pressure limit is attained where the rate of removal of carriers, both in the gas and at the walls, exceeds the rate of production. The reaction then becomes nonexplosive in character. At still higher pressures, represented by the third limit, the explosion may be due in some cases to another chain mechanism not important at lower pressure or it may be thermal in character. In a thermal explosion the rapid reaction is due to an increase in temperature of the gas by the heat generated in the reacting system.

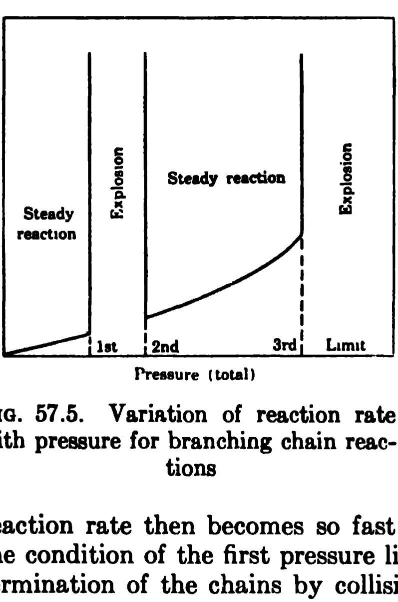


FIG. 57.5. Variation of reaction rate with pressure for branching chain reactions

THEORY OF REACTION RATES

58a. The Effect of Temperature on Reaction Rate: Energy of Activation.—Increase of temperature almost invariably increases the rate of a chemical reaction to a marked extent; for homogeneous processes the specific rate is usually increased by a factor of about two or three for every 10° rise of temperature. The results in Table 58.1, for instance, show the effect of temperature on the rates of two entirely different reactions; they are (I) the decomposition of dibromosuccinic acid in aqueous solution, and (II) the decomposition of nitrogen pentoxide vapor. The actual change of the specific rate varies with the nature of the reaction, but the data in Table 58.1 may be regarded as more or less typical. A rise of about 40° in the temperature is seen to increase the reaction rate from fifty to one hundred fold, in the examples given. It can be readily understood, therefore, why many reactions which are immeasurably slow at ordinary temperatures, e.g., the combination of hydrogen and oxygen, take place with great rapidity as the temperature is raised.

TABLE 58.1. INFLUENCE OF TEMPERATURE ON SPECIFIC REACTION RATE

I		II	
Temp.	Specific Rate	Temp.	Specific Rate
15°C	9.67×10^{-6}	25°C	3.46×10^{-5}
60°	6.54×10^{-4}	45°	4.19×10^{-4}
101°	3.18×10^{-2}	65°	4.87×10^{-3}

The most satisfactory method for expressing the influence of temperature on reaction velocity can be derived by plotting the logarithm of the specific rate, i.e., log k, against the reciprocal of the absolute temperature, i.e., against $1/T$. An illustration of this type of plot, for the decomposition of gaseous hydrogen iodide, is shown in Fig. 58.1; it is seen that the experimental points fall on a straight line, and the same general result has been obtained for almost all reactions. It is evident, therefore, that the variation of the rate constant of a reaction with temperature can be expressed by means of an equation of the form

$$\log k = a - \frac{b}{T}, \tag{58.1}$$

where a and b are constants for the given reaction; T is the absolute temperature. It is usual to write equation (58.1) in the exponential form, involving the Boltzmann factor $e^{-E/RT}$ (§ 3g), where R is the gas constant; thus,

$$k = Ae^{-E/RT}, \tag{58.2}$$

where the constants A and E are related to a and b, respectively. This is one form of the **Arrhenius equation** (S. Arrhenius, 1889); for reasons which will appear later, A is sometimes called the **frequency factor,** whereas E is the **energy of activation** of the reaction.

Upon taking logarithms of equation (58.2), it is found that

$$\log k = \log A - \frac{E}{2.303RT}, \tag{58.3}$$

which is identical in form with the experimental equation (58.1); it requires the plot of log k against $1/T$ to be linear, the slope being equal to $-E/2.303R$. The constant E, which is characteristic of the reaction and determines the influence of temperature on the reaction rate, can thus be calculated from the value of this slope. The slope of the straight line in Fig. 58.1 is -9.70×10^3.

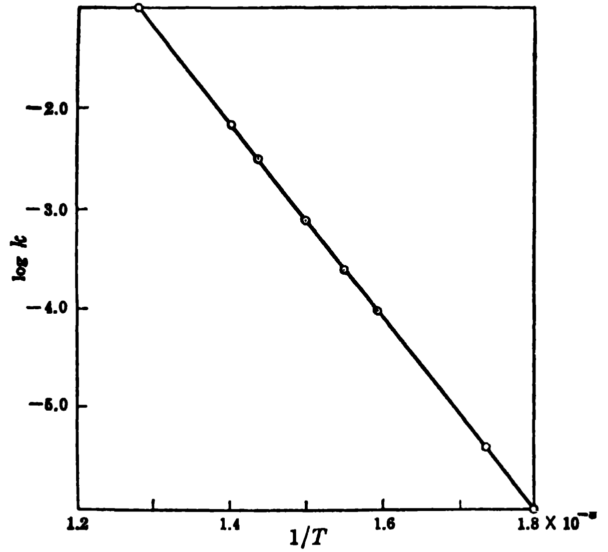


Fig. 58.1. Decomposition of hydrogen iodide

and if R is taken as 1.987 cal, it follows that for the thermal decomposition of hydrogen iodide E is 44,300 cal, or 44.3 kcal.

An alternative method of evaluating E is to take the specific rates k_1 and k_2 for two temperatures T_1 and T_2, and insert them in equation (58.3); if the two resulting expressions are subtracted from one another, it is found that

$$\log \frac{k_2}{k_1} = \frac{E}{2.303R} \cdot \left(\frac{T_2 - T_1}{T_1 T_2} \right). \tag{58.4}$$

Consequently, if the specific rates at two temperatures are known, the value of E can be readily calculated. It may be noted that this expression is similar in form to equation (34.10) which gives the variation with temperature of the equilibrium constant of a reversible reaction. Just as ΔH is an energy quantity in the latter equation, so also is E in equations (58.3) and (58.4).* The ratio k_2/k_1 on the left-hand side of equation (58.4) is dimensionless, and since R has the dimensions of energy per degree, it is evident that E must be an energy term. For the present purpose E is almost invariably expressed in thermal units, i.e., calories or, better, kilocalories.

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* As will be evident shortly, E, like ΔH, is an energy *difference*; it is the common practice, however, to omit the Δ symbol.

Example: Using the data for 25° and 65°C in Table 58.1, calculate E, the energy of activation, for the decomposition of nitrogen pentoxide.

Let 25°C, i.e., 298°K, be T_1, and 65°C, i.e., 338°K, be T_2; then k_1 is 3.46×10^{-5} and k_2 is 4.87×10^{-3}; inserting these values in equation (58.4), the result is

$$\log \frac{4.87 \times 10^{-3}}{3.46 \times 10^{-5}} = \frac{E}{2.303 \times 1.987}\left(\frac{338 - 298}{298 \times 338}\right)$$

$$E = 24{,}800 \text{ cal, or } 24.8 \text{ kcal.}$$

An expression for the actual variation of specific reaction rate with temperature can be readily derived by differentiation of any of the foregoing equations with respect to temperature; the result may be put in the form

$$\frac{d \ln k}{dT} = \frac{1}{k} \cdot \frac{dk}{dT} = \frac{E}{RT^2}.$$

There is evidently a relationship between the temperature coefficient dk/dT and the energy of activation, although it is not possible to state the connection simply in words. However, it can be seen that for two reactions having specific rates of the same order, at approximately the same temperature, the increase of reaction rate with temperature will be greater the greater the energy of activation of the process.

58b. The Collision Theory of Reaction Rates.—Consider a bimolecular reaction between a molecule of A and one of B; for the reaction to occur these two molecules must collide. By the use of equation (3.27) it is possible to calculate the number of such collisions taking place between the molecules of A and B at a given temperature and concentration (or pressure); if this result is compared with the number of molecules reacting, as determined by direct experiment, the number of collisions is almost invariably found to be very much greater. For example, at a temperature of 556°K and a concentration of 1 mole per liter, the number of molecules of hydrogen iodide that collide with each other is calculated to be 6×10^{31} per ml per sec, assuming a collision diameter of 3.5×10^{-8} cm (§§ 3i, 3j). From experiments on the bimolecular dissociation of hydrogen iodide at the same temperature and pressure (concentration), it is found that the number of molecules reacting is only about 2×10^{14} per ml per sec. This means that only one collision in every 10^{17} is effective in bringing about dissociation. Another apparent discrepancy arises when the effect of temperature is considered. It is seen from equations (3.24) and (3.27) that the frequency of binary collisions, i.e., collisions between two molecules, is proportional to $T^{1/2}$. Hence, an increase in temperature, say from 500 to 510°K, will increase the collision frequency by a factor of $(510/500)^{1/2} = 1.01$ or 1 per cent. The rate of chemical reaction, however, may be increased 200 per cent or more.

The experimental facts can be accounted for, however, if it is postulated that reaction occurs when two molecules collide *only if they possess energy in excess of a certain amount;* all other collisions are fruitless and do not lead to reaction. The minimum energy which the molecules must acquire before they can react upon collision is equal, as a first approximation, to the energy of activation E, as derived above from the effect of temperature on reaction rate. As a consequence of the mutual impacts of molecules of gas, there is a continuous interchange of energy between them; as a result there are always a few molecules possessing energies that are greatly in excess of the normal or average value (Fig. 3.2). It is thus possible to have collisions between molecules having the high energy of activation E necessary for reaction, but the number of such collisions will be a very small fraction of the total number of collisions taking place in the gas. This accounts for the fact that only a small proportion of the collisions are effective in leading to reaction. As the temperature is increased, the number of molecules possessing the necessary high energy increases rapidly, and although the total number of collisions is not much changed, the proportion of effective collisions will obviously be greatly increased. The marked effect of temperature on reaction rate can be explained in this manner.

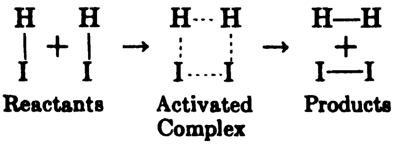
If the molecules A and B taking part in a given reaction could be treated as rigid spheres, possessing only (kinetic) energy of translation, the activation energy would then be restricted to translational energy along the direction in which the molecules collide. In this event, the proportion of collisions in which the molecules possess energy in excess of the minimum amount E required for the reaction is equal to the Boltzmann factor $e^{-E/RT}$. It is the large temperature variation of this factor, rather than of the collision frequency, which can account for the marked increase in reaction rate with temperature. For example, if E is 40,000 cal, then at 500°K, $e^{-E/RT}$ is 4.27×10^{-16}, but at 510°K it is 9.46×10^{-16}, representing an increase by a factor more than two, i.e., over 100 per cent. If Z represents the total number of collisions, as given by equation (3.24) or (3.27), the actual number of collisions leading to reaction should thus be equal to $Ze^{-E/RT}$, since this product gives the number of effective collisions. When the two reacting molecules are the same, as in the dissociation of hydrogen iodide, the number of molecules reacting is equal to twice the number of collisions, and allowance should be made for this fact. Comparison of the theoretical expression $Ze^{-E/RT}$ with the experimental equation (58.2) shows that the former is, at least, of the correct form; the frequency factor A in the Arrhenius equation is thus seen to be equivalent to the collision frequency Z.

As stated earlier, the number of molecules of hydrogen iodide colliding per second at 556°K and a concentration of 1 mole per liter is 6×10^{31} per ml; this is equal to $2Z$, calculated from equation (3.24). Since the activation energy for this reaction was found to be 44,300 cal, it follows that the exponential Boltzmann factor $e^{-E/RT}$, which gives the fraction of effective collisions, at 556°K is $e^{-44{,}300/2 \times 556}$, the value of R being taken, with sufficient accuracy, as 2 cal. This fraction is found to be 5×10^{-18}, and hence the number of molecules reacting per ml should be the product of the total number of molecules colliding, i.e., 6×10^{31} per ml, and the Boltzmann factor 5×10^{-18}, that is, 3×10^{14} molecules per ml. The result is in good agreement with the value given above, i.e., 2×10^{14} molecules per ml, calculated from the experimental data on the dissociation of hydrogen iodide at 556°K and a concentration of 1 mole per liter. Since the value of E used in the foregoing calculations was based on rate measurements over a range of temperatures, equally satisfactory agreement between the observed and calculated reaction rates could be obtained at other temperatures.

It is true that for the dissociation of hydrogen iodide, and also for the combination of hydrogen and gaseous iodine, and in a few other cases, the product of the collision number Z and the exponential factor $e^{-E/RT}$ gives results which agree with the observed reaction rates within a factor of ten. In many other instances, however, the calculated and observed values differ considerably. For the combination of two molecules of ethylene the discrepancy is a factor of about 2,000, while in the reaction between ethanol and acetic anhydride vapors at 79°C, and between carbonyl sulfide and water vapor at about 300°C, the calculated collision theory rates are too large by a factor of 10^5 to 10^6.

In seeking for an explanation of these discrepancies it must be remembered that the identification of $Ze^{-E/RT}$ with the reaction rate is based on the supposition that the reacting molecules behave as rigid spheres, and that the activation energy is translational in character. When the reacting molecules are relatively simple, as in the decomposition of hydrogen iodide or in the combination of hydrogen and iodine, they approximate to rigid spheres, and the calculations given above are roughly applicable. For more complex molecules, on the other hand, the approximation of rigid spheres is not satisfactory, and account must be taken of rotational and vibrational energy, in addition to the translational energy. The molecules acquire the high energy necessary for reaction as a result of interchanges upon impact, but the energy must be properly distributed among the various rotations and vibrations before the reaction can take place. The number of collisions is still given by the value of Z, but the simple factor $e^{-E/RT}$ no longer determines the probability that a collision will result in reaction. No direct method has yet been devised for calculating the fraction of fruitful collisions in the general case of molecules that are not rigid spheres, and so other approaches to the problem have been developed.

58c. The Activated-Complex Theory of Reaction Rates.—One of the most significant treatments of the theory of reaction rates is based on the concept of the existence of an **activated complex** or **activated state** as an intermediate stage in all chemical reactions. In a reaction involving two or more molecules, the reactants, possessing sufficient energy, must approach one another closely; there must then be an appropriate rearrangement of valence bonds and energy so as to give the activated complex characteristic of the given reaction. The activated complex is regarded as a molecule which does not differ from normal molecules, except in one respect; it has a transient existence only, and breaks up at a definite rate to yield the products of the reaction. The bimolecular decomposition of hydrogen iodide, for example, might be represented as follows:



Even in a unimolecular reaction, in which a single molecule takes part in each chemical act, it is necessary for some rearrangement of atoms and energy to occur, giving the requisite activated complex, before reaction can take place. The activation energy of a reaction is then defined as *the additional energy which the reactant molecules must acquire in order to form the activated complex for the reaction.* In other words, it is *the difference in energy of the activated complex and the reactants.*

By supposing that an equilibrium exists between reacting molecules and the activated complex, which decomposes at a definite rate, viz.,

$$\text{Reactants} \rightleftharpoons \text{Activated State} \rightarrow \text{Products},$$

it has been found possible to derive an equation for the specific rate of any reaction, namely

$$k = \frac{RT}{Nh} K^{\ddagger}, \tag{58.5}$$

where R and T have their usual significance; N is the Avogadro number, h is Planck's quantum theory constant (§ 15b), and $K^{\ddagger}$ is the equilibrium constant of the equilibrium between activated state and the reactants (H. Eyring, 1935). In one important development of equation (58.5), the equilibrium constant $K^{\ddagger}$ is expressed in terms of the partition functions (§ 36c) of the substances concerned; the treatment lies beyond the scope of this book, and so it will not be discussed here. Another approach is to utilize the familiar thermodynamic equations (34.1) and (9.6), i.e.,

$$\Delta F^0 = -RT \ln K \qquad \text{and} \qquad \Delta F^0 = \Delta H^0 - T\Delta S^0,$$

to derive the general expression

$$K = e^{-\Delta F^0/RT} = e^{\Delta S^0/R} e^{-\Delta H^0/RT}. \tag{58.6}$$

If the corresponding result for the equilibrium constant $K^{\ddagger}$ is inserted in equation (58.5), it is seen that

$$k = \frac{RT}{Nh} e^{-\Delta F^{\ddagger}/RT} \tag{58.7}$$

$$= \frac{RT}{Nh} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT}, \tag{58.8}$$

where $\Delta F^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ are the standard free energy, entropy and heat of activation, respectively; these quantities represent the difference between the values of the respective thermodynamic functions for the activated complex and the reactants, all the substances being in their standard states of unit activity. Because of the transient nature of the activated complex, there is no hope of being able to determine its thermodynamic properties by direct measurement; useful information can nevertheless be obtained in other ways. It should be noted, incidentally, that the factor RT/Nh in equations (58.5), (58.7) and (58.8) is a universal constant, apart from the temperature, and contains no reference to the reacting substances or to the activated state.

It is seen that according to equation (58.7) *the specific rate of a reaction, at a given temperature, is determined by* $\Delta F^{\ddagger}$, *the free energy of activation.* This is a result of outstanding significance; among other matters, it is evident that *the higher the free energy of activation, the slower the reaction rate at a given temperature.* In equation (58.8) the free energy factor has been replaced by factors involving the entropy and heat of activation. The latter may be identified, at least approximately, with the experimental activation energy E, so that

$$k = \frac{RT}{Nh} e^{\Delta S^{\ddagger}/R} e^{-E/RT}, \tag{58.9}$$

and if this is compared with the Arrhenius equation (58.1), it is seen that the two expressions become identical if the frequency factor A of the latter is represented by

$$A = \frac{RT}{Nh} e^{\Delta S^{\ddagger}/R}. \qquad (58.10)^*$$

In the simple collision theory of reaction rates, discussed in § 58b, the factor A was regarded as equivalent to the collision number Z, but in the present treatment it is seen to have a different meaning. However, for simple molecules, which may be treated as rigid spheres, the value of A as given by equation (58.10) comes out to be the same as the collision frequency. For simple molecules, therefore, the two theories are identical, as they should be. With more complex reactants, when the simple collision theory fails, equation (58.10) is still satisfactory. When the reacting molecules contain relatively large numbers of atoms, the formation of the activated state is usually accompanied by a large decrease of entropy, that is, $\Delta S^{\ddagger}$ has a fairly large *negative* value. In this case the quantity $e^{\Delta S^{\ddagger}/R}$ in equation (58.10) is small, and since RT/Nh is the same for all reactions, it follows that the frequency factor A will be much less than it would be for simple reactants. This accounts for the fact that the experimental value of A is often less than the collision number Z by factors as large as 10^6, as stated in § 58b.

The theory of *unimolecular reactions* is essentially the same as that described above, and equations (58.5), (58.7), etc., are applicable to such reactions. It is, nevertheless, important to consider how the molecules acquire the energy that is necessary before the activated state can be formed. Like all other molecules, those taking part in unimolecular reactions must obtain

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[*] Equations (58.9) and (58.10) provide two alternative ways of calculating $\Delta S^{\ddagger}$ from the Arrhenius equation; the former require E and the latter A.

the energy of activation as the result of interchanges in collisions with other molecules. However, if the molecules decomposed immediately after acquiring the requisite minimum (activation) energy, the reaction rate would be dependent on the number of collisions, and hence on the *square* of the concentration [cf. n^2 in equation (3.24)]. In other words, the reaction would be kinetically of the second order. Nevertheless, first order gas reactions are not uncommon, and the cause of the apparent discrepancy will now be considered.

In order to account for the fact that certain reactions, such as the decomposition of nitrogen pentoxide, are of the first order, it has been suggested that after the molecule of reactant acquires sufficient energy in the course of a collision there is an appreciable delay before decomposition occurs. This delay is presumably due to the necessity for the energy to be distributed in such a way as to form the activated complex appropriate to the reaction. In the period which elapses between the acquisition of the energy and the breaking up of the activated molecule, another collision may ensue in which a large proportion of the energy is removed; if this happens, the molecule will not decompose. At relatively high concentrations (or pressures) the probability of such deactivating collisions is large; hence a fraction only of the molecules which acquire sufficient energy to react actually succeed in doing so. The mathematical treatment, based on the postulate of activation by collision, followed by a delay before decomposition, predicts that, provided the gas concentration is relatively high, the reaction rate will be directly proportional to this concentration, as required for a first order process. At low concentrations (or pressures), on the other hand, the frequency of collisions is diminished and so the probability of deactivating collisions becomes very small; the reaction rate will then be dependent upon the square of the concentration (or pressure). Hence, the unimolecular reaction should behave kinetically as second order; this has been verified experimentally, as indicated by the curve in Fig. 58.2.

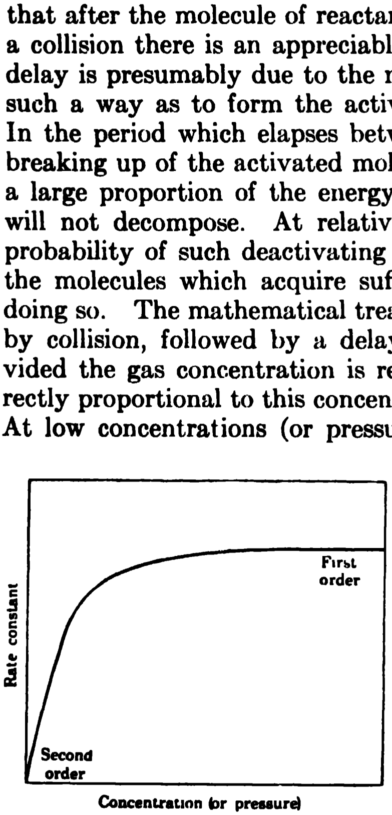

FIG. 58.2. Variation of the rate constant of a unimolecular reaction with concentration or pressure

58d. Prediction of Reaction Rates.—One of the purposes of the theory of reaction rates is to be able to predict the rate of a reaction from a knowledge of the properties of the substances involved. An examination of the Arrhenius equation (58.2) shows that the problem falls into two parts; first, the determination of the frequency factor A, and second, the estimation of the activation energy E. A solution to the first part of the problem is given by equation (58.10), but the theoretical calculation of E is much more difficult. Some progress has been made in this connection by means of quantum (wave) mechanics, but the complex subject is still in the early stages of development. Another method for assessing energies of activation is to make use of the information that is available concerning the strengths of various valence bonds. From a consideration of the nature of the reactants and the products, and the strengths of the bonds that are broken and formed in the course of the reaction, it is often possible to make a fairly reliable estimate of the magnitude of the activation energy. This procedure requires considerable experience and knowledge of the theory of reaction rates.

There is one type of reaction for which it is a simple matter to derive a minimum value, at least, for the energy of activation; thus for an endothermic reaction, for which ΔH is positive, the energy of activation E must be at least equal to the change ΔH in the enthalpy for the complete reaction. In Fig. 58.3 are depicted the energies of reactants, activated state and the products, for exothermic and endothermic reactions, respectively. Since the energy of the activated state must always be in excess of that of both the reactants and the products, it is apparent that for the endothermic reaction, the energy of activation E must be at least as great as ΔH. Hence, *the activation energy of an endothermic reaction must be greater than the heat change accompanying the reaction;* frequently the difference is quite large, but there is no simple method for its estimation.

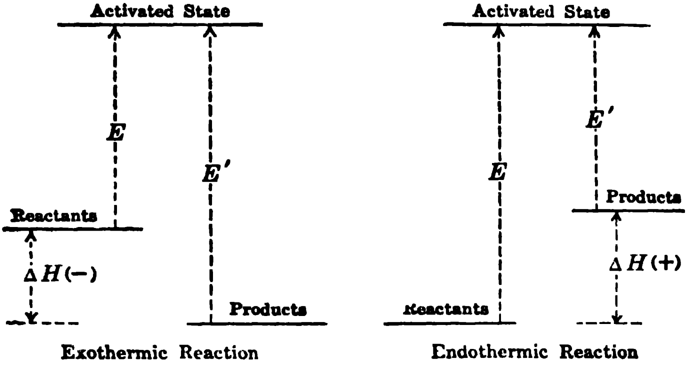

FIG. 58.3. Energy of activation

For an exothermic reaction there is no connection whatever between the activation energy and the overall heat of reaction. However, in the case of a reversible reaction, if E has been determined for the reaction in one direction, the value of E' for the other direction can be readily derived from a knowledge of ΔH for the complete reaction. The activated state is the same for the reaction in either direction, and hence it is seen from Fig. 58.3 that

$$E - E' = \Delta H, \tag{58.11}$$

so that one activation energy can be calculated if the other is known.

Example: For the dissociation of gaseous hydrogen iodide, the energy of activation is 44.3 kcal; determine the activation energy for the reverse reaction, utilizing the fact that ΔH for the formation of a mole of hydrogen iodide from hydrogen and gaseous iodine is -1.35 kcal.

The data given are

$$2\text{HI}(g) = \text{H}_2(g) + \text{I}_2(g) \qquad E = 44.3 \text{ kcal}$$
$$\tfrac{1}{2}\text{H}_2(g) + \tfrac{1}{2}\text{I}_2(g) = \text{HI}(g) \qquad \Delta H = -1.35 \text{ kcal}$$

and from the latter result, it follows that

$$2\text{HI}(g) = \text{H}_2(g) + \text{I}_2(g) \qquad \Delta H = 2 \times 1.35 = 2.70 \text{ kcal.}$$

Combination of this value of ΔH with E for the forward reaction gives E' for the reverse reaction, by equation (58.11), as

$$E' = E - \Delta H = 44.3 - 2.70 = 41.6 \text{ kcal.}$$

The same result may be obtained directly from Fig. 58.4.

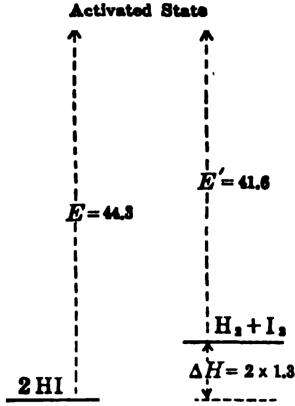

FIG. 58.4. Activation energies in the $2\text{HI} = \text{H}_2 + \text{I}_2$ reaction

In view of the difficulty in deriving the activation energy from theoretical considerations, it is necessary in most cases to obtain the value from measurements of the reaction rate at various temperatures, as explained in § 58a. The problem is then to estimate the frequency factor A for the given reaction, as defined by equation (58.10). The value of R is 8.31×10^7 ergs deg^{-1} mole^{-1}, N is 6.02×10^{23} mole^{-1} and h is 6.62×10^{-27} erg sec; hence

$$A = 2.1 \times 10^{10} T e^{\Delta S^{\ddagger}/R} \text{ sec}^{-1}. \qquad (58.12)$$

There is some uncertainty in assessing $\Delta S^{\ddagger}$ the standard entropy of activation, but from various considerations it is known that for *bimolecular reactions* it usually lies within the range of about -10 to -40 cal deg^{-1} mole^{-1}, if the standard state is taken as corresponding to a concentration of 1 mole per liter; with this standard state the specific reaction rate is given in the familiar (mole/liter)$^{-1}$ sec^{-1} units. If these extreme values for $\Delta S^{\ddagger}$ are inserted into equation (58.12), it follows that for a bimolecular reaction A may be between about 10^8T and 10^2T, so that, utilizing the Arrhenius type of equation,

$$k = 10^2 T e^{-E/RT} \quad \text{to} \quad 10^8 T e^{-E/RT} \text{ liter mole}^{-1} \text{ sec}^{-1}. \qquad (58.13)$$

For simple reacting molecules, such as hydrogen iodide, the frequency factor approaches the higher limit, but with increasing complexity the trend is toward the lower value.

It is evident from equation (58.13) that the rate of a bimolecular reaction is not determined solely by the energy of activation, since the frequency factor can vary over a considerable range. As stated earlier, it is really the *free energy of activation* that is the determining factor. Nevertheless, it is possible to state that for a series of similar reactions, in which the frequency factor does not vary greatly, the higher the energy of activation the slower the reaction at the same temperature. It is found, as a rough approximation, that for a chemical reaction to have an appreciable rate at normal temperatures, i.e., about 300°K, the activation energy must be about 20 kcal, but if the rate does not become measurable until about 600°K, the activation energy will be about 40 kcal.

Example: Estimate the specific rate of the bimolecular dissociation of hydrogen iodide in liters mole^{-1} sec^{-1} units at 556°K, the activation energy being 44.3 kcal.

Since the reacting molecules are simple, it is probable that k is given by the upper limit in equation (58.13), i.e., $k = 10^8 Te^{-E/RT}$; hence, taking R as 2 cal,

$$k = 10^8 \times 556 \times e^{-44{,}300/2\times 556} = 2.8 \times 10^{-7} \text{ liter mole}^{-1} \text{ sec}^{-1}.$$

(The experimental result at 556°K is 3.5×10^{-7} liter mole^{-1} sec^{-1}.)

For *unimolecular reactions* the situation with regard to the entropy of activation is somewhat simpler than for bimolecular reactions; in the majority of unimolecular processes the activated complex has about the same entropy as the reacting molecule, so that $\Delta S^{\ddagger}$ is approximately zero. The expression for A, the frequency factor, then reduces to RT/Nh, and the equation for the specific rate is, from equation (58.9),

$$k = 2 \times 10^{10} Te^{-E/RT} \text{ sec}^{-1}. \tag{58.14}$$

The value of k is, of course, independent of the concentration units, as explained in § 57b. For certain reactions the rates are much slower than is given by equation (58.14), but for a large proportion of unimolecular reactions this equation gives specific rates in fair agreement with those observed experimentally.

It should be noted that if the process under consideration involves chains of appreciable length, the rate constants derived from equations (58.13) and (58.14) are liable to be much too low.

Example: Estimate the specific rate of the unimolecular decomposition of nitrogen pentoxide at 45°C; the activation energy for the reaction is 24.7 kcal.

Since T is $273 + 45 = 318$°K, equation (58.14), with R equal to 2 cal, gives

$$k = 2 \times 10^{10} \times 318 \times e^{-24{,}700/2\times 318} = 0.9 \times 10^{-4} \text{ sec}^{-1}.$$

(The experimental result is 4.9×10^{-4} sec^{-1}, more than five times the estimated value; however, the latter is of the correct order, which is as much as may be expected.)

The equations derived above have referred primarily to gas reactions, but they are probably applicable also to reactions in solution. In a number of cases, e.g., the decomposition of nitrogen pentoxide, the same reactions have been carried out in the gas phase and in an inert solvent; the rates in the two cases have been found to be approximately equal. If there is a tendency for compound formation to take place between the solvent and the reactants, the results may be different.

58e. Ionic Reactions and Salt Effect.—The concept of the formation of an activated complex as an intermediate in the rate-determining stage of a chemical reaction has been used to account for the striking effect of electrolytes on reactions involving ions. The theoretical treatment was originally proposed by J. N. Brønsted (1922), but the simpler form presented by N. Bjerrum (1924) will be given here. Consider a reaction between two species A and B, at least one of which is ionic; it is postulated that the first step is the formation of an activated complex X which subsequently decomposes to form the reaction products; thus

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{X} \xrightarrow{k_x} \text{products.}$$

The rate of reaction, i.e., the rate of formation of products, is proportional to the concentration of activated complex, so that

$$\text{Rate of reaction} = k_x c_x. \tag{58.15}$$

The activated complex is in equilibrium with the reactants A and B, and the equilibrium constant is given by equation (51.2) as

$$K = \frac{a_x}{a_A a_B} = \frac{c_x}{c_A c_B} \cdot \frac{f_x}{f_A f_B}, \tag{58.16}$$

the activities being expressed as the products of the respective concentrations and activity coefficients. Elimination of c_x from equations (58.15) and (58.16) then gives

$$\text{Rate of reaction} = \left(k_0 \frac{f_A f_B}{f_x}\right) c_A c_B, \tag{58.17}$$

where $k_0 = k_x K$.

The ordinary kinetic equation for a bimolecular reaction between A and B is

$$\text{Rate of reaction} = k c_A c_B \tag{58.18}$$

so that, from equations (58.17) and (58.18), the experimental specific rate constant k is given by

$$k = k_0 \frac{f_A f_B}{f_x}$$

or, taking logarithms,

$$\log \frac{k}{k_0} = \log \frac{f_A f_B}{f_x}. \tag{58.19}$$

At infinite dilution, the activity coefficient factor on the right of equation (58.19) would be unity and its logarithm zero; hence, physically k_0 is the specific rate constant of the reaction between A and B extrapolated to infinite dilution. In general, however, $f_A f_B / f_x$ will vary with the ionic strength of the medium, and so the rate constant may also be expected to vary. This is referred to as the **primary salt effect** on ionic reactions.*

The nature of the expected variation is indicated by utilizing the Debye-Hückel equation (51.10) to express the activity coefficients in dilute solutions; thus at 25°C,

$$\log \frac{f_A f_B}{f_x} = -0.509(z_A^2 + z_B^2 - z_x^2)\sqrt{\mu}, \tag{58.20}$$

where z_A, z_B and z_x are the charges carried by A, B and X, respectively. Since $z_x = z_A + z_B$, with the appropriate signs included, equation (58.20) reduces to

$$\log \frac{f_A f_B}{f_x} = +1.018 z_A z_B \sqrt{\mu}.$$

Combination with equation (58.19) then gives

$$\log \frac{k}{k_0} = +1.018 z_A z_B \sqrt{\mu}. \tag{58.21}$$

Thus, if k for the reaction between A and B is determined in the presence of inert electrolyte, at various ionic strengths, the plot of $\log k/k_0$ against $\sqrt{\mu}$ at 25°C should be a straight line of slope $+1.018 z_A z_B$, particularly for dilute solutions.

According to equations (58.21) the variation of the specific rate constant with ionic strength should depend on the magnitude and sign of the product $z_A z_B$. If $z_A z_B$ is positive, i.e., A and B are either both positive or both negative ions, then k should increase with the ionic strength. If one of the reactants is a neutral molecule, $z_A z_B$ will be zero, and k should be independent of the ionic strength. Finally, if $z_A z_B$ is negative, when A and B carry opposite charges, k will decrease as the ionic strength increases. In Fig. 58.5 the small circles represent experimental data for a number of reactions of different types, and the full lines are a plot of equation (58.21) for the corresponding values of $z_A z_B$. The agreement, especially in the more dilute solutions, is seen to be excellent.

HETEROGENEOUS GAS REACTIONS

59a. Kinetics of Heterogeneous Reactions.—The study of the kinetics of heterogeneous reactions between gases taking place on the surfaces of solids has led to the discovery that, in addition to reactions of apparently simple orders, there are others of zero or fractional order. In some cases, further, the reaction is inhibited, instead of accelerated, by increasing the concentration of one of the reacting gases, while in other cases the products may have a retarding influence. The equations for the kinetics of surface reactions

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* Secondary salt effects arise when one of the reactants is a weak electrolyte; the extent of ionization and, hence, the concentration of the ions are then affected by the presence of salts.

