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1 atm $= 1.013 \times 10^6$ dynes/cm^2	Normal atmosphere
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INTRODUCTION TO THE STUDY OF PHYSICAL CHEMISTRY

Louis P. Hammett
Professor of Chemistry
Columbia University

FIRST EDITION

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1952

INTRODUCTION TO THE STUDY OF PHYSICAL CHEMISTRY

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FOREWORD TO THE STUDENT OF PHYSICAL CHEMISTRY

This book is intended to provide you with the materials which you need to start learning about the methods of physical chemistry. I say "methods" intentionally, for I would define physical chemistry as a method, namely, that of using quantitative and mathematical ways of thinking in the attack on the problems of chemistry. Chemists often do try to define physical chemistry in the kind of terms which are used when organic chemistry is defined as the study of carbon compounds. But a word has meaning only by virtue of agreement among those who use it, and there is no agreement whatsoever on any definition of physical chemistry of this kind. On the other hand, there is rarely any dispute among chemists whether the method used in attacking a particular problem is or is not a physical chemical method. The method will be called a *physical chemical* one if it involves quantitative data and if these are correlated, analyzed, and related to other phenomena by mathematical methods. Nor is there uncertainty in recognizing as a physical chemist a scientist who is skilled and habituated in the use of quantitative and mathematical methods in approaching chemical problems.

Now one can learn a method only by practice in the use of the method; you can therefore learn physical chemistry only by solving problems which involve the application of mathematics to quantitative data. Consequently, the problems are the most important part of a book of this sort, and what you will have learned from the study of this text will be measured by the quality of the intellectual effort provided for you by the problems and by your own willingness to make the effort.

The definition I have given of physical chemistry includes things you met when your first contacts with chemistry confronted you with atomic and molecular weights and also things you will continue to learn as long as you are a chemist or use chemistry and have not become incapable of learning. The content of this book is necessarily much narrower and derives from an estimate, based on some experience, of the material you should be able to master in a year of study if your previous studies included general chemistry, analytical chemistry, a year of college physics, and a year of calculus. Within such a framework the decision to include one subject involves a sometimes extremely difficult decision to omit another subject, and you are entitled to a statement of the principles to which I have tried to adhere in making these decisions.

Wisely or not, I have followed the custom which leaves to separate textbooks on the laboratory methods of physical chemistry the important matter of the design of instruments and the details of experimental techniques.

In a world in which there is so much that is interesting to be learned I have tried to avoid wasting your time by repeating things you should have learned in your previous studies. But in case your memory is rusty I have made frequent references to standard texts in these subjects. A list of these references together with the abbreviations which will be used in referring to them follows this foreword. I have equally tried to avoid assuming that you know things, especially in physics and mathematics, that would not normally be included in the preparation listed. Mathematicians naturally and properly teach mathematics, not the application of mathematics to chemical problems. While much of this book is in a sense concerned with the latter subject, some of the more specifically mathematical techniques are collected in an appendix.

Finally, I have been more concerned that the book should offer an introduction to all of the more important methods of thinking used by the physical chemist than that it should survey all of the areas in chemistry in which important results have been obtained by the physical chemical approach.

It is in terms of such rules as these, and not because I fail to appreciate the great importance of the subject, that I have omitted any discussion of the structure of crystalline substances and of the X-ray diffraction method for determining such structures. An elementary discussion of the method and of its results is reported in textbooks on general chemistry and I feel no need of repeating this. The three-dimensional geometry and optical theory involved in the actual interpretation of X-ray diffraction data is so involved that it can be understood only by an effort much too great for inclusion within the bounds of the present undertaking. And the results of such investigations belong more to the fields of descriptive inorganic and organic chemistry than they do to that of physical chemistry. It is for much the same kind of reasons that I have omitted a chapter on atomic structure.

Because, therefore, this book contains such a limited selection from the field of physical chemistry, it is particularly important that you should be supplied with a guide for further study and reading. I have therefore included in the references which follow, a list of books that may be useful for review of your previous work, for study of subjects that I have omitted, and as compendia of data. Furthermore, each chapter will usually be followed by a list of references which should be helpful if you wish to study more intensively subjects that are discussed in the text of that

chapter. Most of the references which appear in parentheses in the text are to books in the list which appears on page xi and employ the abbreviation or codes shown in that list. For the others the bibliography at the end of the chapter in which the reference appears should be consulted.

LOUIS P. HAMMETT

NEW YORK, N.Y.
May, 1952

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CHAPTER I

SOME PROPERTIES OF GASES

Definition. The characteristic property of a gas is the way in which the pressure it exerts upon its surroundings varies with the volume. Pressure is exerted by all matter: with solids and liquids it is called the *vapor pressure* of the substance; it may be too small for direct measurement, but it certainly exists even then. There are, however, two striking differences between the behavior of the gas and that of the condensed phases, *i.e.*, the solids and liquids. The more obvious one in cases where the system can be observed visually is that two phases can be recognized in a certain range of pressure when the pressure applied to a solid or liquid is gradually decreased, whereas a gas remains a single homogeneous phase under the same conditions.

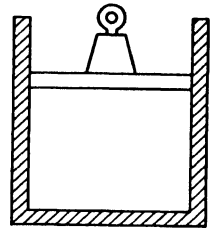


FIG. 1.

Consider a cylinder, such as is shown in Fig. 1, completely filled with a liquid and immersed in a constant-temperature bath. A certain force, symbolized by the weight in the figure, is necessary to prevent expansion. If weights are removed from the piston, the liquid expands very gradually at first, *i.e.*, a large change in force is accompanied by only a small change in volume, and the cylinder remains completely filled with a homogeneous material. When, however, the force drops to a certain sharply defined value, the volume increases by a relatively large amount and the cylinder content separates into two regions of very different properties: a denser *liquid* of relatively high refractive index, and a lighter *gas* of low refractive index. Because of the difference in refractive index it is easy to see the surface which separates the two regions, which we call a *liquid phase* and a *gas phase* (page 50); because of the difference in density the liquid phase occupies the lower part of the container. If the volume is now allowed to increase further, the portion of the space occupied by the gas phase is observed to increase and that occupied by the liquid phase to decrease, *i.e.*, the liquid evaporates. At a sharply defined value of the volume which depends upon the composition, the quantity, and the temperature of the material the liquid phase disappears, and further increase in volume to the largest possible values then fails to yield any break into a heterogeneous mixture of two phases.

This account is oversimplified in one respect because of the phenomena of *metastability* (page 255). In the absence of any bubble, even a very minute one, of gas it is often possible to reduce the pressure appreciably below the equilibrium vapor pressure of the liquid without the occurrence of the separation into two phases. The situation is, however, unstable and essentially temporary, and as soon as any gas appears, the volume and pressure rise to an equilibrium value.

More fundamental than these observable effects is the way in which the force which must be applied to the piston varies with the volume. If the piston were completely frictionless, this force would have to be exactly balanced by the outward force exerted by the material inside the cylinder; this outward force, calculated to unit area, is what is called the *pressure*

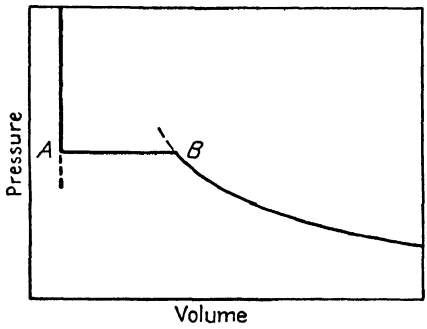


FIG. 2. A schematic isotherm.

exerted by the contents of the cylinder. Of course there is no such thing as a completely frictionless piston; consequently there will always be a certain range of weights within which the piston moves neither upward nor downward. It follows that the most one can say about the pressure of the cylinder contents is that it lies between the limits defined by the largest weight that will not quite make the piston drop and the smallest one that will just fail to let it rise. This fuzziness exists, of course, in all physical measurements, and much of the art involved in studying nature quantitatively consists in the development of methods for reducing the width of the band of uncertainty to the narrowest limits possible. Fortunately the friction of the column of mercury in a manometer tube or of the bent tube of a bourdon gage is quite small.

If now we observe the pressure thus defined in the cylinder of material we have been discussing, we find that it takes a course of the sort represented schematically in the plot of Fig. 2. Such plots are called *isotherms*. There are two sharp breaks in the plot (discontinuities in slope) at A and B. The dotted lines represent the metastable systems. Start-

ing from small volumes, the break at point A coincides exactly with the separation of the system into two phases, *i.e.*, with the appearance of the gas phase. The break at point B coincides with the disappearance of the last drop of the liquid. The segment AB may either be horizontal, this being characteristic of a pure substance, or it may slope downward, as it does with most mixtures.

For any material the length of the segment decreases with rising temperature, and the discontinuities vanish at the critical temperature (Pauling 177, Timm 140, Sears I, 421–423). A material is said to be in the gaseous state when it lies in a region of pressure and volume which puts it to the right of point B in the plot of Fig. 2 or when the temperature is so high that the discontinuities are absent. As a definition then we may say: A gas is a material whose pressure decreases indefinitely and without discontinuity in slope when its volume is increased without limit, the temperature being kept constant.

Boyle's Law. In Table 1 we reproduce some data of Boyle's on the behavior of a sample of air at pressures of a few atmospheres or less and at

TABLE 1. PRESSURE AND VOLUME OF A CONSTANT QUANTITY OF AIR AT ROOM TEMPERATURE*

The pressure P is in inches of mercury, the volume v in arbitrary units

v	P	Pv
48	29 3/16	1400
44	31 15/16	1405
40	35 15/16	1412
36	39 5/16	1415
32	44 3/16	1414
28	50 5/16	1409
24	58 13/16	1411
20	70 11/16	1414
16	87 14/16	1406
12	117 9/16	1411

* Data of Boyle, quoted in Conant, "On Understanding Science," Yale University Press, New Haven, 1947.

approximately constant temperature, the data consisting of a series of values of volume and of corresponding pressure. These values of pressure and volume are plotted in Fig. 3. Data of this sort present one of the most frequent and important problems of the physical scientist, that of obtaining a quantitative relationship between observable quantities, in this case between the pressure and the volume of the sample of air. This

amounts to finding the best possible curve which fits the points of Fig. 3. Of course we know an answer in this case, for Boyle's law is one of the most familiar relationships of physics and chemistry. But let us try to put ourselves in the position of Boyle when he made the first measurements of this sort. Being human, we look for the easiest way and hope for the simplest and most easily manipulated relationship between the two variables. Now when two variables are so related that, when one goes up,

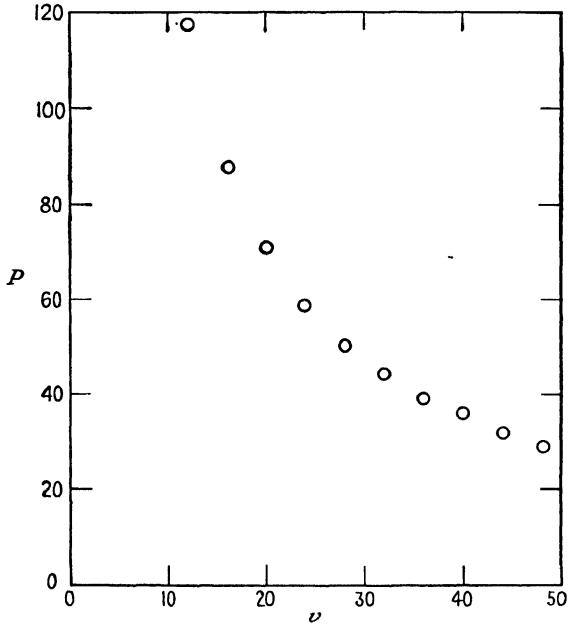


FIG. 3. Pressure P and volume v of a sample of air from Table 1.

the other goes down, the simplest relationship is that of inverse proportionality, namely, volume v is proportional to one over pressure P,

$$v = k\frac{1}{P} \qquad \text{or} \qquad Pv = k \tag{1}$$

where k is a constant so long as composition, quantity of gas, and temperature are held fixed. Because Eq. (1) involves only one constant, k, it is a simple matter both to determine whether the functional relationship represented by this equation is a suitable one and, if it is, to obtain a value of k. We merely calculate the value of the Pv product for each pair of pressure-volume values, as has been done in Table 1, and observe whether or not the product is reasonably constant. Of course we cannot expect the value to be absolutely invariable because of the inevitable scatter of all experimental measurements. We note, however, in this case that the

Pv product varies only from 1400 to 1415, *i.e.*, by 1 per cent, while P and v individually vary by a factor of 4. Further we see no trend in the values, no tendency for low values to predominate at one end or the other or in the middle of the scale of pressures and for high values to concentrate in some other region. Consequently we conclude that Eq. (1) is valid within the precision of the measurements; that the best value of the constant is 1410, the arithmetic mean or average of the values of the Pv product; and that if we use this value to calculate the volume which the gas will possess at a given pressure we are not likely to be in disagreement with experiment by as much as 1 per cent.