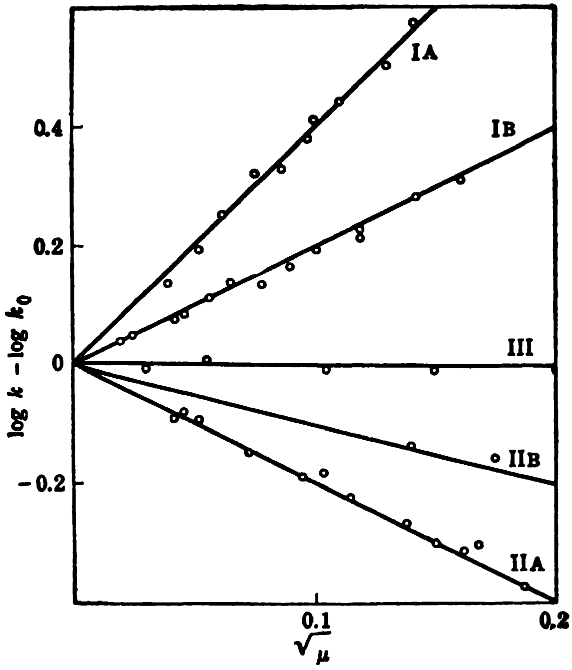

FIG. 58.5. Dependence of reaction rates on ionic strength

IA $2Co[(NH_3)_5Br]^{+2} + Hg^{+2} + 2H_2O = 2Co[(NH_3)_5(H_2O)]^{+3} + HgBr_2$, $z_Az_B = +4$
IB $S_2O_8^{-2} + 2I^- = I_2 + 2SO_4^{-2}$, $z_Az_B = +2$
IIA $Co[(NH_3)_5Br]^{+2} + OH^- = Co[(NH_3)_5(OH)]^{+2} + Br^-$, $z_Az_B = -2$
IIB $H_2O_2 + 2H^+ + 2Br^- = 2H_2O + Br_2$, $z_Az_B = -1$
III $[Cr(NH_2 \cdot CO \cdot NH_2)_6]^{+3} + 6H_2O = [Cr(H_2O)_6]^{+3} + 6NH_2 \cdot CO \cdot NH_2$, $z_Az_B = 0$

may best be developed by following the method of I. Langmuir (1916), as described in connection with the adsorption of gases in § 54d.

Consider, first, the case of a *unimolecular reaction*, involving a single gaseous reactant on the surface of a solid. The rate of reaction will evidently be proportional to the concentration of adsorbed gas on the surface; for a given surface, this is proportional to θ, the fraction of the surface covered by the adsorbed gas. The value of θ is given by equation (54.5) as

$$\theta = \frac{}{kp + k'}, \tag{59.1}$$

where k and k' are constants, and p is the pressure of the gas. The rate of reaction, represented by the general expression dx/dt, is directly proportional to θ, and consequently, by the same procedure as was used in deriving equation (54.6) from (54.5), it follows that

$$\frac{dx}{dt} = \frac{k_1 p}{k_2 p + 1}, \tag{59.2}$$

where k_1 and k_2 are constants.* It is apparent from this result that although the surface reaction is unimolecular, it does not behave, in general, as if it were kinetically of the first order.

At low gas pressures, $k_2 p$ in the denominator of equation (59.2) may be neglected in comparison with unity; hence, the rate equation becomes

$$\frac{dx}{dt} = k_1 p, \tag{59.3}$$

which is the expression for a first order reaction. It is evident, therefore, that a heterogeneous unimolecular reaction is kinetically of the first order only when the reacting gas pressure is low, that is, when the surface of the solid is only sparsely covered. Instances of such behavior are found for the decomposition of phosphine on glass, porcelain and silica surfaces, of nitrous oxide on gold, of hydrogen iodide on platinum, and of formic acid vapor on glass, platinum, and other surfaces.

At sufficiently high pressures, when the surface of the solid is almost completely covered with adsorbed gas, it is possible to neglect unity in comparison with $k_2 p$ in equation (59.2); this equation then becomes

$$\frac{dx}{dt} = \frac{k_1}{k_2} = \text{constant}. \tag{59.4}$$

The rate of the reaction will now be constant, independent of the pressure; such a reaction is said to be kinetically of **zero order.** The decomposition of hydrogen iodide on a gold surface, and of ammonia on surfaces of molybdenum or tungsten, are found to be reactions of zero order, the rates being independent of the pressure over a considerable range. The physical interpretation of this constancy of the reaction rate is that the surface is virtually covered with the reacting gas, and changing the pressure does not have any appreciable effect on the surface concentration of reacting molecules; the rate of decomposition is consequently almost independent of the pressure.

According to equations (59.3) and (59.4) the rate of a surface reaction is proportional to the first power of the gas pressure, at low pressures, and to the zero power at high pressures; it is thus possible to write the general equation

$$\frac{dx}{dt} = kp^n, \tag{59.5}$$

where n varies from unity to zero as the pressure is increased. It can be understood, therefore, why certain surface reactions, such as the decomposition of stibine on an antimony surface, are kinetically of a fractional order, viz., 0.6 in this case. This fractional order would undoubtedly vary with the

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* These values of k_1 and k_2 are, of course, different from those in equation (54.6), because the proportionality constant is not the same.

pressure of the reacting gas, as has been observed in the decomposition of phosphine on a molybdenum surface.

For a *bimolecular reaction* involving two gaseous molecules, it is necessary for the two molecules to be adsorbed adjacent to one another on the surface of the solid. The probability of this occurrence, which determines the reaction rate, is proportional to θ^2, for a single reactant, and to $\theta_A\theta_B$ for two reacting molecules; θ_A and θ_B represent the fractions of the surface covered by the reactants A and B, respectively. If neither of the gases is strongly adsorbed, then at low pressures θ_A and θ_B are proportional to the respective pressures [see equation (54.7)]; the rate of the reaction is then given by

$$\frac{dx}{dt} = k\theta_A\theta_B = k_1p_Ap_B, \tag{59.6}$$

where k and k_1 are constants. Under these conditions the bimolecular heterogeneous reaction would be kinetically of the second order. This type of behavior has been observed for the reaction of ethylene and hydrogen on a copper surface, of hydrogen and carbon dioxide on platinum, and of nitric oxide and oxygen on glass, at low pressures.

The variation with temperature of the specific rate of a simple surface reaction, of the type considered above, can usually be represented by the Arrhenius equation, $k = Ae^{-E/RT}$, where E is the energy of activation. As will be seen later (§ 60d), the activation energy for a heterogeneous reaction is, however, in general, quite different from that for the same reaction taking place in a homogeneous, e.g., gas, phase. Further, although the frequency factor A is still given by equations (58.10) and (58.12), the entropy of activation cannot be estimated in a simple manner, and equations (58.13) and (58.14) are usually not applicable.

If one of the reacting substances is strongly adsorbed, so that it occupies most of the surface, the kinetics of the process is completely changed. In fact, as the pressure of the more strongly adsorbed gas is increased the rate of the surface reaction actually decreases, as will be shown in the following section.

59b. Retardation of Surface Reactions.—Consider a bimolecular heterogeneous reaction between one molecule of a gaseous reactant A and one of a reactant B; if the gas A is strongly adsorbed, the fraction θ_A of the surface covered by this reactant at the pressure p_A is given by equation (59.1) as

$$\theta_A = \frac{kp_A}{kp_A + k'}. \tag{59.7}$$

The fraction of the surface covered by the reactant B will be small, and hence the fraction of the surface that is bare may be taken as equal to $1 - \theta_A$; by equation (59.7) this is

$$1 - \theta_A = \qquad kp_A + k'$$

For a strongly adsorbed gas, k', the rate constant for desorption, will also be small, so that it may be neglected in comparison with kp_A, and hence

$$1 - \theta_A = \frac{k'}{kp_A}. \qquad (59.8)$$

The rate of the surface reaction between A and B will depend on the rate at which the B molecules can reach the bare parts of the surface, because there are always A molecules available in the vicinity for reaction to occur. The rate of adsorption of the B molecules on the bare surface, and hence the reaction rate, is proportional to the product of the pressure of the gas B, i.e., p_B, and the fraction $1 - \theta_A$ of the surface that is bare; hence, making use of equation (59.8),

$$\frac{dx}{dt} = k_1 p_B(1 - \theta_A) = k_2 \frac{p_B}{p_A}. \qquad (59.9)$$

The rate of reaction should thus be proportional to p_B, the pressure of the feebly adsorbed gas, and *inversely proportional* to p_A, the pressure of the strongly adsorbed reactant. *The reacting gas* A *thus retards the rate of the surface reaction because it virtually monopolizes the surface and makes it more difficult for* B *to be adsorbed.* A number of instances of this type of kinetics are known; in the combination of carbon monoxide and oxygen on a platinum or a quartz glass surface, the former gas is strongly adsorbed and retards the reaction. In the ethylene-hydrogen reaction on copper at low temperatures, the rate is inversely proportional to the pressure of ethylene; on a nickel surface the hydrogen is strongly adsorbed and retards the formation of ethane.

Not only can one of the reactants retard a heterogeneous reaction by being strongly adsorbed, but a reaction product can function in a similar manner. The principle is identical with that described above; by occupying a large proportion of the surface the product prevents access of the reactant or reactants. As in the preceding case, the rate of reaction is proportional to the pressure of the reacting gas, assuming a single reactant, and to the fraction of bare surface; this leads to a result analogous to equation (59.9), where p_A now represents the pressure of the strongly adsorbed product. Examples of retardation by a reaction product are the thermal decomposition of nitrous and nitric oxides on a platinum surface, when oxygen is strongly adsorbed, and of ammonia, also on platinum, when hydrogen gas is the strongly adsorbed product. The familiar reaction between sulfur dioxide and oxygen on a platinum catalyst is retarded by the product, sulfur trioxide, which is strongly adsorbed.

There are many other cases of unusual kinetics of surface reactions. Sufficient has been stated, however, to indicate the general nature of the results.

CATALYSIS

60a. The Criteria of Catalysis.—The term **catalysis** is applied generally to cases in which *the rate of a chemical reaction is accelerated by the presence of a substance which is itself unchanged chemically in the process.* The substance causing the acceleration is called a **catalyst.** In some cases an added substance retards the rate of a reaction; this is referred to as **negative catalysis.** Many types of catalyzed reactions, both homogeneous and heterogeneous, are known, but in spite of their many differences there are certain characteristics common to them all; these will now be considered briefly.

(i) *The catalyst is unchanged chemically at the end of the reaction.* The total amount of the catalyst is the same at the end as at the beginning of the reaction; hence, it must be unchanged chemically, although it frequently undergoes a change in physical form. For example, manganese dioxide employed to catalyze the decomposition of potassium chlorate can be changed from relatively large crystals to a fine powder, and platinum gauze used as a catalyst for the oxidation of ammonia shows considerable roughening after a few weeks. Since the catalyst undergoes a physical alteration, it probably takes part *chemically* in a certain stage of the reaction and is regenerated, also chemically, in another stage.

(ii) *A small quantity of catalyst is often sufficient to bring about a considerable amount of reaction.* Since the catalyst is not used up in the course of the reaction, a small quantity will often bring about the combination of large quantities of reactants. In some cases minute traces of catalyst are sufficient to cause considerable acceleration of certain reactions, but as a general rule, in a homogeneous reaction that does not involve a chain mechanism, the rate of a catalytic action is proportional to the concentration of the catalyst. For many heterogeneous reactions, also, the rate increases roughly in proportion to the area of the catalyst surface, although the same material in different forms may have quite different activities (§ 60e).

(iii) *The catalyst does not affect the position of equilibrium in a reversible reaction.* Since a catalyst is unchanged chemically at the end of the reaction, it can contribute no appreciable energy to the system; consequently, it follows from thermodynamics that the same position of equilibrium should be ultimately attained whether a catalyst is present or not. This theoretical expectation has been verified experimentally. The function of the catalyst, therefore, is to speed up the attainment of equilibrium without affecting the value of the equilibrium constant. An important consequence of this fact is that, for a reversible process, the catalyst must affect the rates of the forward and reverse reactions to the same relative extent, since the equilibrium constant K is equal to the ratio k/k' of the respective specific rates (§ 57j). Consequently, a good catalyst for the forward reaction will also accelerate the reverse change. In illustration may be quoted the fact that the same catalyst, namely hydrochloric acid, can be employed to facilitate the esterification of an organic acid and also the hydrolysis of the corresponding ester. Other instances will be found in later parts of the present chapter.

There are some cases, e.g., in the esterification process just mentioned, in which the catalyst, i.e., the hydrochloric acid, appears to affect the equilibrium constant (§ 57j); the reason for this lies in the fact that the acid changes the medium to such an extent that the activities differ markedly from the concentrations. If the true equilibrium constants, involving the activities, were evaluated they would be found to be independent of the catalyst.

(iv) *The catalyst does not initiate the reaction; it merely accelerates a reaction that is already occurring, although perhaps extremely slowly.* The criterion that a given reaction should be possible is that the process should be accompanied by a decrease of free energy (§ 35b), but the fact that the reaction is possible gives no indication of whether it will take place at an appreciable rate. If the *free energy of activation* of the reaction, which may bear no relationship to the over-all free energy, is large, the reaction may be so slow as to be undetectable; nevertheless, it is probably true to say that the reaction is taking place. *The function of a catalyst, which speeds up the reaction, is to make the same over-all process take place by an alternative path involving a smaller free energy of activation.* The catalyzed reaction invariably occurs in stages, and the free energy of activation of the slowest of these stages must be appreciably less than for the reaction in the absence of a catalyst. If the frequency factor A in the Arrhenius equation or, in other words, the entropy of activation, is taken as roughly constant, the reaction rate is determined essentially by the energy (heat) of activation. It is possible to state the foregoing conclusions in the following approximate form: *a catalyst causes a given reaction to take place in such stages that the slowest has an activation energy considerably less than for the uncatalyzed reaction.* Experimental data will be quoted later which support this theoretical deduction.

Consider a reaction involving a substance A and a substance B to give AB, viz.,

$$\mathrm{A + B = AB.}$$

If the free energy ΔF for this reaction is negative under the experimental conditions, the process will be possible theoretically, but it may be very slow. Suppose a catalyst C is added which accelerates the formation of AB; the reaction may occur in the following relatively rapid stages,

$$\begin{gathered}\mathrm{A + C \rightarrow AC}\\ \mathrm{AC + B \rightarrow AB + C,}\end{gathered}$$

so that the result is the formation of AB, the catalyst C being regenerated. Substance A is called the **substrate** for catalyst C.[*] The substance AC, which acts as an intermediate and permits the reaction to take place in stages with low activation energies, is referred to as the **substrate-catalyst complex or intermediate compound,** although it is not always a stable compound capable of isolation. Sometimes the intermediate substance can be identified as a known compound, as, for instance, in the combination of hydrogen and oxygen on a copper catalyst. It has been proved that the reaction occurs in the stages

$$\mathrm{2Cu + \tfrac{1}{2}O_2 \rightarrow Cu_2O} \qquad \text{and} \qquad \mathrm{Cu_2O + H_2 \rightarrow H_2O + Cu,}$$

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[*] The term substrate was originally introduced in connection with enzyme catalysis, but it can be used in a more general sense.

so that the intermediate is the familiar substance cuprous oxide. The same is true in the conversion of ethanol to diethyl ether in the presence of sulfuric acid as catalyst; the intermediate compound is then ethyl sulfuric acid in solution. In other cases, however, the intermediate substance may exist on a surface or it may have a transitory existence only, so that it will not be identical with any known compound. This is probably true for the hydrolysis of esters, the inversion of cane sugar, and similar processes catalyzed by acids or bases (§ 60b). For the heterogeneous gas reactions occurring on the surface of a solid catalyst, the intermediate state is probably represented by the reacting molecules adsorbed on the surface.

60b. Homogeneous Catalysis.—Catalytic processes may be considered in separate categories, depending on whether the catalyst is part of the same phase as the reactants, i.e., **homogeneous catalysis,** or whether it forms a separate phase, i.e., **heterogeneous catalysis.** There may be a further subdivision according as the reactants are in the gaseous or liquid phase. Catalyzed homogeneous gas reactions are not very common; one of the best known is the use of nitric oxide to catalyze the combination of sulfur dioxide and oxygen in the "lead chamber" process. Nitric oxide is also able to catalyze the reaction between carbon monoxide and oxygen. The reactions may be written as

$$\tfrac{1}{2}O_2 + NO \rightarrow NO_2 \quad \text{and} \quad NO_2 + SO_2 \rightarrow NO + SO_3,$$
$$\tfrac{1}{2}O_2 + NO \rightarrow NO_2 \quad \text{and} \quad NO_2 + CO \rightarrow NO + CO_2,$$

the nitrogen dioxide being the intermediate compound. It is probable, however, that the actual reactions are much more complicated than these equations would imply.

Another type of catalyzed homogeneous gas reaction is the thermal decomposition of ethers and aldehydes in the presence of iodine as catalyst. Approximate activation energies for the iodine-catalyzed and uncatalyzed decompositions of a number of ethers have been calculated from measurements of the reaction rates at several temperatures (C. N. Hinshelwood, 1929); the results are recorded in Table 60.1. It is seen that the activation energies of the catalyzed reactions are 16.5 to 32.5 kcal less than for the uncatalyzed reactions. At a temperature of 800°K, in the vicinity of which the latter were studied, the increase in reaction rate would be given approximately by a factor of $e^{16,500/2\times 800}$ to $e^{32,500/2\times 800}$, i.e., about 10^4 to 10^8.

TABLE 60.1. ACTIVATION ENERGIES FOR THE THERMAL DECOMPOSITION OF ETHERS

Substance Decomposed	Uncatalyzed	Iodine Catalyzed
Methyl ethyl ether	54.5 kcal	38.0 kcal
Diethyl ether	53.0	34.3
Diisopropyl ether	61.0	28.5

There are many instances of homogeneous catalysis in solution, and perhaps the most important examples are those generally included under the heading of **acid-base catalysis.** It has long been known that hydrogen ions are able to accelerate the inversion of cane sugar, the hydrolysis of esters, and other reactions in aqueous solution; similarly, hydroxyl ions were found to be particularly effective for the mutarotation of glucose, the conversion of acetone into diacetone alcohol, etc. In recent years, however, it has become evident that for many reactions which are catalyzed by hydrogen ions, any protonic acid, i.e., any substance with a tendency to give up a proton (§ 52a), can act as catalyst; this is known as **general acid catalysis.** Similarly, **general base catalysis,** in which all bases, that is, all substances capable of taking up a proton, can act as catalysts, has been shown to occur with reactions catalyzed by hydroxyl ions. For some processes, e.g , the mutarotation of glucose, the hydrolysis of simple esters and the enolization of acetone, both acids and bases have been found to have catalytic action, although bases are, in general, more effective than the corresponding acids. It is of interest to note that it was the discovery of the phenomena of general acid and base catalysis that led to the development of the proton transfer concept of acids and bases.

The measured specific rate constant may in general be expressed as

$$k = k_0 + \Sigma k_{\text{acid}} c_{\text{acid}} + \Sigma k_{\text{base}} c_{\text{base}},$$

where k_0 is the constant for the uncatalyzed reaction and k_{acid} and k_{base} are the catalytic constants for each species of proton acid and base of concentration c_{acid} and c_{base}, respectively, present. The value of k_{acid} is obtained from measurements in strongly acidic solutions where c_{base} is extremely small and k_{base} in strongly basic solutions where c_{acid} is negligible. By determining the rates of the catalyzed reactions under various conditions, it is possible to determine the catalytic effects of individual acids and bases, including those of water, hydrogen ions, hydroxyl ions, undissociated molecules of acids and bases, anions of weak acids, and cations of weak bases. Some of the results obtained for the mutarotation of glucose are given in Table 60.2. The general conclusions reached from these measurements is that *the catalytic efficiency of an acid or base for a given reaction is related to the ionization constant of the acid or base.* The ionization constant is a measure of the tendency of an acid to lose, or of a base to gain, a proton; it appears, therefore, that the addition and removal of protons play an essential part in the mechanism of the catalyzed reactions under consideration.

Acid	k	Base	k
H_3O^+	1.4×10^{-1}	H_2O	9.5×10^{-6}
H_2O	9.5×10^{-6}	OH^-	6×10^{3}
Acetic acid	2×10^{-3}	Acetate ion	2.7×10^{-2}
Mandelic acid	6×10^{-3}	Mandelate ion	1.1×10^{-2}

The mutarotation of glucose, for example, apparently involves the addition of a proton, from the acid catalyst, to the molecule at one point, folowed, or accompanied, by the removal of a proton, by the basic catalyst, from another point in the molecule. Thus, if GH represents α-glucose and HG is the isomeric β-glucose, the acid catalyzed change in water may be represented by

$$GH + H_3O^+ \rightleftharpoons H\overset{+}{G}H + H_2O$$

$$H\overset{+}{G}H + H_2O \rightleftharpoons HG + H_3O^+,$$

the first proton being supplied by the acid H_3O^+ whereas the one discarded is removed by the base H_2O; the intermediate compound $H\overset{+}{G}H$ probably exists as an ion in solution, although it cannot be isolated. Any other mixture of acid and base of suitable strength would be suitable; thus, in the absence of water the base pyridine is a poor catalyst for the mutarotation of tetramethylglucose, and so also is the acid *m*-cresol, but a mixture of pyridine and *m*-cresol is a powerful catalyst.

The homogeneous catalyzed decomposition of hydrogen peroxide in the presence of halogen and halide ions is an example of a steady state process. If a halide ion, preferably in acid solution, is added to hydrogen peroxide, a steady state is soon reached in which the halogen and halide ion concentrations remain constant, and the net reaction is the decomposition of the peroxide, i.e., $2H_2O_2 = 2H_2O + O_2$. At the steady state two "compensating reactions" occur at the same rate. When the bromine-bromide ion system is the catalyst, the processes, each of which undoubtedly takes place in at least two stages, are

$$H_2O_2 + 2H_3O^+ + 2Br^- \rightarrow Br_2 + 4H_2O$$

$$Br_2 + H_2O_2 + 2H_2O \rightarrow O_2 + 2H_3O^+ + 2Br^-,$$

with the result that the peroxide is decomposed catalytically. It must be remembered, however, that these equations represent over-all reactions, and that intermediate stages are undoubtedly involved. The kinetics of the indicated reactions can, in fact, be explained by postulating that HBrO is an intermediate in each case; this is highly probable since it is a constituent of aqueous solutions of bromine.

60c. Negative Catalysis and Inhibition.—A substance that is able to diminish, rather than increase, the rate of reaction is said to be a **negative catalyst** or **inhibitor.** The oxidation of sodium sulfite solution by oxygen gas is inhibited by small amounts of various organic compounds, e.g., alcohols, aniline and benzaldehyde; similarly, the oxidation of benzaldehyde and of other aldehydes is inhibited by anthracene, diphenylamine and other substances. It has been proved that these oxidations are actually chain reactions (§ 571), and the function of the inhibitors in these instances is to terminate the reaction chains by combining with, and thus destroying, the chain carriers.

Negative catalysis in gas reactions is probably to be ascribed similarly to the breaking of reaction chains. Reference was made earlier to the use of lead tetraethyl to reduce "knocking" in the internal combustion engine, and of the property of nitric oxide and propylene of terminating chains. These are all examples of inhibition or negative catalysis. In the case of tetraethyl lead the actual inhibitor is probably finely divided lead dioxide, formed by oxidation, which reacts with and destroys the chain carriers.

60d. Heterogeneous Catalysis Involving Gases.—Reactions between gaseous substances in the presence of a solid catalyst are very common; in fact, the heterogeneous processes considered from the standpoint of their kinetics in § 59a fall into this category. These reactions are all catalyzed by the material of the surface upon which they occur; in the absence of the solid the reaction rates are usually smaller. A number of processes of industrial importance, such as the combination of nitrogen and hydrogen to form ammonia, the oxidation of ammonia, the reduction of carbon monoxide to methanol, and many reactions involving hydrocarbons, require the use of suitable solid catalysts. Some reactions which were at one time thought to be completely homogeneous have been found to take place, at least partly, on the walls of the containing vessel; thus, the combination of ethylene and bromine vapor is inhibited if the interior of the glass reaction vessel is coated with paraffin, but it occurs even more rapidly if stearic acid is used. The formation of ethylene bromide is evidently a heterogeneous reaction which is catalyzed by a glass or a stearic acid, i.e., a polar, surface, but not by paraffin.

In a catalyzed reaction between two gases taking place on the surface of a solid, it is probably necessary that the reacting molecules should be first adsorbed at adjacent points on the surface (§ 59a). If these adsorbed molecules have sufficient energy, they may combine to form the activated complex for the process (§ 58c); this differs from the activated complex of the corresponding homogeneous reaction in being also adsorbed by the catalyst surface. The adsorbed activated complex then decomposes at a definite rate, forming the reaction products which are finally desorbed from the surface and pass into the gas phase. *The basis of heterogeneous catalysis is consequently adsorption, at adjacent positions on the surface, of molecules with sufficient energy to form the adsorbed activated complex.* If one of the reactants is very strongly adsorbed it will prevent access of the other to the surface, and consequently the reaction will be retarded, as explained in § 59b. On the other hand, if neither of the gases is adsorbed to any appreciable extent, the probability of the reacting molecules being adjacent to one another on the surface will be small, and the catalytic effect will not be great. The ideal conditions for catalysis are that both gases should be adsorbed to a moderate extent, but neither so strongly that it covers virtually the whole of the surface.

If the catalyzed reaction is unimolecular in character, involving a single molecular species, e.g., the decomposition of hydrogen iodide on gold or platinum, or of ammonia on tungsten or molybdenum, the process involves the adsorption of a molecule of reactant with sufficient energy to form the adsorbed activated complex. The latter then decomposes and the products are desorbed. Since there is only one reacting substance it would seem that strong adsorption would be advantageous; the larger the amount of surface covered the greater the probability of the formation of the adsorbed activated complex, and hence also the greater the reaction rate.

Both experimental and theoretical considerations lead to the view that the type of adsorption which is a necessary prerequisite to surface catalysis is that referred to in § 54c as chemisorption or activated adsorption. The more general, van der Waals, type of adsorption involves forces that are too feeble to have any appreciable influence on chemical reaction. The stronger forces of a chemical nature operative in chemisorption tend to bring about a partial loosening of the bonds in the adsorbed reacting molecules; the result is that a much smaller amount of energy is sufficient to form the activated complex for the reaction. It is to be expected, therefore, that the activation energy of a surface reaction should be less than for the corresponding homogeneous reaction; that this is the case is indicated by the results in Table 60.3. It is the marked decrease in the energy of activation that is the main reason for the greatly increased rates of catalyzed reactions. Another important factor is the large surface area of the catalyst, since this permits a greater concentration of the activated complex, but calculations have shown that the reduction of activation energy, as compared with the homogeneous reaction, is chiefly responsible for the acceleration of heterogeneous processes.

TABLE 60.3. ACTIVATION ENERGIES OF HOMOGENEOUS AND HETEROGENEOUS REACTIONS

Decomposition of	Surface	Activation Energy	
		Heterogeneous	Homogeneous
Hydrogen iodide	Platinum	25.0 kcal	44.0 kcal
	Gold	14.0	
Nitrous oxide	Platinum	32.5	58.5
	Gold	29.0	
Ammonia	Tungsten	39.0	~80
	Osmium	47.0	

60e. Properties of the Catalytic Surface: Active Centers.—The catalytic activity of a surface, like chemisorption, is specific in nature; there is, in other words, no universal catalyst for all reactions. Some reactions are accelerated by one substance, while others require a surface of an entirely different material. In spite of the many variations, certain generalizations can be made. The metals copper and nickel, in particular, have a strong attraction for hydrogen; hydrogen gas is chemisorbed on surfaces of these metals, and it probably exists there in a form approaching that of the separated atoms. It is consequently not surprising to find that copper and nickel are among the best catalysts for reactions involving the addition to or removal of hydrogen from a molecule, i.e., hydrogenation and dehydrogenation processes. For example, if ethanol vapor is passed over a copper or nickel catalyst at 300° to 400°C, it is dehydrogenated, with the formation of acetaldehyde, thus,

$$CH_3CH_2OH = CH_3CHO + H_2.$$

Similar reactions, involving removal of hydrogen from various alcohols and other organic compounds, are also catalyzed by copper and nickel. In the reduction of carbon monoxide to methanol, which is a hydrogenation process, viz.,

$$CO + 2H_2 = CH_3OH,$$

the catalyst usually employed is a mixture of zinc oxide and chromium sesquioxide; this mixture is known to exhibit marked chemisorption of hydrogen.

Aluminum oxide, in an appropriate physical form, adsorbs water vapor very strongly; this substance is consequently found to be a valuable catalyst for dehydration processes, involving the removal of the elements of water from a molecule of an organic compound. Thus, when ethanol vapor is passed over a surface of alumina the product is ethylene,

$$CH_3CH_2OH = CH_2:CH_2 + H_2O.$$

If zinc oxide is used in place of aluminum oxide, the product is acetaldehyde, as might have been anticipated; since zinc oxide is able to chemisorb hydrogen, the dehydrogenation process would take place in preference to dehydration.

In addition to the chemical nature of the catalyst, the state of its surface is of great importance in determining the rate of a heterogeneous reaction. Not the whole of the surface may be catalytically active, and the reaction may take place at certain points only. These are generally known as **active centers** (H. S. Taylor, 1925), and in the preparation of a catalytic material it is desirable that there should be as large a number as possible of such active centers.

There is much evidence which indicates the existence of regions or centers of special activity on the surface of a catalyst Ethylene and hydrogen, for instance, are both adsorbed by a copper surface, and there they react to form ethane; a trace of mercury reduces the amount of ethylene adsorbed to about 80 per cent, and that of hydrogen to 5 per cent of their respective values on a clean surface. At the same time, however, the rate of production of ethane, by the combination of ethylene and hydrogen, is decreased to less than 0.5 per cent of its initial value. The fact that the catalytic activity is diminished by the mercury to a much greater extent than is the adsorption of the reacting gases, shows that chemical reaction occurs at only a small fraction of the centers of adsorption. If all the parts of the surface were equally active for catalysis, the adsorption and reaction should be affected to the same extent.

Different reactions apparently occur at different active centers on a given surface, for it has been found that the reaction between carbon dioxide and hydrogen on a platinum catalyst can be largely inhibited, while on the same surface the decomposition of nitrous oxide is hardly affected. The exact nature of the active centers is not known, but they may be associated with the orientation of the many small crystals which constitute the catalyst surface. Experiments with single crystals of metals have shown that catalytic effects vary with the crystal planes upon which the reaction occurs. For example, the rate of reaction between hydrogen and oxygen on the (111) plane of a copper crystal is about three times as rapid as on the (100) plane. Similarly, in the catalytic decomposition of carbon monoxide on a nickel crystal, carbon is selectively deposited on the (111) plane. In the preparation of a catalyst, crystal planes of various kinds are exposed and catalytic effects of different magnitude, and even of different type, may depend upon which planes predominate.

60f. Promoters.—It sometimes happens that a mixture of two catalysts is more effective than either alone, e.g., zinc and chromium oxides in the reduction of carbon monoxide to methanol. Such a mixture is known as a **mixed catalyst.** In the extreme case, a small quantity of a material, which is itself either noncatalytic or a feeble catalyst, is able to increase very appreciably the activity of a given catalyst; a substance of this kind is referred to as a **promoter.** Many examples of promoter action are known, and several are of industrial importance. In the combination of nitrogen and hydrogen, the catalyst that has been used is iron, promoted by the addition of small amounts of potassium and aluminum oxides.

Attempts have been made to explain promoter action by changes in the active centers of the catalytic surface, and also by changes in the adsorptive power of the catalyst. It has been established experimentally that chemisorption occurs more readily at a promoted than at an unpromoted surface, but it is doubtful if this alone will account for promoter action. There are probably several factors which are simultaneously operative; these may include the number, spacing and effectiveness of the catalytically active centers.

60g. Retardation and Poisoning.—It was seen in § 59b that if either one of the reactants or one of the products of a reaction is strongly adsorbed by the catalyst, the rate of the reaction may be considerably decreased. This is the phenomenon of **retardation,** the retarding effect being proportional to a simple power of the pressure (or concentration) of the retarding substance. In other cases, purely extraneous materials, often present in very minute amounts, are able to inhibit catalyzed reactions to a marked extent; such substances are called **catalytic poisons.** An example of poisoning was given in § 60e in connection with the ethylene-hydrogen reaction on copper; traces of mercury reduce very greatly the efficiency of the catalyst. In the manufacture of sulfur trioxide from sulfur dioxide and oxygen, arsenic compounds act as poisons for the platinum catalyst; it was this fact which was the cause of the failure of the early attempts to establish this process on the industrial scale. The vanadium pentoxide catalyst, largely used at the present time, is much less sensitive to poisons.

The behavior of a catalytic poison is evidently based on its strong adsorption at the active centers, thus preventing access of the reacting substances. Since these centers constitute a fraction only of the total surface, it is clear that a small amount of poison may have a very considerable effect in reducing the efficiency of a catalyst. Experiments with poisons have confirmed the view that a catalyst may have active centers with different catalytic activities. For example, the rate of reaction of hydrogen with carbon dioxide on nickel is markedly reduced by methane, but the corresponding reaction with nitrous oxide is only slightly decreased.

60h. Enzyme Reactions.—The most important heterogeneous catalyzed reactions occurring in solution are those in which the catalysts are the **enzymes** derived from living organisms. These substances are proteins and so are macromolecular in nature. Each enzyme is specific for a given reaction, although in the case of reversible processes, enzymes, like other catalysts, are able to accelerate both forward and reverse reactions. Further, like the colloidal metals, which they resemble in some respects, enzymes are readily poisoned by traces of the same substances that poison the former catalysts.

The mechanism of enzyme reaction is represented in simplified form as

$$\mathrm{E} + \mathrm{S} \rightleftharpoons \mathrm{ES} \rightarrow \mathrm{E} + \mathrm{P}$$

where E represents the enzyme, S the reactant or substrate, ES the enzyme-substrate complex, and P the reaction products. The rate equation derived from this mechanism is in harmony with the experimental fact that the rate of an enzyme reaction is proportional to the concentration of the substrate, provided this concentration is small. However, at high concentrations of the substrate, the reaction rate becomes independent of the concentration; the reaction is then of zero order. The behavior is analogous to that observed with some homogeneous gas reactions on solid surfaces (§ 59a); when the surface is almost completely covered with reactant, the rate becomes independent of the pressure (or concentration) of the latter. In the case of the enzyme action, similarly, the process will become of zero order when such parts of the macromolecule as are catalytically active are completely covered with substrate. Even if the concentration of the latter is increased beyond this point there can be no further increase in the rate of the reaction, for the given quantity of enzyme.

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PROBLEMS

1. When hydrogen iodide at a concentration of 1.62 millimole per liter was passed through a tube maintained at 700°C, 0.0189 millimole per liter of iodine was produced in a reaction time of 0.486 sec. This concentration of iodine represents 0.0867 of the concentration which would have been attained if the reaction had been allowed to reach equilibrium. Calculate the specific rate constant.

2. A major product of the thermal decomposition of 2-nitropropane is propylene. Its rate of formation is represented by the equation

$$d\,(C_3H_6)/dt = k(C_3H_7NO_2) \text{ with } k = 1.11 \times 10^{11}\, e^{-39{,}300/RT}\ \text{sec}^{-1}.$$

Determine the half-life of the reaction at 300°C, i.e., the time taken for half the initial amount of reactant to be decomposed.

3. The first order rate constant for the pyrolysis of *t*-butyl chloroacetate follows the equation

$$\log k(\text{min}^{-1}) = 33.91 - \frac{36{,}300}{RT}.$$

How long will it take for (*a*) one mole, (*b*) five moles to decompose 25%, 50% and 75% at 227°C?

4. The gas phase reaction, $2NO + 2H_2 \rightarrow N_2 + 2H_2O$, takes place at high temperatures. When equimolecular amounts of nitric oxide and hydrogen were mixed and heated to 826°C, the half-life was found to vary with the total initial pressure as follows:

Pressure, mm	354	288	243	202
$t_{1/2}$, sec	81	140	176	224

Show that the reaction is third order.

5. The catalytic decomposition of nitrous oxide by gold at 900°C and an initial pressure of 200 mm was 50% complete in 53 min and 73% in 100 min. (*a*) What is the order of the reaction? (*b*) How much will decompose in 100 min at the same temperature but at an initial pressure of 600 mm?

6. When ammonia was decomposed by heating to 856°C by the passage of electricity through a tungsten wire, it was found that after 100 sec the ammonia content decreased 13.5 mm when the initial pressure was 100 mm and 14.0 mm when it was 200 mm. What is the order of the reaction?

7. At high temperature dimethyl ether decomposes as follows, $(CH_3)_2O \rightarrow CH_4 + H_2 + CO$. When the reaction was run at 504°C in a closed container, the pressure increased with time as follows:

Time, sec	0	390	665	1195	2240	3155	∞
Pressure, mm	312	408	468	562	714	779	931

Determine (*a*) the order of the reaction, and (*b*) the rate constant. (*c*) The activation energy is 58.5 kcal mole^{-1}. Calculate the frequency factor.

8. The conversion of β-glucose to α-glucose in water solution is a reversible reaction. At 20°C the following polarimetric data were obtained:

Time, min	20	40	60	80	120	360	1440
Angle of rotation, deg	10.81	13.27	15.10	17.47	18.20	20.32	20.39 (equilibrium)

(*a*) Show that the reaction is first order, (*b*) determine the rate constant.

9. The hydrolysis of dimethyl acetal is catalyzed by hydrogen (H_3O^+) ions; at 20°C, $k = 3.92c_{H_3O^+}\ \text{min}^{-1}$. When dissolved in a 5.00×10^{-3} M solution of chloroacetic acid at 20°, k was $8.29 \times 10^{-3}\ \text{min}^{-1}$. (*a*) Calculate K_a' for chloroacetic acid. (*b*) With the aid of the Debye-Hückel equation, evaluate K_a.

10. The rate law for the reaction, $H_2O_2 + 2H_3O^+ + 2Br^- \rightarrow 4H_2O + Br_2$, is $-dc_{H_2O_2}/dt = kc_{H_2O_2}c_{H_3O^+}c_{Br^-}$. At 25°C, k varies with the hydrogen bromide concentration as follows:

HBr, millimole l^{-1}	13.5	22.0	28.8	43.2	67.7
$k \times 10^3$, $l^2\ \text{mole}^{-2}\ \text{min}^{-1}$	377	347	338	318	297

By a suitable plot of the data, determine k_0, the rate constant for the uncatalyzed reaction.

11. The decomposition of benzenediazonium chloride in aqueous solution, $C_6H_5N_2Cl \rightarrow C_6H_5Cl + N_2$ is first order. The variation of the rate constant with temperature is

t°C	20	30	40	50	60
k, min^{-1}	0.00166	0.00678	0.0210	0.0688	0.251

Calculate A and E of the Arrhenius equation for this temperature range.

12. The rate constants, with pressures in mm of Hg, at several temperatures for the second order (gas phase) dimerization of 1,3-butadiene, $2C_4H_6 \rightarrow C_8H_{12}$, are:

t°C	326	341	370	388
$k \times 10^5$, $\text{mm}^{-1}\ \text{min}^{-1}$	2.50	4.15	10.0	17.5

By a suitable plot determine the energy of activation and the frequency factor. Calculate (*b*) the fraction of molecules which have the activation energy at 341°C and (*c*) the number of collisions per sec at a concentration of one mole l^{-1}. The collision diameter of butadiene is 4.5×10^{-8} cm. (*d*) Evaluate k_{341} in terms of liter $\text{mole}^{-1}\ \text{min}^{-1}$.

13. With the aid of the stationary state concept, derive the rate law for each of the following processes:

(*a*) $A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B$ (fast)

$B \xrightarrow{k_3} C$ (slow).

(*b*) $A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} C$ (slow)

$C + D \xrightarrow{k_3} \text{Products}$ (fast).

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Photochemistry

THE LAWS OF PHOTOCHEMISTRY

61a. Introduction.—The subject of **photochemistry** is concerned mainly with *the characteristics of chemical reactions resulting from exposure of a system to radiation* lying in the visible and ultraviolet regions, that is, in the wave length range from 8000 A to 2000 A. Reactions of many types, e.g., synthesis, decomposition, polymerization, isomeric change, oxidation and reduction, can be brought about by exposure to such radiation. Strictly speaking the term "radiation" includes X-rays and gamma rays, and it has also been applied to beams of particles, such as α-rays, electrons, neutrons and protons. The chemical effects produced by these "ionizing" radiations (§ 62k), belong to the field of **radiation chemistry**. Since some aspects of radiation chemistry are related to photochemistry, a brief discussion of the former will be included in this chapter.

There is one respect in which some, but not all, photochemical reactions differ from ordinary chemical processes, usually referred to as "thermal" or "dark" reactions. The latter, as seen in § 35b, are always accompanied by a decrease of free energy of the reacting system; *certain photochemical processes, however, involve an increase of the free energy.** Illustrations of such reactions are provided by the conversion of oxygen into ozone, the decomposition of ammonia, and the polymerization of anthracene; the photosynthesis of carbohydrates and oxygen from carbon dioxide and water falls into the same category. In all these reactions some of the energy of the radiation is converted into free energy of the products; when the source of light is removed, however, the system tends to return to its original state, since this process is accompanied by a decrease of free energy. The change may, nevertheless, take place extremely slowly at ordinary temperatures, as in the case of the reaction between carbohydrates and oxygen to regenerate carbon dioxide and water. On the other hand, if the reverse (dark) reaction is rapid, it may occur simultaneously with the photochemical reaction, and this leads to a state of photochemical equilibrium.

61b. The Absorption of Radiation.—It is to be expected that there should be some relationship between the light absorbed and the chemical change occurring in a photochemical reaction. Such a connection can be

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* Such reactions do not take place spontaneously, i.e., in the absence of light, and so they are not in conflict with the second law of thermodynamics.

stated in terms of the generalization first proposed by T. von Grotthuss (1817) and rediscovered by J. W. Draper (1841). It is usually known as the **Grotthuss-Draper law,** and may be put in the following form: *only those radiations which are absorbed by the reacting system are effective in producing chemical change.* It should be clearly understood that although photochemical reaction can result only from the absorption of radiation, it does not follow that all, or any, of the light absorbed is effective chemically. In certain cases some or all of the light absorbed is converted into heat; that is to say, the energy of the radiation is transformed into kinetic energy of translation of the absorbing molecules. In other instances, *the absorbed radiation is re-emitted as light of the same or another frequency;* this emission of radiation, which occurs immediately after absorption, is known as **fluorescence.**

The relationship between the extent of light absorption and the depth, or thickness, of the absorbing material is given, for a pure substance, by **Lambert's law** (1760); this law states that *equal fractions of the incident radiation are absorbed by successive layers of equal thickness of the light-absorbing substance.* This may be expressed mathematically as

$$\frac{-dI}{db} = kI, \tag{61.1}$$

where I represents the intensity of the radiation and b the thickness of the absorbing material. Upon integration, this gives

$$I = I_0 e^{-kb}, \tag{61.2}$$

where I_0 is the intensity of the incident light, and I is its intensity after the passage through b cm of the given material; the constant k, which is characteristic of the latter, is known as its **absorption coefficient.** It refers to light of a particular wave length, its value varying with the wave length of the absorbed radiation. The intensity I_{abs} of the light absorbed is equal to the difference between the intensities of the incident (I_0) and the transmitted (I) radiation; thus,

$$I_{\text{abs}} = I_0 - I = I_0(1 - e^{-kb}).$$

The light-absorbing properties of a substance are often described in terms of its **molar absorptivity,** a;* this is defined by an alternative form of Lambert's law equation (61.2), viz.,

$$I = I_0 10^{-ab}. \tag{61.3}$$

It followed from equations (61.2) and (61.3) that

$$k = 2.303a, \tag{61.4}$$

which provides the connection between the absorption coefficient and the molar absorptivity.

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* This quantity was formerly called the *extinction coefficient* ϵ, and the name is still used to some extent.

If the absorbing substance is in solution, the relationship between the intensities of the incident and transmitted radiations is given by **Beer's law** (1852), which states that *equal fractions of the incident radiation are absorbed by equal changes in concentration of the absorbing substance in a path of constant length;* that is

$$\frac{-dI}{dc} = k'I.$$

Combination with equation (61.1) followed by integration leads to the alternative forms of the law

$$I = I_0e^{-kbc} \qquad \text{or} \qquad I = I_0 10^{-abc}, \tag{61.5}$$

where c is the concentration of the solution. The corresponding expressions for the light absorbed are

$$I_{\text{abs}} = I_0(1 - e^{-kbc}) = I_0(1 - 10^{-abc}). \tag{61.6}$$

The absorption coefficient and molar absorptivity of the dissolved substance are k and a, respectively; they are related to each other by an expression identical with equation (61.4). Most solutions obey Beer's law if dilute, but divergences are observed in more concentrated solutions; however, Lambert's law is always followed. Beer's law has been used, in conjunction with light absorption measurements, to determine the quantity of a given light-absorbing substance in solution for analytical purposes.

Example: Light of definite wave length was passed through a cell of 5.00 cm thickness containing a 0.0100 molar solution of a given substance; it was found that the intensity of the transmitted light was 0.245 of the incident light. Calculate the molar absorptivity of the dissolved substance.

For this problem it is convenient to use equation (61.5), in which c is 0.0100, and b is 5.00; I/I_0 is 0.245, and hence,

$$\frac{I}{I_0} = 10^{-abc} \qquad \text{or} \qquad 0.245 = 10^{-a\times 5.00\times 0.0100}$$

Taking logarithms, the result is

$$\log 0.245 = -0.0500a$$

$$a = 12.2.$$

If the absorption coefficient k is required, it is best derived from a by the use of equation (61.4).

61c. The Law of the Photochemical Equivalent.—One of the most fruitful generalizations in photochemistry is the **law of the photochemical equivalent,** first proposed by A. Einstein (1905, 1912); according to this law, *each molecule taking part in a chemical reaction, which is a direct result of the absorption of light, takes up one quantum of the radiation causing the reaction.* If ν is the frequency of the absorbed radiation in vibrations per sec, i.e., in sec^{-1} units, the corresponding quantum is equal to $h\nu$ ergs (§ 15b). The energy E absorbed per mole is then

$$E = Nh\nu \text{ ergs per mole.} \tag{61.7}$$

Since ν is equal to c/λ, where c is the velocity of light and λ is the wave length in cm,

$$E = \frac{Nhc}{\lambda} \text{ ergs per mole.}$$

Upon substituting numerical values for N, h and c, this gives

$$\begin{aligned} E &= \frac{6.025 \times 10^{23} \times 6.625 \times 10^{-27} \times 2.998 \times 10^{10}}{\lambda} \\ &= \frac{1.196 \times 10^{8}}{\lambda} \text{ ergs per mole.} \end{aligned}$$

If the wave length is expressed in Angstrom units, i.e., 10^{-8} cm, as is commonly done, this equation becomes

$$E = \frac{1.196 \times 10^{16}}{\lambda} \text{ ergs per mole.}$$

It is more convenient to state the energy in calories or kilocalories, and since 1 cal is equivalent to 4.184×10^7 ergs, it follows that

$$\begin{aligned} E &= \frac{1.196}{\lambda} \times \frac{10^{16}}{4.184 \times 10^{7}} \text{ cal per mole.} \\ &= \frac{2.859}{\lambda} \times 10^{5} \text{ kcal per mole.} \end{aligned} \tag{61.8}$$

The quantity E is sometimes referred to as one **einstein** of radiation of the given wave length λ. The value is seen to decrease with increasing wave length, so that the energy absorbed per mole (or per molecule) is greater at the violet or ultraviolet end of the spectrum and smaller at the red end. The values of the einstein for radiations of different wave lengths, at intervals of 1000 A, in the spectral region of photochemical interest are given in Table 61.1.

TABLE 61.1. VALUES OF THE EINSTEIN AT DIFFERENT WAVE LENGTHS

Wave Length	Color Region	E
2000 A	Ultraviolet	142.95 kcal
3000	Ultraviolet	95.30
4000	Violet	71.48
5000	Blue-green	57.18
6000	Yellow-orange	47.65
7000	Red	40.84
8000	Near infrared	35.74

PHOTOCHEMICAL REACTIONS

62a. The Quantum Yield or Efficiency.—The results of a photochemical process are frequently expressed by means of the **quantum efficiency** or **quantum yield** of the reaction; this is defined as *the number of moles of the light-absorbing substance that react for each einstein of absorbed radiation.*[*] By the law of the photochemical equivalent, *one mole* of the substance should be involved in the reaction which is a *direct result* of the absorption of light, for each einstein absorbed. It is to be expected, therefore, that if the only reaction which occurred in a given process was the one associated with the light absorption, the quantum yield should be unity.

The experimental determination of the quantum yield constitutes one of the main aspects of the study of photochemical changes. For this purpose it is convenient to represent the quantum yield by the expression

$$\text{Quantum yield } (\phi) = \frac{\text{Number of moles reacting}}{\text{Number of einsteins absorbed}}, \qquad (62.1)$$

which is, of course, equivalent to the definition given earlier. The number of moles of the light-absorbing substance that react in a given time can be determined by familiar analytical procedures, adapted to the materials concerned and the experimental conditions. The measurement of the number of einsteins, i.e., of the energy, absorbed requires some consideration. Since the value of the einstein depends on the wave length (or frequency) of the radiation [equation (61.8)], it is desirable in photochemical work that light of a definite wave length, i.e., monochromatic light, or light falling within a narrow range of wave lengths, should be used. Much of the older photochemical research is of little value because of failure to observe this condition. Monochromatic radiation is generally obtained by using discharge tubes which give atomic line spectra; the line of desired wave length is isolated by means of a filter or by passage through a prism in a spectrograph. A device of this kind is called a **monochromator.** The energy of the monochromatic radiation is determined most accurately by means of a thermopile, made up of a large number of junctions of two dissimilar metals, i.e., of thermocouples. The radiation is converted into heat, and the E.M.F. produced by the resulting thermoelectric effect is observed; this provides a measure of the energy of the radiation falling on the thermopile. The measurements are made with and without the reacting system, and the difference gives the amount of energy actually absorbed by the latter.

For many purposes the accuracy of the thermopile is not required, and the energy of the absorbed light is determined by means of an **actinometer;** this is a device for using a photochemical reaction to estimate the absorbed energy. One of these, which has been used in recent years, is the uranyl-oxalate actinometer, consisting of a dilute solution of oxalic acid containing

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[*] An alternative, equivalent definition is the number of *molecules* reacting for each *quantum* of absorbed radiation.

uranyl sulfate. When exposed to ultraviolet or violet light, within the range of about 2540 to 4350 A, the oxalic acid is decomposed;* the extent of decomposition at the conclusion of the experiment is determined by titration with permanganate. The uranyl-oxalate actinometer has been standardized with radiations of various wave lengths, and from the amount of oxalic acid decomposed the amount of energy absorbed can be evaluated. As before, the measurements are made with and without the reacting system in the path of the light; the difference in the energies taken up by the actinometer is equal to the energy absorbed by the reacting substance.

Example: Radiation of wave length 2540 A was passed through a cell containing 10 ml of a solution of 0.0495 molar oxalic acid and 0.01 molar uranyl sulfate; after the absorption of 8.81×10^8 ergs of radiation, the concentration of the oxalic acid was reduced to 0.0383 molar. Calculate the quantum yield for the photochemical decomposition of oxalic acid at the given wave length.

The magnitude of the einstein for radiation of 2540 A is given by equation (61.8); this is in kcal, and upon multiplying by $4.184 \times 10^7 \times 10^3$ the result will be in ergs, i.e.,

$$E = \frac{2.859}{2540} \times 10^5 \times 4.184 \times 10^{10} \text{ ergs.}$$

The number of einsteins absorbed in the experiment is obtained if the 8.81×10^8 ergs is divided by this value of the einstein. The concentration of the oxalic acid is decreased by $0.0495 - 0.0383 = 0.0112$ mole per liter; the quantity of oxalic acid decomposed in 10 ml, the volume of the cell, is therefore 1.12×10^{-4} mole. Hence by equation (62.1)

$$\text{Quantum yield} = \frac{1.12 \times 10^{-4} \times 2.859 \times 4.184 \times 10^{15}}{8.81 \times 10^8 \times 2540}$$

$$= 0.599.$$

The quantum yields of a number of photochemical reactions of different types are given in Table 62.1; the approximate wave length, or range of wave length, of the effective radiation is given in each case. Only in a few instances is the quantum yield equal or close to unity, as required by the law of the photochemical equivalent. In some cases the yields are approximately integers, but in general they range from small fractions, e.g., 0.04 to very large values, e.g., 10^5.

The apparent discrepancies between the Einstein law of the photochemical equivalent and the experimental results can, however, be readily explained. The view is now held that the law applies to what is called the **primary process** of the reaction, in which the light is actually absorbed; that is why the phrase "*direct result* of the absorption of light" is included in the statement of the law (§ 61c). One mole of the light-absorbing substance reacts in the primary process for every einstein, or one molecule per quantum, of absorbed radiation. It frequently happens, however, that the products of the primary process are involved in subsequent thermal (dark) reactions,

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[*] The uranyl ion acts as a photosensitizer for the reaction (§ 62h).

TABLE 62.1. QUANTUM YIELDS OF PHOTOCHEMICAL REACTIONS

Reaction	Wave Length	Yield
Gas Phase		
$2NH_3 = N_2 + 3H_2$	~2100 A	~0.2
$CH_3COCH_3 = CO + C_2H_6$	~3000	~0.3
$2NO_2 = 2NO + O_2$	4050	0.7
$2NO_2 = 2NO + O_2$	3660	1.5
$2HI = H_2 + I_2$	2070-2820	2
$2HBr = H_2 + Br_2$	2070-2530	2
$2Cl_2O = 2Cl_2 + O_2$	3130-4360	3.5
$CO + Cl_2 = COCl_2$	4000-4360	$\sim 10^3$
$H_2 + Cl_2 = 2HCl$	~4000	$\sim 10^5$
Liquid Phase		
Maleic acid → fumaric acid	2000-2800	~0.04
$2Fe^{+2} + I_2 = 2Fe^{+3} + 2I^-$	5790	1
$CH_2ClCOOH + H_2O = CH_2OHCOOH + HCl$	2537	1
$2HI = H_2 + I_2$	3000	1.84
$2H_2O_2 = 2H_2O + O_2$	3100	>7

referred to as the **secondary processes**, in which the molecules of reactant take part. As a result, the *total number* of moles reacting for each einstein of radiation absorbed may differ from unity. In other words, although the quantum efficiency of the primary photochemical process is unity, the over-all yield, as determined from the ultimate results of the reaction, may be quite different. The actual value of the quantum yield provides information which makes it possible to understand the nature of the secondary processes; this will be made clear shortly, when specific photochemical reactions are considered.

62b. The Primary Process and Molecular Spectra.—Since photochemical reaction requires absorption of energy as the first step, the result is that the reacting molecule is raised to a higher energy level. Although energies in the infrared region (see Table 61.1) are, theoretically, sufficient to bring about some chemical reactions, as a result of a vibrational transition alone, no case is known of photochemical reaction in this part of the spectrum. This means that an electronic transition, which accompanies absorption of radiation in the visible or ultraviolet region, is a preliminary to photochemical reaction. The nature of the resulting primary process then depends on the relationship between the upper and lower electronic states of the molecule. The problem can best be considered with the aid of the potential energy curves for the two states.

Four types of behavior are of interest in connection with the primary photochemical process; these are depicted in Fig. 62.1. The transition from the lower to the upper electronic state is represented by a vertical line, starting from a point representing a vibrational level in the lower curve. This is in accordance with the principle enunciated by J. Franck (1925) and E. U. Condon (1926) which states (1) that an electronic transition is more probable when the nuclei are in their extreme positions in an oscillation, and (2) that

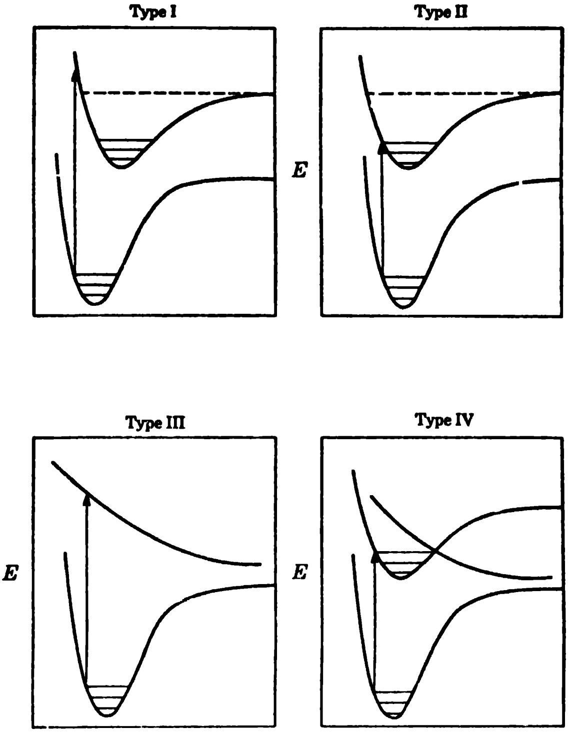

Fig. 62.1. Four types of photochemical primary process

the time required for the electronic transition is so small that the internuclear distance remains unchanged.

In type I, the nature of the potential energy curves is such that in the transition indicated the vibrational energy of the molecule in the upper electronic state exceeds the maximum value. This means that after absorption of energy the molecule will dissociate in its first oscillation. Transitions from lower vibrational levels in the lower electronic state will not be accompanied by dissociation. The electronic spectrum in a case of this kind will consist of a series of discrete vibrational-rotational bands converging to a limit and followed by a region of continuous absorption. The absorption of light in the continuous region of the spectrum results in dissociation of the molecule as the primary photochemical process. In the region of discrete (or banded) structure, dissociation will not occur. The molecule will be in an electronically excited state, with a considerable amount of energy in excess of its normal value. The subsequent behavior of the excited molecule depends upon circumstances, as will be seen below.

In type II, no transition from lower to upper state can result in dissociation of the molecule. The electronic spectrum consists of a series of bands with no continuous region. Absorption of energy can result only in the formation of an electronically excited molecule. The primary photochemical process is then excitation of the absorbing molecule, just as in the banded region in case I.

In case III, which is uncommon, the upper electronic state is completely unstable and has no vibrational levels. The molecular spectrum then has no bands, but is continuous throughout. In these circumstances the electronic transition is always accompanied by dissociation of the molecule.

Finally, there is case IV which is, in a sense, a combination of II and III. There are two upper electronic levels close together; one is like that in case II (stable) and the other like case III (unstable). Transition from the lower state occurs to the stable upper state. However, during the course of a vibration the excited molecule is changed into the unstable state, at the point where the two curves cross; the molecule then dissociates. Behavior of this type is referred to as **predissociation.** The electronic spectrum has a banded structure, but in the region of predissociation the rotational lines are absent, the vibrational bands having a diffuse appearance. The reason for this is that dissociation occurs during a shorter period than is required for the molecule to rotate. If absorption occurs in the diffuse region of the spectrum, the primary photochemical process is dissociation; in the banded region it is electronic excitation, as in cases I and II.

In the following sections some examples will be considered of various kinds of primary photochemical processes and the nature of the subsequent secondary (or thermal) reactions will be discussed.

62c. The Decomposition of Hydrogen Iodide and Hydrogen Bromide.—The photochemical decomposition of hydrogen iodide has been studied with radiations of wave lengths of 2070, 2530 and 2820 A; the quantum yield was found to be very close to 2.0 moles of hydrogen iodide decomposed per einstein of absorbed energy in each case (E. Warburg, 1918). The electronic spectrum of hydrogen iodide is continuous in the region from about 3320 A to below 2000 A wave length; hence, it is clear that, in the experiments referred to, the absorption of radiation must be accompanied by dissociation of the absorbing molecule. The primary photochemical stage may be represented by the equation

$$(1)\quad \mathrm{HI} + h\nu \rightarrow \mathrm{H} + \mathrm{I},$$

where $h\nu$ represents a single quantum of radiation which is absorbed by a molecule of hydrogen iodide, in accordance with the law of the photochemical equivalent. The hydrogen and iodine atoms then undergo the secondary processes

$$(2)\quad \mathrm{H} + \mathrm{HI} \rightarrow \mathrm{H_2} + \mathrm{I}$$

$$(3)\quad \mathrm{I} + \mathrm{I} \rightarrow \mathrm{I_2}.$$

The over-all photochemical process is obtained by adding the primary and secondary stages, i.e., reactions (1), (2) and (3); thus,

$$2HI + h\nu \rightarrow H_2 + I_2,$$

so that two molecules of hydrogen iodide should be dissociated for each quantum, or two moles for each einstein, of radiation absorbed, as found experimentally. The observed results can thus be interpreted by means of the proposed mechanism. It is of interest to note that in the thermal decomposition of hydrogen iodide two molecules interact directly to form a molecule of hydrogen and one of iodine. There are no intermediate steps involving atoms.

As the photochemical decomposition of hydrogen iodide proceeds, the quantum yield is found to fall appreciably below 2.0; the reason is that as the iodine molecules accumulate, the thermal reaction

$$H + I_2 \rightarrow HI + I$$

becomes appreciable. Since this reaction regenerates hydrogen iodide, it will evidently cause a decrease in the over-all efficiency of the photochemical process.

The results of the photochemical dissociation of hydrogen bromide are very similar to those for hydrogen iodide; the quantum yield is initially about 2.0, but it falls off as the proportion of molecular bromine increases. The mechanism of the reaction is presumably analogous to that proposed above for hydrogen iodide. The process involving the regeneration of hydrogen bromide, by the reaction between hydrogen atoms and bromine molecules, probably occurs more readily than does the corresponding reaction with iodine.

62d. The Hydrogen-Halogen Reactions.—One of the most interesting, if perplexing, photochemical processes is the long known reaction occurring between hydrogen and chlorine gases upon exposure to visible or ultraviolet light of wave length less than about 5460 A. The most effective radiation is that of wave length less than 4785 A, which is in the region of continuous absorption of the electronic spectrum of molecular chlorine. The quantum efficiency of the photochemical hydrogen-chlorine reaction is exceptionally high; it varies somewhat with the conditions, but values from 10^4 to 10^6 are not uncommon.

Since the photochemically active radiation falls within the region of continuous absorption of chlorine, the primary stage of the reaction is undoubtedly the dissociation of one molecule per quantum, i.e.,

$$(1) \quad Cl_2 + h\nu \rightarrow 2Cl,$$

in agreement with the Einstein law, and this is followed by the fast reactions

$$(2) \quad Cl + H_2 \rightarrow HCl + H \qquad \text{and} \qquad (3) \quad H + Cl_2 \rightarrow HCl + Cl.$$

The regeneration of the chlorine atom in reaction (3), after the production of two molecules of hydrogen chloride, permits reactions (2) and (3) to occur again, so that a reaction chain is propagated, as explained in § 571. It is seen, therefore, that once the process has been started by the absorption of a single quantum, a very large number of molecules of hydrogen chloride can be formed as a result of the continued repetition of reactions (2) and (3). This accounts for the high observed quantum yield.

The actual efficiency of the photochemical hydrogen-chlorine reaction is determined by the length of the reaction chains, i.e., the number of times reactions (2) and (3) can be repeated, on the average, before the chain is terminated by the removal of either the hydrogen or chlorine atom which is propagating the chain. The most probable chain-terminating process appears to be the recombination of chlorine atoms to form molecules; this may occur either on the walls of the containing vessel or in the gas phase, the relative extents of the two reactions depending on the experimental conditions. It might be supposed that the chains could also be terminated by combination of two hydrogen atoms or of a hydrogen and a chlorine atom, but this is not the case. Since reactions (2) and (3) take place rapidly, the concentration of hydrogen atoms is very much smaller than that of chlorine atoms, so that the rate of the $2H \rightarrow H_2$ and $H + Cl \rightarrow HCl$ reactions are very small.

The recombination of chlorine atoms at the wall involves adsorption of the chlorine atoms as the first (slow) step, followed by combination of two adjacent adsorbed atoms. The process is thus first order with respect to chlorine atoms and is therefore

$$\text{(4a)} \quad Cl \rightarrow \tfrac{1}{2}Cl_2 \text{ (on wall).}$$

Recombination in the gas phase occurs when the two chlorine atoms collide with some third body which serves to remove the energy liberated in the reaction; the reaction is second order with respect to the chlorine atoms, i.e.,

$$\text{(4b)} \quad Cl + Cl \rightarrow Cl_2 \text{ (in gas).}$$

The variation of the overall rate of the photochemical hydrogen-chlorine reaction depends upon which of the two reactions (4a) or (4b) predominates, as will be seen shortly. Comparison of the experimental results and the theoretical equations thus makes possible a distinction between the two mechanisms.

The steady state concept (§ 57g) may be applied to the chlorine atoms and hydrogen atoms since their concentrations are always relatively small. Chlorine atoms are formed in reactions (1) and (3), the rates being $k_1 I_{abs}$ and $k_3(H)(Cl_2)$, respectively.* They are removed by reactions (2), (4a) and (4b) at rates of $k_2(Cl)(H_2)$, $k_4(Cl)$ and $k_4'(Cl)^2$, respectively. For simplicity, the two cases of chain termination at the walls (4a) and in the gas phase (4b) will be considered separately. In the steady state, the total rate of formation of chlorine atoms is equal to the rate of their removal; thus,

$$\text{Case (4a):} \quad k_1 I_{abs} + k_3(H)(Cl_2) = k_2(Cl)(H_2) + k_4(Cl)$$

$$\text{Case (4b):} \quad k_1 I_{abs} + k_3(H)(Cl_2) = k_2(Cl)(H_2) + k_4'(Cl)^2.$$

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* For purposes of clarity, the symbols (H), (Cl_2), etc., are used here in place of the familiar c_H, c_{Cl_2}, etc., to represent concentrations.

Hydrogen atoms are formed in reaction (2) and removed in (3), so that in the steady state

$$k_2(\mathrm{Cl})(\mathrm{H_2}) = k_3(\mathrm{H})(\mathrm{Cl_2}).$$

If this equation is added to each of the preceding ones, the results are, upon rearrangement,

$$\text{Case (4a):} \quad (\mathrm{Cl}) = k_1 I_{\mathrm{abs}}/k_4$$

$$\text{Case (4b):} \quad (\mathrm{Cl}) = (k_1 I_{\mathrm{abs}}/k_4')^{1/2}.$$

The rate of formation of HCl is the sum of the rates of reactions (2) and (3); thus

$$\frac{d(\mathrm{HCl})}{dt} = k_2(\mathrm{Cl})(\mathrm{H_2}) + k_3(\mathrm{H})(\mathrm{Cl_2})$$
$$= 2k_2(\mathrm{Cl})(\mathrm{H_2}),$$

since the steady state conditions for hydrogen atoms requires the rate of reactions (2) and (3) to be equal. Upon inserting the expressions for (Cl) derived above, it follows that

$$\text{Case (4a):} \quad \frac{d(\mathrm{HCl})}{dt} = k(\mathrm{H_2})I_{\mathrm{abs}}$$

$$\text{Case (4b):} \quad \frac{d(\mathrm{HCl})}{dt} = k'(\mathrm{H_2})I_{\mathrm{abs}}^{1/2},$$

the rate being proportional to I_{abs} if the chains are terminated at the walls and to $I_{\mathrm{abs}}^{1/2}$ if termination occurs in the gas phase. The observed rates are found to be proportional to values between $I_{\mathrm{abs}}^{1/2}$ and I_{abs} depending on the experimental conditions.

In the presence of small amounts of oxygen the quantum yield for the photochemical combination of hydrogen and chlorine is greatly reduced; the primary process and the chain-propagating reactions, viz., (1), (2) and (3), are the same as before, but the chain-breaking reactions, upon which the chain length and the quantum yield depend, are quite different. Both chlorine atoms and hydrogen atoms can react with oxygen, ultimately producing chlorine dioxide and water, respectively, so that there are two additional processes whereby the chain carriers can be removed from the reacting system. It can thus be readily understood why the efficiency of the formation of hydrogen chloride is much less in the presence of oxygen than in its absence.

It is somewhat surprising, at first sight, to find that the photochemical hydrogen-bromine reaction has a quantum yield as small as 0.01 molecule of hydrogen bromide per quantum of absorbed radiation at ordinary temperatures, although it increases somewhat as the temperature is raised. From the fact that the active radiation lies in the continuous region of the spectrum of bromine vapor, the primary stage is the dissociation

$$(1) \quad \mathrm{Br_2} + h\nu \rightarrow 2\mathrm{Br}.$$

This is probably followed, as in the chlorine reaction, by

(2) $Br + H_2 \rightarrow HBr + H$ and (3) $H + Br_2 \rightarrow HBr + Br$

but, in contrast to the chlorine reaction which is fast, reaction (2) with bromine atoms is slow, so that rapid propagation of a chain cannot occur. The activation energy for the reaction between chlorine atoms and molecular hydrogen is small, about 5 kcal, and the process occurs very rapidly, thus permitting the propagation of chains. The corresponding reaction between bromine atoms and molecular hydrogen is endothermic to the extent of about 18 kcal, and hence the activation energy must be at least equal to this value (§ 58d); this means that the reaction will undoubtedly be slow. Furthermore, as the reaction proceeds, the reverse of reaction (2) becomes increasingly important, and so the rate of formation of hydrogen bromide is decreased. As a consequence, too, the alternative reaction of bromine atoms, i.e., the recombination to form molecules, takes place more readily. Thus, the efficiency of the formation of hydrogen bromide, occurring through reaction (2), may fall below one molecule per quantum, as is actually the case. If the temperature is raised, the rate of reaction (2) is increased, and so the over all quantum yield is also increased to some extent.

It should be noted that the mechanism of the thermal and photochemical reactions of hydrogen with chlorine and bromine are the same. The first step is the dissociation of the halogen molecule into atoms, in each case, but the source of the energy of dissociation is different. In the thermal reaction it is heat (or kinetic energy) and in the photochemical reaction it is the absorbed radiation. It is for this reason that the photochemical reactions will take place at ordinary temperatures whereas temperatures above 200°C are required for the thermal reactions.

The mechanism of the hydrogen-iodine reaction is quite different from that of the other halogens; the former takes place by direct interaction of the molecules of hydrogen or iodine, even though iodine atoms are undoubtedly present. The reason is that a chain mechanism is impossible because step (2), i.e., the reaction $I + H_2 \rightarrow HI + H$, requires an even greater energy, namely 34 kcal, than does the corresponding step in the hydrogen-bromine reaction. The direct reaction $H_2 + I_2 \rightarrow 2HI$ thus occurs more readily.

62e. Decomposition of Ammonia.—Ammonia gas can be decomposed by radiations of wave length from 1600 to 2200 A; the quantum yield is about 0.15 molecule per quantum, or 0.15 mole per einstein, at 20°C, and about 0.5 at 400°C, the value depending somewhat on the pressure. The electronic spectrum of ammonia in the region of the photochemically active radiation indicates that the primary stage of the reaction involves dissociation, probably

$$NH_3 + h\nu \rightarrow NH_2 + H.$$

The final products of the reaction are nitrogen, hydrogen and hydrazine, which result from the secondary processes

$$NH_2 + NH_2 \rightarrow N_2 + 2H_2, \quad NH_2 + NH_2 \rightarrow N_2H_4 \quad \text{and} \quad H + H \rightarrow H_2.$$

Addition of these equations would indicate a quantum yield of unity; the fact that it is less suggests that the products of the primary stage, i.e., NH_2 and H, recombine to some extent to form ammonia, so that not every molecule absorbing a quantum succeeds in taking part in the secondary reactions following the initial decomposition.