Deviations from Boyle's Law. The data of Table 1 are, however, data of the seventeenth century, obtained with what by our present standards was very crude apparatus, and covering a range of from 1 to 6 atm only. It is characteristic of the way scientific knowledge develops that such data as these are revised in two directions, namely, in the direction of greater precision of measurement and in that of a wider range of conditions. With respect to the former, Table 2 presents recent precise

TABLE 2. RELATION BETWEEN PRESSURE P IN ATMOSPHERES AND MOLAR VOLUME V IN LITERS AT 0°C*

P	V	PV
Oxygen:		
1.00000	22.3939	22.3939
0.75000	29.8649	22.3987
0.50000	44 8090	22.4045
0.25000	89 6384	22.4096
Neon:		
1.00000	22.4280	22.4280
0.66667	33 6360	22.4241
0.33333	67.2567	22 4189
Carbon dioxide:		
1.00000	22.2643	22.2643
0.66667	33.4722	22.3148
0.50000	44.6794	22 3397
0.33333	67.0962	22.3654
0.25000	89.5100	22.3775
0.16667	134.3382	22.3897

* Data on oxygen and neon from Baxter and Starkweather, *Proc. Natl. Acad. Sci. U.S.*, **12**, 699 (1926); **14**, 50 (1928). Data on carbon dioxide from Dietrichson, Miller, and Whitcher, quoted in Millard, "Physical Chemistry for Colleges," 6th ed., McGraw-Hill Book Company, Inc., New York, 1946.

Strictly speaking, the experimental data involved are measurements of the weight of a given volume of the gas, but it has been amply demonstrated (see page 9) that volume at constant pressure and temperature is exactly proportional to weight, and the above-cited volumes per mole were calculated on this basis.

data on the volumes of 1 mole of oxygen, of neon, and of carbon dioxide at pressures of 1 atm and less and at 0°C. It is clear that the principle that the Pv product is constant at constant temperature, *i.e.*, Boyle's law, cannot be upheld to the precision of these data because the indication of a trend in the Pv value is unmistakable, especially when Pv is plotted against P as in Fig. 4. With carbon dioxide, for which 0°C lies below the critical temperature, Pv varies regularly over a total range of more than one-half of 1 per cent between $\frac{1}{6}$ and 1 atm. With oxygen and neon, which are well above the critical temperatures, the variation is less than $\frac{1}{10}$ per cent, but the trend is still obvious.

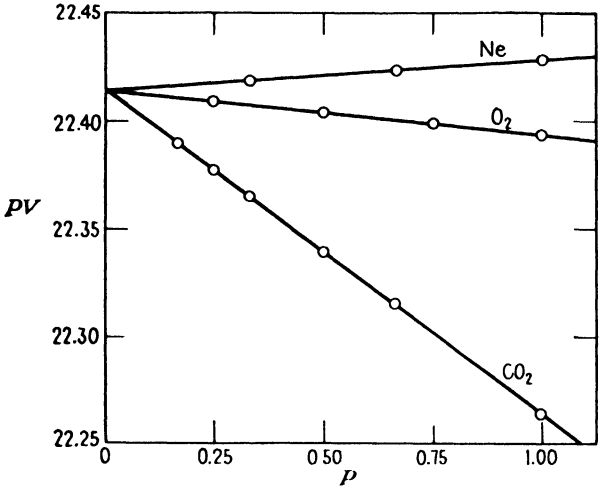


FIG. 4. Plots of PV, the product of pressure in atmospheres and molal volume in liters per mole, against pressure P in atmospheres at 0°C and at pressures of 1 atm and less. (*Data of Table* 2.)

We must conclude that Boyle's law is not exact, even at low pressures, although it is not a bad approximation. And the plot of Fig. 4 suggest a very characteristic procedure, that of taking Boyle's law as a first approximation and adding corrections, for it is rather obvious that Pv is at least close to being a linear function of P. A two-constant equation of the type

$$Pv = a + bP \tag{2}$$

is then a better representation of the facts than the one-constant equation, Eq. (1). The gain in precision in representing the facts is not, however, without cost, for it is a more complicated process to verify the validity of a two-constant equation and to obtain the best values of the constants than it is to do the same thing with a one-constant equation.

It is, of course, a simple matter to lay a straightedge on the graphs of Fig. 4 and to see whether the points lie reasonably close to a straight line or whether they exhibit a pronounced curvature. And one can do a respectable job of estimating the constants from the slope and intercept of what looks like the best straight line through the points. There are, however, better methods involving computation rather than graphical techniques. These are described in Appendix A. By such techniques it can be shown that the data of Table 2 on oxygen satisfy the formula

$$Pv = 22.4148 - 0.0211P$$

and that the *probable error* (page 403) of the Pv values is 0.0002, or 1 part in 100,000.

When we examine the other direction of development, toward a wider range of pressures, we get the kind of data shown in Table 3 and Fig. 5.

TABLE 3. BEHAVIOR OF OXYGEN AT 0°C AT HIGH PRESSURES*

P, atm	PV, liter-atm/mole
24.9475	21.9075
24.9934	21.9030
25.0730	21.8977
49.7212	21.4390
49.7513	21.4379
73.7436	21.0411
73.8134	21.0440
98.4855	20.7079
99.2037	20.6980

* Data from Holborn and Otto, *Z. Physik*, **10**, 367 (1922).

Quite obviously no linear formula of the type of Eq. (2) can fit these curved lines with even moderate precision.

Virial Equations. Confronted with this sort of situation we may (1) search for a quantitative theory leading to an equation which fits the data; (2) merely search for any kind of suitable equation, which, if found, is called an *empirical* equation; (3) combine these procedures to obtain what is called a *semiempirical* equation. In the present case there are theoretical equations which give a better fit than Boyle's law does, but people who have to deal with the most exact possible representation of the facts for such purposes as engineering design find that certain kinds of empirical equations give better fits and are otherwise more useful. For instance the fact that Pv is so nearly a linear function of P at low pressures suggests strongly that Pv may be expressed as a power series in P, namely,

$$Pv = a + bP + cP^2 + dP^3 + \cdots \tag{3}$$

because if the coefficients c and d are small enough the terms cP^2, dP^3, etc., will become negligible at low pressures, leaving the linear relationship of Eq. (2). But just as a two-constant equation is less manageable than a one-constant equation, so a three-constant equation is much more difficult to verify and to use than a two-constant equation. Consequently we must use the smallest number of terms in equations of the type of Eq. (3) that the problem in hand permits. The number depends both on

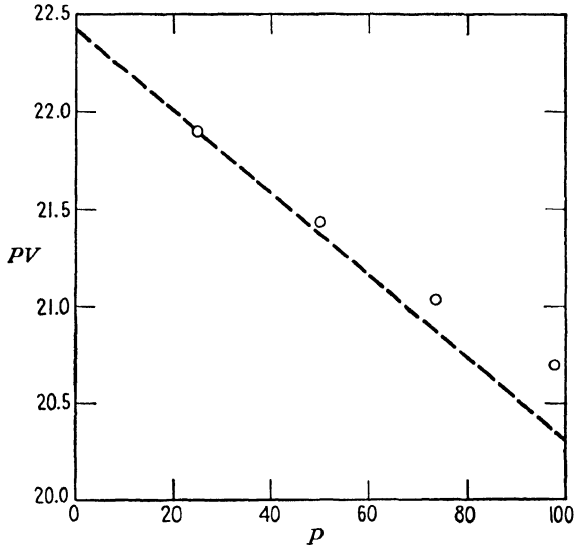


FIG. 5. Data on oxygen at high pressures. Plot of PV, the product of pressure in atmospheres and molal volume in liters per mole, against the pressure P in atmospheres. Temperature 0°C. (*Data of Table* 3.) The straight line is an extrapolation of the low-pressure plot of Fig. 4.

the precision required and on the range of pressures to be covered. Thus the data of Table 3 can be fitted to the equation

$$Pv = 22.414 - 0.02226P + 4.90 \times 10^{-5}P^2$$

with a maximum deviation of 0.1 per cent over the whole range from 0 to 100 atm. But at pressures below 20 atm the last term of this equation is less than 0.1 per cent of the sum and can be neglected if this is sufficient precision. And at pressures of 1 atm and less only the first term on the right suffices to yield a precision of 0.1 per cent, *i.e.*, Boyle's law applies in this range to this precision. If no greater precision than 1 per cent is necessary, Boyle's law is adequate up to 10 atm and a two-term equation suffices up to 70 atm. Equation (3) can be fitted to the data on oxygen

at 0°C to higher pressures than 100 atm by using more than three terms, and such cumbersome equations are necessary for the accurate representation of the Pv-P relationships of many gases even at pressures below 100 atm.

Power-series expressions of the type of Eq. (3) and similar equations involving the concentration c, such as

$$\frac{P}{c} = \alpha + \beta c + \gamma c^2 + \cdots \tag{4}$$

are called *virial equations.*

Concept of the Perfect Gas. It should be clear from this discussion that there is no such thing in nature as a perfect gas, *i.e.*, a substance which among other properties obeys Boyle's law, but that Boyle's law may nevertheless be an extremely useful approximation to the actual behavior of real gases. It is true that scientists often speak of *the* perfect gas or of the properties of the perfect gas, but this is merely a kind of technical slang used to indicate that for the purposes of the problem in hand the perfect-gas approximation is good enough or that more exact relationships would demand information that is not available or would make the mathematics impossibly difficult. For the first 10 chapters of this book we shall in fact work almost entirely within the precision of the perfect-gas approximation and of similar approximations for solutions. We shall, however, try to remember that these are approximations and to learn something about the magnitudes of the errors involved in using the approximations.

Dependence on Mass. There is one property of real gases which we may describe very simply yet as precisely as our most accurate measurements demand, namely, the effect of the quantity of substance present. It is found that at a given temperature and pressure the volume of any particular kind of gas is exactly proportional to the mass, *i.e.*, the density is constant at constant temperature and pressure. The only way in which this can be true at all pressures for a gas whose behavior is satisfactorily described by Eq. (3) is that the coefficients a, b, c, d, etc., must each have a value exactly proportional to the mass. That is, we may write $a = mA$, $b = mB$, etc., with the quantities A, B, etc., independent of the mass m. From this

$$\frac{Pv}{m} = A + BP + CP^2 + \cdots$$

or

$$PV = A + BP + CP^2 + \cdots \tag{5}$$

where $V = v/m$ is the volume of unit mass. As unit mass we may take any convenient quantity, for instance the gram or the pound. But for chemical problems it turns out here, as it does usually, that the mole is the convenient unit.

Avogadro's Law. Two other familiar relationships are, however, valid only to the same kind of approximation as is Boyle's law, namely, Avogadro's law and Charles' law. The former states that equal volumes of all gases at a given temperature and pressure contain the same number of molecules. It follows that the same number of molecules of two different gases must occupy the same volume at the same temperature and pressure. But actually 44.01 g, 1 mole, or 6.023×10^{23} molecules, of carbon dioxide at 0° and 1 atm occupies a volume of 22.2643 liters, while 20.183 g, 1 mole of neon occupies 22.4280 liters. The two values differ by 0.7 per cent. At $\frac{1}{3}$ atm these molar volumes have, however, become 67.0962 and 67.2567 liters, respectively, and differ only by 0.24 per cent. This is an example of the fact that Avogadro's law becomes more nearly exact the lower the pressure. The situation is particularly intelligible in terms of the plots of Fig. 4, for it is clear that the straight lines which follow the experimental points all intersect on the axis of zero pressure. If therefore we represent these plots by equations of the type

$$PV = A + BP \tag{6}$$

the A coefficient has the same value for the three gases and indeed for all gases at this temperature but the B coefficient has different values for different gases. It turns out also that the C, D, etc., coefficients of Eq. (5) have different values for different gases.

Another way of stating the situation is to recognize that the coefficient A can be defined by the relation

$$A = \lim_{P \to 0} PV \tag{7}$$

It is a limit, not an actual value of the PV product, because V becomes infinite and therefore inaccessible to measurement as P approaches zero. However, the variation of PV with P follows such definite laws that we have considerable confidence that these laws may properly be extrapolated to the limit of zero pressure, and this confidence is fully justified by the fact that the resulting limit has the same value for all gases.

The accepted value of the coefficient A at 0°C obtained by careful analysis of all available data is 22.4140 liter-atm/mole. This familiar quantity is often called the molar volume of the perfect gas at 0°C and 1 atm, but it is more properly described, as we have done it, as the limiting value for zero pressure of the product of molar volume by pressure.