The photochemical decomposition of ammonia and the hydrogen-bromine reactions have one feature in common; the primary stage in each case, i.e., decomposition of ammonia and bromine molecules, is a process involving an *increase* of free energy, made possible only because energy is supplied from an outside source, namely, the absorbed radiation. Consequently, if the products of this stage are not removed rapidly by subsequent, i.e., secondary, processes, they will tend to recombine, since this reaction would be accompanied by a decrease of free energy.

62f. Reactions Involving Excited Molecules.—The photochemical processes described so far have all involved dissociation as the primary stage; some reference will now be made to reactions in which the active radiation falls within the banded spectral region of the absorbing molecule. In these cases the primary stage is not dissociation, but the formation of an "excited" or "activated" molecule possessing energy in excess of the normal due chiefly to an increase in its electronic energy. The excited molecule may then react when it collides with another molecule, or it may lose its energy if it does not, or is unable to, react or combine within a short time. The energy of an excited molecule may undergo a rearrangement whereby the electronic energy is partially converted into vibrational energy, and if this is large enough the molecule may undergo dissociation spontaneously or in a collision with another molecule which may be of the same kind or different. The life of an excited molecule is usually about 10^{-7} to 10^{-8} sec, and hence it can undergo many vibrations and rotations before dissociating; the spectrum will thus exhibit definite structure, in spite of the ultimate dissociation. The term predissociation, used in connection with Fig. 62.1, IV, has been extended to cover behavior of this kind.

Acetone vapor can be decomposed photochemically over a range of wave lengths in the ultraviolet region; some of these lie within the continuous spectrum of acetone 2000 to 2900 A, and the primary photochemical process is then the dissociation of the molecule. The mechanism is probably

$$CH_3COCH_3 + h\nu \rightarrow CH_3\cdot + CH_3CO\cdot$$

followed mainly by the reactions

$$CH_3\cdot + CH_3CO\cdot \rightarrow C_2H_6 + CO \qquad \text{and} \qquad CH_3CO\cdot \rightarrow CH_3\cdot + CO$$

The overall process is, to a large extent,

$$CH_3COCH_3 = CO + C_2H_6.$$

However, photochemical decomposition, although with a low quantum yield, does occur with light that is absorbed in the banded portion of the spectrum 2900-3200 A, so that the primary stage is presumably the formation of an electronically excited molecule; thus, indicating the excited molecule by an asterisk,

$$CH_3COCH_3 + h\nu \rightarrow CH_3COCH_3^*.$$

The electronic excitation is in the C═O bond and in a short time some of the excess energy is transferred to an adjacent C—C bond in amount sufficient for a $CH_3\cdot$ radical to split off. The subsequent reactions are then the same as when the radiation absorbed is in the continuous region. However, because the rearrangement of energy in the excited molecule takes an appreciable time, some of the molecules lose energy in this interval either by re-emission as fluorescence, or by conversion into kinetic energy, i.e., into heat, in a nonreactive collision. The quantum yield is, therefore, less than in the continuous region. Further support for these arguments is provided by the fact that acetone exhibits a faint fluorescence in the blue region of the spectrum.

Another instance of the predissociation phenomenon is provided by the hydrogen-bromine reaction (§ 62d); the rate of reaction is almost the same in the discontinuous (banded) region as in the continuous portion of the bromine spectrum, provided the energy in the former case is sufficient to dissociate the molecule into normal atoms. In the banded region the primary process is the formation of excited Br_2^* molecules, and these subsequently dissociate, probably as the result of a collision, viz.,

$$Br_2 + h\nu \rightarrow Br_2^* \quad \text{and} \quad Br_2^* + X \rightarrow 2Br + X,$$

where X is any molecule, not necessarily bromine.

An example of where dissociation apparently takes place when an excited molecule collides with another molecule of the same species is the photochemical decomposition of nitrosyl chloride in the discontinuous region of light absorption. The first stage is the production of an excited molecule $NOCl^*$, and this reacts when it encounters another nitrosyl chloride molecule,

$$NOCl + h\nu \rightarrow NOCl^*$$

$$NOCl^* + NOCl \rightarrow 2NO + Cl_2,$$

thus accounting for a quantum yield of approximately two.

62g. The Dimerization of Anthracene: Photochemical Equilibrium. —A photochemical reaction that presents a number of particularly interesting aspects is the dimerization, or doubling, of the anthracene molecule, i.e.,

$$\underset{\text{anthracene}}{2C_{14}H_{10}} \rightleftharpoons \underset{\text{dianthracene}}{C_{28}H_{20}},$$

occurring when a solution of anthracene in benzene, or other inert solvent, is exposed to ultraviolet light. In dilute solution the reaction is accompanied by emission of part of the absorbed radiation in the form of fluorescence, and the quantum yield of the dimerization reaction is then small. As the concentration of the anthracene is increased, the fluorescence falls off and the quantum yield of the dimerization increases, at the same time, toward a limiting value; when the latter is attained there is very little fluorescence (Fig. 62.2). This behavior can be accounted for by a simple mechanism.

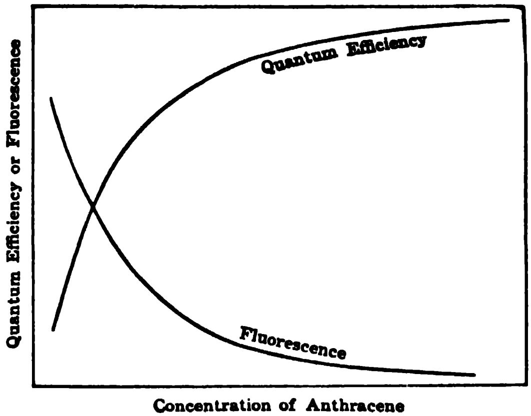

FIG. 62.2. Dimerization and fluorescence of anthracene in solution

The primary process associated with the absorption of the radiation by a molecule A of anthracene is the formation of an electronically excited molecule A*, i.e.,

$$A + h\nu = A^*.$$

This is followed by combination of the excited molecule with another molecule of anthracene, to form a molecule A_2 of dianthracene, i.e.,

$$A^* + A = A_2.$$

When the concentration of anthracene is small, a large proportion of the excited molecules lose their energy as fluorescence, i.e., by the emission of light, before they can encounter another anthracene molecule with which to react. The fluorescence will then be considerable while the quantum yield for the formation of dianthracene will be small. At higher concentrations, however, the frequency of collisions between A* and A molecules is increased, and consequently fewer excited molecules lose their energy by the emission of radiation. The quantum yield thus increases while the fluorescence diminishes correspondingly.

If every excited A* molecule succeeded in combining with another molecule to form A_2, the quantum yield would be two; the maximum observed value is, however, about 0.5. The probable reason for the difference is that some of the A* molecules lose their energy as a result of colliding with solvent molecules; this is a possibility which must always be taken into consideration for photochemical reactions in solution. The energy of the absorbed radiation that is lost in this manner ultimately appears in the form of heat.

As the concentration of anthracene increases another factor becomes operative, namely, the thermal decomposition of dianthracene to regenerate two molecules of anthracene. This, of course, will result in a decrease of the overall efficiency of the photochemical process, but it introduces a new feature into the situation. After the reaction has been proceeding for some time a state of **photochemical equilibrium** is attained, when the rate of formation of A_2 as a result of the action of light on anthracene is exactly balanced by the rate at which A_2 dissociates into simple anthracene molecules as a result of the thermal (dark) reaction. At sufficiently high concentrations of anthracene, when little or none of the absorbed radiation is re-emitted as fluorescence, the rate of photochemical formation of A_2 is proportional to the intensity I_{abs} of the absorbed light; hence,

$$\text{Rate of formation of dianthracene} = kI_{\text{abs}}.$$

It should be noted that the rate of the photochemical process depends only on the energy of the absorbed light, and is apparently independent of the concentration of the anthracene molecules. Actually, of course, the light absorption itself depends on the concentration, in accordance with Beer's law, equation (61.6). The rate of the thermal dissociation of A_2 into anthracene molecules is proportional to the concentration A_2, in accordance with the usual requirements for a unimolecular (thermal) reaction; hence,

$$\text{Rate of dissociation of dianthracene} = k'c_{A_2}.$$

At the photochemical equilibrium state the rates of formation and decomposition of dianthracene are equal, so that

$$kI_{\text{abs}} = k'c_{A_2}$$

$$c_{A_2} = \frac{k}{k'} I_{\text{abs}}. \tag{62.2}$$

The equilibrium concentration of A_2 should thus be proportional to the intensity of the absorbed light; if this intensity is kept constant, the value of c_{A_2} at equilibrium should be independent of the concentration of anthracene. These results emphasize the fact that the ordinary equilibrium constant is not applicable to photochemical equilibrium; the latter is determined by the absorption of energy by the reacting system, and as soon as the source of radiation is removed the system would immediately begin to change toward its normal, or thermal, equilibrium state. Another indication of the difference between photochemical equilibrium and true (or thermal) equilibrium is the fact that the former is unaffected by temperature.

62h. Photosensitized Reactions.—In some photochemical processes the reacting substance is itself unable to absorb the radiation directly, but a suitable atom or molecule, known as a **sensitizer**, absorbs the radiation and passes it on to the reacting molecule. Processes of this type are known as **photosensitized reactions.** A hydrogen molecule, for instance, is unable to absorb the radiation of wave length 2537 A that is emitted in the passage of an electrical discharge through mercury vapor, e.g., in a mercury vapor lamp. Consequently, this radiation cannot bring about dissociation of the hydrogen, in spite of the fact that the value of the einstein corresponding to 2537 A, i.e., 113 kcal, is more than would be required, namely 103 kcal, to dissociate 1 mole of hydrogen molecules into atoms. If a small amount of mercury vapor is added to the hydrogen gas, however, exposure to the 2537 A radiation immediately leads to dissociation. The reaction is photosensitized by the mercury in the following manner. The atoms of mercury in the vapor are able to absorb the radiation, thus forming electronically excited Hg* atoms, possessing 113 kcal per gram atom of excess energy. When these excited atoms collide with hydrogen molecules the 103 kcal required for dissociation are transferred to the latter, and the reaction

$$\mathrm{Hg}^* + \mathrm{H}_2 \rightarrow \mathrm{Hg} + 2\mathrm{H}$$

takes place; the additional 10 kcal are converted into kinetic energy of translation, that is, into heat.

When hydrogen is mixed with oxygen, carbon monoxide, ethylene, nitrous oxide or nitrogen, and a small amount of mercury vapor added, exposure to ultraviolet light of 2537 A wave length leads to a variety of photosensitized hydrogenation reactions. With oxygen, one of the products isolated is hydrogen peroxide, in addition to water. Mercury vapor is also able to sensitize the decomposition of ammonia, water, ethanol and acetone, and the conversion of oxygen into ozone, by means of the 2537 A radiation.

Examples of photosensitization in solution are known; in the uranyl-oxalate actinometer (§ 62a) the uranyl ion acts as a sensitizer for the photodecomposition of the oxalic acid. The processes occurring are excitation of the UO_2^{+2} ion

$$\mathrm{UO}_2^{+2} + h\nu \rightarrow (\mathrm{UO}_2^{+2})^*$$

followed by transfer of the energy to the oxalic acid with resulting decomposition; thus

$$(\mathrm{UO}_2^{+2})^* + \mathrm{H}_2\mathrm{C}_2\mathrm{O}_4 \rightarrow \mathrm{UO}_2^{+2} + \mathrm{CO}_2 + \mathrm{CO} + \mathrm{H}_2\mathrm{O}.$$

In the absence of the uranium compound the quantum efficiency is very low, generally less than 0.01, but for the sensitized reaction it is about 0.5. Uranyl salts also sensitize the photochemical decomposition of formic acid solutions, and ferric salts sensitize the oxidation of potassium ferrocyanide in alkaline solution and other reactions.

The most outstanding illustration of photosensitization is the action of chlorophyll in permitting carbon dioxide and water to react in sunlight, with the eventual formation of carbohydrates and oxygen; this is the process of **photosynthesis** occurring in green plants under the influence of visible light of almost any wave length from 4000 to 7000 A. Neither water nor carbon dioxide absorbs radiations in the visible region, but chlorophyll absorbs over almost the whole range, and particularly in the blue-violet (4700 A) and red

(6500 to 7000 A) regions. The energy of the light absorbed by the chlorophyll is transferred to the reactants, so that the over all reaction

$$CO_2 + H_2O = \tfrac{1}{6}(C_6H_{12}O_6) + O_2$$

can occur. It is a remarkable fact, however, that this process requires energy to the extent of 112 kcal per mole of carbon dioxide and water reacting, and yet, in the presence of chlorophyll, it can take place in red light of 7000 A wave length, which corresponds to only 41 kcal per mole (Table 61.1).

The photosynthetic process is a very complex one, the photochemical and dark stages each consisting of several steps. Since the value of the einstein for red light is 41 kcal, whereas the formation of carbohydrate requires 112 kcal per mole of carbon dioxide, the maximum quantum yield for the reaction in red light will be 41/112, i.e., 0.37, molecule of carbon dioxide and water per quantum of absorbed radiation. The experimental values of the quantum yield apparently vary with the conditions; it rarely exceeds 0.2 and so little more than half of the absorbed energy is actually utilized in photosynthesis. During recent years there has been considerable elucidation of the complicated mechanism of the photosynthetic process by using the isotopic tracer technique (§ 64f). It has been demonstrated that the oxygen liberated in the process comes entirely from the water, and that the oxygen of the carbon dioxide is incorporated into the organic compounds. In the photochemical stage, the energy absorbed by the chlorophyll is transferred to, and activates, an unknown organic compound which then undergoes an oxidation-reduction reaction with water. In the dark stage carbon dioxide reacts with a pentose phosphate to form a product which is readily reduced as the first step in a complicated series of other oxidation-reduction reactions. It should be noted that all of these oxidation-reduction reactions are enzyme catalyzed; some of the enzymes have been identified and isolated.

Another type of photosensitization, in which energy is absorbed at one point but the effect ultimately appears elsewhere, is that involved in the photographic process. A photographic plate consists essentially of a layer of gelatin in which are suspended microcrystals, 10^{-5} to 10^{-4} cm diameter, of a silver halide, usually the bromide. However, traces of certain impurities, e.g., metallic silver or gold or, more commonly, silver sulfide, must be present; these are called sensitizers, although their function is different from that of photosensitizers described above. Silver bromide is ionic in nature and when exposed to light the primary photochemical process is the removal of an electron from the bromide ion, i.e.,

$$Br^- + h\nu \rightarrow Br + \epsilon,$$

to form a bromine atom and a free electron. The quantum yield of this process is unity. The electron is eventually captured by a silver ion, so that a silver atom is produced; the overall reaction is thus the decomposition of silver bromide into elemental silver and bromine.

So far the situation would appear to be relatively simple. A difficulty arises in connection with the fact that, although light is absorbed all over an exposed microcrystal of silver bromide, experiments show that the silver ultimately appears only at a very few isolated points. This pattern of invisible specks of silver, which can be revealed by a mild reducing agent, is called the **latent image.** Upon development each speck acts as a catalytic center for the reduction to visible silver of much of the silver bromide in the exposed microcrystals. The dark color of the small silver crystals, which remain after the unexposed bromide has been dissolved out, gives the familiar blackening of a photographic negative. It is a striking fact that, although something like 10 to 100 silver and bromine atoms are produced in each crystal by exposure to light, approximately a million times this number of silver atoms appear in the final negative.

The mechanism of the formation of the latent image has long been a subject of speculation. The following explanation, however, appears to account for the observations. The removal of a negatively charged electron from the bromide ion in the primary stage leaves a bromine atom which is thus, effectively, a center of positive charge; this is sometimes referred to as a "positive hole" resulting from the removal of an electron. By transfer of an electron from an adjacent bromide ion, which then becomes an atom, the "hole" is transferred to another point in the silver bromide lattice. In a short time, however, the positive "hole" reaches an impurity, e.g., silver sulfide, center and here it is trapped, probably by accepting an electron from the sensitizer.

While this is happening, the electron originally removed from the bromide ion by the light is also moving through the lattice. Since the bromine atom has been trapped, the electron must eventually be captured in another way, and it is apparently a silver ion, located at a crystal imperfection, which takes up the electron to form a silver atom. The latter now becomes an effective center of negative charge. This attracts a free positive silver ion which can migrate through the lattice because the removal of electrons from the bromide ions has made the silver bromide a photoconductor (§ 19d). The second silver ion can now capture another electron released by the absorption of light, thus forming a second silver atom adjacent to the first one. A third silver ion is then attracted, and so on. Thus, essentially the 10 to 100 silver atoms equivalent to the bromine atoms produced in a particular crystal by the primary photochemical process will collect as an invisible speck at one point in the crystal.

62i. Fluorescence and Phosphorescence.—The term **luminescence** is used to describe *the emission of visible radiation that is due to some cause other than temperature*; in other words, luminescence may be regarded as light without heat, or "cold light." At temperatures below about 500°C a body does not normally emit visible or ultraviolet radiation to any appreciable extent, but if by some means it is made to do so, it is described as **luminescent.** The phenomena of fluorescence and phosphorescence, in which radiation absorbed by a molecule is re-emitted at the same or another wave length, are examples of luminescence.

Fluorescence is a general phenomenon; it is exhibited by gases, liquids and solids and by both atoms and molecules. If, as a result of the absorption of radiation, the atom or molecule is raised to a higher electronic state, there is a probability that the excess energy will be emitted within a short time, e.g., about 10^{-8} sec, as fluorescence. Thus electronic excitation is a preliminary step and the wave length of the radiation necessary to achieve this, i.e., visible or ultraviolet, will depend on the energy separation of the two levels. With atoms the wave length of the fluorescence is the same as that of the absorbed radiation; this is referred to as **resonance fluorescence.** With molecules, however, such is rarely the case, the wave length of the fluorescence radiation being longer, i.e., lower frequency, than the absorbed radiation.

The reason for this may be understood from Fig. 62.3 which shows a number of vibrational levels in each of two electronic states of the molecule. Before the absorption of light, most of the molecules are in their lowest ($v = 0$) vibrational level in the lower electronic (ground) state. Upon absorption of radiation, the molecules will occupy several of the vibrational levels of the excited electronic state, as shown in Fig. 62.3. During the 10^{-8} sec (or so) life of the excited state, some of the vibrational energy may be lost by collisions with other molecules, especially in solutions. In any event, when the excess energy is emitted, transitions will take place to various vibrational levels of the ground state. In most cases, the energy of the fluorescent radiation will be less, and hence its wave length will be greater, than that of the exciting (or absorbed) radiation.

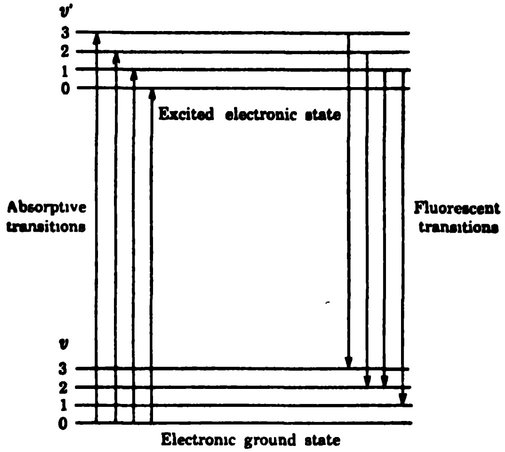

FIG. 62.3. Origin of fluorescence

Emission of fluorescence radiation ceases immediately when the exciting radiation is cut off; if light emission continues for some time, of the order of seconds or more, the phenomenon is called **phosphorescence.** Many dyestuffs, which exhibit fluorescence in aqueous solution, become phosphorescent when dissolved in either fused boric acid or glycerol and the mixture then cooled until its viscosity is very high. In a medium of this type the number of collisions which would remove energy from the excited molecule is greatly decreased.

Phosphorescence has been explained by postulating the existence of an excited energy state somewhat below the upper level involved in fluorescence. Thus, in Fig. 62.4, N represents the normal (or ground) state of the molecule; F is the electronically excited state involved in fluorescence and P is the other excited state. To simplify the representation, vibrational levels are not shown. Transitions from N to P are "forbidden"; that is to say, their probability is very low. Absorption of radiation leads to the $N \rightarrow F$ transition, and the reverse $F \rightarrow N$ transition represents fluorescence. While in the F level, the electronically excited molecule can lose a small amount of energy and make the transition to the P state. The $P \rightarrow N$ transition, like the reverse, is, however, forbidden, and so the molecule will have a relatively long life in the P state. It is possible for the molecule to return to the F state, and then lose its energy in a $F \rightarrow N$ transition accompanied by the emission of radiation. However, in order to do so, the molecule in the P state must acquire an activation energy equal to the energy difference between the F and P states. The process will thus take place relatively slowly and radiation emission will persist for some time.

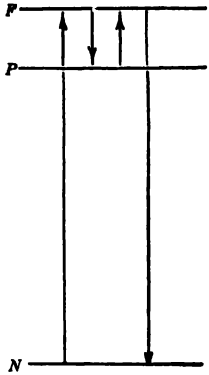

FIG. 62.4. Mechanism of phosphorescence

62j. Chemiluminescence.—When the emission of light, at a temperature at which light rays are not normally to be expected, is the result of a chemical reaction, the effect is known as **chemiluminescence.** In a sense chemiluminescence may be regarded as the reverse of photochemical reaction; in the latter the absorption of radiation leads to chemical change, whereas in the former a chemical reaction is accompanied by the emission of visible radiation. The explanation of chemiluminescence probably lies in the formation of one of the products of the reaction in an electronically excited state. The loss of the excitation energy then occurs by the emission of radiation of the appropriate wave length. In chemiluminescence the energy is such that this wave length falls within the visible region of the spectrum

Many chemical oxidations are associated with luminescence; one of the most familiar is the glow of the element phosphorus and of its trioxide in air. Many Grignard reagents exhibit chemiluminescence when oxidized by air or oxygen, but not when hydrogen peroxide is the oxidizing agent. The oxidation of alkaline aqueous solutions of 5-aminophthalic hydrazide, and of other cyclic hydrazides, by various substances, including hydrogen peroxide, is accompanied by spectacular luminescence. Reference may also be made to the cold light produced by several living organisms; this occurs when a protein derivative, known as luciferin, is oxidized by atmospheric oxygen in the presence of the enzyme luciferase.

62k. Radiation Chemistry.—The chemical effects produced by ionizing radiations have some aspects in common with photochemistry whereas others are different. As with a photochemical reaction, the processes due to ionizing radiation may be distinguished as primary, in which energy is absorbed, and subsequent secondary reactions. In photochemical reactions the primary process yields atoms, free radicals or excited molecules; in a radiochemical reaction ions and electrons are produced in addition. The ions then apparently react with one another to form atoms and free radicals which then undergo thermal reactions in the usual manner.

Whereas the primary photochemical process may depend on the energy of the absorbed light, reactions produced by high-energy particles and radiations are independent of the particle or photon energy. However, the extent of reaction is roughly proportional to the energy absorbed by the reactants. A quantitative measure of these radiation induced effects is given by what is called the **G value** of the reaction. It is defined as *the number of molecules reacting per 100 electron volts of energy absorbed.* This definition may be expressed in another manner which more clearly emphasizes the significance of the G value in chemical terms. The absorption of 1 electron volt (§ 15c) by a molecule is equivalent to N electron volts per mole, where N is the Avogadro number. If ϵ is the electronic charge, $N\epsilon$ is equal to 1 faraday or 96,500 coulombs; hence, N electron volts is equivalent of 96,500 volt-coulombs, or $96{,}500 \times 0.2390 = 23{,}060$ cal. The G value is thus the number of *moles* reacting per 2306 kcal of energy absorbed.

The experimental G values for a few reactions are given in Table 62.2;

TABLE 62.2. G VALUES FOR RADIATION INDUCED REACTIONS

Radiation	Reaction	G
X-rays γ-rays Fast electrons	H_2O (0.01N in H_2SO_4 to neutral) →	H_2 0.45 H 2.57 H_2O_2 0.80 OH 2.05
	Fe^{+2} + air-saturated 0.8NH_2SO_4 → Fe^{+3}	15.45
Co^{60} γ-rays	Styrene → polystyrene	2.08
	Methyl methacrylate → polymer	36.0
Neutrons and fission products (in a nuclear reactor)	$N_2 + 2O_2 \rightarrow 2NO_2$ $N_2 + O_2 \rightarrow NO$ } concurrent	3
	CO_2 (liquid) → $CO + O_2$	4-5

it is seen that G is generally a small number. In other words, only a few moles react for the absorption of over 2000 kcal of energy from the radiation. Normally, chemical reactions rarely require more than 50 kcal per mole, and so it is apparent that, from the energy standpoint, reactions induced by ionizing radiations are not very efficient. Actually, most of the energy of the absorbed radiation appears ultimately as heat and only a small part is utilized in chemical reactions.

When a beam of high-energy radiation (or particles) is passed through matter, very roughly half of the energy absorbed causes ionization of the molecules by ejecting electrons; the remainder produces electronic excitation. In a photochemical process, the excited molecule is in the first electronic level above the ground state. But with high-energy radiation, the energy available is so large that several excited states can be formed in the primary process. The complexity of the secondary stages, involving free radicals, ions and excited molecules, is therefore much greater than in most photochemical reactions.

The chemical effects of various high-energy radiations have been studied in gaseous, liquid and solid phases. The results may be illustrated by a brief consideration of the decomposition of water, although the mechanism of even this reaction has not been definitely established. Following the absorption of energy, the earliest detectable products are hydrogen and hydrogen peroxide, and transient reactive species with properties to be expected from H atoms and OH radicals. These facts may be represented by

$$H_2O \rightsquigarrow \text{Ions and excited molecules} \rightarrow H + OH,$$

where the symbol $\rightsquigarrow$ is conventionally used to represent the absorption of ionizing radiation, followed by

$$H + H \rightarrow H_2 \qquad \text{and} \qquad OH + OH \rightarrow H_2O_2.$$

There is a possibility, too, that H_2 and H_2O_2 are formed directly from two molecules of water without H and OH as intermediates. Competitive with the foregoing reactions are reactions which reform water, e.g., recombination of H and OH, and reactions of the radicals with H_2 and H_2O_2. The yields of the various decomposition products depend to some extent on the nature of the ionization. This difference in behavior is associated with the loss of energy per unit path length of the ionizing radiation. Thus, the relatively heavy alpha particle (helium nucleus) produces a greater concentration of ions and excited molecules than does a beta particle (electron) of the same total energy. The probability of like radicals, i.e., 2H or 2OH, combining to form H_2 and H_2O_2 is thus larger in the former case; in the latter, the recombination reaction of H and OH may be expected to predominate.

Since H atoms can act as reducing agents and OH radicals as oxidizing agents and hydrogen peroxide as both, various oxidation and reduction reactions can result from exposure of aqueous solutions to ionizing radiations. For example, alcohol and ferrous ions are oxidized whereas ceric and dichromate ions are reduced. The oxidation of ferrous sulfate in dilute sulfuric acid is the basis of an "actinometer" for the measurement of ionizing radiation

The detection of H and OH radicals in water exposed to radiation is possible by adding a substance capable of reacting with them. For example, acrylonitrile, which can be polymerized by free radicals, is converted, in water solution, into a polymer containing OH groups when exposed to X-rays or gamma rays. A similar polymer is obtained with OH radicals produced by the photochemical dissociation of hydrogen peroxide. It appears, therefore, that OH radicals are formed in water by the high-energy radiation. If D_2O (heavy water) is used instead of ordinary water, the infrared spectrum of the resulting polymer indicates the presence of C—D bonds. The conclusion to be drawn is that D atoms are formed by the high-energy radiation and so it is probable that H atoms are produced in ordinary water.

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PROBLEMS

1. In the photochemical decomposition of ethylene iodide, $C_2H_4I_2 + h\nu \rightarrow C_2H_4 + I_2$, with radiation of 4240 A, the iodine formed after 20 min required 41.14 ml of 0.00500 N sodium thiosulfate solution. The intensity of the light source was 9.15×10^3 ergs sec^{-1}. Calculate the quantum yield assuming absorption of the energy was complete.

2. The photochemical dissociation of gaseous hydrogen iodide to form normal hydrogen and iodine atoms requires radiation of 4040 A or less. (*a*) Determine the molar heat of dissociation of hydrogen iodide. (*b*) If radiation of 2537 A is used, how much energy will appear as kinetic energy of the atoms?

3. A cell 5.50 cm long and 125 cm^3 capacity contains a gas of molar absorptivity 2.50, at a pressure of 10.0 cm Hg and a temperature of 27°C. If light of 4000 A and intensity 9.05×10^4 erg sec^{-1} is passed through the gas, what percent will be absorbed?

4. When acetone vapor is irradiated with light of wave length 3130 A, it decomposes to form ethane and carbon monoxide, $(CH_3)_2CO + h\nu \rightarrow C_2H_6 + CO$. Using a reaction cell of 60.3 ml capacity and a temperature of 56.0°C, irradiation for 23,000 sec at a rate of 85,200 erg sec^{-1} produced a change in pressure from 760.0 mm to 790.4 mm. Calculate (*a*) the number of molecules of acetone decomposed and (*b*) the quantum yield.

5. Irradiation of *o*-nitrobenzaldehyde in the solid state or in acetone solution by light of 4360–3130 A converts it to the isomeric *o*-nitrosobenzoic acid. In a typical

experiment a solution containing 0.0300 g was irradiated for 220 min at a rate of 3.96×10^{-2} cal sec^{-1}, resulting in the formation of 0.00572 g of acid. Determine the quantum yield.

6. In the photochemical decomposition of acetaldehyde by light of wave length 3100 A, carbon monoxide is produced with a quantum yield of 0.50. Calculate the rate of CO formation for an incident light intensity of 10^6 erg sec^{-1}.

7. The following mechanism has been proposed for the photochlorination of trichloroethylene:

$$\begin{aligned}
&Cl_2 + h\nu \rightarrow 2Cl\\
&Cl + C_2HCl_3 \rightarrow C_2HCl_4\\
&C_2HCl_4 + Cl_2 \rightarrow C_2HCl_5 + Cl\\
&2C_2HCl_4 \rightarrow \text{inert products.}
\end{aligned}$$

With the aid of the steady state treatment, determine the rate law.

8. The photochemical reaction of carbon monoxide and chlorine to form phosgene is a chain reaction for which the mechanism seems to be

$$\begin{aligned}
&Cl_2 + h\nu \rightarrow 2Cl\\
&Cl + CO \rightarrow COCl\\
&COCl \rightarrow CO + Cl\\
&COCl + Cl_2 \rightarrow COCl_2 + Cl\\
&COCl + Cl \rightarrow CO + Cl_2.
\end{aligned}$$

Shows that this mechanism leads to the rate law $d(COCl_2)/dt = kI_{abs}^{1/2}(CO)^{1/2}(Cl_2)$.

18

Nuclear Chemistry

RADIOACTIVITY

63a. Nuclear Reactions.—In chemical reactions there is a rearrangement of the atomic electrons, but the nuclei remain unaffected; that is to say, there is no change in the atomic species taking part in the reaction. It was seen in Chapter 6 that, according to the presently accepted theory, atomic nuclei consist of protons and neutrons; the only exception to this rule is the nucleus of the common hydrogen atom which is a single proton. In a nuclear reaction there is a change in the number of protons or neutrons (or both); the result is, therefore, the formation of a new atomic species. In other words, nuclear reactions lead to atomic transformations or transmutations.

For convenience of discussion, nuclear reactions may be divided into two broad categories: those in which a nucleus undergoes a spontaneous change and those in which the reaction is brought about artificially. The phenomena associated with spontaneous changes of relatively unstable nuclei will be considered in the present section. Many artificial nuclear processes result from the interaction of two nuclei, at least one of which has a large amount of energy. As a general rule, the lighter of the interacting nuclei, commonly a nucleus of hydrogen, i.e., a proton, or of helium, is the one to which the necessary energy is supplied. The manner whereby this is achieved will be described later. An important class of nuclear reactions results from the capture of a neutron by a nucleus. In this case, it is frequently not necessary that either of the interacting particles have energy in excess of its kinetic energy at ordinary temperatures.

63b. Phenomena of Radioactivity.—It was discovered by H. A. Becquerel (1896) that compounds of uranium are capable of spontaneously emitting radiations that are able to effect a photographic plate and produce charged particles, i.e., gaseous ions and electrons, in their passage through air. This phenomenon, which was subsequently called **radioactivity**, was found to be unaffected by the state of combination of the uranium or by the previous history of the element or compound. It was concluded, therefore, that the ability to emit radiations was a characteristic property of the uranium atom. According to modern views, radioactivity is a property of the nucleus, rather than of the atom as a whole, and thus it is a manifestation of spontaneous nuclear reaction.

In the course of an examination of the uranium mineral *pitchblende*, P. and

M. Curie (1898) discovered the element radium, which was even more radioactive than uranium itself. Shortly afterward, G. C. Schmidt and M. Curie independently found that thorium compounds were also active, and since that time over forty radioactive species have been identified as existing in nature. It may be mentioned here that, in addition, several hundred radioactive nuclear species have been obtained as the result of a variety of artificial nuclear reactions of the type indicated above (see § 65e).

The radiations emitted from radioactive substances are of three types, identified by the Greek letters α (alpha), β (beta) and γ (gamma). By deflection of **alpha rays** in electric and magnetic fields, it has been shown that they consist of *particles carrying two unit positive charges and having a mass of four units* on the conventional atomic weight scale. The particles are, in fact, identical with the nuclei of helium atoms. The kinetic energies of the α-particles emitted by a given radioactive substance are either all the same or they fall into a few groups of definite energy. In the study of nuclear reactions, it is the common practice to express energies in terms of the million electron volt (or Mev) unit, where the electron volt (or ev) was defined in § 15c; thus, 1 Mev is equivalent to 1.602×10^{-6} erg. The initial kinetic energies of α-particles emitted by radioactive substances generally lie in the range from 4 to 10 Mev, the corresponding velocities being about 1.4×10^9 to 2.2×10^9 cm per sec.

In its passage through a gas, the energy of an α-particle is largely expended in the removal of extranuclear electrons from the atoms or molecules of the gaseous medium. The result is the formation of a considerable number of **ion-pairs,** as they are called, consisting of separate positive gaseous ions and electrons.* When the energy of the particle has fallen to a low value, it takes up two electrons and thus becomes a neutral helium atom. It then no longer has the characteristic properties of an α-particle. Because of their relatively large mass and high velocity, very few α-particles are deflected by the nuclei of the medium they traverse (cf. § 14a). Consequently, α-particles have essentially straight-line paths of definite length, depending on their initial energy. The distance from its source to the point at which it can no longer be detected, e.g., by its ionization, is called the **range** of the α-particle. In air, the ranges are from 2.8 cm (for an initial energy of 4 Mev) to about 10 cm (for 10 Mev initial energy). In general, the range of an α-particle varies approximately directly as the square root of the (mean) atomic weight and inversely as the density of the medium through which it passes. Thus, α-particles are unable to penetrate a moderately thick sheet of paper or very thin aluminum foil.

The behavior of **beta rays** in electric and magnetic fields shows them to consist of *charged particles that are identical with electrons.* The β-particles emitted by the radioactive substances found in nature are negatively charged; that is to say, they are ordinary electrons. However, some of the radioactive species which have been produced artificially, by suitable nuclear

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* The ion-pairs produced in a gas by the radiations from radioactive substances are, of course, quite different from the ion-pairs present in an electrolytic solution (§ 45f).

reactions, expel β-particles having a positive charge; these are positive electrons or positrons (§ 13d). Unlike α-particles, the β-particles do not have well defined energies; from a given source, the energies vary from quite small values to a maximum which is characteristic of the emitting substance. This variation is referred to as a **β-particle energy spectrum.** In general, the energies of β-particles are of the order of a million electron volts, and their speeds approach that of light.