Charles' Law. Charles' law states that a plot of the PV product against temperature is a straight line and the same straight line for all gases. That is,

$$PV = j + kt \tag{8}$$

where t is a measure of temperature, for instance the value on the centigrade scale, and j and k are coefficients which have the same value for all gases. This again is a reasonably good approximation, especially at low pressures, but more exact measurements or measurements covering a wider range of temperature and pressure show that the plot of PV against t is not exactly straight and that the curves for different gases do not exactly coincide. Here also it is found that the separation between the curves for the different gases gets smaller the lower the pressure, so that we may predict that in the limit of zero pressure the curves would all coincide exactly. In terms of the virial equation this means that the coefficients B, C, D, etc., vary with temperature in a different way for different gases but that the quantity A depends upon temperature in exactly the same way for all gases.

Definition of Temperature. If now we determine the value of A at a series of temperatures by the kind of extrapolation described in the discussion of Avogadro's law and plot these values against the temperature as it is measured by the rise of the thread of mercury in the tube of an ordinary thermometer, we find that the plot is not exactly linear. And if we use alcohol or pentane instead of the mercury, we find that the plots do not coincide exactly with the one obtained from temperatures determined by the mercury thermometer. And even if we use a different kind of glass in the mercury thermometer, we get slightly different results, because the rise of the mercury column depends upon the difference in expansion of the mercury and the glass. To use any one of these liquid-in-glass thermometers as an exact measure of temperature would be entirely arbitrary, and scientists have therefore agreed to use the value of the quantity A. This definition of temperature has the virtue that it depends upon a property which is common to all substances in the gaseous state but which differs so little from the measure of temperature obtained by our familiar liquid-in-glass thermometers that only slight corrections need be made to the latter and those only for very precise work. It has the further advantage that many of the important laws of nature take a relatively simple yet completely exact form in terms of this scale and would be either more complicated or less exact if we were to use some one of the liquid-in-glass or other possible thermometer scales. Finally it can be shown by the reasoning of thermodynamics that this definition of temperature is a special case of a more general definition which makes it

possible to give the concept of temperature a definite and exact experimental meaning in regions, such as those near the absolute zero, where the exact study of the properties of gases becomes impracticable.

As we have seen the value of A at the temperature of melting ice is 22.4140, it has been found to be 30.6194 at the normal boiling point of water. If we adopt the centigrade convention that these temperatures shall be designated 0° and 100°, respectively, we have from Eq. (8)

$$\begin{aligned} 22.4140 &= j \\ 30.6194 &= j + 100k \end{aligned}$$

from which the values of j and k follow as 22.4140 and 0.082054. We have therefore as the definition of the centigrade scale

$$A = 22.4140 + 0.082054t \tag{9}$$

This may also be written

$$A = 0.082054(273.16 + t)$$

and if we define absolute temperature by the equation

$$T = 273.16 + t \tag{10}$$

we have finally

$$A = 0.082054T \tag{11}$$

Just as we write °C for centigrade temperature we write °K (Kelvin) for absolute temperature. The constant 0.08205 is called the *gas constant* and is generally represented by the symbol **R**. When pressures are given in atmospheres and volumes in liters, the units of **R** are liter-atm/deg-mole. Its dimensions are molar energy divided by temperature because a pressure is a force divided by a length squared, and a pressure multiplied by a volume (length cubed) is therefore force times distance, which is energy. The best values in various units are:

$$\begin{aligned} 0.0820544 \text{ liter-atm/deg-mole} &\pm 3.4 \times 10^{-6} \\ 8.31439 \text{ abs joules/deg-mole} &\pm 3.4 \times 10^{-4} \\ 1.98719 \text{ cal/deg-mole} &\pm 1.3 \times 10^{-4} \end{aligned}$$

Perfect-gas Law. To the perfect-gas approximation, $PV = A$, and since, by the definition of T, $A = \mathbf{R}T$, we can write

$$PV = \mathbf{R}T \tag{12}$$

This equation is called the *perfect-gas law*. From what we have said it is clear that it is an approximation valid only in the limit of zero pressure but extremely useful provided its limitations are understood.

Since we have defined V as v/n where n is number of moles, we may also write

$$Pv = n\mathbf{R}T \tag{13}$$

and by substituting $n = w/M$ where w is mass and M is molecular weight we have also

$$Pv = \frac{w}{M}\mathbf{R}T \tag{14}$$

This equation contains five variables and one known constant. Given the values of any four of the variables, the other can therefore be calculated to the precision which this approximate formula permits. It is of course necessary that R be expressed in units which correspond to those in which P, V, and T are expressed. Two other useful forms of the equation are

$$P = \frac{\rho\mathbf{R}T}{M} \tag{15}$$

where $\rho = w/V$ is density in, for instance, grams per liter, and

$$P = c\mathbf{R}T \tag{16}$$

where $c = n/V$ is concentration in moles per liter.

Mixtures of Gases. It has been found that to the perfect-gas approximation, but to this approximation only, a mixture of gases satisfies the equation

$$Pv = (n_1 + n_2 + n_3 + \cdots)\mathbf{R}T \tag{17}$$

where n_1, n_2, n_3, etc., are the numbers of moles of the individual substances. This equation may be put in a more condensed form (see page 386) as

$$Pv = \mathbf{R}T \sum_i n_i \tag{18}$$

and may also be given the equivalent forms

$$Pv = \mathbf{R}T \sum_i \frac{w_i}{M_i} \tag{19}$$

and

$$P = \mathbf{R}T \sum_i c_i \tag{20}$$

Partial Pressure. The partial pressure of a gas in a mixture is defined by the equation

$$P_i = \frac{n_i}{\Sigma n_i} P \tag{21}$$

in which P_i is the partial pressure of substance i, P is total pressure, n_i is number of moles of substance i, and Σn_i is the total number of moles of all gaseous substances present. This may also be put in the form

$$P_i = N_i P \tag{22}$$

where

$$N_i = \frac{n_i}{\Sigma n_i} \tag{23}$$

is called the *mole fraction* of substance i.

To the perfect-gas approximation we may combine Eqs. (18) and (21) to get

$$P_i = \frac{n_i}{v} \mathbf{R}T \tag{24}$$

and can further use the definition of concentration c to get

$$P_i = c_i \mathbf{R}T \tag{25}$$

The relation between partial pressure and concentration in a gas mixture is therefore the same to the *perfect-gas approximation* as the relation between total pressure and concentration of a single gas [Eq. (16)]. It should be emphasized that partial pressure as defined by Eq. (21) or (22) has unambiguous meaning even when the deviations from the perfect-gas equations are large, but that Eqs. (24) and (25) are valid only to the perfect-gas approximation.

Determination of the Extent of a Chemical Reaction from Measurement of Gas Density. Consider the reaction

$$N_2O_4 \rightleftharpoons 2NO_2 \tag{I}$$

and let n represent the number of moles of N_2O_4 introduced into a space of volume v and temperature T and x the fraction of this N_2O_4 which is converted to NO_2 by reaction (I). We may then write

$$\begin{aligned} \text{Actual moles } N_2O_4 &= n(1 - x) \\ \text{Actual moles } NO_2 &= n \cdot 2x \\ \text{Total moles} &= n(1 + x) \end{aligned}$$

The weight w of the gas is nM, where M is the molecular weight of N_2O_4, its volume v is given by Eq. (18) as

$$v = \mathbf{R}T \sum_i \frac{n_i}{P} = \frac{n(1 + x)\mathbf{R}T}{P}$$

and consequently its density $\rho = w/v$ is given by

$$\rho = \frac{MP}{(1 + x)\mathbf{R}T} \tag{26}$$

It follows that if the pressure, the temperature, and the density or, what amounts to the same thing as the density, the weight and the volume of the gas are measured, the fractional extent of the dissociation process can be immediately calculated. Since Eq. (18) was used, the result will be valid only to the perfect-gas approximation. This limitation will be

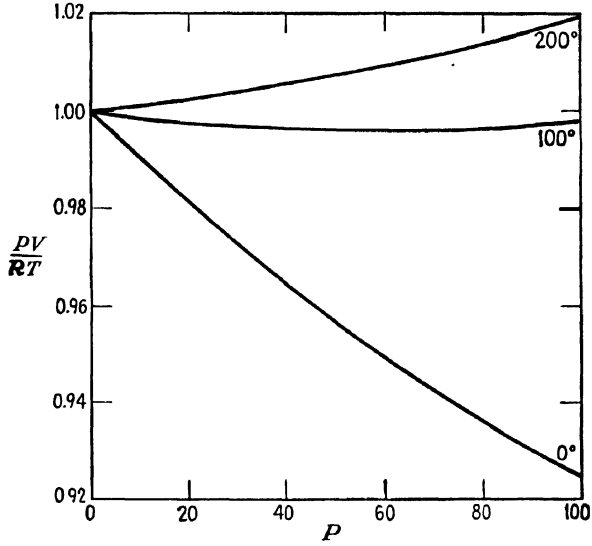


FIG. 6. Plot of the quantity $PV/\mathbf{R}T$ against pressure P in atmospheres for oxygen at 0, 100, and 200°C. (*Data from International Critical Tables, Vol. III, p.* 4.)

especially serious if the dissociation is either very small or very large. If x is nearly zero, Eq. (26) will differ from the equation $\rho = MP/(\mathbf{R}T)$, which would apply if there were no dissociation, by an amount no greater than the uncertainty of the perfect-gas approximation; if x is nearly 1, Eq. (26) will differ from $\rho = MP/2\mathbf{R}T$, which would apply if dissociation were complete, by a similar amount.

Effect of Temperature on the Deviations from the Perfect-gas Law. Since the coefficient A in the virial equation [Eq. (5)] equals $\mathbf{R}T$, the equation may conveniently be put in the form

$$\frac{PV}{\mathbf{R}T} = 1 + B'P + C'P^2 + \cdots \tag{27}$$

with $B' = B/\mathbf{R}T$, $C' = C/\mathbf{R}T$, etc. Figure 6 presents plots of $PV/\mathbf{R}T$ against P for oxygen at 0, 100, and 200°C. Other gases behave similarly

in the sense that the initial slope, *i.e.*, the slope at zero pressure, is negative at low temperatures and positive at high temperatures. The words "low" and "high" in this connection are to be taken relative to the critical temperature of the gas concerned. As Fig. 4 illustrates, this slope is positive at 273°K for neon (critical temperature 44°K), negative at the same temperature for oxygen (critical temperature 154°K), and much more negative for carbon dioxide (critical temperature 304°K). Since this initial slope can be both positive and negative, there must be for any gas a temperature at which it is zero and this temperature is called the *Boyle temperature.* As a rough rule the Boyle temperature may be expected to be about 2.5 times the critical temperature, both being on the absolute scale.

At temperatures approaching the critical value or lower the initial curvature of such plots as these is downward; at higher temperatures it is upward. The curvature is in any case positive at high pressures.

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PROBLEMS

1. The density in grams per liter of a certain gas at 0°C and 1 atm is 1.9804. What is the best value of the molecular weight that can be calculated from this information alone?

2. To the perfect-gas approximation what is the concentration in moles per liter of this gas at 0°C and 1 atm? What is the value at 100°C and 1 atm?

3. To the perfect-gas approximation what pressure will be exerted by 1 g of this gas in a volume of 1 liter at 25°C?

4. The densities ρ in grams per liter and the specific volumes V in liters per gram of this gas show at 0°C the following dependence on pressure P in atmospheres:

P	1.0000	0.66667	0.50000	0.33333
ρ	1.9804	1.3164	0.9861	0 6565
V	0.50495	0.7596	1.0140	1.5232

Plot the PV product against P, and obtain the constants of the best straight line. From the result calculate the best value of the molecular weight of the substance. By how many per cent was the result of Prob. 1 in error?

5. By a historical accident exact molecular weights are usually calculated by plotting values of the ratio ρ/P against P, fitting a straight line to the plot, and calculating the molecular weight from the value of the quantity $\lim_{P\to 0} \rho/P$. Carry out this operation on the data of Prob. 4.

6. How can you account for the fact that both PV, which is equal to P/ρ, and ρ/P plot linearly against P in this case?

7. Show that the linear equation obtained by employing only the first two terms on the right of Eq. (4) also fits the data of Prob. 4. What relations exist between the constants of this equation and those of the equation $PV = A + BP$?

8. At pressures up to a few atmospheres the properties of carbon dioxide at 25°C are described to a considerable precision by the equation $PV/\mathbf{R}T' = 1 - 0.0051P$. To this precision what volume will be occupied by 1 mole of carbon dioxide at 25° and 5 atm?

9. To the same precision what pressure will be exerted by 1 mole of the gas when confined in a volume of 5 liters at 25°?

10. Compressibility β is defined by the equation

$$\beta = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$$

What is the compressibility of a perfect gas? Show that, if the equation $PV = A + BP + CP^2$ applies to a real gas with $C \ll B \ll A$, the compressibility will be closely approximated by the equation

$$\beta = \frac{1}{P} - \frac{B}{A} - \frac{2AC - B^2}{A^2}P$$

11. Fit an equation of the form $PV = A + BP + CP^2$ to the following data on argon at 0°C. Pressure is given in meters of mercury; the unit of volume is the volume occupied by the same weight of gas at 0°C and under a pressure of 1 m Hg.

P	1.00000	19.230	37.552	55.421	74.395
PV	1.00000	0.97826	0.95817	0.94192	0.92746

12. What volume will be required to contain a mixture of 1000 g of hydrogen and 13,900 g of nitrogen at 25°C and 1 atm, assuming perfect-gas behavior and no chemical reaction?

13. At 380.5°C and 813.8 mm pressure the vapor of ammonium chloride has a density of 0.5257 g/lit. What would be the density if the vapor consisted of NH_4Cl molecules? How do you account for the difference?

14. Sufficient NO to produce a pressure of 173.8 mm Hg was introduced into a vessel of 1054.7 cc volume maintained at 299.9°K. A bulb containing 0.660 g of Br_2 was then broken into the vessel, and the total pressure was observed to be 192.7 mm when equilibrium was attained. It can be shown that the only substances present in appreciable quantity are NO, Br_2, and NOBr. What is the partial pressure of each in the equilibrium system?

15. A small bulb containing 1.2798 g of N_2O_4 was broken inside a vessel whose volume was 1.1042 liters, which was maintained at 25°C. The resulting mixture of N_2O_4 and NO_2 exerted a total pressure of 299.6 mm. What was the partial pressure of each substance?

CHAPTER II

AN ELEMENTARY DISCUSSION OF THE KINETIC MOLECULAR THEORY AND OF SOME IDEAS ABOUT INTERMOLECULAR FORCES

The behavior of gases may be interpreted in terms of a model, the kinetic molecular theory, which has proved extremely useful. Such models as this have two important virtues. They satisfy the insatiable human demand for an "explanation," *i.e.*, for the interpretation of the unfamiliar in terms of the familiar. And if they are good theories, which is to say useful ones, they are effective tools for the prediction of new facts and new relationships which may be verified by experiment. The kinetic molecular theory possesses both these virtues in high degree.

General Characteristics of the Kinetic Theory of Gases. In a qualitative form and in its first approximation this theory is a familiar subject of both elementary chemistry and elementary physics (Pauling 174, Timm 110–119). It supposes that the molecules of a gas are in motion and that the bombardment of the walls of the container by these moving molecules is responsible for the pressure which the gas exerts on the walls. The pressure depends upon the frequency and upon the intensity of the collisions. The frequency obviously goes up if the number of molecules contained in the vessel increases; hence the pressure increases if more molecules are crowded into the same volume and decreases if a given number of molecules are allowed a greater volume. This is qualitatively Boyle's law. The intensity of the collisions depends upon the velocity with which the molecules are moving, and the theory supposes that this velocity increases with the temperature of the gas, thus accounting for the fact that the pressure of a gas in a closed container increases with the temperature.

Approximate Derivation. (MWM 276–278, Sears I, 457–460.) We can give these ideas a certain amount of quantitative meaning without becoming involved in the complexities of an exact treatment, in the following way: We suppose as a first approximation that the actual volume of the molecules is negligible compared with the total volume of the space in which they are contained and further that the forces of attraction between molecules which are responsible for the existence of liquids and solids may be neglected. The first of these approximations should obviously be

more nearly justified the greater the volume of the space occupied by the gas. The same thing turns out to be true of the second because the attractive force decreases with the distance between the molecules and the average distance between the molecules increases as the volume increases. Because these conditions are those for which the perfect-gas approximation is most nearly valid, it is not surprising that the assumptions lead to the perfect-gas formula and not to a more exact description of the behavior of a gas. We further assume that the collisions which the molecules of the gas make with each other and with the walls of the container are perfectly elastic. It is a consequence of the fundamental laws of motion (MWM 122, Sears I, 147) that the elastic collision of a molecule

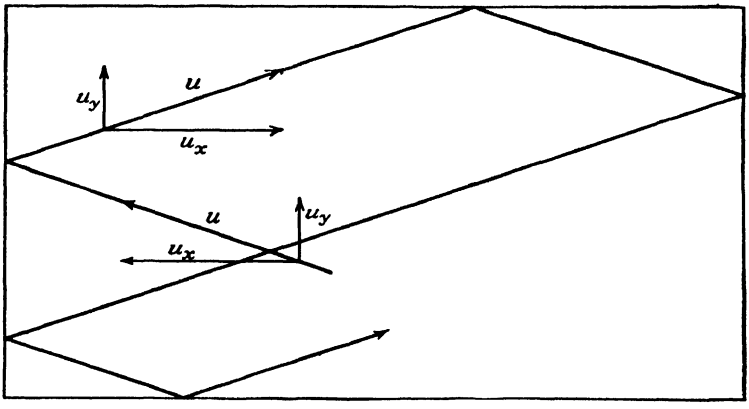


FIG. 1.

with the wall requires, if the wall is not to move, that the wall exert a force F on the molecule during the collision whose impulse J given by

$$J = \int F\, dt \tag{1}$$

is equal to the change in momentum of the molecule. Since the force is normal to the wall, only the component of momentum normal to the wall changes and, if the wall does not move, this component merely changes in sign. If, therefore, we take the x axis perpendicular to the wall, we see that the molecule must bounce off with its y and z components unchanged. If the x component of the velocity before the collision is $-u_x$, the value after the collision must be $+u_x$ and the total increase in momentum during the collision is therefore $2mu_x$, where m is the mass of the molecule. Consider now a single molecule in the rectangular container of Fig. 1. Every time it collides with the left-hand wall, its momentum increases by $2mu_x$. The time required for the molecule to move from the point where it makes one collision with this wall to the point where it makes

its next collision, is easily seen to be $2l/u_x$. Since, therefore, collisions occur at the constant time interval $2l/u_x$, the number of collisions in unit time must be the reciprocal of this quantity, namely, $u_x/2l$. Multiplying this by the change in momentum per collision, we get mu_x^2/l as the total change in momentum impressed on the molecule in unit time by the left-hand wall. For the time interval between t_1 and t_2 the change in momentum is $(t_2 - t_1)mu_x^2/l$. This must be the total impulse of the force which the wall exerts in withstanding the bombardment of the molecules; consequently from Eq. (1)

$$\int_{t_1}^{t_2} F\,dt = \frac{(t_2 - t_1)mu_x^2}{l}$$

or

$$\frac{\int_{t_1}^{t_2} F\,dt}{t_2 - t_1} = \frac{mu_x^2}{l} \tag{2}$$

The left side of this equation is the average force exerted by the wall.

If the container should contain n molecules and if these do not interfere with each other, as would be the case if the volume of the molecule were so small that collisions between the molecules were very rare, the n molecules would suffer n times as great a change in momentum in a given time as would one molecule. The average force, which we represent by $\bar{F}$, would therefore be given by

$$\bar{F} = \frac{nmu_x^2}{l} \tag{3}$$

We defined the pressure P of a gas (page 2) as the force per unit area required to withstand the expansive tendency of the gas; consequently if A is the area of the left-hand wall of Fig. 1,

$$P = \frac{nmu_x^2}{lA} \tag{4}$$

The n molecules must, of course, be moving in all sorts of directions, some with large components in the x direction and small components in the other directions, some with small components in the x and large in the other directions. There is no reason why one direction should be preferred over any other; consequently if all the molecules have a total velocity u, for which

$$u^2 = u_x^2 + u_y^2 + u_z^2 \tag{5}$$

the average value of u_x^2 for all the molecules must be $\frac{1}{3}u^2$. Substituting $\frac{1}{3}u^2$ for u_x^2 in Eq. (4), we have

$$P = \frac{\frac{1}{3}nmu^2}{lA} \tag{6}$$

Further, since lA equals v, the volume of the container, we have

$$Pv = \tfrac{1}{3}nmu^2 \tag{7}$$

A particle of mass m moving through space with velocity u possesses by virtue of that motion a kinetic energy $\tfrac{1}{2}mu^2$. This is called its *translational* kinetic energy, to distinguish it from the kinetic energy which may reside in the rotation of the particle or in motion of the parts of the particle relative to each other. If we represent the translational kinetic energy of n molecules ($\tfrac{1}{2}nmu^2$) by e_t, Eq. (7) takes the form

$$Pv = \tfrac{2}{3}e_t \tag{8}$$

This equation is clearly equivalent to Boyle's law if e_t is constant at constant temperature, which we suppose to be the case.

Some Inadequacies of This Development. A little thought will show that there are some bad gaps in this development. We have derived Eqs. (7) and (8) for a rectangular container and have slipped in the known rule that the pressure of a gas is the same on all parts of a container no matter what its shape. A more complete but considerably more complicated treatment derives this rule from the assumptions of the theory. And the assumption that n molecules exert n times as great a pressure as one molecule appears a bit troublesome, although a consideration of the nature of perfectly elastic collisions (Sears I, 152) shows that with molecules of the same mass the loss in velocity component in the x direction that one molecule suffers in a collision is just compensated by the gain of another. Thus a collision between molecule A moving toward the left and molecule B moving toward the right may increase the time interval before molecule A strikes the left-hand wall, but it decreases the interval before molecule B strikes it. The more complete treatment shows that, provided the volume of the molecules is negligible compared with the total volume occupied by the gas, this just averages out in counting up the total number of collisions per unit time which all the molecules make with the left-hand wall.

Finally we have tacitly assumed that all the molecules have the same velocity u, which cannot possibly be so. Even if it were true at one instant, it would not remain true because the collisions between two molecules or between a molecule and the wall are elastic only in a sort of average sense. If, for instance, two molecules strike a glancing blow, they are set spinning and the energy of this spinning motion must be subtracted from the translational energy which the two molecules possessed before the collision in order to compute the translational motion they possess after the collision. On the other hand, molecules which are

spinning may lose some of their spin in a collision so that the translational energy of the molecules is greater after the collision than it was before.

Averaging of Molecular Velocities. In any sample of gas there will therefore be what is called a *distribution* of velocities, some molecules moving rapidly, some slowly. Since the total pressure which the molecules exert on the wall is the sum of a series of pressure increments P_i each due to the molecules of velocity u_i, we may write for the total pressure

$$P = \sum P_i = \frac{1}{3v} \sum m u_i^2 \tag{9}$$

The quantity mu_i^2 equals twice the kinetic energy of a molecule having velocity u_i; the sum Σmu_i^2 is therefore equal to twice the total translational energy of all the molecules, which is the e_t of Eq. (8). This equation applies therefore even when the molecules have a distribution of velocities instead of a constant velocity. If the molecules did all have the same velocity, the quantity e_t/n would be the kinetic energy $\frac{1}{2}mu^2$ of a single molecule; since this is not so, the quantity represents the average kinetic energy of a molecule, which we represent by $\bar{\epsilon}_t$. If then we calculate a velocity u_s by the equation

$$\frac{1}{2} m u_s^2 = \bar{\epsilon}_t = \frac{e_t}{n} = \frac{\frac{3}{2} Pv}{n} \tag{10}$$

this will be a special kind of average velocity defined by the equation

$$u_s = \sqrt{\frac{1}{n} \sum n_i \bar{u_i^2}} \tag{11}$$

and called the root-mean-square velocity.

Relation to Avogadro's Law. It is a consequence of the laws of collisions between elastic bodies that a head-on collision between two molecules of different mass moving at the same velocity slows down the heavy molecule and speeds up the light one. A generalization of this rule leads to the result that in a mixture of two different kinds of molecules of masses m_a and m_b such interchanges will lead eventually to a situation in which the heavy molecules are moving on the average more slowly and the light ones more rapidly. A detailed analysis shows that the average kinetic energies of the two kinds of molecules will then be equal and the same as they would have been if each kind of molecule were present alone. It follows that the value of the Pv product for n molecules of kind a should be the same as it is for n molecules of kind b. This is Avogadro's law, with which the kinetic theory is therefore consistent.

If we set n in Eq. (7) equal to $\mathbf{N}$, the number of molecules in a mole, the volume v becomes the molar volume V and we have

$$PV = \tfrac{1}{3}\mathbf{N}mu^2 = \tfrac{1}{3}Mu^2 = \tfrac{2}{3}E_t \tag{12}$$

with u the root-mean-square velocity, M the molecular weight, and E_t the total translational energy of the molecules in a mole.