In passing through a gas, β-particles ionize the atoms (or molecules) of the medium and thereby lose energy. The number of ion-pairs produced per centimeter of path, i.e., the **specific ionization,** is much less than for α-particles. Hence, in any given medium, a β-particle will travel much farther than an α-particle of the same energy. However, whereas the latter moves in a straight line, β-particles are easily deflected, due to their small mass, and follow tortuous paths in traversing matter. Nevertheless, the net distance penetrated by a β-particle of sufficient energy may be quite considerable, e.g., several meters of air. Because of the nonlinear path and the energy spectrum, the ranges of β-particles are not well defined, but most of these particles can be stopped in a thickness of about 0.2 cm of aluminum foil. As a rough generalization, it appears that the range is inversely proportional to the density of the medium.

Finally, the **gamma rays** differ from the other radiations in the respect that they are not charged particles and are not deflected in electric or magnetic fields. They are *electromagnetic radiations of very short wave length,* generally between 10^{-8} and 10^{-11} cm; the corresponding energies, as derived from the Planck equation (15.6), are roughly 0.01 to 10 Mev. As far as their general properties are concerned, there is no difference between γ-rays and X-rays, except possibly in their energies. For the same energy, the two types of radiation are indistinguishable, but the term γ-rays is applied to those of nuclear origin, whereas X-rays arise from energy changes involving electrons. Most radioactive substances emit *either* α- *or* β-particles and this emission is frequently, although apparently not always, accompanied by γ-radiation. As a result of the nuclear reaction, which is associated with the expulsion of an α- or β-particle, the product nucleus may be in a high-energy (or excited) state. The excess energy, above that in the normal (or ground) state of the nucleus, is then emitted as a photon of γ-radiation. Thus, γ-rays are a kind of nuclear spectrum, related to nuclear energy levels, just as optical and characteristic X-ray spectra are associated with electronic energy levels (see Chapter 6).

As may be expected from their similarity to X-rays, the γ-rays are able to penetrate considerable distances even of fairly dense matter. As they pass through a gas, γ-rays produce ion-pairs, but the process is indirect, in contrast to the direct ionization caused by α- and β-particles. In certain interactions with atoms (or molecules), the γ-ray photon is able to eject an extranuclear electron with high energy. It is this energetic electron, behaving just like a β-particle, which produces ionization in its path. Whereas α- and β-particles have more or less definite ranges, that is to say, they can be stopped within a specified thickness of a given medium, such is not the case for γ-rays. These radiations can be attenuated to the extent that they are essentially undetectable, but, in principle, they cannot be absorbed completely (§ 65h).

63c. Detection of Ionizing Radiations.—The same general methods are used for the detection and measurement of α- and β-particles, γ-rays and, in fact, all kinds of ionizing particles (or radiations). Observations of the tracks of such particles can be made with the **Wilson cloud chamber,** the operation of which is based on the tendency of drops of moisture to condense on gaseous ions. When an ionizing particle passes through air that is supersaturated with water (or other) vapor, the liquid droplets condensing on the ions and electrons form a visible "cloud track" indicating the path of the particle. In the **bubble chamber,** which is a more modern development, the passage of an ionizing particle through a superheated liquid, e.g., liquid hydrogen or isopentane, produces a track consisting of a series of closely spaced bubbles. In this case, the ions and electrons serve as nuclei for bubble formation in the superheated liquid.

Tracks of ionizing particles can also be made apparent in photographic plates. The phenomenon of radioactivity was discovered by the action of the radiations on a photographic emulsion, but in this case there was only a general blackening observed after development. By the use of special **nuclear track emulsions,** however, it is possible to observe the tracks of individual particles. Because of the relatively high density of the emulsions, compared with air, the tracks are very short and must be observed under a microscope.

For the quantitative measurement as well as the detection of ionizing radiations, a number of methods are used which depend upon the fact that the ion-pairs produced in a gas make the gas capable of conducting electricity. Suppose two metal electrodes, which may be two parallel plates or, more commonly, a cylinder with a wire along its central axis, are placed in a gas and connected to a source of potential. Provided the applied voltage is not high, no current will flow, because the gas is a very poor conductor. If now ion-pairs are produced in the gas, a flow of current will be observed, as the positive ions and negative electrons move toward the respective oppositely charged electrodes. If the applied potential is relatively low, e.g., roughly 100 to 200 volts, only those ions and electrons formed by the ionizing particles will be collected at the electrode, and the magnitude of the current is a direct measure of the rate at which these particles enter the gas. A detecting instrument operating on this principle is called an **ionization chamber.**

By suitable adjustment of the external circuits, it is possible to count each individual particle as it enters the chamber by the pulse of current produced. The magnitude of the pulse is proportional to the number of ion-pairs formed in the chamber. Consequently, in a given chamber of moderate size, an α-particle will yield a larger pulse than a β-particle or γ-ray photon, of the same energy, because of its much greater specific ionization; that is to say, the α-particle forms more ion-pairs in the chamber than do the other radiations. Discrimination between various radiations, and even among α-particles of different energies, is thus possible by means of an ionization chamber.

Ionization chambers are simple and convenient instruments but they have the drawback of a small output, so that they must be used in conjunction with highly sensitive electrometers or with vacuum-tube amplifiers. However, if the potential applied to the electrodes in the detection device is increased to something like 500 to 800 volts, internal amplification occurs. The energy acquired by an electron in moving toward the positive electrode is now such that it is capable of producing secondary ion-pairs; the electrons of the latter can produce further ion-pairs, and so on. It is thus possible for each primary ion-pair to yield a total of approximately 10^4 ion-pairs due to secondary ionization. The size of the current pulse produced by an ionizing particle is thus increased enormously and external amplification is unnecessary. If the applied voltage is in the proper range, the total number of ion-pairs produced is proportional to the number formed by the original ionizing particle. A detection system operating under these conditions is consequently called a **proportional counter,** as it is invariably used to count individual particles. Like the ionization chamber, a proportional counter can discriminate among particles having different energies and different specific ionizations.

By increasing the potential between a cylindrical and a central wire electrode to the region of 1000 to 1500 volts, the result is a **Geiger-Müller counter,** sometimes abbreviated to **Geiger counter.** The internal amplification may now be as high as 10^8 and the total number of ion-pairs formed is independent of the primary number produced by the ionizing particle. Thus, output pulses of essentially the same size are obtained from α- and β-particles and γ-ray photons and, of course, no discrimination is possible. Because of the enormous amplification, Geiger counters, in a great variety of forms, have been extensively used for the detection of γ-rays, since these radiations have a relatively low specific ionization. The main disadvantage of the Geiger counter is that it is not satisfactory for fast counting because of the relatively long resolving time between pulses.

It has been known for many years that ionizing radiations are able to produce luminescence in certain substances, e.g., zinc sulfide, diamond and barium platinocyanide. Examination of this luminescence under a microscope showed it to consist of a large number of individual flashes or scintillations, and visual observation of these scintillations were used at one time to count α-particles. The procedure was tedious and with the development of ionization counters of the type described above the method was discarded. Since 1947 there has been a great revival of interest in **scintillation counters** as a result mainly of two circumstances. First, the discovery of scintillators that are transparent to the light they emit permits the use of relatively large volumes, thus insuring a high probability of interaction with the radiation. Second, the availability of photomultiplier tubes makes possible the conversion of the feeble light of a single scintillation into an electric pulse capable of operating a counter. Although scintillation counters detect ionizing radiations, their operation depends upon electronic excitation rather than ionization. Essentially, the production of a scintillation involves the initial formation of a high-energy (or excited) electronic state of the atoms, molecules, or, in some cases, a small region of the scintillator. The excess energy is then emitted in a very short time as a flash of light.

Numerous scintillators (or **phosphors**) have been developed in solid, liquid and even gaseous forms; they may be organic or inorganic in nature. The best organic phorphors have molecules consisting of two or more linked benzene rings, e.g., naphthalene, anthracene and terphenyl. The organic phosphors were first employed in the form of large, transparent crystals, but the discovery that scintillations could be produced in liquid and plastic media has made possible the construction of large and, hence, very efficient counters without the necessity for growing crystals. Among the solid, inorganic phosphors, the one most widely used, especially for γ-rays, is sodium iodide containing a trace of thallium as activator. Zinc sulfide, activated with a trace of silver, is a highly efficient phosphor, but large crystals are difficult to obtain and so it is mainly employed in counting α-particles, since they have a very short range in solids and there would be no advantage to the use of a large crystal.

Scintillation counters have the great merit of simplicity and high sensitivity to all types of ionizing radiations. In some forms they can discriminate between photons of different energies, so that they are used in γ-ray spectrometers. For the detection and measurement of γ-rays, scintillation counters are superior to Geiger counters because of their greater efficiency and shorter resolving time, so that fast, accurate counting is possible.

63d. Radioactive Decay.—In the course of the earliest studies of radioactive substances it was found that virtually all the activity of uranium and of thorium solutions could be carried down by certain precipitates. The uranium or thorium remaining in solution was inactive. It appeared, therefore, that most of the observed activity of compounds of uranium, for example, was not due to this element but to another, separable from it, to which the name uranium-X was given. On standing for some weeks, however, the uranium solution gradually regained its initial activity, but that of the precipitate fell off at about the same rate, so that the total activity remained virtually constant. This process of separating the active uranium-X, followed by its regeneration in the solution and decay in the precipitate, can apparently be repeated indefinitely.

These and other remarkable phenomena led E. Rutherford and F. Soddy (1902) to propose the revolutionary theory of **radioactive disintegration.** In more modern language, this theory postulates that *the nucleus of a radioactive species undergoes a spontaneous change accompanied by the emission of an α- or a β-particle and the formation of the nucleus of a new element.* This new element, which is quite different physically and chemically from its parent, may in turn also be unstable and emit a particle with the production of still another element. There may, in fact, be a succession of radioactive transformations, each accompanied by its characteristic rays.

The results described above in connection with the removal of the activity of uranium in certain precipitates can now be readily explained. The solution contains the feebly active parent radioelement uranium and the highly active product uranium-X, which is now known to be a mixture of two or three elements. Upon the formation of a suitable precipitate, e.g., of ferric hydroxide, the uranium-X is carried down with it, giving an active precipitate and an almost inactive filtrate. In the course of time, the uranium-X in the precipitate gradually disintegrates, the product being less active; hence, there is a gradual decrease of its radioactivity. The uranium in solution, however, also continues to disintegrate, and in doing so produces more uranium-X; the activity consequently increases until a certain equilibrium amount, equal to that initially present, is attained. The disintegration stages may thus be represented (approximately) by the following scheme:

$$\underset{\text{(feeble activity)}}{\text{Uranium}} \rightarrow \underset{\text{(strong activity)}}{\text{Uranium-X}} \rightarrow \underset{\text{(feeble activity)}}{\text{Products.}}$$

The rate at which radioactive atoms (or nuclei) decay or disintegrate, which is equal to the rate of emission of α- or β-particles, is directly proportional to the number of atoms (or nuclei) present. Radioactive decay is thus a first order process expressed by

$$\frac{-dN}{dt} = \lambda N, \tag{63.1}$$

where N is the number of radioactive atoms present at any instant and λ, called the **decay constant**, is a characteristic property of the given radioactive species. Upon integration it follows that

$$N = N_0 e^{-\lambda t}, \tag{63.2}$$

where N_0 is the number of atoms present at any arbitrary zero time and N is the number remaining at a time t later. It follows, therefore, from equation (63.2) that radioactive disintegration (or decay) is an exponential process.

An interesting consequence of the exponential decay is that every radioactive species has a definite **half-life period**, i.e., the time required for the amount (or activity) of a radioactive material to be reduced to half its initial value. The condition for the half-life is then $N/N_0 = 0.5$, and if the half-life period is represented by T, it follows from equation (63.2) that

$$e^{-\lambda T} = 0.5$$

or

$$T = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}. \tag{63.3}$$

The half-life, which is inversely related to the decay constant, is thus seen to be independent of the initial amount of radioactive material.

The situation may be illustrated by reference to Fig. 63.1, in which the proportion of the initial amount of radioactive material is plotted against time, in units of its half-life. The curve is, of course, exponential in nature.

It is seen that in each half-life period the *amount* of material disintegrating is less than in the preceding period, but it is always the same *fraction*, namely one half, of the amount present at the beginning of that period. In general, the fraction of the initial activity remaining after n half-life periods is $(\frac{1}{2})^n$, so that after seven such periods, for example, the quantity of radioactive material left is somewhat less than 1 per cent of that present initially.*

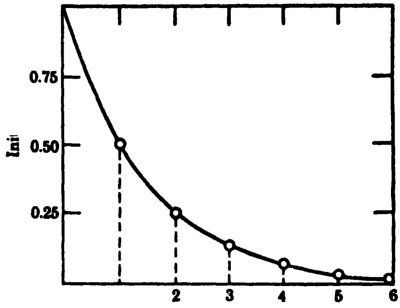

FIG. 63.1. Radioactive decay, illustrating the half-life principle

Upon combining equations (63.2) and (63.3), taking logarithms and rearranging, the result is

$$\log N = \log N_0 - \frac{0.301t}{T}.$$

Thus, a plot of $\log N$ against t should be a straight line with slope equal to $-0.301/T$, so that if the slope is obtained, from experimental observations, the half-life can be evaluated. Instead of determining N, the actual number of radioactive atoms present at any time t, the half-life can be obtained by observing the rate of decay or, its equivalent, the rate of emission of α- or β-particles. Since N is proportional to $-dN/dt$, the half-life period of the radioactive species can be obtained by plotting $\log(-dN/dt)$ against t. This procedure is commonly used for determining radioactive half-lives, the rate of particle emission being measured by means of one of the devices described above, e.g., a proportional or scintillation counter.

If a radioactive parent element, e.g., uranium, produces a daughter element which is also radioactive, a state of equilibrium will be attained when the daughter element decays at the same rate as it is being formed from its parent. Denoting the parent by the subscript 1 and the daughter by the subscript 2, the condition for **radioactive equilibrium** is given by

$$\lambda_1 N_1 = \lambda_2 N_2,$$

since, by equation (63.1), $\lambda_1 N_1$ is the rate of decay of the parent, and hence the rate of formation of the daughter, and $\lambda_2 N_2$ is the rate of decay of the daughter. In general, for a series of decay stages, it follows that, at equilibrium,

$$\lambda_1 N_1 = \lambda_2 N_2 = \lambda_3 N_3 = \lambda_4 N_4 = \cdots = \text{constant}, \qquad (63.4)$$

where N_1, N_2, N_3, etc., are the numbers of atoms of the various radioactive

---

* Since $(\frac{1}{2})^n$ can never become zero, no matter how large n is, it would appear that a radioactive substance can never decay completely. However, the exponential law of radioactive decay is a statistical law, based on large numbers of atoms (or nuclei), so that it may well break down when the number of atoms is small.

species present in the system at equilibrium. After introducing equation (63.3) relating the half-life to the decay constant, it is seen that

$$\frac{N_1}{T_1} = \frac{N_2}{T_2} = \frac{N_3}{T_3} = \cdots = \text{constant.} \tag{63.5}$$

In other words, at radioactive equilibrium, the number of atoms present of any member of a given decay series is proportional to its half-life.

If A and B represent any two members of a radioactive decay series, irrespective of whether they are parent or daughter or are separated by several generations, it follows from equation (63.5) that

$$\frac{N_A}{T_A} = \frac{N_B}{T_B} \tag{63.6}$$

when radioactive equilibrium is attained. This result provides an alternative method for determining half-lives which is particularly useful for species having such long half-lives that the rates of decay, i.e., rates of particle emission, are too slow to be determined with any degree of accuracy.

Example: Uranium minerals, which are old enough for radioactive equilibrium to have been established, contain 1 atom of radium to 2.8×10^6 atoms of uranium. The half-life of radium has been found by direct measurement to be 1620 years; estimate the half-life of the uranium.

Let A and B represent uranium and radium, respectively; then, from equation (63.6),

$$\begin{aligned} T_A &= \frac{N_A}{N_B} T_B \\ &= \frac{2.8 \times 10^6}{1} \times 1620 = 4.5 \times 10^9 \text{ years.} \end{aligned}$$

The half-life of uranium is thus 4.5×10^9 years.

63e. Mechanism of Radioactive Change.—The basic requirement for a spontaneous nuclear process to occur is that the *mass of the parent nucleus must be greater than the sum of the masses of the daughter nucleus and of the emitted particle.* In other words, a radioactive decay process must be accompanied by a decrease in mass. As will be seen later (§ 65g) this "lost" mass appears as an equivalent amount of energy carried by the α- or β-particle and frequently by a γ-ray photon. The nature of the particles emitted, that is, whether it is an α-particle or a positive or a negative β-particle, depends upon various circumstances, some of which are outlined below.

Because of the complexity of their structure, all nuclei containing at least 84 protons, i.e., elements having atomic numbers of 84 (polonium) or more, are fundamentally unstable. In many cases, such nuclei emit α-particles, although these particles are probably not normal constituents of the nucleus. If the energy required to remove two protons and two neutrons from a particular nucleus is numerically less than that gained by combining them to form an α-particle, then that nucleus will probably emit α-particles. The combining energy (or binding energy) of the α-particle has a definite value (28.2 Mev), but the energy of removal of the protons and neutrons varies with the nature of the nucleus. With a considerable number of heavy nuclei, the latter energy becomes small enough (23 Mev or so), for α-particle emission to be theoretically possible. Some α-particle emitters are known among lighter nuclei, but the number is very small.

When the energy requirement indicated above cannot be met, the nuclei of high atomic number emit β-particles, i.e., negative electrons. Because of the existence of radioactive β-particle emitters, it was thought, at one time, that atomic nuclei actually contain electrons, but this view was discarded after the discovery of the neutron. The present theory is that β-particle emission accompanies the conversion of a neutron into a proton, when the conditions are such that the energy required to remove a neutron from a particular nucleus is numerically less than that gained by the addition of a proton to the residual nucleus. The process taking place in the nucleus may be written as

	neutron →	proton +	electron +	neutrino
Mass	1	1	0	0
Charge	0	+	−	0
Spin	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$

It will be noted that an additional particle, called a **neutrino,** is postulated as accompanying the conversion of a neutron into a proton plus an electron, which is immediately emitted as a negative β-particle. The neutrino is not required to conserve either mass or charge, but it is necessary to satisfy conservation of spin. The neutron, proton and electron each have spin quantum numbers of $+\frac{1}{2}$ or $-\frac{1}{2}$, and conservation is not possible without an additional particle of similar spin. Further, the formation of the neutrino, for which there is direct experimental evidence, accounts for the β-particle energy spectrum. The energy released in the radioactive decay of the parent nucleus into its daughter is shared in a random manner between the electron and the neutrino. The β-particle energy may thus range from almost zero to a definite maximum value equal to the total energy released in the radioactive change (§ 63b).

An examination of the numbers of neutrons and protons in stable nuclei reveals that, for a nucleus to be stable, the ratio of neutrons to protons must lie within a restricted range for any given number of protons (or neutrons) (Fig. 63.2). When the neutron-to-proton ratio in a particular nucleus is greater than is required for stability, then the conditions for β-particle emission, described above, will exist. The conversion of a neutron into a proton results in a decrease of the neutron-to-proton ratio, so that the change is in the direction of increasing stability. In many nuclei, most of which have been obtained as the result of a variety of artificial nuclear reactions and

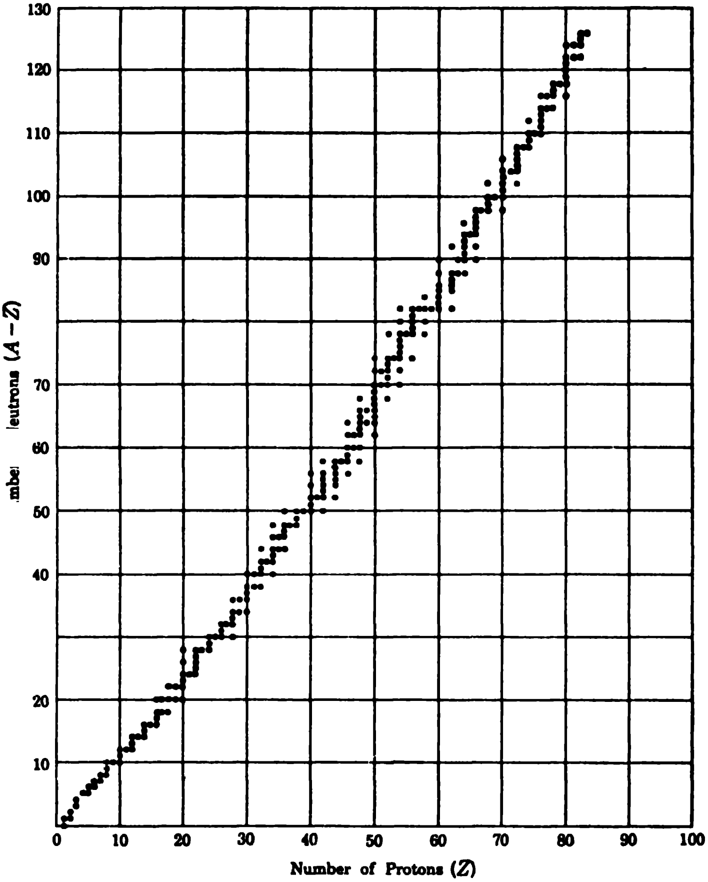

Fig. 63.2. Plot of the numbers of neutrons and protons in stable nuclei

which cover the whole range of atomic numbers, the neutron-to-proton ratio is too large for stability. These nuclear species are consequently radioactive and emit negative β-particles.

If the neutron-to-proton ratio of a nucleus lies below the stability range, for the given number of protons, i.e., atomic number, then there are three ways in which the radioactive species can approach stability. For nuclei of high atomic number the most common process is α-particle emission, but this is very rare among other nuclei. As an alternative, the radioactive species can undergo a change which is the reverse of negative β-particle decay; a proton spontaneously changes into a neutron plus a positron (and a neutrino). This is the process of positive β-particle decay, which is accompanied by the emission of a positron. Apparently, there are no positive β-particle emitters among the radioactive nuclei found in nature, but many have been prepared by artificial nuclear reactions. A third possibility, which has been observed with some unstable nuclei of low, medium or high atomic number, obtained artificially, is for the nucleus to capture an extranuclear electron; this process is known as **orbital electron capture.** The electron then combines with a proton in the nucleus to form a neutron (and a neutrino). The net result, as in positron emission, is the conversion of a proton into a neutron, thus leading to an increase in the neutron-to-proton ratio in the nucleus.

63f. Radioactive Series.—When a radioactive species emits an α-particle, which has a mass of approximately 4 units on the conventional atomic weight scale and a charge of +2 units, the atomic weight of the daughter element will be roughly 4 units less and the atomic number 2 units less than the parent. Since the atomic number gives the ordinal position of the element in the periodic system, it follows that when a particular radioactive species emits an α-particle, the product occupies a position in the periodic table that is two places to the left of the parent element. Expulsion of a β-particle, on the other hand, is accompanied by a very small change in the atomic weight but since there is gain of a proton, the atomic number of the daughter is one unit greater than that of its parent. The daughter element thus occupies a position in the periodic system that is one place to the right of the parent. These conclusions provide the basis of the **group displacement law** of radioactivity; this law, which was proposed independently by K. Fajans, A. S. Russell and F. Soddy (1913), before the development of the modern ideas concerning nuclear structure, has been put in the following form. *When an α-particle is emitted in a radioactive change, the product is displaced two places (or groups) to the left in the periodic table; the emission of a negative β-particle results in a displacement of one place (or group) to the right.* The law may be extended, of course, to include positive β-particle emitters and nuclei which exhibit orbital electron capture; in these cases, the daughter element occupies one place (or group) to the left of its parent.

By making physical and chemical separations when possible, by studying radioactive decay and growth curves, by determining the specific properties of the emitted radiations and in other ways, it has been found that the forty or more different radioactive species of high atomic number occurring in nature* fall into three distinct series. These are known as the **thorium series,** the **uranium series** and the **actinium series.** The first two series are named after the longest-lived precursors, thorium and uranium, with half-lives of 1.39×10^{10} and 4.51×10^{9} years, respectively. These elements undoubtedly had parents, but owing to their relatively short half-lives, they no longer exist in detectable amounts. The parent of the actinium series is not actinium, as was originally supposed, but rather a much longer-lived element, sometimes called actinouranium, having a half-life of 7.1×10^{8} years. After a number of successive radioactive changes, all involving the emission of an α- or a β-particle, there is finally formed in each series a

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* There are, in addition, probably about ten elements of lower mass number found in nature which contain traces, at least, of radioactive forms, e.g., potassium and rubidium, that are not included.

stable nonradioactive **end product.** As will be seen shortly, for the three natural radioactive series, the end product is a form of the element lead. Thus, each radioactive series is complete with a definite number of stages from the initial parent to the end product. In the great majority of cases, all the nuclei of a given species emit either α- or β-particles, but a few instances are known of **branched disintegration,** in which a certain proportion of the nuclei emit α-particles whereas the others expel β-particles.

The atomic weight of thorium is 232, to the nearest integer, and this is 4×58. Since an α-particle disintegration results in a decrease of 4 units in the atomic weight, whereas there is only a very small change accompanying β-particle emission, it is evident that the atomic weights of all the members of the thorium series may be represented by $4n$, where n is an integer varying from 58 (for thorium) to 52 (for the end product). In exactly the same way, it can be shown that all the atomic weights of the uranium series can be expressed by $4n + 2$, where n ranges from 59 (for uranium I) to 51 (for the end product), and for the actinium series by $4n + 3$, where n decreases from 58 (for actinouranium) to 51 (for the end product).

It will be noted that there is no natural radioactive series with atomic weights represented by $4n + 1$. However, such a series has been obtained by artificial means and it has been called the **neptunium series,** from the member, which is not found in nature, having the longest life, i.e., half-life 2.20×10^6 years. The end product of this series is not lead, but bismuth. It is very probable that the neptunium series existed billions of years ago, but natural decay has reduced the amounts of even the longest lived members to such an extent that they have ceased to be detectable.

ISOTOPES

64a. Radioactive Isotopes.—Some of the results obtained by applying the group displacement law and the expected atomic weight changes to part of the uranium series is shown in Fig. 64.1, in which the atomic weights are plotted as ordinates and the atomic numbers as abscissae. An α-particle is represented by a line sloping downward and to the left, corresponding to a decrease of 4 units in atomic weight and 2 units in atomic number. The emission of a negative β-particle is indicated by a horizontal line pointing to the right, because the atomic weight remains essentially constant while the atomic number increases by unity.

An examination of Fig. 64.1 shows that the three substances radium A, radium C′ and radium F, which have different atomic weights and different radioactive properties, have the same atomic number, viz., 84, and hence must occupy the same position in the periodic table. A similar conclusion is reached for the pair, radium C and radium E, atomic number 83, and for the trio, radium B, radium D and radium G, atomic number 82. *Such species possessing the same atomic number and requiring to be placed in the same position in the periodic table, are called* **isotopes** (Greek: *same place*).

In addition to the isotopes in the uranium series, others have been found

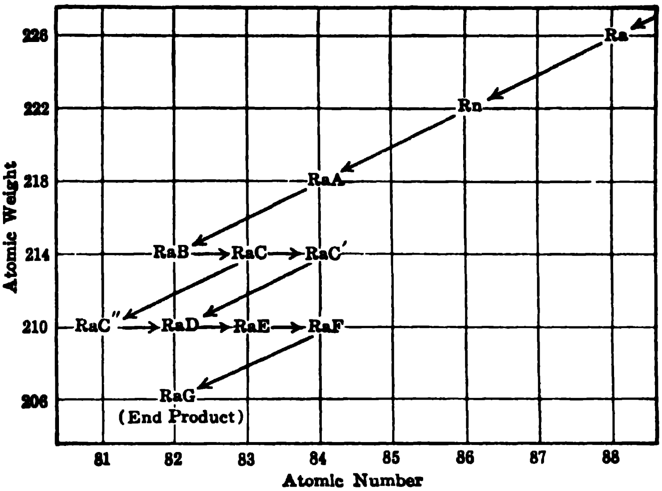

FIG. 64.1. Radioactive disintegration in the uranium series

to occur in the thorium and actinium series. It can be easily deduced from the group displacement law, that *whenever there are three successive stages involving one α-particle and two β-particle emissions, the resulting element will be isotopic with the first element.* Further, isotopes are not restricted to one radioactive series; for instance, the following seven substances, three belonging to the uranium series and two to each of the other two natural series, all have the atomic number 84 and hence are isotopic:

Radium A, C′ and F; Thorium A and C′; Actinium A and C′.

The atomic weights of these isotopes range from 210 to 218.

Since the nuclei of isotopic forms of a given element all contain the same number of protons, they must have different numbers of neutrons to account for the differences in atomic weight. Hence, isotopes are sometimes defined as *nuclear species having equal numbers of protons but different numbers of neutrons.* The total number of protons and neutrons in a nucleus, which is the integer closest to the atomic weight, is called the **mass number**; the ordinates in Fig. 64.1 give, in fact, the mass numbers of the various species. An alternate definition of isotopes is thus *nuclear species having the same atomic number but different mass numbers.*

It will also be observed from Fig. 64.1 that there are instances in which different substances have almost the same atomic weight or, more exactly, they have the same mass numbers, although their atomic numbers are different. Such species are said to be **isobars** (Greek: *same weight*). Thus, radium B, radium C and radium C′ are isobars, and many other instances are known. The total number of neutrons (n) and protons (p) is the same in each case, but the individual numbers are different, viz., $82p + 132n$,

$83p + 131n$ and $84p + 130n$, respectively, for the three radioactive species mentioned.

The general term **nuclide** is frequently used to describe *an atomic species that is characterized by the composition of its nucleus*, that is, by the numbers of neutrons and protons it contains. Thus, radium A, radium C′ and radium F are said to be isotopic nuclides, whereas radium B, radium C and radium C′ are isobaric nuclides. As will be seen shortly the existence of isotopic and isobaric forms is, however, by no means restricted to radioactive nuclides (or radionuclides).

Mention may be made of the existence of **isomeric nuclei** or **nuclear isomers**; these are nuclei having the same mass number and atomic numbers, so that they have the same composition, but which differ in their energy states. If the transition from the upper to the lower energy state, accompanied by the emission of γ-rays, is "forbidden," the former state may have an appreciable life. Nuclear isomerism has been observed with many nuclides, both radioactive and stable.

Isotopic forms of a given element contain the same number of protons in their nuclei and so they must have the same number of extranuclear electrons. It is these electrons that determine the chemical behavior of an atom and so the isotopes should, and do in fact, have essentially identical chemical properties. For this reason, the separation of isotopes by chemical methods is extremely difficult, although it has been achieved in some instances. Isobaric nuclides, on the other hand, have different numbers of protons and, hence, of extranuclear electrons; they are, consequently, quite different chemically. Radioactive properties are determined by the composition of the nucleus, and so differences in radioactive behavior are observed among both isotopic and isobaric nuclides.

64b. Nonradioactive Isotopes.—An important conclusion to be drawn from the group displacement law is in connection with the nonradioactive end products of the uranium and thorium disintegration series. It was found that these substances should, in each case, possess an atomic number of 82, which happens also to be that of the element lead. The end products should thus be isotopic with lead; further, since, like the latter, they are not radioactive, they should be identical with ordinary lead. Nevertheless, there should be one important although somewhat astonishing difference: the end product of the uranium series should have an atomic weight of about 206 (see Fig. 64.1), whereas that of the end product of the thorium series should be 208, compared with 207.2 for the atomic weight of ordinary lead.

Uranium and thorium minerals in nature are almost invariably associated with lead, and if some, at least, of this element were of radioactive origin, having been formed by the gradual disintegration from its parent over a long period of time, the atomic weight should differ from that of lead obtained from a nonradioactive source. This expectation has been confirmed, for lead derived from a number of uranium minerals has been found to have an atomic weight of 206.01 to 206.08, whereas that extracted from thorium minerals has an atomic weight of 207.8 to 207.9. It may be regarded as established, therefore, that the lead associated with radioactive minerals can exist in two isotopic forms, at least, with mass numbers of 206 and 208. Ordinary lead, from nonradioactive sources, with an atomic weight of 207.2, is, therefore, either a mixture of these two isotopes, or it consists of a third isotope of mass 207; actually it contains all three, together with a small amount of a fourth isotope of mass number 204. The occurrence of nonradioactive lead in isotopic forms not only provides strong support for the theories of radioactivity, it also proves the possibility of the existence of isotopes of a nonradioactive element.

The discovery of the isotopes of nonradioactive lead stimulated the search for isotopic forms of other elements, and in this connection the most valuable results came from a study of the positive rays in discharge tubes (§ 13d). These rays are made up of atoms and molecules, present in the tube or derived from the anode material, that have lost an electron (or occasionally two or three electrons), and so have acquired a positive charge. By applying electric and magnetic fields to a stream of positive rays, it is possible to sort them into groups, each made up of particles having the same ratio of charge to mass. Since most of the particles carry the same charge, it is apparent that *by means of the electric and magnetic fields the positive rays are divided into groups of particles of equal mass;* in other words, a sort of **mass spectrum** is produced. Since isotopic forms of the same element have different masses, they can evidently be separated from each other by the use of positive rays. In this way, not only can the presence of isotopes be detected, but their masses and proportions (or **relative abundances**) can be determined.

The first application of positive rays to the study of isotopes was made by J. J. Thomson (1913), and the procedure was developed and improved by F. W. Aston, from 1919 onward, and by others in more recent years. Modern instruments fall into two broad classes: **mass spectrographs,** generally used for determining isotopic masses, in which the positive rays are focused onto a photographic plate, and **mass spectrometers,** largely applied for relative abundance measurements, in which the rays are made to fall on a fixed slit where they are detected and measured electrically. Simple examples of the two types of instrument are shown in Figs. 64.2A and 64.2B, respectively.

In the mass spectrograph (Fig. 64.2A), a beam of positively charged ions from an ion source, in which the atoms in the vapor of the element (or a compound) under examination are ionized by bombardment with electrons, passes through the slits S_1 and S_2. They are then acted upon simultaneously by opposing electric and magnetic fields, so that the positive ions emerging from the third slit S_3 are those for which the displacements produced by the two fields compensate exactly. It can be shown that in these circumstances the ions all have the same velocity, in spite of differences in mass. The procedure is known as **velocity focusing.** After leaving the slit S_3, the positive ions enter another magnetic field which causes them to be deflected into a semicircular path so that they strike the photographic plate F.

According to equation (13.1), which is applicable to all charged particles,

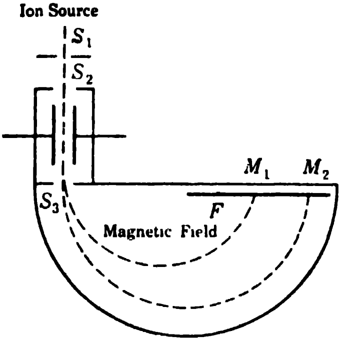

FIG. 64.2A. Mass spectrograph with velocity focusing

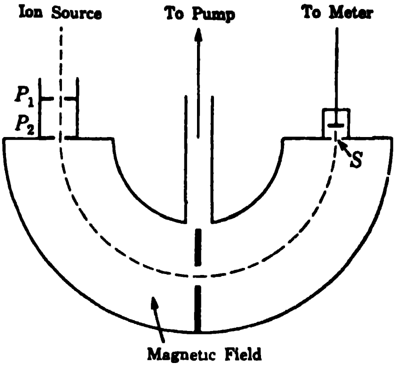

FIG. 64.2B. Dempster's mass spectrometer (direction focusing)

when a positive ion of mass m, charge ϵ and velocity v is deflected by a magnetic field H, then

$$m \qquad \frac{v}{Hr}, \tag{64.1}$$

where r is the radius of curvature of the path of the ion. In the present case, H and v are constant, and so ϵ/m is proportional to $1/r$. Assuming the charge carried by all the positive ions to be the same, it is seen that the radius of curvature of the path is directly proportional to the mass of the ions. Thus, all the ions of a given isotopic species will follow a particular path and will produce a definite line, such as M_1 or M_2, on the photographic plate. From the positions of the lines, the masses of the isotopic ions can be determined by comparison with a standard line (or lines), utilizing the proportional relationship between mass and path radius. From the relative intensities of the lines, the proportions of the various isotopes can be determined. An example of a mass spectrum obtained in the manner described above is shown in Fig. 64.3.