Relation to Temperature. The equation $PV = \mathbf{R}T$ is our definition of temperature within the precision of the perfect-gas law or for the limiting case of very dilute gases. We see from this and Eq. (12) that the kinetic theory makes the absolute temperature a direct measure of the average translational kinetic energy of the molecules of a gas and that

$$E_t = \tfrac{3}{2}\mathbf{R}T \tag{13}$$

and

$$\bar{\epsilon}_t = \frac{3}{2}\frac{\mathbf{R}}{\mathbf{N}}T \tag{14}$$

Distribution of Molecular Velocities. Because of our well-justified faith in the reproducibility of nature we expect not merely that the average kinetic energy of the molecules of a particular gas at a given temperature should have a constant value but also that the distribution of the energies should be fixed. That is, it seems reasonable that the fraction of the molecules having any particular velocity should be determinate. Such a distribution may be described by the equation

$$\frac{dn}{n} = D\,du \tag{15}$$

in which n is the total number of molecules and dn the number having velocities between u and $u + du$. The quantity $D\,du$ is therefore the fraction of the molecules which have velocities in this range. It was shown by Maxwell from elementary considerations of probability and can be derived as a special case of the general laws of quantum statistics (Appendix B) that the quantity D satisfies the equation

$$D = \frac{4}{\pi^{1/2}}\left(\frac{M}{2\mathbf{R}T}\right)^{3/2} u^2 e^{-Mu^2/2\mathbf{R}T} \tag{16}$$

The value of the quantity D for oxygen at 0° and at 100°C is plotted against the velocity u in Fig. 2. The value of u at which the maximum in this curve appears is clearly the most probable velocity. This is easily shown to be given by

$$u_m = \sqrt{\frac{2\mathbf{R}T}{M}} \tag{17}$$

The value of u_m, the most probable velocity, therefore increases with increasing temperature and with decreasing molecular weight. Since the root-mean-square velocity u_s is given by Eq. (10) as $\sqrt{3RT/M}$, this velocity is greater than the most probable velocity in the ratio $\sqrt{3/2}$. The value of D at the maximum is shown by substitution of u_m in Eq. (16) to be

$$D_m = \frac{4}{e}\sqrt{\frac{M}{2\pi RT}} \tag{18}$$

This quantity decreases with increasing temperature or with decreasing molecular weight. Since the total area under the curve from zero to

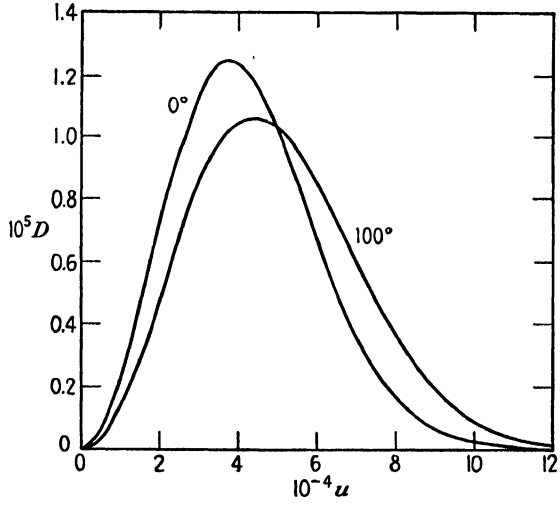


FIG. 2. Distribution of molecular velocities for oxygen at 0 and at 100°C.

infinite velocity

$$\int_0^\infty D\,du = \int \frac{dn}{n}$$

must equal unity, the integral on the right being merely the sum of all the fractions dn/n, the lower ordinate of the maximum with higher temperatures or lower molecular weights implies a broader and flatter curve. With respect to temperature all these effects are easily appreciated from the two curves of Fig. 2. Since temperature and molecular weight appear in these formulas only as the ratio M/T, the effect of an increase in molecular weight is in all respects the same as that of a proportionate decrease in temperature.

Evidence for the Theory. One might say that the whole structure of chemical and physical science is evidence in support of the usefulness of

the kinetic molecular theory and hence in support of the only kind of validity a theory can have. A very direct kind of evidence has come from the study of molecular beams.

Suppose a vessel A, containing a gas, communicates with a vessel B, in which the pressure is maintained at an extremely low value by efficient pumps, through an orifice so small that the molecules streaming through the orifice have a negligible chance of colliding with each other within the orifice. The molecules which leave A will then proceed through B with the same velocity and direction that they had in A provided the pressure in B is small enough so that the chance of a collision with the residual gas molecules in B is negligible. By a system of successive orifices the molecules which have a particular direction can be allowed to enter a third vessel C, the remainder being pumped out or condensed on a surface cooled with liquid air or the like. The beam of molecules in C consists then of a stream of molecules moving in nearly parallel lines and consequently not colliding with each other. Their velocities are necessarily the velocities which the molecules possessed in the original vessel A and should therefore be determined by the temperature of that vessel and by the molecular weight of the substance.

Although the density of molecules in such beams is inevitably low, sensitive methods for detecting the beam have been developed. A variety of devices then become available for determining the time required for a molecule to traverse the known length of vessel C and hence to determine the velocity of the molecule. One of these involves the interposition of a pair of toothed wheels on a common axis rotating at high speed. If the speed of rotation is properly adjusted to the velocity of the molecules, those which get through a gap on the first wheel will also get through a later gap on the second wheel and register on the detecting device; otherwise they will be stopped by a tooth on the second wheel. The results of such experiments as these are in satisfactory agreement with the predictions of the kinetic molecular theory, not only with respect to the most probable velocity but also with respect to the distribution of velocities according to Eq. (16).

The van der Waals Equation. We noted earlier that the problem of obtaining a quantitative description of the properties of nature may be approached either empirically or from theoretical reasoning (page 7). A moderately successful theoretical approach to the behavior of real gases leads to the van der Waals equation. This takes account both of the fact that the volume of the molecules is not negligible compared with the total volume occupied by the gas and also of the existence of attractive forces between the molecules.

With respect to the volume problem let us return to our consideration

(page 22) of the effect of collisions between molecules. Suppose a molecule j coming from the left-hand wall of Fig. 1 strikes head on a molecule k coming with the same velocity in the opposite direction. After the collision molecule j will be moving toward the wall with the same velocity that molecule k possessed before the collision. Molecule j acts, therefore, after the collision in just the way that molecule k would have acted in the absence of the collision except that it will at any instant be ahead of the position which k would have had by an amount equal to the diameter of the molecules. The net effect is that the collisions with the wall occur a little more frequently than would have been the case if the molecules had zero volume, which is to say as frequently as if the space occupied by the gas were a little smaller than is actually the case. This is taken account of in the van der Waals equation by subtracting from the volume occupied by the gas a quantity b which is proportional to the volume of the molecules.

The very existence of liquids and solids indicates that there are attractive forces acting between molecules which are strong when the molecules are crowded closely together in the liquid or solid state. These forces must, however, become very weak when the molecules are widely separated; otherwise the perfect-gas law could not so closely approximate the behavior of real gases at low pressures when the average distance between the molecules is large. In reckoning the total force exerted on a particular molecule we need therefore consider only the effects deriving from its fairly near neighbors and can neglect the force exerted by distant molecules. It follows that the intermolecular forces act equally in all directions on a molecule well within the body of a gas but exert a one-sided pull away from the wall on a molecule which is just approaching the wall. As a result the force with which the wall must resist the collisions of the molecules is somewhat reduced, which is to say that the pressure exerted by the gas is less than it would have been in the absence of the intermolecular forces. Van der Waals supposed that the effect varies inversely as the square of the volume and obtained the equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = \mathbf{R}T \tag{19}$$

Validity of the van der Waals Equation. This equation is qualitatively in agreement with the behavior of real gases over very wide ranges of pressure and temperature, although the quantitative agreement is not close. This is illustrated in Fig. 3 for the case of carbon dioxide at three temperatures. Of course, a continuous function such as Eq. (19) cannot possibly duplicate the discontinuities which appear in the behavior of real

gases below the critical temperature, but the curve for 13.1°C illustrates how the equation makes a noble effort to match the condensation phenomena by means of a sort of wriggle. It will be noted that the agreement between the equation and the facts is best for the critical temperature (31.1°C). This is because, as is customary in the application of the van der Waals equation, the values of the constants a and b were so

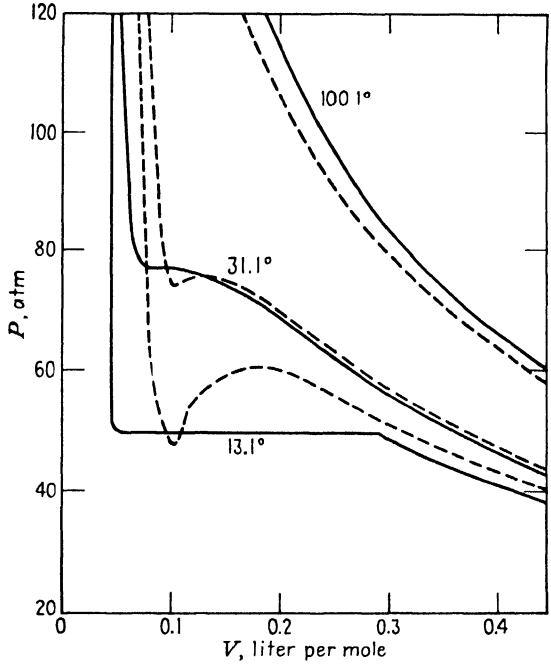


FIG. 3. Solid-line experimental isotherms for carbon dioxide at 13.1, 31.1, and 100.1°C. Dashed-line plots of the van der Waals equation with $a = 3.57$ and $b = 0.0424$. (*Taken from Fig. 34 of Loeb, "Kinetic Theory of Gases," McGraw-Hill Book Company, Inc., New York,* 1934.)

chosen as to make the equation coincide with experiment at the critical point.

By proper choice of the values of the constants the equation can be made to fit the data over more limited ranges quite closely. Thus column II under the heading of Calculated pressure in Table 1 contains values of pressure for oxygen at 0°C calculated from the van der Waals equation, with the values $a = 1.143$ and $b = 0.030$ chosen to give the best fit to these data. These calculated pressures agree with the observed values to within 1 part in 10,000—considerably better in fact than do the figures of column III, which were calculated using the virial equation. But if the values $a = 1.36$ and $b = 0.0316$, computed from the critical proper-

TABLE 1. PRESSURE-VOLUME RELATIONS OF OXYGEN AT 0°C*

Observed		Calculated pressure		
P, atm	V, liter/mole	I	II	III
24 9475	0.87814	24.72	24.944	24.926
49.7212	0.43118	48.76	49 772	49.697
73 7436	0.28532	70.49	73 749	73.738
98 4855	0.21026	94.65	98.48	98.436

* Experimental data from Table 3 of Chap. 1.

ties, are employed in the van der Waals equation, the pressures contained in column I are obtained. These are obviously in much poorer agreement with experiment.

It is a reasonable and generally accepted conclusion that the van der Waals equation represents at least a good beginning toward a theoretical interpretation of the deviations from the perfect-gas law and that the ideas involved in the derivation of the equation are qualitatively sound even though not exact in a quantitative sense.

Nature of the Forces between Molecules. The van der Waals reasoning assumes that there is an attractive force between the molecules of a gas which is large when the molecules are close together but which dies off very rapidly with increasing distance. It also treats the molecules as impenetrable bodies with a definite volume. These ideas are most easily visualized in terms of a plot of the potential energy ϵ of a pair of molecules against the distance r between their centers. The negative value of the slope of such a plot is then equal to the force F of repulsion between the bodies (MWM 212–214, Sears I, 134)

$$F = -\frac{d\epsilon}{dr} \tag{20}$$

The choice of a zero value of potential energy is purely arbitrary, and the energy is usually taken to be zero when the molecules are separated by an infinite distance. The van der Waals assumption is then that as r decreases from infinity there is at first an attractive force (F negative, $d\epsilon/dr$ positive) so that the curve slopes downward and the energy ϵ decreases. When the molecules come in contact, however, r can no longer decrease. This is to say that the force of repulsion suddenly and discontinuously becomes infinitely repulsive and the energy plot takes, therefore, the form shown in Fig. 4. We know, however, that solids and liquids can be compressed, although their compressibility is 10^4 to 10^6 times smaller than that of dilute gases, and that this compressibility

shows no sign of disappearing as the temperature is lowered toward the absolute zero. And our successful theories of atomic structure very definitely indicate, not that the force between two molecules changes over discontinuously from attractive to infinitely repulsive but rather that there is a change that can be represented by a smooth curve in the energy diagram of the sort shown in Fig. 5.

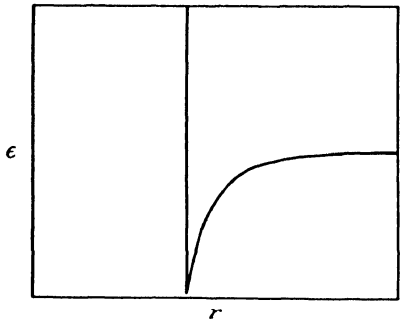


FIG. 4. Potential energy ϵ and intermolecular distance r according to the van der Waals assumptions.

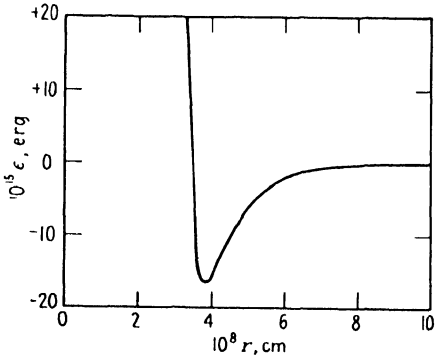


FIG. 5. Relation between potential energy ϵ and intermolecular distance r for two argon atoms.

Relation between Intermolecular Energy and Distance. Figure 5 is actually a plot of the equation

$$\epsilon = ar^{-12} - br^{-6} \tag{21}$$

with $a = 1.78 \times 10^{-103}$ and $b = 1.08 \times 10^{-58}$. This represents the best current estimate of the variation with distance of the potential energy of a pair of argon atoms, the constants being derived by Lennard-Jones from the deviations of argon from the perfect-gas law. The general form of this equation is consistent with quantum-mechanical theories of atomic and molecular structure and with such known facts as the way in which the compressibilities of solids and liquids vary with pressure. The most important numerical properties of the plot, namely, the values of r and ϵ at the minimum, are consistent with such facts as the distance between adjacent atoms in crystalline argon and with the heat of evaporation of that substance. At large values of r the first term is negligible because it involves a much higher inverse power of r than does the second. Consequently the situation in this region is that of an energy varying as the inverse sixth power of r and hence of an attractive force varying as the inverse seventh power. At small values of r, by the same token, the second term is negligible, and the force is one of repulsion varying as the inverse thirteenth power of the distance.

All the experimental knowledge we have about the properties of gases, liquids, and solids and all our theoretical information about the nature of atoms and molecules are consistent with the idea of an energy of interaction between electrically neutral molecules which is of the sort represented by Fig. 5 and Eq. (21). In particular it seems clear that the energy can be represented to an excellent approximation as the sum of two terms of opposite sign and that the negative term, which is responsible for the attraction, involves the distance to the inverse sixth power. The total strength of the binding, *i.e.*, the depth of the minimum of the plot of Fig. 5, varies considerably according to the structure of the molecule. It is measured in hundreds of calories per mole for very symmetrical structures like those of the inert gases, is materially greater in magnitude with molecules whose charge distribution corresponds to the presence of a dipole moment (Pauling 216, 329, Timm 289), and reaches as much as a few thousands of calories when the structure is such as to permit what is called *hydrogen bonding* (Pauling 331–335, Timm 292–293).

An inverse-sixth-power variation represents, of course, a very rapid disappearance of the attractive effect as the distance increases. Doubling the distance decreases the term by a factor of 64; multiplying the distance by 10 decreases the term by 1,000,000. Consequently these effects disappear for all practical purposes when the distance between the molecules is a few times the molecular diameter.

Forces between Ions. When molecules are electrically charged, *i.e.*, when they are ions, there is an electrical interaction varying as the inverse first power of the distance. If we suppose that there is a repulsion of the same sort as that which exists between neutral molecules, the total potential energy of a pair of ions is given by

$$\epsilon = \frac{a}{r^{12}} + \frac{e_1 e_2}{Dr} \tag{22}$$

If the charges e_1 and e_2 on the two ions have opposite sign, the second term is negative and corresponds to an attraction; it corresponds to a repulsion if they have the same sign. The interaction, whether attractive or repulsive, is smaller the greater the dielectric constant D. It is clear that these effects persist to a much greater distance than do those operating between neutral molecules; doubling the distance halves the magnitude of the second term of Eq. (22) instead of reducing it by a factor of 64.

Energy of a Gas. A molecule of a gas possesses, therefore, a potential energy which derives from the forces which operate between it and the other molecules of the gas. If the gas is dilute and the average distance between the molecules is consequently large, the magnitude of this energy

is very small. If therefore we are considering only gases at low pressures, *i.e.*, at high dilutions, we shall make only a small error if we assume that the potential energy is zero and therefore constant. By the kinetic theory the kinetic energy of the molecules of a gas depends only on the temperature and is unaffected by changes in pressure or volume at constant temperature. Hence we arrive at the conclusion that the total energy of a portion of a gaseous substance at a fixed temperature should to a good approximation be independent of the pressure of the gas provided that the pressure is low enough so that forces of interaction between the molecules may be neglected, which is to say provided the conditions are such that the perfect-gas law is also a good approximation. This conclusion is supported by experiment (page 69) and has many important implications.

Relation between the van der Waals Equation and the Virial Equation. The fact that the pressure-volume relationships of real gases can be reasonably well approximated either by the virial equation or by the van der Waals equation brings up a question of a sort which is of frequent occurrence. The two equations have very different mathematical forms and appear to be completely unrelated. How then can it happen that both equations fit the facts so well, and what are the conditions which make this coincidence possible? The first part of this question is immediately answered by the mathematical principle that a continuous function may be closely approximated over a greater or smaller range by a power series in one of the variables. The degree of approximation that may be attained depends on the nature of the particular function; for any particular function it is usually better the larger the number of terms in the series and poorer the wider the range covered. The virial equation obviously expresses the variable PV as a power series in the variable P; it is not immediately obvious that the van der Waals equation represents a functional relation between these variables because it is not possible to manipulate it into a form in which PV is given as an explicit function of P, that is, into a form in which the variable PV can be set down equal to an expression which involves P as the sole variable. Nevertheless it is possible by substituting a series of values of V in the equation to calculate the corresponding values of P and from these the values of PV. A tabulation of these corresponding values of PV and P or the plot of PV against P which can be constructed from the tabulation is then a functional relationship between the variables PV and P. Consequently Maclaurin's theorem (ST 396–399) in the form

$$PV = \lim_{P\to 0}(PV) + \left[\lim_{P\to 0}\frac{d(PV)}{dP}\right]P + \frac{1}{2!}\left[\lim_{P\to 0}\frac{d^2(PV)}{dP^2}\right]P^2 + \cdots \quad (23)$$

may be used to approximate the relationship by a power series. Now the van der Waals equation may easily be put into forms in which either P or PV is an explicit function of V, namely,

$$P = \frac{\mathbf{R}T}{V - b} - \frac{a}{V^2} \tag{24}$$

$$PV = \frac{\mathbf{R}TV}{V - b} - \frac{a}{V} \tag{25}$$

Hence the derivatives $d(PV)/dV$ and dV/dP are easily obtained as functions of V. By a fundamental principle of the calculus the desired first derivative $d(PV)/dP$ is then given by

$$\frac{d(PV)}{dP} = \frac{d(PV)}{dV}\frac{dV}{dP} \tag{26}$$

and the second derivative by

$$\frac{d^2(PV)}{dP^2} = \frac{d}{dV}\left[\frac{d(PV)}{dP}\right]\frac{dV}{dP} \tag{27}$$

The necessary substitutions are complicated but not difficult and are reported in Appendix A; the result is that the three-constant virial equation which most closely approximates the van der Waals equation is

$$PV = \mathbf{R}T + \frac{\mathbf{R}Tb - a}{\mathbf{R}T}P + \frac{a}{(\mathbf{R}T)^3}(2\mathbf{R}Tb - a)P^2 \tag{28}$$

That is, the best agreement between the two equations is obtained if the constants B and C of the virial equation [Eq. (5) of Chap. I] are related to the van der Waals constants a and b by the relations

$$B = \frac{\mathbf{R}Tb - a}{\mathbf{R}T} \qquad C = \frac{a}{(\mathbf{R}T)^3}(2\mathbf{R}Tb - a) \tag{29}$$

Since (page 8) a three-constant virial equation fits the data for oxygen at 0°C to 0.1 per cent and the van der Waals equation fits the same data to 0.01 per cent, the agreement between the van der Waals and the virial equation is in fact good.

Since the van der Waals equation is qualitatively in agreement with the properties of real gases over wide ranges of temperature (Fig. 3), Eq. (28) makes it possible to estimate the effect of temperature on the nature of the PV-P plots as this is illustrated in Fig. 6 of Chap. I (see Probs. 10 and 11) and also to estimate the temperature coefficients of the virial equation. A more accurate set of relations between the constants of the

virial equation and the temperature is the essential content of the Beattie-Bridgeman equation of state, which is the most satisfactory equation we have for representing the properties of real gases.

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PROBLEMS

1. What is the root-mean-square velocity of a molecule of oxygen at 0° and at 500°C? What is the root-mean-square velocity of a molecule of hydrogen at 0°C?

2. What is the average translational kinetic energy in ergs of a molecule of oxygen at 0°C? What is the translational energy in joules and in calories of 1 mole of oxygen at 0°C?

3. Develop an equation based on the considerations of pages 19 to 22 for the number of molecules of a gas striking unit area of the wall of the container in unit time.

4. Derive Eqs. (17) and (18).

5. What is the value of D in Eq. (16) for hydrogen at 0°C for the most probable velocity and for a velocity 10 times the most probable velocity?

6. For carbon monoxide van der Waals constants $a = 1.43$ atm-liters^2/mole^2 and $b = 0.0386$ liter/mole have been reported. What is the pressure predicted for this gas at $T = 273.2$°K and $V = 0.5$ liter/mole?

7. What volume is predicted on the same basis for 1 mole of carbon monoxide at 273.2°K and 50 atm?

8. What values of α, β, and γ in the equation

$$\frac{P}{c} = \alpha + \beta c + \gamma c^2$$

where $c = 1/V$, most closely approximate the van der Waals equation?

9. The Landolt-Börnstein Tables and the "Handbook of Chemistry and Physics" report values of a and b in the equation

$$\left(P + \frac{a}{v^2}\right)(v - b) = xT$$

in which v is the volume of that quantity of gas which would occupy 1 liter at 0°C and 1 atm if the substance were a perfect gas, and P is pressure in atmospheres. The values given for chlorine are $a = 0.01294$, $b = 0.002510$. What values of a and b in Eq. (19) with P in atmospheres and V in liters per mole can be calculated from these data?

10. The Boyle temperature of a gas is the temperature at which the initial slope of the PV-P plot is 0, that is, the temperature for which $\lim_{P \to 0} [d(PV)/dP] = 0$. Obtain a relation between the Boyle temperature of a gas and the constants of the van der Waals equation for that gas.

11. At low temperatures the low-pressure portion of the PV-P plot is concave downward, at high temperatures concave upward. What relation does the van der Waals equation predict between the temperature at which the curvature changes sign and the Boyle temperature?

12. Calculate from the data given on page 30 for the interaction energy of two argon atoms the value of r_0, the distance apart of the atoms in the state of lowest potential energy. Calculate also the energy ϵ_0 which must be supplied to separate them from this distance to infinity. Finally calculate the energy in joules and in calories required to separate $\frac{1}{2}$N pairs of argon atoms, and compare with the experimental heat of evaporation. How do you account for the difference?

CHAPTER III

SOLUTIONS, WITH SPECIAL REFERENCE TO DILUTE SOLUTIONS

Nature of Solids and Liquids. It is a familiar fact of experience that a solid or a liquid has a temperature just as much as a gas does, that a solid or a liquid may transfer thermal energy to a gas or receive it from a gas. Our picture of the nature of a gas makes its thermal energy proportional to the kinetic energy of the translational motion of the molecules. We inevitably suppose that the thermal energy of a solid or liquid consists also of molecular motion but must recognize that this motion is not the translational motion of the molecules, for diffusion in liquids is very much slower than it is in gases, and it is very much slower again in solids. Ease of diffusion is obviously a measure of the velocity of the translational motion of the molecules.

The case of solids is the easiest to understand because X-ray diffraction has furnished a convincing picture of the molecular properties of these materials. A crystalline solid consists of units arranged in a definite repetitive pattern (Pauling 37–46, 64–66, 245–246, Timm 153–158). These units may be all of one kind, or they may be of several kinds; they may be individual atoms, or they may be aggregates of atoms. They may be uncharged electrically, or they may be ions. The forces between the units may be the attractions and repulsions arising from the charges on ions as in sodium chloride; they may be valence forces arising from electron sharing as in diamond; they may be merely the relatively weak forces which we discussed in the last chapter and which are often called van der Waals forces. In all cases, however, the cohesive energy of the crystal arises from interactions between individual units which vary with distance in the general sort of way pictured in Fig. 5 of Chap. II. It is to this pattern of structure and forces that we attribute the rigidity and elasticity of crystalline substances because the pattern requires that work be done if a crystalline unit is to be displaced from its equilibrium position either toward or away from a neighboring unit, and because it implies that once the unit is displaced in either direction a force operates which tends to restore it to the equilibrium position. Now the existence of such a force whose magnitude increases with the displacement in either direction from the equilibrium position is exactly the condition which

allows a vibratory motion (MWM 173*ff.*, Sears I, 253*ff.*). Consequently we have every reason to suppose that the thermal energy of a crystal consists in part at least in the vibrational motion about their normal or equilibrium positions of the units which make up the crystal and that the total thermal energy of a solid is proportional to the energy of this vibrational motion. The transfer of heat from a moving gas molecule to a solid in contact with it is therefore analogous to the setting into vibration of a drumhead by the impact of the stick. The reverse process of transfer from solid to gas may be thought of as occurring when the collision of gas molecule with vibrating solid molecule occurs in the proper phase, *i.e.*, when the vibrating solid molecule is moving toward the gas molecule at the instant of the collision.