In the mass spectrometer (Fig. 64.2B), the positive ions, from an ion source, emerging from the slit in the plate P_1 are accelerated by means of a variable electric field applied between the plates P_1 and P_2. The beam of ions emerging from P_2 is deflected into a semicircular path by means of a magnetic field H and, as a result, particles having the appropriate mass are able to pass through the slit S and on to a small plate connected to an electrometer

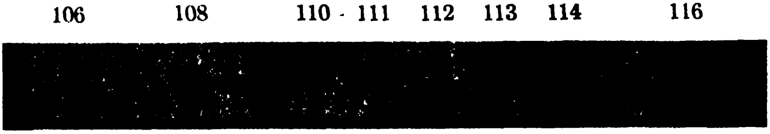

FIG. 64.3. Mass spectrum of cadmium (Dempster)

or similar device for measuring the ion current. All particles having the same m/ϵ value are brought to a focus at S, in spite of the different directions in which they leave the slit in P_2. A mass spectrometer of this type thus has the feature of **direction focusing.**

The ions emerging from the slit in P_2 will all have virtually the same energy $V\epsilon$, where V is the potential difference of the electric field. This energy is kinetic in nature and so is equal to $\frac{1}{2}mv^2$, where v is the velocity of the particles as they leave the slit; consequently

$$V\epsilon = \tfrac{1}{2}mv^2. \tag{64.2}$$

By combining equations (64.1) and (64.2), so as to eliminate v, it is seen that

$$\frac{m}{\epsilon} = \frac{H^2r^2}{2V}. \tag{64.3}$$

Only those ions having a specific radius can enter the slit S and be recorded, and since the magnetic field is maintained constant, the m/ϵ value of these ions is inversely proportional to the potential applied between P_1 and P_2. For a given potential only those isotopic ions having the same mass, as determined by equation (64.3), will pass through S and contribute to the observed ion current. The strength of the ion current is a measure of the relative abundance of that particular isotopic species. By changing the potential V, ions of a different mass are collected, the mass being proportional to $1/V$; the constant of the apparatus is determined by means of substances of known mass. An illustration of the variation of the ion current with mass, corresponding to change in the applied potential, is given in Fig. 64.4, in which the ordinates indicate the relative abundances of the four isotopes of ordinary lead.

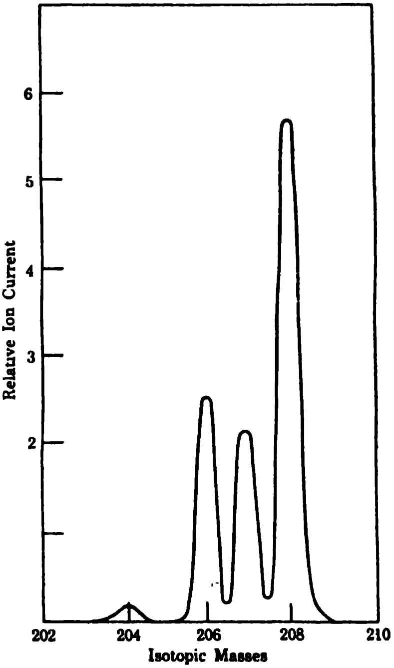

FIG. 64.4. Relative abundances of the isotopes of ordinary lead

64c. Isotopic Masses and Abundances.—All the naturally occurring elements have been subjected to mass spectroscopic study, and it has been found that there are only twenty elements which are simple and consist of only a single stable nuclide. Some elements have many isotopes—tin, for example, has ten which are stable—whereas others have two, three or more isotopic forms. The masses and relative abundances of the isotopes of a few common elements are recorded in Table 64.1. It is the custom in stating isotopic masses to express them relative to the value of the most abundant isotope of oxygen, to which is assigned the mass of 16.0000. Attention may be called to the fact that the isotopic masses are all very close to whole numbers. This is to be expected since the masses of the proton and neutron are only slightly greater than unity, on the same scale, and the electron mass is very small. The subject is discussed further in § 65g.

TABLE 64.1. ISOTOPIC MASSES AND ABUNDANCES

Element	Mass Number	Isotopic Mass	Abundance per cent
Hydrogen	1	1.008145	99.985
	2	2.014740	0.015
Boron	10	10.01612	18.7
	11	11.01280	81.3
Carbon	12	12.00380	98.89
	13	13.00748	1.11
Nitrogen	14	14.00752	99.635
	15	15.00486	0.365
Oxygen	16	16.00000	99.759
	17	17.00453	0.037
	18	18.00486	0.204
Sulfur	32	31.9822	95.018
	33	32.9819	0.750
	34	33.9786	4.215
	36	35.9784	0.017
Chlorine	35	34.97990	75.53
	37	36.97754	24.47
Lead	204	204.037	1.5
	206	206.039	23.6
	207	207.041	22.6
	208	208.042	52.3
Uranium	234	234.114	0.006
	235	235.118	0.720
	238	238.125	99.274

The masses and relative abundances of isotopes can now be determined with great accuracy, as is implied by the number of significant figures in Table 64.1. Hence, it should be possible to determine mean atomic weights of the elements as they occur in nature and compare them with the accepted chemical values. In doing this, it must be remembered that the latter are based on the assignment of 16.0000 to the atomic weight of atmospheric oxygen, which consists of three isotopes in the proportions given in the table.

On the other hand, the mass spectroscopic results, called **physical atomic weights,** are based upon the value of 16.0000 for the oxygen isotope of mass number 16. To convert physical into chemical atomic weights, it is necessary to determine the mean physical atomic weight of atmospheric oxygen; from the data in Table 64.1 this is seen to be

$$(0.99759 \times 16.00000) + (0.00037 \times 17.00453) + (0.00204 \times 18.00486) = 16.0045.$$

It follows, therefore, that

$$\frac{\text{Physical atomic weight}}{\text{Chemical atomic weight}} = \frac{16.0045}{16.0000} = 1.00028,$$

so that mass spectroscopic atomic weights must be divided by 1.00028 to obtain the corresponding values on the conventional chemical scale.*

The mean atomic weights derived from mass spectroscopic measurement are in excellent agreement with those obtained by chemical methods. In fact, in a few instances, notably, boron and antimony, the accepted chemical values were found to be in error and were subsequently corrected. The atomic weight of hydrogen in common use, namely, 1.0080, is actually derived from mass spectroscopic values; thus

$$\frac{(0.99985 \times 1.008145) + (0.00015 \times 2.014740)}{1.00028} = 1.00801.$$

64d. The Separation of Isotopes.—The earliest success in connection with the separation of isotopes was achieved by the **gaseous diffusion method,** making use of the different rates of diffusion of gaseous isotopic molecules. The rate of diffusion of a gas is inversely proportional to the square root of its density (§ 2i), and hence also to the square root of its molecular weight. The lighter isotopic form of a given substance will thus diffuse more rapidly than the heavier form, and a partial separation should be possible. By using a number of diffusion units in series, significant separations were obtained of the isotopes of a number of the lighter elements (G. Hertz, 1932).

An outstanding application of the gaseous diffusion method has been in the separation of the isotopes of uranium of mass numbers 235 and 238, the lighter, uranium-235, being important because it is the basic material for the release of nuclear energy (§ 66d). The material used is uranium hexafluoride vapor which diffuses or, more correctly, effuses through a series of porous barriers; the vapor passing through any barrier is richer in uranium-235 than

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* The existence of two atomic weight scales is an unfortunate situation. Ideally, a scale based on an assigned value to an individual nuclide is preferable to one based on a mixture, but chemical atomic weights are so well established that the adoption by chemists of the physical system is virtually a practical impossibility. A suggested compromise, which has been supported both by chemists and by workers in mass spectroscopy, is to adopt a single scale in which the value of 12.0000 is assigned to the carbon-12 isotope. The resulting atomic weights would differ from present chemical values by only 43 parts per million, so that, in most cases, the atomic weights in common use would not be changed.

is that left behind. If f is the atomic fraction (or percentage) of uranium-235 in the uranium hexafluoride before diffusion and f' is the fraction after diffusion, the **separation factor** s is defined by

$$s = \frac{f'}{f}. \tag{64.4}$$

The ideal (or maximum) separation factor is equal to $\sqrt{M_2/M_1}$, where M_1 and M_2 are the molecular weights of two isotopic molecules undergoing diffusion. In the case under discussion, M_1 is $(235 + 6 \times 19) = 349$ and M_2 is $(238 + 6 \times 19) = 352$, so that

$$s \text{ (ideal)} = \sqrt{\frac{352}{349}} = 1.004.$$

In practice, the separation factor is considerably less, probably not more than 1.002, since only part of the gas is permitted to diffuse through each barrier. The degree of isotopic enrichment per stage, as expressed by equation (64.4), is thus very small. However, by the use of several thousand diffusion stages in a cascade, which operates something like a fractionation column in distillation, it has been possible to obtain uranium containing over 90 atomic per cent of uranium-235, starting with natural uranium having 0.72 per cent of this isotope.

The **electromagnetic method** for separating isotopes is based on a similar principle to that used in obtaining mass spectra. A strong beam of positive ions, from a suitable ion source, is first accelerated by passage through an electric field and then deflected in a magnetic field. The radius of curvature of the ion path, under given conditions, is proportional to the ionic mass, so that the different isotopic species follow different paths, as in Fig. 64.2A. By placing vessels at the appropriate locations, e.g., corresponding to M_1 and M_2, the separated ions can be collected simultaneously. The electromagnetic procedure has been used for the separation of isotopes of many elements, ranging from some of the lightest, e.g., boron, to the heaviest, e.g., uranium. Many stable, i.e., nonradioactive, isotopes are now available in reasonable quantity as a result of the application of this technique.

The **thermal diffusion method** for separating isotopes (K. Clusius, 1938), that has proved to be very successful on the laboratory scale, involves a combination of diffusion and convection. A long vertical tube has a central wire which can be heated electrically to a temperature of 500°C or more, so that a temperature gradient is maintained between the hot wire and the colder wall of the tube. If a gas (or liquid) is placed in the tube, the lighter isotope molecules tend to collect near the hot wire, as a result of thermal diffusion, whereas the heavier ones move preferentially toward the cold wall. Convection then causes the hotter gas in the center to flow upward while the colder gas at the outside flows downward. The combination of thermal diffusion and convection leads to a concentration of the lighter isotope at the top of the tube and of the heavier one at the bottom.

One of the consequences of the mass difference of isotopes is that liquids which differ in their isotopic compositions have different vapor pressures and, hence, boiling points. Except for the very lightest element, these differences are too small to be useful, but for such elements, isotopic separation has been achieved by the **fractional distillation method.** It is of interest that, in the very first attempts at separating isotopes, namely, those of neon, distillation was employed (Aston, 1912), but these efforts met with failure. Success was subsequently achieved and the method was used in the discovery of the heavier isotope of hydrogen, as mentioned below. By the distillation of water, it has been possible to obtain some separation of the isotopes of both hydrogen and oxygen. In general, the form containing the lighter isotope has the higher vapor pressure and so the distillate tends to be enriched in this isotope in comparison with the residue.

Although the isotopic forms of an element or compound undergo the same chemical reactions, the rates are often different because of differences in activation energies (§ 58a). Although small, these differences in reactivity, which are usually more marked for the lighter than for the heavier elements, have been utilized to achieve the partial separation of the isotopes of a number of elements, e.g., hydrogen, carbon, nitrogen and sulfur (H. C. Urey, 1936). The **chemical exchange method** is based on the fact that one isotope of an element in a particular state of combination will exchange with a second isotope of the same element in another compound. In general, whenever an isotopic atom in a gaseous substance can exchange with another isotopic form in a liquid or in a solution, the gas will have a different isotopic composition from the liquid when equilibrium is attained.

As an example, consider the exchange of the isotopes of nitrogen, of mass numbers 14 and 15, represented by N^{14} and N^{15}, respectively, between ammonia gas and the ammonium ion, present as an ammonium salt, in solution. The reaction can be represented by

$$N^{15}H_3\,(\text{gas}) + N^{14}H_4^+\,(\text{soln}) \rightleftharpoons N^{14}H_3\,(\text{gas}) + N^{15}H_4^+\,(\text{soln}),$$

the rate of the exchange from left to right being somewhat greater than that from right to left. The equilibrium constant has been calculated to be 1.033 at 25°C, and so it follows that

$$\frac{[N^{14}\,(\text{gas})][N^{15}\,(\text{soln})]}{[N^{15}\,(\text{gas})][N^{14}\,(\text{soln})]} = \frac{[N^{14}\,(\text{gas})]}{[N^{15}\,(\text{gas})]} \bigg/ \frac{[N^{14}\,(\text{soln})]}{[N^{15}\,(\text{soln})]} = 1.033.$$

In other words at equilibrium the ratio of N^{14} to N^{15} in the gas phase is greater than that in solution, so that the heavier isotope tends to concentrate in the solution. In operating the exchange process, the ammonia gas flows upward through a packed column down which trickles a solution of ammonium nitrate; this insures thorough mixing and the rapid attainment of equilibrium. The system operates like a fractionation column in distillation, the solution becoming richer and richer in N^{15} as it moves toward the bottom of the column.

Partial separation of the stable isotopes of carbon, C^{12} and C^{13}, has been realized in a similar manner by the reaction between HCN gas and CN^- ions in solution; thus,

$$HC^{12}N \text{ (gas)} + C^{13}N^- \text{ (soln)} \rightleftharpoons HC^{13}N \text{ (gas)} + C^{12}N^- \text{ (soln)},$$

for which the calculated equilibrium constant is 1.026 at 25°C. It will be noted that, in this case, the heavier isotope, C^{13}, tends to concentrate in the gas phase.

The isotopic exchange reaction between oxygen gas and water is of interest since it is responsible for the atomic weight of atmospheric oxygen being greater than that of oxygen derived from lake water. Considering the two most abundant isotopes only, viz., O^{16} and O^{18}, the reaction is

$$O_2^{16} \text{ (gas)} + 2H_2O^{18} \text{ (liq)} \rightleftharpoons O_2^{18} \text{ (gas)} + 2H_2O^{16} \text{ (liq)},$$

with an equilibrium constant of 1.012 at 25°C. Using the arguments presented above, it can be readily shown that at equilibrium, the ratio of O^{18} to O^{16} will be greater in the gas phase than in liquid water. The reactions are too slow to be of practical value for the separation of the oxygen isotopes, but it does account for the difference in the atomic weights of oxygen in air and water.*

64e. Heavy Hydrogen.—From a comparison of the mass spectrographic and chemical atomic weights of hydrogen, it was concluded that this element normally contained a small proportion of a heavier isotope, probably of mass number 2. The first partial separation of the isotopes of hydrogen was achieved by the fractional distillation of liquid hydrogen (H. C. Urey, 1931), but better results were obtained shortly thereafter by the electrolysis of aqueous solutions. It appears that the overvoltage (§ 50g) associated with the discharge of hydrogen ions at a cathode is somewhat smaller for the lighter isotope. As a result, the electrolytic gas tends to contain a higher proportion of this isotope whereas the remaining aqueous solution becomes richer in the heavier isotope. Prolonged electrolysis, therefore, leads to the accumulation in the liquid of the isotope of mass number 2. Appreciable quantities of water have been obtained in this manner containing over 99 atomic per cent of the hydrogen in the heavier isotopic form; this may be compared with the 0.015 per cent in the starting material, ordinary water.

The heavier isotope of hydrogen, whose chemical atomic weight is 2.01418, is often called **heavy hydrogen** and water in which the hydrogen is in this form is known as **heavy water.** The density of the latter is more than 10 per cent greater than that of ordinary water. Because the atomic weights of the two stable isotopes of hydrogen are in the approximate ratio of 2 to 1, which is greatly in excess of that for any other element, the differences in properties between the isotopes are quite marked. For this reason it has been found convenient to devise a special name for the heavier isotope; it is called

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* This provides another argument against the use of ordinary oxygen as the atomic weight standard.

deuterium (Greek: *the second*) and the corresponding symbol is D. The nucleus of the deuterium atom, made up of a proton and neutron, is called a **deuteron,** by analogy with the proton.

The differences in the physical properties of the isotopic forms of hydrogen are very apparent; for example, the boiling point of liquid deuterium is more than 3°C higher than that of liquid hydrogen. The molar heats of vaporization are 303.1 and 217.7 cal per mole, respectively, while the molar volumes are 23.17 and 26.15 cc per mole. Analogous differences occur between the physical properties of light and heavy water, i.e., H_2O and D_2O, as may be seen from the data in Table 64.2.

TABLE 64.2. PHYSICAL PROPERTIES OF ISOTOPIC FORMS OF WATER

Property	H_2O	D_2O
Relative density at 25°C	1.0000	1.1079
Boiling point	100.00°C	101.42°C
Freezing point	0.00°	3.82°
Maximum density at	4.0°	11.6°
Surface tension at 20°C	72.75	67.8 dynes cm^{-1}

Large quantities of heavy water are being produced at the present time for use in various aspects of the atomic energy program (§ 66f). The first stages of concentration of the deuterium are achieved by distillation of water or by chemical exchange (or both), and this is followed by electrolysis to yield a product containing 99.75 mole per cent D_2O. At one time the isotopic exchange reaction between hydrogen gas and ordinary water, in the form of steam, was used, but equilibrium is attained slowly and requires the presence of a catalyst. More recently better results have been obtained with hydrogen sulfide gas and liquid water. Equilibrium is established rapidly over a large range of temperatures without the use of a catalyst.

64f. Applications of Isotopes.—Since the isotopes of a given element behave chemically in a virtually identical manner, but are distinguishable because of differences in mass or radioactivity, they have been employed as **indicators** or **tracers** in connection with many different phenomena. The use of radioactive isotopes, both those occurring in nature and others that have been prepared by special methods (§ 65e), is particularly advantageous, because they can be detected and estimated in amounts that are so small as to be beyond the limits of chemical analysis. A very large number of applications of isotopes in research and in industry have been reported. The few examples given here have been chosen because of their special chemical interest.

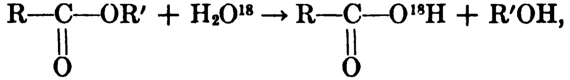
The behavior of such elements as hydrogen, carbon, nitrogen, oxygen, phosphorus or sulfur in various biological processes, for instance, can be followed by employing compounds having a small quantity of one or other of these elements in isotopic forms that differ from those normally present. By employing the mass spectroscope or an instrument for detecting radioactivity (§ 63c) to trace the fate of these isotopes, it is possible to obtain valuable data concerning the processes in which their compounds are involved. For example, when water or carbon dioxide enriched in the oxygen isotope O^{18} was used in photosynthesis, the oxygen evolved in the process was found to come entirely from the water while the oxygen of the carbon dioxide was contained in the organic compounds. The overall reactions are thus

$$CO_2^{16} + H_2O^{18} = \tfrac{1}{6}(C_6H_{12}O_6^{16}) + O_2^{18}$$

and

$$CO_2^{18} + H_2O^{16} = \tfrac{1}{6}(C_6H_{12}O_6^{18}) + O_2^{16}.$$

By using water enriched in the oxygen isotope O^{18}, information has been obtained concerning the mechanism of ester hydrolysis. It was found that, of the products of the reaction, only the acid contained excess of O^{18}; the O^{18} content of the alcohol was normal. The reaction may then be written as



$$\underset{\underset{\displaystyle O}{\|}}{R\text{—}C\text{—}OR'} + H_2O^{18} \rightarrow \underset{\underset{\displaystyle O}{\|}}{R\text{—}C\text{—}O^{18}H} + R'OH,$$

indicating that the reaction proceeds by the scission of the C—OR′ bond.

With the aid of deuterium or a radioactive isotope of hydrogen, called tritium, of mass number 3 (§ 65d), or by employing radioactive halogen isotopes, interesting information can be obtained relating to the mechanisms of chemical changes. As an illustration, reference may be made to the familiar Friedel-Crafts reaction in which aluminum chloride acts as a catalyst for the interaction of an aromatic hydrocarbon and an acyl chloride. When the aluminum chloride catalyst contained some radioactive chlorine, the hydrogen chloride gas evolved was found to possess the same activity as the chloride remaining in the solution, so that the reaction can be represented approximately by

$$C_6H_6 + CH_3COCl(+AlCl_3^*) \rightarrow C_6H_5COCH_3 + HCl^*(+AlCl_3),$$

for example, where the asterisk indicates the presence of radioactive chlorine. It is evident that the chlorine in the hydrogen chloride must have come from the aluminum chloride catalyst, rather than from the CH_3COCl. It appears, therefore, that the chlorine atom is first removed from the latter and becomes attached to the aluminum chloride, forming $(CH_3CO)(AlCl_4)$. The particular atom of chlorine which is then removed from the $AlCl_4$ grouping, as hydrogen chloride, depends upon chance; hence, the proportion of radioactive chlorine present in the evolved gas will be the same as that in the liquid, as found experimentally.

Radioactive substances have been used to determine the solubilities of sparingly soluble salts of isotopic elements. A trace of radium D, isotopic with lead, and of known activity, is mixed with a definite amount of an ordinary, nonradioactive, lead salt. This gives the proportion of radium D to lead in the mixture, and because of the virtual identity of properties it remains unchanged in the course of the subsequent treatment. The mixture is converted into the sulfate, or other sparingly soluble salt, and a saturated solution is prepared; a known volume is then evaporated to dryness and its radioactivity measured to determine the amount of radium D present. Since the proportion of this isotope in the system is known, the quantity of lead, and hence the solubility of the lead sulfate, can be calculated. The same general principle, called **isotopic dilution**, has been used in a procedure for determining low vapor pressures by the transpiration method (§ 11c).

An entirely different application of isotopes arises from the formation of a radioactive form of carbon, C^{14}, produced by the action of neutrons from cosmic rays on the N^{14} in the upper atmosphere (§ 65d). As a result, the carbon dioxide present in the air contains a definite proportion of C^{14} and this is assimilated into living plants during photosynthesis. After removal from the plant, the C^{14} present in "dead" carbonaceous materials, such as wood, cotton, etc., decays and is not replaced, as it is in the living plant. By comparing the radioactivities of the "dead" and "live" materials, the age of the former can be determined, since the half-life of C^{14} is known (5600 years). The radiocarbon method of dating has been used to estimate the ages of archeological and geological specimens that are up to 50,000 years old.

ARTIFICIAL NUCLEAR REACTIONS

65a. The Interaction of Nuclei.—For two nuclei to interact they must be brought so close together that nuclear attractive forces begin to exceed the force of electrostatic repulsion between the two positively charged nuclei. If two nuclei of atomic number Z and Z', respectively, are brought together from a distance, their mutual repulsion results in an increase in the potential energy (Fig. 65.1). If Coulomb's law is obeyed, the potential energy, when the nuclear centers are a distance d apart, is equal to $ZZ'\epsilon^2/d$, where ϵ is the unit (or electronic) charge. When the distance between the nuclei is equal to d_0 in Fig. 65.1, the short range attractive forces become dominant, so that the potential energy decreases sharply. The two nuclei then fuse and reaction occurs. It would appear, therefore, that a minimum energy of $ZZ'\epsilon^2/d_0$ must be supplied to make the nuclei interact. The distance d_0 is approximately equal to a nuclear diameter, i.e., 10^{-12} cm, and since ϵ is 4.8×10^{10} esu, the minimum energy is found to be 2.3×10^{-7} ZZ' ergs or about 0.15 ZZ' Mev (cf. § 63b). Because of the effect of wave mechanical barrier penetration, often referred to as the **tunnel effect**, detectable nuclear interaction occurs at somewhat lower energies. Nevertheless, the main conclusions to be drawn from the result

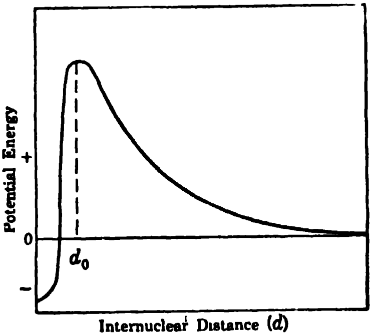


FIG. 65.1. Potential energy curve for the interaction of two nuclei

just obtained are correct: first, energies of the order of a million electron volts are necessary to bring about nuclear reactions, and, second, the required energy increases with the atomic numbers of the interacting nuclei.

The first artificial nuclear reaction was reported by E. Rutherford in 1919 who observed protons of long range, i.e., high energy, when α-particles of about 4.8 Mev kinetic energy were passed through nitrogen gas. The reaction occurring was

$$_7N^{14} + {}_2He^4 \rightarrow {}_8O^{17} + {}_1H^1,$$

where each symbol represents the nucleus of the corresponding species, the subscript giving the atomic number and the superscript the mass number. There is no change in the numbers of protons and neutrons in the reaction and so the atomic numbers and mass numbers must balance on the two sides of the equation. It is evident, therefore, that the interaction of an α-particle ($_2He^4$) with a $_7N^{14}$ nucleus must yield a nucleus of $_8O^{17}$ in addition to a proton ($_1H^1$). In the abbreviated notation commonly used to describe nuclear reactions the process would be represented by

$$N^{14}(\alpha,p)O^{17},$$

where the first symbol in the parentheses indicates the bombarding particle or **projectile** and the second represents the emitted particle, i.e., a proton. At the left is the symbol for the **target nucleus**, with which the projectile interacts, and that of the product or **recoil nucleus** is given at the right.

65b. The Acceleration of Charged Particles.—Following the discovery that α-particles of radioactive origin could bring about a nuclear reaction, efforts were made to develop devices whereby nuclei of hydrogen (protons), deuterium (deuterons), helium (α-particles) and even of heavier atoms could be accelerated to high velocities and energies. In 1929, J. D. Cockcroft and E. T. S. Walton described a voltage multiplier system which permitted a source of moderate voltage to be built up to high values. The basic principle of this accelerator is that a number of capacitors are charged in parallel from the source and then discharged in series; the discharge voltage is then the sum of the voltages on the individual capacitors.

An instrument that has bnee widely used to accelerate nuclei is the **cyclotron** (E. O. Lawrence, 1932). In its most general form it consists of two flat, semicircular boxes, called **dees** because of their shape, which are indicated by D_1 and D_2 in Fig. 65.2,I. These are surrounded by a vessel, containing gas at a low pressure, between the poles of a magnet (Fig. 65.2,II). A high-frequency (H.F.) alternating potential, of several million cycles per second, is applied across the dees, as shown. At S positive ions are produced by the bombardment of hydrogen, deuterium or helium atoms by electrons. Suppose that, at any particular instant, the direction of the alternating potential is such that D_1 is positive and D_2 is negative. A positive ion starting from S will then move into D_2 following a semicircular path due to the deflection caused by the magnetic field. While in the interior of the dee the velocity of the ion remains constant and its path has a definite radius.

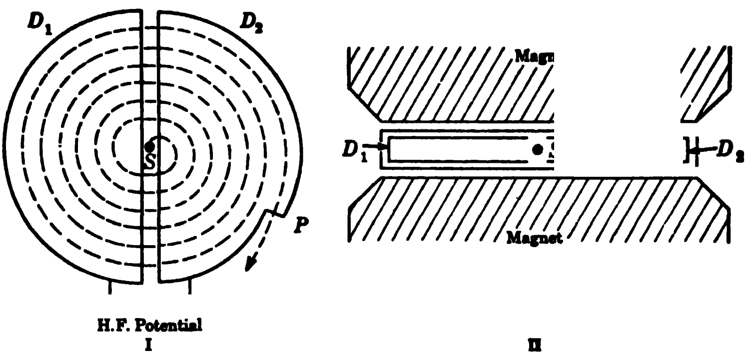


FIG. 65.2. Simplified representation of cyclotron with two dees

When the ion reaches the gap between the dees it becomes subject to the action of the applied potential. If the oscillation frequency is such that in the time of passage through D_2 the sign of the potential is reversed, so that D_1 is negative and D_2 is positive, the ion will then be accelerated toward D_1. Since it now moves faster than before, the radius of its path is increased; however, the time taken to traverse the dee remains unchanged because the increased path length is exactly compensated by the increased speed of the ion. This means that, if the oscillation frequency of the applied potential is properly adjusted, the charged particle will always keep in phase with the changing potential between the dees. Thus, each time an ion crosses the gap from D_1 to D_2 it will be accelerated toward D_2, and when it crosses from D_2 to D_1, it will receive an impulse toward D_1, for the direction of the potential will then be reversed. As a result of these repeated impulses, the energy of the ions is steadily increased, while they describe a flat spiral path of increasing radius (Fig. 65.2,I). Eventually, the ions, having acquired an energy which may be as high as several hundred million electron volts, are deflected from the spiral path and emerge at P.

Among several other devices for producing charged particles (or nuclei) of high energy, mention may be made of the **linear accelerator**; this instrument was the precursor of the cyclotron, but interest in it has been revived because it appears to be useful for producing large currents of relatively heavy ions of high energy (§ 65f). A linear accelerator is made up of a series of tubes of increasing length (Fig. 65.3); alternate tubes are connected to-

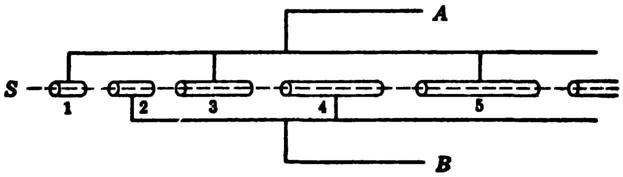


FIG. 65.3. Linear accelerator for positively charged particles

gether and to the respective terminals A and B of a source of high-frequency potential. At a particular instant, when tubes 1, 3, 5, etc., have a negative potential, ions are attracted from the source S and move through tube 1 with a constant velocity. The tube length and the frequency of the alternating potential are adjusted so that, by the time the ions reach the gap between tubes 1 and 2, the potentials are reversed and tube 2 is now negative. The ions will thus be accelerated as they traverse the gap. An analogous situation occurs at each gap, so that the ions acquire additional energy each time they pass from one tube to the next. In this manner, energies of several million electron volts may be built up.

65c. Charged Particle Reactions.—When a projectile ion acquires sufficient energy to permit it to interact with a given target nucleus, the two particles first combine to form a **compound nucleus.** This is a nucleus of either a normally stable or unstable species in a highly excited state. The excess energy arises from two sources: first, the kinetic energy of the projectile is converted into internal energy and, second, a certain quantity of energy is generally released by the combination of the projectile and target nuclei. Within a very short time, e.g., 10^{-12} sec or less, the compound nucleus, in an effort to attain stability, expels one or, sometimes, more particles, e.g., a neutron (n), proton (p), deuteron (d), α-particle, etc., or the excess energy is emitted as γ-rays. The particular nuclear reaction which occurs depends on the excitation energy of the compound nucleus and the amount required to expel one particle or another. Consequently, it often varies with the energy of the projectile particle. In many instances two or more reactions may occur simultaneously, if they are energetically possible.

Some of the main types of nuclear reactions involving charged nuclear particles are summarized below; for each projectile, the order is very roughly that of decreasing probability. If sufficient energy is available, two or more particles may be emitted. Thus with projectiles of high energy such reactions as $(p,2n)$, (p,np), $(d,2n)$, $(\alpha,2n)$, $(\alpha,3n)$, etc., have been observed. With target nuclei of large atomic number, reactions of an entirely different character, namely, **fission** and **spallation,** often occur if the projectile has sufficient energy. In fission, the compound nucleus breaks up into two more or less equal parts and at the same time emits a small number of neutrons, but in spallation, as many as 20 to 30 neutrons and protons are split off, leaving a nucleus with considerably smaller mass and atomic number than the target.

Projectile	Reaction Type			
Proton	(p,n)	(p,γ)	(p,α)	(p,d)
Deuteron	(d,p)	(d,n)	(d,α)	(d,γ)
Alpha particle	(α,n)	(α,p)		

Some mention will now be made of a few nuclear reactions of special interest. The neutron was discovered as the result of (α,n) reactions with certain light nuclei, especially those of beryllium; thus,

$$_4\mathrm{Be}^9 + {}_2\mathrm{He}^4 \rightarrow ({}_6\mathrm{C}^{13})^* \rightarrow {}_6\mathrm{C}^{12} + {}_0n^1,$$

where the compound nucleus is a highly excited state of the normally stable C^{13} nucleus. At the present time, convenient laboratory sources of neutrons consist of a mixture of beryllium and an α-particle emitter, such as radium or polonium.

As stated earlier, the first artificial nuclear reaction to be discovered was of the (α,p) type. On the other hand, the first such reaction with artificially accelerated particles, using protons as the projectiles, was of the (p,α) type; thus

$${}_3Li^7 + {}_1H^1 \rightarrow ({}_4Be^8)^* \rightarrow {}_2He^4 + {}_2He^4,$$

where the residual nucleus is also an α-particle.

In most cases the nature of the residual (or recoil) nucleus can only be inferred from the atomic and mass numbers of the target, projectile and emitted particles. However, reactions in which the products were directly identified, occurred in the bombardment of bismuth with deuterons; both (d,p) and (d,n) reactions take place, viz.,

$${}_{83}Bi^{209} + {}_1H^2 \rightarrow {}_{83}Bi^{210} + {}_1H^1$$

$${}_{83}Bi^{209} + {}_1H^2 \rightarrow {}_{84}Po^{210} + {}_0n^1.$$

The products, namely Bi^{210} and Po^{210}, have been found to be identical with the naturally occurring nuclides, radium E and radium F (polonium) respectively (cf. Fig. 64.1).

65d. Neutral Particle Reactions.—When a neutron approaches a nucleus, there is no repulsion and consequently, no appreciable increase in the potential energy, but when the neutron is close enough for the short range attractive force to become effective, the potential energy decreases sharply (Fig. 65.4). Consequently, it is not necessary to use neutrons of high energy to bring about reaction with many nuclei. In numerous instances, in fact, slow neutrons, i.e., neutrons with energies of a fraction of an electron volt, undergo reaction more readily than do fast neutrons of high energy. It is only when the emission of a particle (or of two particles) requires the compound nucleus to have a large excitation energy that high energy neutrons are necessary.

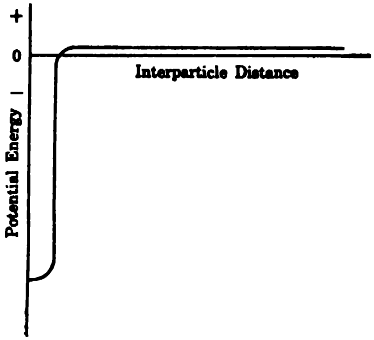


FIG. 65.4. Potential energy of a slow neutron and a nucleus

The familiar neutron sources generally yield neutrons of high energy. To slow down these fast neutrons a substance called a **moderator** is used. As a result of "billiard ball" type of collisions, referred to as **elastic scattering** collisions, with the moderator nuclei, the neutrons transfer much of their energy to these nuclei. By simple mechanics, it can be shown that the fraction of the neutron energy transferred per collision increases with decreasing mass number. Hence, the elements of low mass number are the best moderators. Water and paraffin have been largely used in the laboratory to produce slow neutrons from fast neutron sources. Neutrons whose average energy has been reduced to the value kT, i.e., $8.6 \times 10^{-5}T$ ev, where T is the temperature of the moderator in °K, are known as **thermal neutrons.** At ordinary temperatures, i.e., around 300°K, the average energy of thermal neutrons is therefore 0.026 ev. Much of the work on interaction with nuclei has been done with such slow neutrons.