Liquids are more difficult to discuss in any theoretical fashion because they have less regularity of structure than crystalline solids and little if any rigidity. It is, however, reasonable to suppose that the molecules of a liquid vibrate much as do those of a solid and under the influence of the same intermolecular forces but that the center of motion of the vibration moves relatively slowly from one part of the volume occupied by the liquid to another.

Evaporation and Condensation. Just as the translational velocities of the different molecules of a gas vary around an average value and the velocity of a single molecule varies with time around the same average (page 22), so also must the vibrational energy of the molecules of a solid or liquid fluctuate around a mean. Occasionally this fluctuation will put into a single molecule on the surface sufficient energy and hence amplitude of oscillation (MWM 180, Sears I, 255, 264) to enable it to escape beyond the range of effective action of the attractive forces of the neighboring molecules and to become a free-moving gas molecule. This is evaporation. Occasionally also a gas molecule striking the surface will lose so much of its kinetic energy by transfer to the molecules of the condensed phase that it becomes captured by the latter. This is condensation. In any closed space there will be equilibrium in this process when the rates of evaporation and condensation are equal (Pauling 47–49, Timm 136–137); *i.e.*, when the rates are equal, the amounts of condensed phase and of gas will remain unaltered indefinitely.

If the temperature is held constant, the rate of evaporation is nearly independent of the pressure (there is a small effect because the force of attraction between the molecules depends upon their distance apart, and this decreases slightly with increasing pressure). But the rate at which the gas molecules strike the surface is to a first approximation proportional to the concentration in the gas phase (see Prob. 3 of Chap. II), and the concentration is proportional to the pressure at constant tempera-

ture. Since the capture of the gas molecule by the surface is a random matter, we expect that a certain constant fraction of the molecules which strike the surface will be condensed so that the rate of condensation should be proportional to the pressure of the gas. If a liquid or solid is brought into a space containing very little of its own vapor, the rate of evaporation must then be greater than the rate of condensation so that there is a net transfer from condensed phase to gas. As more and more gas is formed, the rate of condensation must increase until at a definite value of the pressure of the vapor the rates of condensation and evaporation will just balance and no further change will take place. The pressure of the vapor when this situation is attained is called the *vapor pressure of the condensed phase.* The change of pressure with time will therefore be something like the lower curve of Fig. 1. If, however, the condensed phase is brought into a space containing its vapor at a higher pressure than the equilibrium value (a supersaturated vapor), the rate of condensation will be greater than that of evaporation. The pressure of the vapor will therefore decrease with time until the same condition of equality between rate of evaporation and rate of condensation as in the other case is attained. The pressure-time curve will be of the nature of the upper curve of Fig. 1.

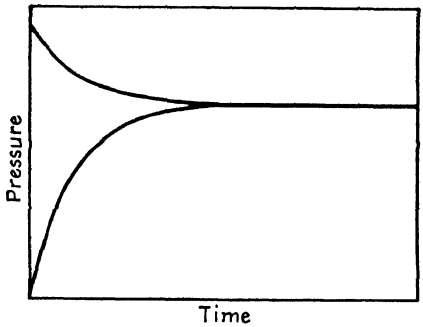


FIG. 1.

A rise in temperature increases the kinetic energies both of the condensed-phase molecules and of the gas molecules and must therefore increase the rates of both evaporation and condensation. The net effect, an increase in vapor pressure, can be accounted for only in terms of principles to be discussed later (page 147).

Evaporation of Solutions. In a solution, liquid or solid, *i.e.*, in a homogeneous mixture of two or more substances, we must expect the rate of evaporation of any one of the constituents to be smaller than would be the case if that substance made up the whole of the phase, because only a part of the surface from which evaporation takes place is made up of that substance. Specifically consider the evaporation of molecules of kind A from a liquid solution containing also molecules of kind B. Because of the dilution effect we have just mentioned the rate of evaporation of A from the solution is less than it would be from pure liquid A at the same temperature. But this dilution effect may be considerably modified according as the work required to separate an A molecule from

a B molecule against the attractive force operating between them is greater or less than the work required to separate two A molecules. If it is greater, the rate of evaporation is reduced to a still smaller value than the dilution effect alone would produce, because the A molecule has less chance of getting the larger vibrational energy required. If it is less, the rate of evaporation is greater than would be predicted from the dilution effect alone (although always less than it would be from the pure liquid). Only if the energy of interaction between unlike molecules happens to be exactly equal to the energy of interaction between like molecules should we expect the pure dilution effect. With this equality of energy the rate of condensation of A molecules from vapor of any given concentration must be the same on the surface of the solution as it is on that of the pure liquid A, for an A molecule will then be just as effectively trapped by a B molecule as by an A molecule. With unequal interaction energies the rate of condensation of A on the solution will be greater or less than it is on pure liquid A according as the energy of interaction between unlike molecules is greater or less than that between like molecules.

Quantitative Measures of Composition of Solutions. Before we look into the quantitative aspects of this situation, we must specify the quantitative measures of composition used in describing solutions. One kind of solution, gaseous mixtures, has already been considered from this point of view (page 13).

The *weight fraction* f_i of component i is

$$f_i = \frac{w_i}{\Sigma w_i} = \frac{w_i}{w} \tag{1}$$

where w_i is the weight of constituent i and w is the total weight of the solution. *Weight per cent* is obviously $100f$.

Mole fraction N_i of constituent i is defined by

$$N_i = \frac{n_i}{\Sigma n_i} \tag{2}$$

where n_i is the number of moles of constituent i. This is identical with the definition of mole fraction in a gaseous mixture [Eq. (23) of Chap. I]. While weight fraction is an exactly defined experimental quantity, mole fraction is sometimes a bit indeterminate because of uncertainty about the actual constituents of the solution.

Two other measures are particularly useful in solutions in which one constituent is present in much larger proportion than the other. Such solutions are called *dilute solutions;* the major constituent is called the *solvent,* and the other constituents are called *solutes.* The *molality* m_B of

a solute B is defined as the number of moles of solute in 1000 g of the solvent A, that is,

$$m_B = \frac{n_B \cdot 1000}{w_A} \tag{3}$$

where n_B is number of moles of B and w_A is weight of A in grams. *Concentration* c_B of solute B is defined as the number of moles of B per liter of solution, *i.e.*,

$$c_B = \frac{n_B}{v} \tag{4}$$

where v is volume of solution in liters. Note particularly that the definition of molality involves the weight of the solvent, not that of the solution, whereas the definition of concentration involves the total volume of the solution, not the volume of solvent employed in preparing the solution.

By a common convention, which we shall follow, the symbol 1 m KCl means a solution in which the molality of KCl is 1; the symbol 1 M KCl means a solution in which the concentration of KCl is 1 mole/liter.

Interconversion of Composition Measures. Problems involving the conversion of one composition scale into another occur frequently and are most easily handled by defining all the units in terms of one or more weight ratios. Thus for a binary solution of substances A and B we may write

$$f_B = \frac{w_B}{w_B + w_A} = \frac{1}{1 + (w_A/w_B)} \tag{5}$$

$$N_B = \frac{w_B/M_B}{(w_B/M_B) + (w_A/M_A)} = \frac{1}{1 + (M_B/M_A)(w_A/w_B)} \tag{6}$$

$$m_B = \frac{1000 w_B/M_B}{w_A} = \frac{1000}{M_B(w_A/w_B)} \tag{7}$$

$$C_B = \frac{w_B}{M_B v} = \frac{1000\rho}{M_B\{1 + (w_A/w_B)\}} \tag{8}$$

If the molecular weights M_A and M_B and, where Eq. (8) is involved, the density ρ of the solution are known, the weight ratio w_A/w_B may be calculated from any one of the other composition measures by the suitable equation of this list and any other composition measure may then be calculated from this ratio.

When more than two substances are present, the situation is more complicated but it is still useful to express each composition measure in terms of the minimum number of weight ratios.

Raoult's Law. Returning now to the evaporation and condensation of a liquid solution, we may reasonably suppose that in those cases where the interaction energy between like molecules has the same value as that

between unlike molecules the rate of evaporation r_e of A should be proportional to the fraction of the total volume of the solution which consists of A. If the molecular volumes are not too different, this volume fraction will be essentially the same as the mole fraction N_A and we may therefore write

$$r_e = k_e N_A \tag{9}$$

Similarly we may expect the rate of condensation r_c to be proportional to the partial pressure P_A of A in the gas phase but to be independent of the

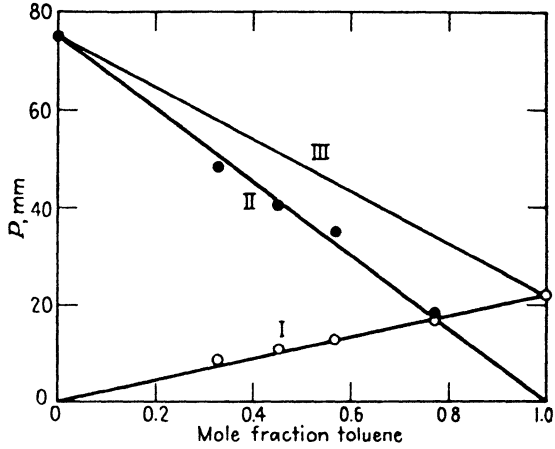


FIG. 2. Partial vapor pressure of benzene-toluene solutions: ○, partial pressures of toluene; ●, partial pressures of benzene. [*Data of Bell and Wright, J. Phys. Chem.*, **31**, 1884 (1927).]

composition of the liquid

$$r_c = k_c P_A \tag{10}$$

At equilibrium these two rates become equal; hence at equilibrium

$$P_A = \frac{k_e}{k_c} N_A \tag{11}$$

Since P_A must equal P_A^0, the vapor pressure of pure liquid A when $N_A = 1$, that is, in the pure liquid, k_e k_c must equal P_A^0 and

$$P_A = P_A^0 N_A \tag{12}$$

This equation is known as *Raoult's law*. The partial pressure P_A of substance A in equilibrium with a solution containing A is called the *partial vapor pressure* of A from the solution.

The previous discussion leads us to expect that Raoult's law may be a useful approximation for solutions composed of very similar substances. Figure 2, in which the points represent experimental data and the lines

are graphs of the law, shows that it does agree with the facts for solutions composed of benzene and toluene. Other frequently cited examples of what are called *ideal solutions*, for which Raoult's law applies for both constituents over the whole range of composition, are chlorbenzene-brombenzene, carbon tetrachloride–silicon tetrachloride, and *n*-butyl chloride–*n*-butyl iodide.

In Fig. 2 we have plotted three different quantities as ordinates against mole fraction of toluene as abscissas. If we let N_A and P_A represent mole fraction and partial pressure of toluene and N_B and P_B the corresponding

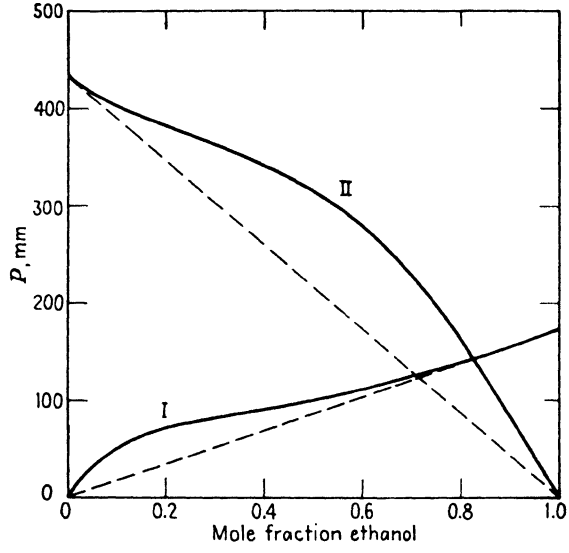


FIG. 3. Partial vapor pressures of (I) ethanol, (II) chloroform in mixtures at 45°C. Dotted lines represent Raoult's law; the full lines follow closely the numerous experimental points. [*Data of Scatchard and Raymond, J. Am. Chem. Soc.*, **60**, 1278 (1938).]

quantities for benzene, then line I in this figure is simply the plot of Eq. (12). Raoult's law applied to benzene leads to

$$P_B = P_B^0 N_B = P_B^0(1 - N_A) \tag{13}$$

which is plotted as line II in the figure. Finally total pressure P is given by

$$P = P_A + P_B = P_A^0 N_A + P_B^0(1 - N_A)$$

or

$$P = P_B^0 + (P_A^0 - P_B^0)N_A \tag{14}$$

This likewise linear equation is plotted as line III in Fig. 2.