The most common type of neutron reaction is of the (n,γ) type, in which a neutron is captured and the excess energy of the compound nucleus is emitted as γ-rays; such processes are called **radiative capture reactions.** The great majority of nuclides, He^4 being an outstanding exception, exhibit radiative capture of neutrons, to some extent at least. A number of (n,γ) reactions will be described later, but one will be mentioned here, namely, that involving Cd^{113}, a naturally occurring isotope of cadmium. The reaction is

$$_{48}Cd^{113} + {_0n^1} \rightarrow (_{48}Cd^{114})^* \rightarrow {_{48}Cd^{114}} + \gamma,$$

so that the product is an isotope of the target nucleus but with a mass number 1 unit larger. This is the case for all radiative capture reactions. The reaction with Cd^{113} occurs very readily with neutrons of low energy and it is, in fact, used for the absorption of such neutrons, e.g., in the control of nuclear reactors (§ 66f).

If sufficient energy is available, a (n,p) reaction is possible; in a few instances reactions of this type occur with slow neutrons, although generally fast neutrons are required. An interesting case is that involving N^{14}, the common isotope of nitrogen; thus,

$$_7N^{14} + {_0n^1} \rightarrow (_7N^{15})^* \rightarrow {_6C^{14}} + {_1H^1},$$

so that the product is C^{14} which, as stated above, is formed in the upper atmosphere. Considerable quantities of C^{14} for isotopic tracer work are prepared by exposure of a nitrogen compound, e.g., beryllium nitride, to neutrons.

With neutrons of high energy (n,α) reactions are observed, and with some target nuclei of low atomic number even slow neutrons are adequate. Thus, with boron-10, the process $B^{10}(n,\alpha)Li^7$ occurs very readily and the reaction is used for the detection of neutrons. The chamber of a proportional counter may be filled with boron trifluoride gas or the walls lined with a boron compound. The α-particle and Li^7 nucleus, formed when a neutron is captured, produce a burst of ionization which is recorded as a pulse on the counter. Another important (n,α) reaction is that with Li^6, i.e.,

$$_3Li^6 + {_0n^1} \rightarrow (_3Li^7)^* \rightarrow {_2He^4} + {_1H^3},$$

in which the product is the hydrogen isotope of mass number 3, generally called **tritium** (Greek: *the third*) and represented by the symbol T. This reaction is the one whereby tritium is prepared for various experimental studies.

Of outstanding significance among neutron reactions is that of nuclear fission. Because of its application in connection with the release of nuclear energy, the treatment of fission by neutrons will be deferred to a later section (§ 66d).

Another electrically neutral particle with which nuclei can interact is the photon; the processes which take place are referred to as **photonuclear reactions.** The most common are those of the (γ,n) type, where γ represents the photon of radiation, since the energy required is invariably in the million electron volt range. The energy which the photon must have depends upon the energy which binds the neutron in the target nucleus. In deuterium and beryllium the neutron binding energy is relatively small, namely, 2.2 and 1.6 Mev, respectively; hence the (γ,n) reactions can be produced by γ-rays from various radioactive materials. **Photoneutron sources,** consisting of beryllium and a γ-ray emitter, are commonly used in the laboratory for experimental work. In most nuclei, however, the binding energy of the neutron is about 8 Mev and so γ-rays having at least this amount of energy are needed for the (γ,n) reaction. Very few radioactive nuclides emit γ-rays of such high energy, and so the radiations, which are really a form of X-rays, are obtained by allowing electrons of high energy to fall upon a suitable anticathode (cf. Fig. 13.1). Photons of 8-Mev energy or more can also cause (γ,p) reactions and with higher energies reactions of the (γ,α), (γ,np), $(\gamma,2n)$, etc., types can occur.

65e. Artificial Radioactivity.—While studying the (α,n) reaction with boron, magnesium and aluminum, I. Joliot-Curie and F. Joliot (1934) noted that positrons were produced in addition to neutrons. When the α-particle source was removed, the emission of neutrons ceased, but the positrons continued to come off for some time, the intensity falling off gradually. The explanation is that the recoil nucleus is one of an unstable nuclide which exhibits radioactive decay with the emission of positive β-particles. The reaction with aluminum, for example, is

$$_{13}\mathrm{Al}^{27} + {}_2\mathrm{He}^4 \rightarrow {}_{15}\mathrm{P}^{30} + {}_0n^1,$$

so that the product contains one neutron less than the only stable isotope of phosphorus, P^{31}. From the arguments presented in § 63e, it is not surprising that P^{30}, which does not occur in nature, emits positive β-particles; thus,

$$_{15}\mathrm{P}^{30} \rightarrow {}_1\beta^0 + {}_{14}\mathrm{Si}^{30},$$

so that the final product, identified by its atomic number, is the stable nuclide Si^{30}. Proof of the foregoing arguments was provided by irradiating aluminum foil with α-particles and then subjecting it to various chemical treatments; the positive β-activity appeared in all precipitates or gases where phosphorus was to be expected.

After the initial discovery of **artificial radioactivity** (or **induced radioactivity**), it was found that many artificial radionuclides could be obtained by the bombardment of stable isotopes by protons, deuterons, α-particles or neutrons. A large number of others have been produced in nuclear fission and spallation reactions, so that some eight hundred such unstable isotopes, of all the elements from hydrogen to uranium, have been identified. Among them are several radioactive isotopes of the two "missing" elements with atomic numbers 43 (technetium) and 61 (promethium), neither of which has been found on earth. Although the earliest artificial radionuclides possessed positive β-activity, because they contained too few neutrons for stability, the majority now known emit negative β-particles.

Not all nuclear reactions, of course, lead to the formation of unstable nuclei; in many cases the products are stable with neutron-to-proton ratios lying within the stability range for the given atomic number. Reactions which are likely to lead to residual nuclei which are negative β-emitters, although all will not necessarily do so, are those accompanied by an increase in the neutron-to-proton ratio, e.g., (d,p), (α,p), (n,γ), (n,p), (n,α). On the other hand, the (p,n), (p,γ), (d,n), (α,n), $(n,2n)$ and (γ,n) reactions are accompanied by a decrease in the neutron-to-proton ratio, so that the products often emit positive β-particles or exhibit orbital electron capture. These rules are not obeyed rigorously, since special circumstances arise, but they are useful as a rough guide.

65f. The Transuranium Elements.—The product of the radiative capture of neutrons by uranium-238 (atomic number 92), namely, uranium-239, emits negative β-particles (half-life 23 min) and so its daughter must have an atomic number of 93. Since no element of this atomic number exists in nature, this product is an isotope of a new, artificial element to which the name **neptunium** (symbol Np) has been given.* This is the first of the **transuranium elements,** i.e., elements with atomic numbers exceeding that of uranium. The (n,γ) reaction with uranium-238 and the subsequent negative β-decay are represented by

$$_{92}U^{238} + {}_0n^1 \rightarrow {}_{92}U^{239} + \gamma$$

$$_{92}U^{239} \xrightarrow{23\text{ min}} {}_{-1}\beta^0 + {}_{93}Np^{239}.$$

The product, Np^{239}, also emits negative β-particles (half-life 2.3 days) and its daughter has an atomic number of 94; this second transuranium element is called **plutonium,** symbol Pu.† Its formation is expressed by

$$_{93}Np^{239} \xrightarrow{2.3\text{ days}} {}_{-1}\beta^0 + {}_{94}Pu^{239}.$$

The isotope Pu^{239} is an α-particle emitter with the relatively long half-life of 24,400 years; its decay product is the naturally occurring uranium-235. Both of these nuclides play an important role in the release of nuclear energy.

Several other isotopes of neptunium and plutonium have been obtained, mainly as a result of the interaction of accelerated deuterons and α-particles, respectively, with the isotope of uranium. Mention may be made of the $U^{238}(\alpha,n)Pu^{241}$ reaction because the product, Pu^{241}, is a negative β-emitter

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* After the planet Neptune which lies beyond Uranus in the solar system.

† After the last of the known planets, Pluto, which lies beyond Neptune.

whose daughter, called **americium** (symbol Am), has the atomic number 95; thus,

$$_{94}\mathrm{Pu}^{241} \rightarrow {}_{-1}\beta^0 + {}_{95}\mathrm{Am}^{241}.$$

The nuclide Am^{241} is an α-particle emitter with a half-life of about 500 years. Other isotopes of the new element americium have also been obtained, some of which are negative β-emitters.

As a result of various (α,n), $(\alpha,2n)$, (n,γ) and other reactions, often followed by negative β-decay, it has been possible to build up the series of transuranium elements, up to atomic number 102. With increasing atomic number, the amount of target material available becomes less and less. Consequently, attention is being turned to the use of fairly heavy accelerated ions, such as C^{12}, C^{13}, N^{14}, O^{16}, etc., as projectiles, with the relatively abundant uranium-238 and plutonium-239 as the target nuclei. Among the reactions which have been definitely established, the following are of interest:

$$\begin{gathered}
_{92}\mathrm{U}^{238} + {}_{6}\mathrm{C}^{12} \rightarrow 4\ {}_{0}n^1 + {}_{98}\mathrm{Cf}^{246} \\
_{92}\mathrm{U}^{238} + {}_{7}\mathrm{N}^{14} \rightarrow 5\ {}_{0}n^1 + {}_{99}\mathrm{Es}^{247} \\
_{92}\mathrm{U}^{238} + {}_{8}\mathrm{O}^{16} \rightarrow 4\ {}_{0}n^1 + {}_{100}\mathrm{Fm}^{250}
\end{gathered}$$

where the symbols Cf, Es and Fm represent the elements **californium, einsteinium** and **fermium,** respectively. In the earlier work with heavy ions, cyclotrons were used for acceleration, but the ion currents were fairly small. Larger currents, leading to increased yields of the products, can be obtained with linear accelerators of suitable design.

Apart from the fact they do not exist in nature, the transuranium elements are of particular chemical interest because they are part of a series, probably commencing with the element actinium (89), analogous to the rare earth elements (§ 15i). As is to be expected from this analogy, the trivalent state is the most stable among the **actinide series** of elements, although other states exist, especially with the earlier members of the series.

65g. Energy Changes in Nuclear Reactions.—The energy changes accompanying nuclear reactions are large, being of the order of a million times greater than those associated with chemical reactions. The basic reason for this is that electronic energy changes, which are involved in chemical reactions, are in the electron volt range (§ 15c), whereas nuclear energies are millions of electron volts. Nuclear reaction energies are sometimes determined directly, from the energies of the interacting and product particles, as estimated from their ranges or from their deflections in an electric or magnetic field. An alternative approach is to make use of the Einstein relationship for the equivalence of mass and energy, i.e.,

$$E = mc^2,$$

where E is the energy equivalent to the mass m, and c is the velocity of light. The mass change in a nuclear reaction is often known from the isotopic masses of the nuclei involved, and so the energy change can be calculated.*

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* Chemical reactions are undoubtedly also accompanied by mass changes, but they are far too small to be detectable by any known experimental technique.

If m is in grams then, since c is 2.998×10^{10} cm per sec, the equivalent value of E in ergs will be

$$E \text{ (ergs)} = m \text{ (grams)} \times (2.998 \times 10^{10})^2 = m \text{ (grams)} \times 8.990 \times 10^{20}.$$

Since nuclear energy changes are usually given in million electron volt units, use of the conversion factor 1 Mev = 1.602×10^{-6} erg gives

$$E \text{ (Mev)} = m \text{ (grams)} \times 5.614 \times 10^{26}. \tag{65.1}$$

In most calculations of mass-energy equivalence, masses are expressed in terms of the physical atomic weight scale; the unit of mass on this scale, referred to as an **atomic mass unit** (amu), is then one-sixteenth of the actual mass of an O^{16} atom. Since the Avogadro number, on the physical scale, is 6.025×10^{23}, it follows that 1 amu = $1.000/(6.025 \times 10^{23}) = 1.658 \times 10^{-24}$ gram. Upon inserting this factor into equation (65.1), the result is

$$\begin{aligned} E \text{ (Mev)} &= m \text{ (amu)} \times 5.614 \times 10^{26} \times 1.658 \times 10^{-24} \\ &= 931.1m \text{ (amu)}. \end{aligned} \tag{65.2}$$

It is seen, therefore, that 1 amu is equivalent to 931.1 Mev, so that the *energy change in Mev, in any process is equal to the change in mass, in amu, multiplied by 931.1.*

As an illustration of the application of equation (65.2), consider the historically interesting $Li^7(p,\alpha)He^4$ reaction which may be written as

$$Li^7 + H^1 \rightarrow He^4 + He^4.$$

In determining the mass change, it is customary to use the atomic (or isotopic) masses, which include the masses of the electrons, rather than those of the nuclei. Since the number of electrons is unaffected by the nuclear process, the increase or decrease of the atomic masses will be identical with that of the nuclear masses. The mass spectroscopic values of the atomic species are given below:

Interacting Particles		Product Particles	
Li^7	7.01823 amu	He^4	4.00387 amu
H^1	1.00815	He^4	4.00387
	8.02638		8.00774

$$\text{Mass change in reaction} = 8.00774 - 8.02638 = -0.01864 \text{ amu}.$$

The energy released, which is the equivalent of this decrease in mass, is consequently $0.01864 \times 931.1 = 17.34$ Mev. Measurement of the ranges of the two helium nuclei (α-particles) produced in the reaction gave a value of 17.2 Mev for the energy liberated, in good agreement with the more exact result calculated from the change in mass.

Nuclear reaction energy values are invariably given for a single reacting atom (or nucleus) whereas those for chemical reactions are based on a gram atom (or mole) of reactant. To compare the magnitudes of the two types of energy change, the former must be multiplied by the Avogadro number, thus

$$1 \text{ Mev per atom} \equiv 6.025 \times 10^{23} \text{ Mev per gram atom.}$$

Utilizing the conversion factors $1 \text{ Mev} = 1.602 \times 10^{-6}$ erg and $1 \text{ cal} = 4.184 \times 10^{7}$ erg, it follows that

$$1 \text{ Mev per atom} \equiv 23.06 \times 10^{6} \text{ kcal per gram atom.}$$

Since nuclear reaction energies are in the Mev range compared with kcal values for chemical reactions, it is evident, as stated earlier, that the former are of the order of a million times the latter.

An interesting consequence of the study of mass and energy changes in nuclear reactions was the discovery that the mass spectroscopic isotopic weights of the lighter elements in use prior to 1935 were in error. In a number of instances there appeared to be a discrepancy between the energy changes calculated from mass changes and those obtained experimentally. This led to a redetermination of the isotopic masses and with the new values the discrepancies disappeared. At the present time, nuclear energy changes, e.g., those accompanying β-decay, are used to supplement mass spectroscopic data to obtain accurate isotopic weights, especially for unstable nuclides which do not occur naturally.

65h. Rates of Nuclear Reactions: Cross Sections.—Nuclear reaction rates are expressed in terms of a quantity called the nuclear **cross section** indicated by the symbol σ (Greek: *sigma*); it has the dimensions of an area and is a measure of *the probability that a projectile particle of specified energy will undergo a given reaction with a particular nucleus.* Suppose the projectile source provides a density of n particles per cm^3 moving with a velocity v cm per sec in a given direction, then the product nv particles per cm^2 per sec is called the projectile particle **flux.** It is numerically equal to the total distance traveled by all the particles present in 1 cm^3 in 1 sec, and so is sometimes referred to as the **track length.** Suppose the projectile particles impinge on a material containing N target nuclei per cm^3; if σ cm^2 is the cross section of the given nuclear species for the reaction under consideration, then $N\sigma$ per cm is the probability that a particle will react with a nucleus in traversing 1 cm of the target material. Upon multiplying the probability $N\sigma$ per cm by the track length nv, the result $nvN\sigma$ gives the number of nuclei (or projectile particles) interacting per cm^3 per sec; hence, in a total volume of V cm^3

$$\text{Number of nuclear interactions per sec} = nvNV\sigma. \qquad (65.3)$$

In general, two methods have been used to determine nuclear cross sections, especially for reactions involving neutrons. One procedure, called the **activation method,** is applicable only if the reaction product is radioactive; in this case, the rate of formation of the radioactive nuclei in the target material is given by equation (65.3). The rate of decay will initially be less than the rate of formation, but as the number of radioactive nuclei increases their decay rate also increases. After moderate reaction time, a state of equilibrium is reached in which the rates of formation and decay are equal. Hence, equation (65.3) then also gives the rate of decay of the product, and since this can be measured by means of a suitable counter, σ can be calculated. It is necessary, of course, that n and v for the projectile particles be known; for neutrons, the product nv, i.e., the neutron flux, can be readily determined experimentally.

From the definition of cross section, it follows that the change dn in the particle density due to nuclear interactions, in traversing a thickness dx of target material is $-nN\sigma\, dx$. Hence, if n_0 is the density of the particles falling on a target x cm thick and n is the density of the emerging particles,

$$n = n_0 e^{-N\sigma x}, \tag{65.4}$$

so that, if n and n_0 are measured, σ can be obtained. This is the basis of the **transmission method** for the determination of nuclear cross sections.

It is of interest that a relationship of the form of equation (65.4) represents the absorption of γ-rays (and X-rays) by various materials; it is usually written in the form

$$I = I_0 e^{-\mu x},$$

where I_0 and I are the radiation intensities before and after passage through a material x cm thick and μ cm^{-1} is called the **linear absorption coefficient** of the material. The value of μ varies with the energy of the γ-ray photon, but for any specified energy it is roughly proportional to the density. This accounts for the fact that, for a given thickness, the more dense the material the more effective it is as an absorber of γ-rays. Incidentally, it is the exponential nature of γ-ray absorption that explains why these radiations can be attenuated but, at least in principle, not absorbed completely.

It should be noted that the nuclear cross section determined by the transmission method is the total cross section for all the different interactions which can occur between the given particles and target nuclei. The activation method, on the other hand, yields the cross section for a specific reaction, namely, the one leading to the formation of a particular radioactive nuclide.

Nuclear reaction cross sections vary with the energy of the projectile particles; for charged particles, there is generally an increase with energy, but with neutrons, especially for (n,γ) reactions, the cross section may be quite large for low energies, i.e., for slow neutrons, and the value decreases with increasing energy. For many nuclides of moderate and high mass number, the neutron capture cross section exhibits a sudden and marked increase for certain values of the neutron energy. This phenomenon is known as **resonance** and is attributed to the formation of the compound nucleus at, or close to, one of its energy levels.

Since nuclear diameters are of the order of 10^{-12} cm, the geometrical cross sections are about 10^{-24} cm^2. In many instances, nuclear reaction cross sections are in the vicinity of this order of magnitude; hence, 10^{-24} cm^2, called a **barn**, has been chosen as the unit for expressing cross sections. For (n,γ) reactions, the cross sections range from a small fraction of a barn, e.g., 4.6 ×

10^{-6} barn for the capture of thermal neutrons by deuterium, to a few millions, e.g., 3×10^6 barns, for the analogous reaction with xenon-135.

THE RELEASE OF NUCLEAR ENERGY

66a. Nuclear Binding Energies.—When isotopic weights were first determined by means of the mass spectrograph, it was noted that the results were close to integers. The departure from integral values was expressed by F. W. Aston (1927) as the **packing fraction,** defined by

$$\text{Packing fraction} = \frac{\text{Isotopic atomic weight} - \text{Mass number}}{\text{Mass number}} \times 10^4.$$

It was realized that the packing fraction was related to the stability of the nucleus, a negative fraction implying stability whereas a positive fraction indicated instability. However, a quantitative determination of relative stability had to await the discovery of the neutron and the development of the neutron-proton theory of nuclear structure.

If A and Z are the mass number and atomic number of a nuclide, then its nuclei contain $A - Z$ neutrons and Z protons; in addition, there will be Z orbital electrons. Let m_n, m_p and m_e be the masses of a neutron, proton and electron, respectively; the sum of the masses of the constituents of an atom is then $(A - Z)m_n + Zm_p + Zm_e$. Suppose the observed isotopic weight of the atom is M; the change in mass, called the **mass defect,*** accompanying the hypothetical formation of the atom from its constituents is thus

$$\begin{aligned}\text{Mass defect} &= (A - Z)m_n + Z(m_p + m_e) - M \\ &= (A - Z)m_n + Zm_{\text{H}} - M, \qquad (66.1)\end{aligned}$$

where $m_p + m_e$ has been replaced by m_{H} the mass of the hydrogen atom. The mass defect is equivalent to the energy that would be released in the hypothetical formation of the nucleus from individual protons and neutrons; this is the **binding energy** of the nucleus. It is numerically equal to the energy that would have to be supplied to break up the nucleus into its constituents.

If m_n, m_{H} and M in equation (66.1) are expressed in amu, the binding energy is obtained in Mev upon multiplying the mass defect by 931.1. For various purposes, it is convenient to determine the mean binding energy per nucleon, the term **nucleon** being used to describe a nuclear constituent, i.e., a neutron or a proton. This quantity is obtained upon dividing the total nuclear binding energy by the mass number; thus,

$$\text{Mean binding energy per nucleon} = \frac{931.1}{A}[(A - Z)m_n + Zm_{\text{H}} - M]\ \text{Mev}.$$

Taking m_n and m_{H} as 1.008986 and 1.008145 amu, respectively, and using the known isotopic weights, which are also in amu (cf. Table 64.1) the mean

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* The mass defect was originally defined by F. W. Aston as the difference between the isotopic weight and the mass number, i.e., $A - M$.

binding energy per nucleon can be determined. In Fig. 66.1, the values obtained in this manner for a number of nuclides are plotted against the mass number.

With the exception of He^4, C^{12} and O^{16}, the points fall on, or close to, a single curve. The fact that the binding energies of these nuclei lie above the curve implies that they are exceptionally stable; this stability appears to be associated with the presence of equal even numbers of protons and neutrons.* It is seen from Fig. 66.1 that, over a considerable range of mass numbers, the mean binding energy per nucleon is about 8 Mev. This consequently, is roughly the amount of energy required to remove a proton or a neutron from a nucleus. For the removal of a proton, however, additional energy is needed to permit the charged particle to overcome the potential energy barrier (cf. Fig. 65.1).

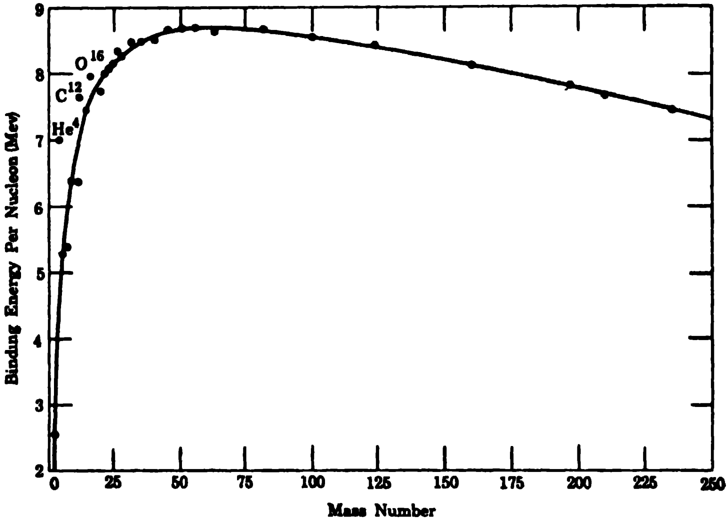

FIG. 66.1. Binding energy per nucleon as a function of the mass number of stable nuclides

From the standpoint of the release of **atomic energy,** more correctly called **nuclear energy,** since it is the energy accompanying nuclear reactions, the important aspect of Fig. 66.1 is that the binding energy first increases with increasing mass number and then decreases. It can be readily shown that, in any nuclear process in which the mean binding energy per nucleon is greater in the product nuclei than it is in the reacting nuclei, there must be a release of energy. It follows, therefore, that there are two general ways

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* The nonexistence of a stable Be^8 nucleus is probably due to the much greater stability of $2He^4$.

whereby nuclear energy can be obtained; they are (a) by **fusion reactions,** in which the lightest nuclei are combined to form somewhat heavier nuclei, and (b) by **fission reactions,** in which the heaviest nuclei are split into two (or more) lighter nuclei. In order to be of practical value, however, these reactions must be self-sustaining, that is to say, like combustion, they must be able to continue throughout a quantity of material, once they have been started. Unfortunately, although there are many nuclear reactions accompanied by a release of energy, there are few which can be made self-sustaining under conditions attainable on earth.

66b. Thermonuclear Fusion Reactions.—Many fusion reactions can be brought about by accelerating protons, deuterons, etc., and allowing them to react with various target nuclei of light elements. The amount of energy released is, however, very small in comparison with that expended in accelerating the particles. An alternative method of supplying the required kinetic energy to permit the nuclear reaction to take place is by raising the temperature of the reacting system. Nuclear processes occurring under these conditions are called **thermonuclear reactions.** The possibility then exists for the reaction to become self-sustaining by a mechanism similar to that involved in combustion. Once the process has been initiated, the energy produced is sufficient to raise the temperature of other nuclei to that necessary for reaction to take place at an appreciable rate. If the nuclear reactions occur fast enough, more energy may be released than is needed to maintain the temperature of the system. In this manner, nuclear fusion energy could be made available for use in various ways.

Because of the Maxwell distribution of velocities among the nuclei, the temperatures required for appreciable fusion reactions to occur, although very high, are lower than might be expected from the high energies, approaching the Mev range, that appear to be needed.* The rate at which a thermonuclear reaction occurs is determined by the product of the number of nuclei having a certain energy and the reaction probability (or cross section) at that energy, summed over the whole Maxwellian energy distribution at the existing temperature. Although the proportion of nuclei with energies greatly in excess of the average is not large, this is compensated by the marked increase in cross section with increasing particle energy. As a result, fusion reactions may take place at a useful rate at temperatures of the order of 10^7 °K, such as exist in the interiors of many stars.

There are undoubtedly several different thermonuclear fusion reactions, accompanied by the release of energy, which occur in stars, but two appear to be most important. They both involve, ultimately, the combination of four protons to form a helium nucleus (plus two positrons), but the intermediate stages are quite different. In the **carbon cycle,** which is the main process at the higher stellar temperatures, the nuclear reactions occurring are believed to be the following:

* Assuming the particle energy to be $\frac{3}{2}kT$, an energy of 0.1 Mev would imply a *particle* temperature of 8×10^8 ° K.

$$\begin{aligned} {}_6\mathrm{C}^{12} + {}_1\mathrm{H}^1 &\quad {}_7\mathrm{N}^{13} + \text{energy} \\ {}_7\mathrm{N}^{13} &\quad {}_6\mathrm{C}^{13} + {}_{+1}\beta^0 \\ {}_6\mathrm{C}^{13} + {}_1\mathrm{H}^1 &\rightarrow {}_7\mathrm{N}^{14} + \text{energy} \\ {}_7\mathrm{N}^{14} + {}_1\mathrm{H}^1 &\rightarrow {}_8\mathrm{O}^{15} + \text{energy} \\ {}_8\mathrm{O}^{15} &\rightarrow {}_7\mathrm{N}^{15} + {}_{+1}\beta^0 \\ {}_7\mathrm{N}^{15} + {}_1\mathrm{H}^1 &\rightarrow {}_6\mathrm{C}^{12} + {}_2\mathrm{He}^4. \end{aligned}$$

The over all reaction, obtained upon adding the six equations, is seen to be

$$4\,{}_1\mathrm{H}^1 \rightarrow {}_2\mathrm{He}^4 + 2\,{}_{+1}\beta^0 + \text{energy},$$

where ${}_{+1}\beta^0$ represents a positron, so that the C^{12}, regenerated in the last stage of the cycle, acts in the nature of a catalyst. From the known masses of the hydrogen and helium nuclei and that of the positron, which is the same as for an electron, it is found that the energy release is 26.7 Mev per four protons. Using the conversion factor given in § 65g, this is seen to be equivalent to the very large value of 1.54×10^8 kcal per gram of hydrogen consumed.

The stages in the alternative **proton-proton chain,** which predominates at lower stellar temperatures, are as follows:

$$\begin{aligned} {}_1\mathrm{H}^1 + {}_1\mathrm{H}^1 &\quad {}_1\mathrm{D}^2 + {}_{+1}\beta^0 + \text{energy} \\ {}_1\mathrm{D}^2 + {}_1\mathrm{H}^1 &\quad {}_2\mathrm{He}^3 + \text{energy} \\ 2\,{}_2\mathrm{He}^3 &\quad {}_2\mathrm{He}^4 + 2\,{}_1\mathrm{H}^1 + \text{energy}. \end{aligned}$$

To obtain the two helium nuclei for the third reaction the first two must occur twice, so that the net result is the same as in the carbon cycle. In the sun and similar stars, with interior temperatures of the order of 2×10^7 °K, the carbon cycle and proton-proton chain make almost equal contributions to the total energy produced.

66c. Thermonuclear Reactions on Earth.—The possibility of bringing about thermonuclear (fusion) reactions on earth, to serve as a source of energy, has attracted much attention. Bearing in mind the masses of material available on earth, it is certain that the reactions of the carbon cycle and the proton-proton chain would occur too slowly to be of any practical value. Calculations show that, even at the temperature of the sun, it would take several million years to convert 1 gram of hydrogen into helium. It is only because of its enormous mass that the sun produces energy at a high rate.

To obtain useful thermonuclear energy on earth, it is necessary to seek for other fusion reactions which occur more rapidly. The only ones which appear to offer any prospects for success are three reactions among the nuclei of the hydrogen isotopes, deuterium and tritium; they are

$$\begin{aligned} {}_1\mathrm{D}^2 + {}_1\mathrm{D}^2 &= {}_2\mathrm{He}^3 + {}_0n^1 + 3.2\ \text{Mev} \\ {}_1\mathrm{D}^2 + {}_1\mathrm{D}^2 &= {}_1\mathrm{T}^3 + {}_1\mathrm{H}^1 + 4.0\ \text{Mev}, \end{aligned}$$

which take place at approximately the same rate at a given temperature, and

$${}_1\mathrm{T}^3 + {}_1\mathrm{D}^2 = {}_2\mathrm{He}^4 + {}_0n^1 + 17.6\ \text{Mev},$$

the rate of which, at equivalent concentrations, is about a hundred times as great. If sufficiently high temperatures could be attained, the deuterium present in all natural waters would represent an almost inexhaustible source of energy.

One way in which temperatures of the order of millions of degrees can be obtained on earth is by means of a nuclear fission bomb (§ 66f). By combining a quantity of deuterium or tritium (or a mixture) with such a bomb, it has been possible to bring about tremendously powerful explosions due to the very rapid release of large amounts of energy in the thermonuclear reactions occurring among the isotopes of hydrogen. This is the basis of the hydrogen (or thermonuclear) bomb. In the explosion of such devices, the energy is released in an uncontrolled manner, but there is a possibility that the energy could be stored, as heat, underground and utilized over a period of time.

Methods are being sought for bringing about the thermonuclear fusion reactions mentioned above in a controlled manner, by means of high temperatures obtained by electrical heating. In order to provide useful energy, the energy released must be greater than that required to heat the gas plus that which is lost in various ways, especially as radiation. The latter is not strictly a loss, since the radiation energy can be absorbed outside the reacting system and utilized, but it is not available to maintain the temperature of the reacting nuclei. With increasing temperature, both the rate of energy release and the rate of loss increase, but the former goes up more rapidly, so that at a certain temperature a self-sustaining thermonuclear reacting system is theoretically possible. For the D-D reaction, this temperature is about 3.5×10^8 °K and for the T-D reaction it is roughly 4.5×10^7 °K. The most obvious problems, therefore, are the attainment of such high temperatures and the containment of the reactants at these temperatures. Since the hydrogen isotopes are completely ionized at temperatures above 50,000°K, magnetic fields offer the best prospect for containing the nuclei and electrons present at high temperatures. As mentioned above, initial heating of the ionized **plasma,** as it is called, may perhaps be achieved by electrical means.

66d. Nuclear Fission.—It was observed by O. Hahn and F. Strassmann (1939) that one of the products resulting from the action of neutrons on uranium (atomic number 92) was an isotope of barium (atomic number 56). This led L. Meitner and O. R. Frisch to suggest that, after the capture of a neutron, the uranium nucleus splits up into two approximately equal parts; that is to say, the neutron causes the uranium to undergo **fission.** By separating the isotopes of uranium, it was later found that only the uranium-235 is fissionable by neutrons of all energies, but uranium-238 requires neutrons of energy in excess of 1 Mev to cause fission. The adjective "fissionable" is generally applied only to those nuclides which can undergo fission as a result of the capture of neutrons of all energies. Uranium-235 is the only fissionable species of relatively long half-life found in nature. Several other fissionable nuclides have been made artificially by nuclear reactions, but only two have sufficiently long half-lives to be of practical value for the release of nuclear energy by fission. One of these is plutonium-239, obtained by the (n,γ) reaction with uranium-238 followed by two stages of β-decay, and the other is uranium-233 obtained in an analogous manner from thorium-232.

The energy released in fission can be calculated from the known masses of the neutron and the uranium-235 atom and of the ultimate products of the reaction. A simple approximate approach is to make use of the mean binding energies per nucleon. It is seen from Fig. 66.1 that in elements of the highest mass number, e.g., uranium, this is about 7.6 Mev, but in the intermediate mass range, where the products of fission are found, the value is close to 8.5 Mev. This means that the formation of uranium-235 from its constituent nucleons would be accompanied by the release of 235 × 7.6 Mev. On the other hand, the formation of fission product nuclei would result in the liberation of 235 × 8.5 Mev. Thus, it is possible to write

$$92p + 143n \rightarrow \text{Uranium-235} + 235 \times 7.6 \text{ Mev}$$
$$92p + 143n \rightarrow \text{Fission products} + 235 \times 8.5 \text{ Mev}$$

and, upon subtraction, the result is seen to be

$$\text{Uranium-235} \rightarrow \text{Fission products} + 210 \text{ Mev.}$$

Consequently, the fission of a single uranium-235 (or other) nucleus is accompanied by the release of over 200 Mev of energy. Expressed in another form, the nuclear energy accompanying the fission of 1 gram of uranium-235 is close to 2×10^7 kcal.

The importance of nuclear fission lies not only in the large amount of energy released, but also in the fact that the reaction resulting from the capture of a neutron is accompanied by the emission of two (or more) neutrons. Thus, in principle, a fission chain reaction, with neutrons acting as the chain carriers, is possible. Hence, once started, the process will be self-sustaining and energy will be produced continuously. Fission can be initiated by neutrons of virtually zero energy, so that essentially all the energy released is available.

In nuclides of high atomic and mass numbers, the neutron-to-proton ratio e.g., 1.55 in uranium-235, is greater than it is for the stable nuclides of lower atomic numbers, e.g., about 1.44 for barium. It is this difference which accounts for the emission of neutrons in fission. However, the neutron-to-proton ratios of the nuclei formed in the fission process are still high for stability, so that they are negative β-particle emitters. Each fission product nucleus undergoes, on the average, three stages of β-decay before a stable species is formed.

A detailed study of the complex mixture of nuclides produced in fission shows that the nuclei of a given species can split up in some forty different ways; there are, consequently, roughly 80 primary fission products, forming a complex mixture of some 250 nuclides as a result of the average of three stages of β-decay. The mass numbers of these nuclides range from 72, probably an isotope of zinc (atomic number 30), to 160, believed to be an isotope of gadolinum (atomic number 64). The most probable fission mode of uranium-235, which takes place with 6.4 per cent of the nuclei undergoing fission, leads to products with mass numbers 95 and 139. In only 0.01 per cent of the cases does symmetrical fission occur, yielding two products with mass numbers of 117. The energy released depends somewhat on the mode of fission, but the value given above, of approximately 200 Mev per nucleus, is a good average for the three fissionable nuclides.

66e. The Fission Chain Reaction.—The number of neutrons emitted in the fission process also varies, to some extent, with the fission mode, but the weighted average values are close to 2.5 for uranium-233 and -235, and 2.9 for plutonium-239. Since only one neutron is required, per fission, to maintain the fission chain, it would appear, at first sight, that a self-sustaining chain could be realized without difficulty. That such is not the case, is apparent from the fact that considerable amounts of uranium-235 exist in nature in normal uranium compounds without undergoing fission, in spite of the availability of neutrons. The reason natural uranium is stable against fission is that not all the neutrons produced in fission are available for maintaining the fission chain. A large proportion of the neutrons is lost in nonfission reactions, mainly radiative capture by uranium-238, as well as by the fissionable uranium-235 and other nuclides that may be present; in addition fission neutrons are lost by escaping from the system altogether. As a result, less than one neutron is available per fission and so the chain reaction cannot be maintained.

In any material containing a fissionable nuclide, the condition for a self-sustaining chain reaction is that the number of neutrons produced in the fission process must be equal, at least, to the number absorbed in both fission and nonfission reactions plus the number that escape entirely. Since fission neutrons are produced throughout the whole volume of the system, but escape occurs only at the surface, the *fraction* of neutrons lost by escape can be diminished by increasing the size, thereby decreasing the ratio of area to volume. For any given fissionable system, there is thus a minimum **critical size,** below which the maintenance of a fission chain is impossible.

The critical size, and **critical mass** of fissionable nuclide present, depends on the nature and isotopic abundance of that nuclide in the system; the presence, nature and amount of moderator present to slow down the fast fission neutrons; the shape and arrangement of the materials; the presence of extraneous substances which capture neutrons, etc. However, for any specific system, the critical mass always has a definite value. It may range from less than 1 kg of uranium-235 for an aqueous solution of a salt of uranium containing about 90 per cent of this isotope, to some 200 kg (or more), present in a total mass of over 30 tons of natural uranium, with carbon as the moderator.

It should be mentioned that, in the absence of a moderator, a fission chain cannot be maintained in natural uranium, no matter how great the size or mass. With neutrons that are not slowed down appreciably, the proportion captured by the uranium-238 in nonfission reactions is so large that a self-sustaining fission chain in the uranium-235 is impossible. If the abundance of the latter isotope is increased, e.g., by the thermal diffusion process (§ 64d), or if a suitable moderator is included with the natural uranium to slow down the neutrons, the fraction of nonfission capture is decreased and a sufficiently large mass can become critical.

66f. The Utilization of Fission Energy.—The large amounts of energy that accompany the fission process have been utilized in two ways: first, uncontrolled, rapid release of the energy to cause an explosion, and second, the controlled, relatively slow release to produce heat which can be utilized for electrical power. In the **atomic bomb,** a subcritical quantity of fissionable material, i.e., less than the critical size for the given conditions, is suddenly made highly supercritical, i.e., greatly in excess of critical. In the latter state, approximately two neutrons are available per fission, so that a branching (or divergent) chain reaction is possible. This leads to a very rapid increase in the overall fission rate and, hence, an extremely rapid release of energy. Two general procedures have been described for quickly converting a subcritical system of fissionable material into a supercritical one. In the first method, two or more masses of subcritical size are brought together very rapidly, by means of a high-explosive charge, so as to form a highly supercritical mass. The second method is based on the fact that a subcritical quantity of fissionable material can be made supercritical by compression. The surface area is decreased without changing the mass, and so the proportion of neutrons that escape is diminished. Sufficient neutrons thus become available to maintain the fission chain.

The controlled release of nuclear fission energy is achieved in a device called a **nuclear reactor.*** Although there are numerous variations in the design and components of nuclear reactor systems, there are, nevertheless, a number of features which they all possess in common. In outline, a reactor consists of an active core wherein the fission chain is sustained and where most of the energy is released as heat. The core contains the **nuclear fuel,** consisting of a fissionable nuclide and often a **fertile material,** namely, uranium-238 or thorium-232, which can be converted into a fissionable species, i.e., plutonium-239 or uranium-233, respectively, as a result of neutron capture. If it is required to slow down the neutrons released in fission, a moderator is included in the core. The moderators in general use are ordinary water, which requires enriched fuel, heavy water, carbon (as graphite) and, to some extent, beryllium or its oxide. The relative amounts and nature of the fuel and moderator determine the energy of the neutrons causing most of the fissions. Certain reactors, called **fast reactors,** contain no moderator and the majority of the fissions are caused by neutrons having energies of 0.5 Mev or more. **Thermal reactors,** at the other extreme, have a sufficient amount of moderator to reduce the energies of most of the fission neutrons to thermal values. The reactor core is surrounded by a neutron reflector to decrease the loss of neutrons from the core by scattering back many of those which have escaped.

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* The name "pile" was originally used because the first nuclear reactor was made by piling blocks of graphite (moderator) upon one another and inserting pieces of uranium at predetermined locations.

The heat generated in the core is removed by circulation of a suitable coolant. Among the coolants which have been used or proposed for various reactors, the most important are ordinary water, heavy water, liquid sodium (or sodium-potassium alloy), organic compounds of high boiling point having stability against ionizing radiations (cf. § 63c), and the gases helium, air and carbon dioxide. If the heat liberated in the reactor is to be converted into electrical power, it must be transferred to a working fluid to produce steam or a hot gas. By the second law of thermodynamics, the temperature of the latter should be as high as possible, so as to increase the efficiency of the conversion of heat into useful work (§ 8i). Hence, operating temperatures in the reactor core must be high.

In order that a chain reaction may be sustained, the reactor core is designed to be slightly supercritical. However, to prevent the propagation of a divergent fission chain, the excess neutrons are removed either by means of a neutron absorber, such as boron or cadmium, or they are allowed to escape by temporarily removing part of the core or reflector. It is by varying the loss of neutrons in this manner that the operation of a nuclear reactor is controlled. When not operating, the controls permit neutrons to be lost, so that the system is subcritical. To start up the reactor, the controls are moved in such a manner as to decrease the losses and the system becomes slightly supercritical. This condition is continued until the desired rate of fission, and hence of heat release, is attained. By changing the controls once more, so that the reactor is just critical, the rate of fission is held essentially constant. To shut the reactor down, the controls are adjusted so as to increase the loss of neutrons, thereby making the system subcritical once more.

66g. Chemistry and the Release of Nuclear Energy.—The economic future of nuclear power from fission is closely bound up with the solution of a number of chemical problems, some of which will be mentioned here. The raw materials are uranium and thorium, and simple and efficient methods must be developed for extracting them from their ores, especially those containing very small proportions of these elements. The fission energy of the uranium-235 present in ordinary granite is roughly equivalent to that obtainable from the combustion of the same weight of coal. But the separation of the nuclear fuel from the granite is, at the present time, prohibitively expensive.

The ideal coolant is one that has a low melting point and a high boiling point, is stable at high temperatures and to ionizing radiations, has a small cross section for neutron capture, is noncorrosive and chemically inactive, and has good heat transfer properties. None of the coolants employed at present satisfies all these requirements, but chemical research will undoubtedly lead to the development of better materials. With some of the coolants in use at the present time, e g., water (at high temperature and pressure) and liquid sodium, corrosion is a major problem. The containing material must be able to withstand high temperatures and have a small cross section for neutron capture, in addition to being inexpensive and noncorrosive. These requirements are currently being met by the use of zirconium (and its alloys) and stainless steels, but neither of these is ideal. For operation at lower temperatures the demands are less severe and aluminum and magnesium alloys have been employed, especially with carbon dioxide gas as the coolant.

Perhaps the outstanding chemical problem in connection with nuclear reactors is that associated with the treatment of spent reactor fuels. Because of the consumption of some of the fissionable species and the accumulation of fission products, it is not possible to maintain criticality, although the reactor fuel still contains a large proportion of valuable nuclides which must be recovered. If the fuel consists initially of uranium-235 and -238, for example, the spent material will contain considerable amounts of these two isotopes and also of fissionable plutonium-239, resulting from neutron capture by uranium-238. The separation of the uranium and plutonium from one another and from the highly radioactive, complex mixture of fission products involves problems of considerable physicochemical interest. By simplifying the extraction processes, chemistry can make a significant contribution to the economics of power derived from nuclear fission.

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PROBLEMS

1. The C^{14} content of living matter undergoes 15.3 disintegrations min^{-1} g^{-1}. A fragment from the Dead Sea Scrolls gave a count of 12.0 disintegrations min^{-1} g^{-1}. The half-life of C^{14} is 5600 years. Determine the age of the scrolls.

2. Hg^{198} has been prepared from gold by a (n, γ) reaction. Write equations for the transformations which take place.

3. When sulfur-33 is irradiated with protons, it emits neutrons. Shortly thereafter positrons are emitted. What reactions have taken place?

4. The number of α particles emitted per sec by one gram of radium is 3.608×10^{10}. Determine (*a*) the decay constant and (*b*) the half-life of radium.

5. In the reaction $N^{14}(\alpha, p)O^{17}$, 1.16 Mev of energy is absorbed. Determine the isotopic mass of O^{17}. The isotopic mass of He^4 is 4.00387.

6. The average energy of thermal neutrons at 300°K is 0.026 ev. Calculate the equivalent wave length.

7. The α particles emitted by radium have energies of 4.795 Mev and 4.611 Mev. What is the wave length of the gamma ray accompanying the decay?

8. The half-life for the beta decay of K^{40} is 1.83×10^9 years. The isotope constitutes 0.012% of natural potassium. Determine (*a*) the decay constant and (*b*) the number of beta particles emitted per sec by one gram of potassium chloride.

9. The final (stable) products of the fission reaction

$$_{92}\mathrm{U}^{235} + {}_0n^1 \rightarrow {}_{56}\mathrm{Ba}^{141} + {}_{36}\mathrm{Kr}^{92} + 3\ {}_0n^1,$$

after radioactive (beta) decay of the initial products, are $_{59}\mathrm{Pr}^{141}$ and $_{40}\mathrm{Zr}^{92}$, whose isotopic masses are 140.951 and 91.934, respectively. Calculate the total energy in calories released as a result of the fission of one gram of U^{235} in this manner.

10. Determine the number of nuclei which react per sec when a sheet of gold 0.040 cm thick and 10 cm^2 in area is subjected to a thermal neutron flux of 8.0×10^7 neutrons cm^{-2} sec^{-1}. The cross section of Au^{197} is 98 barns and its density is 19.3 g cm^{-3}.

TABLE OF ATOMIC WEIGHTS

	Symbol	Atomic no.	Atomic wt.
Aluminum	Al	13	26.98
Antimony	Sb	51	121.76
Argon	Ar	18	39.944
Arsenic	As	33	74.91
Barium	Ba	56	137.36
Beryllium	Be	4	9.013
Bismuth	Bi	83	209.00
Boron	B	5	10.82
Bromine	Br	35	79.916
Cadmium	Cd	48	112.41
Calcium	Ca	20	40.08
Carbon	C	6	12.011
Cerium	Ce	58	140.13
Cesium	Cs	55	132.91
Chlorine	Cl	17	35.457
Chromium	Cr	24	52.01
Cobalt	Co	27	58.94
Copper	Cu	29	63.54
Dysprosium	Dy	66	162.51
Erbium	Er	68	167.27
Europium	Eu	63	152.0
Fluorine	F	9	19.00
Gadolinium	Gd	64	157.26
Gallium	Ga	31	69.72
Germanium	Ge	32	72.60
Gold	Au	79	197.0
Hafnium	Hf	72	178.50
Helium	He	2	4.003
Holmium	Ho	67	164.94
Hydrogen	H	1	1.0080
Indium	In	49	114.82
Iodine	I	53	126.91
Iridium	Ir	77	192.2
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.92
Lead	Pb	82	207.21
Lithium	Li	3	6.940
Lutetium	Lu	71	174.99
Magnesium	Mg	12	24.32
Manganese	Mn	25	54.94
Mercury	Hg	80	200.61
Molybdenum	Mo	42	95.95
Neodymium	Nd	60	144.27
Neon	Ne	10	20.183
Nickel	Ni	28	58.71
Niobium	Nb	41	92.91
Nitrogen	N	7	14.008
Osmium	Os	76	190.2
Oxygen	O	8	16.000
Palladium	Pd	46	106.4
Phosphorus	P	15	30.975
Platinum	Pt	78	195.09
Potassium	K	19	39.100
Praseodymium	Pr	59	140.92
Rhenium	Re	75	186.22
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.48
Ruthenium	Ru	44	101.1
Samarium	Sm	62	150.35
Scandium	Sc	21	44.96
Selenium	Se	34	78.96
Silicon	Si	14	28.09
Silver	Ag	47	107.880
Sodium	Na	11	22.991
Strontium	Sr	38	87.63
Sulfur	S	16	32.066
Tantalum	Ta	73	180.95
Tellurium	Te	52	127.61
Terbium	Tb	65	158.93
Thallium	Tl	81	204.39
Thorium	Th	90	232.05
Thulium	Tm	69	168.94
Tin	Sn	50	118.70
Titanium	Ti	22	47.90
Tungsten	W	74	183.86
Uranium	U	92	238.07
Vanadium	V	23	50.95
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.92
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.22

PHYSICAL CONSTANTS AND CONVERSION FACTORS

1 liter = 1000 ml = 1000.027 cc

1 absolute joule = 10^7 ergs

1 international joule = 1.0002×10^7 ergs

1 defined calorie = 4.184 abs joules
= 4.184×10^7 ergs

1 standard atm = 76.0 cm of mercury
= $76.0 \times 13.595 \times 980.66 = 1.0132 \times 10^6$ dynes cm^{-2}

Ice point (0° C) = 273.15° K

Volume of 1 mole of ideal gas at S.T.P. = 22.414 liters

Gas constant (R) = 0.08205 liter-atm deg^{-1} mole^{-1}
= 8.314×10^7 ergs deg^{-1} mole^{-1}
= 1.987 cal deg^{-1} mole^{-1}

$\ln x = 2.3026 \log x$

$2.3026R$ = 4.576 cal deg^{-1} mole^{-1}

Avogadro number (N) = 6.023×10^{23} molecules mole^{-1}

Boltzmann constant (k) = 1.380×10^{-16} erg deg^{-1} molecule^{-1}

Faraday (F) = 96,500 coulombs g-equiv^{-1}

1 abs volt-coulomb = 1 abs joule = 0.2390 (defined) cal

Acceleration due to gravity (g) = 980.66 cm sec^{-2}

Planck constant (h) = 6.624×10^{-27} erg sec

Velocity of light (c) = 2.998×10^{10} cm sec^{-1}

1 electron volt (ev) = 1.602×10^{-12} erg
= 23.06 kcal mole^{-1}

Answers to Problems

CHAPTER 2

1. 92.9 cm **2.** 0.694 g l^{-1} **3.** (*a*) 7.05 atm; (*b*) 3.04 atm **4.** (*a*) 95.23 A, 4.77 He; (*b*) A 66.7, He 33.9 **5.** (*a*) 3.78×10^{26}; (*b*) 3.23×10^{26} **6.** 134 kg **7.** 273.165°K **8.** (*a*) 1.17 g; (*b*) 3.29×10^{13} **9.** (*a*) 6.8×10^{14}; (*b*) 9.6×10^{9}; (*c*) 2.7×10^{-48} **10.** 675g (ideal); 1400g (van der Waals) **11.** (*a*) 1.177 mg ml^{-1}; (*b*) 1.169 mg ml^{-1} **12.** (*a*) 7.73 atm; (*b*) 0.363 atm **13.** $M = 44.019$; N = 14.010 **14.** M 78.108, C 12.010 using H = 1.0080) **15.** 39°C **16.** (*a*) 0.788×10^{-5} cm; (*b*) 3.38×10^{-8} cm; (*c*) 9.87×10^{28} collisions sec^{-1} ml^{-1} **17.** (*a*) 167 sec; (*b*) 91.6 ml **18.** 7.1×10^{23} **19.** 1.154

CHAPTER 3

1. 4.89×10^{11} erg; 11,680 cal **2.** (*a*) $w = RT \ln \frac{V_2 - b}{V_1 - b} + a\left(\frac{V_1 - V_2}{V_1V_2}\right)$; (*b*) 11.2×10^{8} joules **3.** — **4.** $w = -A \ln \frac{P_2}{P_1} + \frac{c}{2}(P_2^2 - P_1^2)$ **5.** a/v^2 **6.** — **7.** (*a*) 917 g; (*b*) 3.71×10^4 cal; (*c*) 4.58×10^5 cal **8.** −85.8 kcal **9.** (*a*) $q = w = -1240$ cal, $\Delta E = \Delta H = 0$: (*b*) $q = 0$, $w = -1579$ cal, $\Delta E = +1579$ cal, $\Delta H = +2630$ cal **10.** −17.5 kcal **11.** 57.0 kcal **12.** 5 moles **13.** $\Delta E = 1337$ cal, $\Delta H = 1338$ cal **14.** −233.88 kcal $mole^{-1}$ **15.** (*a*) *n*-butane, −29.82 kcal; *iso*-butane, −31.46 kcal; (*b*) - 1.64 kcal **16.** (*a*) −41.698 kcal; (*b*) −74.430 kcal **17.** (*a*) +30.1 kcal; (*b*) +56.5 kcal **18.** ΔH(cis → trans) = −13.04 kcal $mole^{-1}$ **19.** −647.1 kcal **20.** (*a*) −26.8; (*b*) −7.4 kcal **21.** (*a*) solute, −11.70 kcal $mole^{-1}$; solvent, −0.029 kcal $mole^{-1}$; (*b*) −6.10 kcal **22.** (*a*) 43.5 kcal; (*b*) 43.3 kcal **23.** (*a*) *ca.* 2250°K; (*b*) over 4000°K **24.** (*a*) 32.08 kcal (*b*) 135.95 kcal for 1 CO + 1 H_2 **25.** 1 mole of steam to 2.83 moles of air **26.** Sodium **27.** (*a*) −19 kcal; (*b*) +17 kcal; (*c*) +3 kcal

CHAPTER 4

1. (*a*) 0; (*b*) −1254 eu; (*c*) +1468 eu **2.** (*a*) $\Delta S = 13.8$ eu, $\Delta A = -4125$ cal, $\Delta F = -4125$ cal; (*b*) same values **3.** T/C_p, T/C_v **4.** (*a*) 2.42 eu; (*b*) 5.2 eu **5.** (*a*) 2.19 eu; (*b*) 3.80 eu; (*c*) −136.64 kcal **6.** (*a*) −5.00 eu; (*b*) −5.15 eu **7.** 44.5 eu, −1407 cal, 0 **8.** 27.5 eu, −1257 cal, −515 cal **9.** $\Delta S = \int_0^{173°K} C_p(c)\,\frac{dT}{T} + \frac{L_f}{173} + \int_{173°K}^{273°K} C_p(l)\,\frac{dT}{T} + \frac{L_v}{273} + \int_{273°K}^{298°K} C_p(g)\,\frac{dT}{T}$ **10.** 8.06 eu **11.** 7300 cal **12.** (*a*) 0.535; (*b*) 0.214 **13.** (*a*) −121.5 kcal; (*b*) −121.4 kcal **14.** Diphenyl **15.** (*a*) 4377 cal; (*b*) 10,215 cal; (*c*) −292 eu; (*d*) +292 eu, +292 eu **16.** — **17.** (*a*) 0; (*b*) 1775 cal **18.** V/C_p **19.** 58.8 cal g^{-1} **20.** −101.6 cal **21.** —

CHAPTER 5

1. $d_l = 0.383$, $d_v = 0.172$ g ml^{-1} 2. (*a*) 1.908 ml g^{-1}; (*b*) 79.4 (using 3.64), 109 (using 2.67) atm, experimental value 77.8 atm; (*c*) $\frac{d_l + d_v}{2} = 0.7344 - 0.001334t$; (*d*) 0.526 g ml^{-1} 3. (*a*) 2.21, 2.20 cm deg^{-1}; (*b*) 79.84°; (*c*) 112 mm 4. (*a*) $a = 1.345$, $b = 0.03219$; (*b*) 0.4136 g ml^{-1} 5. 9.70 mm 6. 4.95 atm 7. 78°C 8. (*a*) $\log p = -\frac{a}{2.303RT} + \frac{b}{R}\log T + \text{constant}$; (*b*) $\log p = -\frac{a}{2.303RT} + \frac{v}{R}\log T + \frac{cT}{2.303R}$ 9. (*a*) Liquid 570 g, vapor 430 g; (*b*) liquid 739 ml, vapor 2261 ml 10. (*a*) $a = 3\,P_cV_c{}^2T_c$, $b = \frac{1}{3}\,V_c$, $R = \frac{8}{3}\,\frac{P_cV_c}{T_c}$; (*b*) 2.67; (*c*) $(\pi + 3)(3\theta - 1) = 8\theta$ 11. (*a*) 14.73 kcal mole^{-1}; (*b*) $L_v = 15{,}229 - 1.685T$ cal mole^{-1} 12. (*a*) (*b*) 150.8 cal g^{-1} 13. 84.73°C 14. (*a*) 103.9 l; (*b*) $w = 10{,}520$ joules, $\Delta E = 25.73$ kcal, $\Delta F = 0$ 15. (*a*) 11.1 kcal mole^{-1}; (*b*) 66°C 16. 0.01 mm 17. 0.0143 cm 18. 7.14 cm 19. 234°C 20. 4.25 millipoise 21. 69.5 atm

CHAPTER 6

1. (*a*) 1.33×10^9 cm sec^{-1}; (*b*) 0.548 A 2. Mo, $Z = 42$ 3. 1.3×10^{-21} A 4. 4.96×10^4 volt cm^{-1} 5. 6200 A 6. 3.29 kv 7. (*a*) 4102, 950, 10,050 A; (*b*) 0.38, 0.54, 0.28 ev 8. (*a*) 303.8 A; (*b*) 54.40 ev

CHAPTER 7

1. (*b*) 0.68 2. (*a*) Fe, Ni; (*b*) Fe, 75°38′ 3. (*a*) 111, 200, 220, 311, 222, 400, 331, 420; (*b*) 3.602 A; (c) Face centered, Cu 4. (*a*) Face centered; (*b*) 1.432 A 5. Face centered 6. 4.29 A 7. 4.46 g cm^{-3} 8. (*a*) 21.93°; (*b*) 3.300 A; (*c*) 3.300, 2.330, 1.903 A 9. 4 g cm^{-3} 10. 6.50 A 11. (*a*) 0.037 cm^3; (*b*) rhombic 12. (*a*) 562 cal g-atom^{-1}; (*b*) 7630 atm 13. 8.18 cal g^{-1} (exp. value 7.85) 14. 15.1°C 15. (*a*) 24.7 kcal mole^{-1}; (*b*) 14,500 mm 16. (*a*) 221°C; (*b*) 0.0053 mm; (*c*) 220°C; (*d*) 9.3 kcal g-atom^{-1} 17. 146°C exp. value 18. 25.4 kcal mole^{-1} P_4

CHAPTER 8

1. 182 2. (*a*) 676 mm; (*b*) 84.3°C; (*c*) −2.6°C 3. 0.50°C 4. (*a*) 434 g; (*b*) 0.0438 5. 35.5 cal g^{-1} 6. ±0.005°C 7. 99 mole% 8. (*a*) 1 methanol to 1.94 ethylene glycol; (*b*) 14.7% methanol, 25.3% ethylene glycol, by wt 9. $a = 0.760$, $\gamma = 0.910$ 10. S_8 11. 22.8 12. (*a*) 59000; (*b*) −0.0006°C 13. 49.4 atm (Morse eq.), 58.4 atm (thermodynamic eq.) 14. $a_1 = 0.998$ 15. −40.1 cal

CHAPTER 9

1. 1.44 D 2. 1.05 D 3. *o* 1.44, *m* 1.80, *p* 1.95 D 4. (*a*) 0; (*b*) linear 5. 1.350 6. (*a*) 21.32 cm^3; (*b*) 7.72 cm^3 7. (*a*) 4; (*b*) 207.6 cm^{-1} 211.2, by eq. 29.4; (*c*) 2.69×10^{-40} g cm^2 8. (*a*) 2890 cm^{-1}; (*b*) 4.82×10^5 dyne cm^{-1} 9. 2.39, 2.44 μ

Chapter 10

1. — 2. Mole% I_2 = mole% H_2 = 11.1, mole% HI = 77.8 3. (*a*) 36.8 kcal mole^{-1}; (*b*) 0.279 4. (*a*) 10.82 kcal; (*b*) No 5. No 6. 2.485 g 7. $\Delta H^0 = 90.16$ kcal, $\Delta F^0 = 38.65$ kcal, $\Delta S^0 = 32.2$ eu 8. −38.65 kcal mole^{-1} 9. (*a*) $\log K_p = \frac{3904}{T} - 8.010 \log T + 2.514 \times 10^{-3}T - 2.77 \times 10^{-7}T^2 + 10.30$, $\Delta F^0 = -17{,}870 + \underbrace{15.916T \ln T}_{36.654T \log T} - 11.505 \times 10^{-3}T^2 + 12.70 \times 10^{-7}T^3 - 47.182T$; (*b*) 973 atm 10. 1.30% 11. (*a*) $\Delta F^0 = +43.47$ kcal, no; (*b*) $K_p = 3.36 \times 10^{-4}$ (pressure in atm), $\Delta F^0 = +15.50$ kcal 12. 44.54 eu mole^{-1} 13. 53.17 eu mole^{-1} 14. 7.5×10^{-5}% 15. 16.904 eu 16. (*a*) $K_p = 1.08 \times 10^{-3}$; (*b*) −14.0 kcal mole^{-1} 17. 15.1 (pressure in atm) 18. 4.28×10^{30} 19. 7.824

Chapter 11

1. (*a*) $k = 3.40 \times 10^{-8}$ mole cc^{-1} atm^{-1}; (*b*) 12.4 kcal mole^{-1} 2. 0.0024°C 3. (*a*) 0.0146 mole fraction; (*b*) 4.83 g 4. (*a*) 0.614 mole fraction ethyl bromide, $P = 435$ mm; (*b*) 0.667 mole fraction ethyl iodide, $P = 327$ mm. 5. (*a*) 6; (*b*) 8; (*c*) 35.5 mole% toluene 6. (*b*) alcohol; (*c*) 208 g 7. 41.3 g methylethylketone-rich layer 8. 0.096 mole l^{-1}; 4 (nearest whole number to 3.84) 9. Dimeric 10. (*a*) $x = 1$, $y = 2$, $p = 193.8$ mm; $x = y = 1$, $p = 8.1$ mm; $x = 2$, $y = 1$, $p = 2.9$ mm; (*b*) $K_p = 0.255$, 1.07×10^{-2}, 3.8×10^{-3} (pressure in atm); $\Delta F^0 = 0.74$, 2.47, 3.03 kcal mole^{-1} 11. (*a*) Eutectic at 360°, 34.5 atom% Sb; compound $AuSb_2$, peritectic at 460° 12. Solid solution 13. (*a*) Solid phases are $(NH_4)_2SO_4$, $BeSO_4 \cdot 4H_2O$ and $(NH_4)_2SO_4 \cdot BeSO_4 \cdot 2H_2O$ (*b*) $BeSO_4 \cdot 4H_2O$, $(NH_4)_2SO_4$

Chapter 12

1. 3 hr 47 min 2. 336 3. 2.59 g 4. Anode 0.4861, cathode 0.4882, mean 0.4871 5. Anode 0.3109, cathode 0.3109 6. 2150 ohms 7. (*a*) 88.86; (*b*) 80.5 (calc.), 85.0 (exp.); (*c*) 388.6 8. (*a*) 0.6038; (*b*) 0.5095 9. Ba^{+2} 48.2, 4.99×10^{-4}; Cl^- 63.3, 6.56×10^{-4} 10. 0.3893 11. 0.4341 12. 2.85 mg l^{-1} 13. 0.0284 N

Chapter 13

1. (*a*) $2Ag(s) + Hg_2Br_2(s) = 2AgBr(s) + 2Hg(l)$; (*b*) $\Delta H^0 = 2.600$ kcal, $\Delta F^0 = -3.154$ kcal, $\Delta S^0 = 19.3$ eu (*c*) 47.1 eu 2. (*a*) 0.0711 v; (*b*) −0.0711 v; (*c*) 0.909 3. 1.8×10^{-6} 4. (*a*) $Pt|Fe^{+2}$, $Fe^{+3}|Br_2(l)$, $Br^-|Pt$; (*b*) 0.294 volt, −6.8 kcal, 9.25×10^4; (*c*) 0.294 volt, −13.6 kcal, 8.55×10^9 5. (*a*) $Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O$; (*b*) −1.676 volt 6. (*a*) $Pt|Cu^+$, $Cu^{+2}|Cu^+|Cu$; (*b*) 0.368; (*c*) −0.521 v 7. (*a*) −1.64, −1.61, −1.49, −1.43; (*b*) 1.40, 1.37, 1.25, 1.19 v 8. 2 9. (*a*) $Cu|Cu^{+2}|Ag^+|Ag$; (*b*) $Cu + 2Ag^+ = Cu^{+2} + 2Ag$; (*c*) 4.0×10^{15} 10. (*a*) −0.0520 v; (*b*) $\frac{1}{2}\,Zn(c_2) = \frac{1}{2}\,Zn(c_1)$ 11. (*a*) 0.0354; (*b*) 0.891 12. (*a*) $Ag|AgCl(s)|KCl(0.50\ \text{N})|KCl(0.05\ \text{N})|AgCl(s)|Ag$ (*b*) $2KCl(0.50\ \text{N}) = 2KCl(0.05\ \text{N})$; (*c*) 0.501 13. 6.5×10^{-2} 14. 0.92

Chapter 14

1. +0.8 mv 2. 1.81×10^{-10} 3. 1.975×10^{-5} 4. 14.42 kcal mole^{-1} 5. (*a*) 2.00, 12.71; (*b*) 12.71, 2.00; (*c*) 7.36, 7.36 6. 14.00 7. (*a*) 4.51, 4.75; (*b*) 4.49, 4.47; (*c*) 4.62, 4.75

8. (*a*) 0.781; (*b*) 0.712; (*c*) 1.731 $\times$ 10^{-4} mole l^{-1} **9.** (*a*) 1.95 $\times$ 10^{-4}; (*b*) 3.10 $\times$ 10^{-6}; (*c*) 1.73 $\times$ 10^{-4} mole l^{-1} **10.** (*a*) 1.04 $\times$ 10^{-5}; (*b*) 1.08 $\times$ 10^{-8}; (*c*) 1.03 $\times$ 10^{-5} mole l^{-1} **11.** (*a*) 0.773; (*b*) 9.15 $\times$ 10^{-4} mole l^{-1}, 0.756 **12.** (*a*) 1.67; (*b*) 6.11; (*c*) 11.44 **13.** (*a*) 2.58; (*b*) 1.91; (*c*) 8.65; (*d*) 3.60 **14.** (*a*) 0.585; (*b*) 0.114 volt **15.** (*a*) 4.27; (*b*) 0.954; (*c*) 4.31

CHAPTER 15

1. (*b*) $k_1 = 4.0 \times 10^2$, $k_2 = 21.6 \times 10^2$; (*c*) 0.185 ml of STP; (*d*) 12.5 A^2, 2.0 A **2.** (*a*) 11.05 ml of STP; (*b*) 2.76 m^2 g^{-1} **3.** (*a*) 3.4 $\times$ 10^{-10} mole cm^{-2}; (*b*) 20 $\times$ 10^{13} molecules cm^{-2}; (*c*) 20 $\times$ 10^{-3} molecules A^{-2}; (*d*) 2.4 $\times$ 10^{-10} **4.** (*a*) 21.0 A^2; (*b*) 23.4 A **5.** 2.50 $\times$ 10^5 **6.** $K = 3.60 \times 10^{-4}$, $a = 0.64$ **7.** 86,000 **8.** $\overline{M}_n = 105{,}000$, $\overline{M}_w = 140{,}000$ **9.** 178,000

CHAPTER 16

1. 30.6 $\times$ 10^{-3} **2.** 4850 sec ($RT = 2 \times 573$), 5970 sec ($RT = 1.987 \times 573.2$) **3.** (*a*) (*b*), 120, 289, 578 min **4.** 2.8 order $\approx$ 3 **5.** (*a*) First; (*b*) 73% **6.** Zero **7.** (*a*) First; (*b*) 4.43 $\times$ 10^{-4} sec^{-1}; (*c*) 1.26 $\times$ 10^{13} sec^{-1} **8.** (*b*) 0.0148 min^{-1} **9.** (*a*) 1.55 $\times$ 10^{-3}; (*b*) 1.40 $\times$ 10^{-3} **10.** 0.467 **11.** 2.63 $\times$ 10^{15} sec^{-1}, 24.45 kcal **12.** (*a*) 24.7 kcal mole^{-1}; (*b*) 1.66 $\times$ 10^{-9}; (*c*) 8.10 $\times$ 10^{31}; (*d*) 1.59 **13.** (*a*) $-d\text{A}/dt = d\text{C}/dt = \dfrac{k_1k_3}{k_2}(\text{A})$, (*b*)

$$-d\text{A}/dt = \frac{k_1k_3(\text{A})(\text{B})(\text{D})}{k_2 + k_3(\text{D})} \approx \frac{k_1k_3}{k_2}(\text{A})(\text{B})$$

CHAPTER 17

1. 26.4 **2.** (*a*) 70.8 kcal mole^{-1}; (*b*) 41.9 kcal mole^{-1} **3.** 15.6% **4.** (*a*) 5.38 $\times$ 10^{19} (*b*) 0.17 **5.** 5.5 $\times$ 10^{-3} **6.** 1.3 $\times$ 10^{-8} mole sec^{-1} **7.** $d(\text{C}_2\text{HCl}_5)/dt = kI_{\text{abs}}{}^{1/2}(\text{Cl}_2)$

CHAPTER 18

1. 1960 years **2.** ${}_0n^1 + {}_{79}\text{Au}^{197} \pm {}_{79}\text{Au}^{198} + \gamma$, ${}_{79}\text{Au}^{198} \rightarrow {}_{80}\text{Hg}^{198} + {}_{+1}-$ **3.** ${}_{16}\text{S}^{33} + {}_1\text{H}^1 \rightarrow {}_{17}\text{Cl}^{33} + {}_0n^1$, ${}_{17}\text{Cl}^{33} \rightarrow {}_{16}\text{S}^{33} + {}_{+1}\beta^0$ **4.** (*a*) 1.354 $\times$ 10^{-11} sec^{-1}; (*b*) 162 years **5.** 17.00449 **6.** 48 μ **7.** 0.0674 A **8.** (*a*) 1.7 $\times$ 10^{-17} sec^{-1}; (*b*) 17 sec^{-} **9.** 1.93 $\times$ 10^7 kcal g^{-1} **10.** 1.9 $\times$ 10^6

INDEX

	LOGARITHMS										Proportional Parts								
No.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
No.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

LOGARITHMS

											Proportional Parts								
No.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	[illegible]						1	1	2	2	3	3	3	4
No.	0	1	2	3	4								3	4	5	6	7	8	9