Deviations from Raoult's Law: the Dilute Solution. Figure 3 presents data on a system, chloroform-ethanol, which deviates widely from the

predictions of Raoult's law. The deviation in this case is what is called a *positive* one, *i.e.*, the actual pressures are greater than those predicted from the law, but equally large negative deviations are common. It will be noted that the plot of the vapor pressure of ethanol deviates only slightly from the predictions of Raoult's law in solutions which contain much more ethanol than they do chloroform and that the vapor pressure of chloroform follows the law rather closely in solutions which consist almost entirely of chloroform. This kind of behavior is a constant and characteristic feature of such plots, no matter how widely the curve as a whole deviates from Raoult's law. In terms of our definition of dilute solution and of solvent (page 39) we may therefore state a very important and general rule.

There is for any liquid system of more than one constituent a region of dilute solutions in which the vapor pressure of the solvent agrees closely with Raoult's law, i.e., for which at a fixed temperature

$$P_A = P_A^0 N_A \tag{12}$$

the subscript A indicating the solvent.

This rule is a reasonable one. Even in the dilute solution there will be a dilution effect of normal magnitude which depresses the vapor pressure of the solvent according to Raoult's law. But because there are many more solvent molecules than there are solute molecules the near neighbors of any given solvent molecule are much more likely to be solvent molecules than solute molecules. Consequently the interaction energy against which a solvent molecule must operate in order to escape into the gas phase is in most cases the same as in the pure solvent, and the cases where a solute molecule is a near enough neighbor to produce a significant effect lead only to small deviations from the pure dilution effect.

Henry's Law. It will be noted also that, while the vapor pressure of the chloroform in solutions consisting mostly of ethanol deviates widely from Raoult's law, the plot is very nearly linear over a considerable range. The same is true of the vapor pressure of ethanol from solutions consisting mostly of chloroform, although the region of linearity is narrower. This result also is perfectly general and may be put in the form known as *Henry's law.*

The vapor pressure of a solute from a dilute solution is closely proportional to its mole fraction, i.e., at a fixed temperature

$$P_B = K_N N_B \tag{15}$$

the subscript B referring to the solute. *Except in the special case of the truly ideal solution the Henry's law constant K_N is not equal to the vapor pressure of the pure liquid solute P_B^0.*

This rule also is a reasonable one. A solute molecule in a dilute solution is surrounded by solvent molecules and is so far from any other solute molecule that their mutual interaction energy is small. Consequently the interaction energy against which the solute molecule must operate in order to escape is very closely the interaction energy between solute and solvent molecules. Except for the ideal solution this is quite different from the interaction between solute molecules. But so long as the solution is dilute and the solute molecules far apart, the energy should be independent of the concentration of the solute molecules.

Since the interaction energy of a given solute with different solvents has different values, we must also expect that the K_N value of a given solute should have different values in different solvents. And we find, for instance, that at 35.2°C the constant for the solute acetone in the solvent carbon disulfide is 7 times greater at 35.2°C than the vapor pressure of pure acetone but the constant for the same solute in the solvent chloroform is only 0.4 times the vapor pressure of pure acetone.

Henry's law is a relation between the mole fraction of the solute in a dilute solution and the partial pressure of the vapor of the same substance in the gas phase in equilibrium with the solution. There is nothing in fact or in theory which restricts its application to cases where the pure solute is a liquid at the pressure and temperature of the experiment. Indeed one of the commonest applications of the law is in connection with what is called the *solubility* of a gas in a liquid. Thus Table 1 lists the

TABLE 1. HENRY'S LAW DATA FOR THE SOLUTE HCl IN THE SOLVENT TOLUENE AT 25°C*

P, atm	N	K_N	m	K_m	ρ	c	K_c
0.0338	0 00154	21 9	0.0167	2 02	0.8604	0.0144	2 35
0.0965	0 00429	22.5	0 0468	2.06	0 8606	0.0402	2 40
0.158	0.00697	22.6	0 0762	2.07	0.8609	0 0655	2 41
0.282	0 0125	22.6	0.137	2.06	0.8614	0.117	2.41

* Data of O'Brien and Bobalek, *J. Am. Chem. Soc.*, **62**, 3227 (1940).

mole fractions N_{HCl} of HCl in saturated solutions in the solvent toluene, *i.e.*, in solutions of HCl in toluene which are in equilibrium with gaseous HCl at the partial pressure P_{HCl} listed. The corresponding Henry's law constants $K_N = P_{HCl}/N_{HCl}$ are satisfactorily constant.

Henry's Law in Terms of Molality and of Concentration. Table 1 also lists the molalities m_{HCl} and the concentrations c_{HCl} of these solutions and the constants K_m and K_c of two frequently used variations of Henry's law,

$$P_B = K_m m_B \tag{16}$$
$$P_B = K_c c_B \tag{17}$$

These quantities are as satisfactorily constant as is K_N, the average deviation from the mean being approximately 1 per cent in each case. The result illustrates a general rule that any relation involving the solute in a dilute solution has the same mathematical form when the composition of the solution is expressed in terms of the molality or of the concentration as when it is expressed in terms of the mole fraction of the solute. The numerical values of the constants involved in the equations are of course different with the different measures of composition.

The rule follows from the nature of dilute solutions as the following considerations show. From Eqs. (6) and (7) we get, using r for the ratio w_A/w_B,

$$\frac{N_B}{m_B} = \frac{r}{1000\{(1/M_B) + (r/M_A)\}} \tag{18}$$

In the most concentrated solution listed in Table 1 the quantity $r/M_A = 2.2$, whereas $1/M_B = 0.027$. Consequently the error involved if the latter term is neglected compared with the former is a little over 1 per cent; in the more dilute solutions r is larger, and the error involved in the approximation is even smaller. But Eq. (15) is not itself valid to better than 1 per cent, as the data of the table clearly show, and we have therefore no right whatsoever to be worried by an approximation of the same order of magnitude. Consequently we have, to as good a precision as that of Eq. (15) itself,

$$\frac{N_B}{m_B} = \frac{r}{1000r/M_A} \qquad \text{or} \qquad N_B = \frac{M_A}{1000} m_B \tag{19}$$

From this

$$P_B = \frac{K_N M_A}{1000} m_B \tag{20}$$

Eq. (20) has the same essential content as Eq. (16).

Similarly we have from Eqs. (6) and (8)

$$\frac{N_B}{c_B} = \frac{1}{1000\rho} \frac{1 + r}{1/M_B + r/M_A)} \tag{21}$$

As we have seen the term $1/M_B$ may be neglected compared with r/M_A to a sufficient precision in the most concentrated solution; for the same solution, $r = 200$, and $1 + r$ may therefore be replaced by r with similar precision. Consequently Eq. (21) reduces to

$$\frac{N_B}{c_B} = \frac{M_A}{1000\rho} \tag{22}$$

Furthermore the density ρ of the solution will not differ largely from the density ρ_A of the pure solvent, as indeed the data on densities listed in the table clearly show. Consequently we may write

$$N_B = \frac{M_A}{1000\rho_A} c_B \tag{23}$$

and from Eq. (15)

$$P_B = \left(K_N \frac{M_A}{1000\rho_A}\right) c_B \tag{24}$$

Equation (24) is identical in content with Eq. (17).

The Dilute Solution. As Fig. 3 indicates, the region of compositions in which Raoult's law holds for the solvent is approximately the same as that in which Henry's law holds for the solute. This is true both for the region on the right of the diagram in which the solvent is ethanol and for that on the left in which the solvent is chloroform. Examination of other systems of this sort shows that they all exhibit this agreement in the range of validity of the two laws, and the generalization may be supported by thermodynamic reasoning. As we shall see, a large number of other important rules, notably the ideal law of chemical equilibrium and the laws of chemical kinetics, are applicable to a useful precision over about the same range of compositions as that in which Raoult's law for the solvent and Henry's law for the solute apply. Fundamentally this region is, as we have seen, the one in which the solute molecules are far enough apart so that the forces between solute molecule and solute molecule may be neglected.

For these reasons it is customary to assign to the term *dilute solution* the specialized meaning of a solution sufficiently dilute so that Raoult's and Henry's laws are useful approximations. The limit of the region of dilute solutions thus defined is obviously vague, for, like the region of applicability of the perfect-gas law, it depends both on the magnitude of the forces which produce the deviations from dilute solution behavior and also on the precision required for the problem in hand. Except for solutions of electrolytes and for solutions of high polymers in solvents of low molecular weight we normally expect the dilute-solution laws to be good to at least 1 per cent at concentrations running from zero to 0.1 mole/liter and good to within a few per cent up to 1 mole/liter.

The much larger deviations observed with ionic solutes arise from the fact that the forces between ions are much greater than those between electrically neutral molecules and die off less rapidly with the distance (page 31). The large deviations in the high-polymer solutions may be attributed to the large difference in molar volume between solute and solvent (page 41).

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On the properties of solutions of nonelectrolytes:

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PROBLEMS

1. A separatory funnel of volume V contains V_1 ml of an aqueous solution whose vapor pressure is P_1, and the remainder of the funnel contains air plus water vapor in equilibrium with the solution. An amount V_2 ml of chloroform, whose vapor pressure is P_2, is introduced, and the funnel is stoppered before any significant quantity of chloroform has evaporated. If the atmospheric pressure is normal, what pressure will be reached in the funnel when it is shaken until equilibrium is reached?

2. Prove that, in the limiting case of the dilute solution, $c/m = \rho$, where c and m are concentration and molality of solute and ρ is density of solvent.

3. The density of a 5 per cent solution of ethanol in chloroform at 25°C is 1.419 g/ml. Calculate the mole fraction, the molality, and the concentration of ethanol in this solution.

4. What is the molality of a solution of ethanol in chloroform in which the mole fraction of ethanol is 0.05?

5. The vapor pressure of liquid benzene at 20°C is 74.7 mm Hg; that of toluene is 22.3. Assuming the solutions to be ideal, what is the composition of the liquid which boils at 20°C under 40 mm pressure?

6. On the same assumption calculate the mole fraction of toluene in the first drop of distillate obtained when a large quantity of a benzene-toluene mixture in which the mole fraction of toluene is 0.1 is distilled at 20°C.

7. If the solution of Prob. 6 is evaporated at 20°C in a closed container whose volume is gradually increased by motion of a closely fitting piston, what is the composition of the last drop of liquid?

8. Estimate from Fig. 3 the mole fraction of ethanol in the first drop of distillate from a chloroform-ethanol mixture in which the mole fraction of ethanol is 0.1 at 45°C. How do you account for the fact that the distillate is richer in the less volatile constituent than is the liquid being distilled in this case, whereas it was poorer in the case of Prob. 6?

9. One gram of *t*-butyl chloride is dissolved in 100 g of a 50 per cent by weight mixture of ethanol and water. In a second solution 1 g of the butyl chloride is dissolved in 100 g of an ethanol-water mixture containing 75 per cent by weight ethanol. Calculate the mole fraction of *t*-butyl chloride in each case.

10. At 20°C the vapor pressure of water is 17.535 mm Hg. A solution of 20 g of a certain nonvolatile substance in 1000 g of water has a vapor pressure 0.0343 mm less than that of water at this temperature (the difference can be measured experimentally with greater certainty than can the absolute vapor pressure of solvent or solution). Using Raoult's law, calculate the molecular weight of the solute.

11. Many tables list values of the "Bunsen coefficient" α, which is the amount of gas in milliliters, measured at 0°C and 1 atm, that dissolves in 1 ml of solvent when the partial pressure of the solute is 1 atm. What is the relation between α and the K_c of Eq. (17)?

12. From Fig. 3 estimate the Henry's law constant for the solute chloroform in the solvent ethanol at 45°C.

13. At 35.17°C a solution of chloroform in acetone whose mole fraction of chloroform is 0.0588 has a total vapor pressure of 332.4 mm Hg. At this temperature the vapor pressure of pure chloroform is 293.1 mm; that of pure acetone is 344.5 mm. Assuming that this is a dilute solution, answer the following questions: (*a*) Are acetone-chloroform solutions ideal, and if not is the deviation positive or negative? (*b*) What should be the total vapor pressure of a solution whose mole fraction of chloroform is 0.03? (*c*) What is the partial vapor pressure of chloroform from the 0.0588 solution? (*d*) What is the mole fraction of chloroform in the vapor in equilibrium with the 0.0588 solution?

CHAPTER IV

THE FIRST LAW OF THERMODYNAMICS

Systems, Surroundings, and Properties. Those who work in any field of science inevitably develop a specialized language, and this frequently employs words in a sense different from that of their common usage or in a definitely limited specialization of the common meaning. A most important part of the task of learning a science is that of becoming familiar with the exact sense of these specialized meanings.

In physical science a *system* is any part of the universe under consideration for a particular problem. All of the rest of the universe makes up the *surroundings* of the system. The surroundings include such measuring instruments as thermometers, manometers, balances, refractometers, the human eye, and all other devices used for investigating the system. With such instruments as these we determine the *properties* of the system, by which we mean the various behaviors it exhibits toward these instruments.

We define as an *isolated* system one which is completely isolated from the rest of the universe. To attain this complete isolation, the system would have to be surrounded by a rigid wall which is a perfect thermal insulator and across which no forces operate. Since our instruments could not operate through such a barrier, we should have no way of observing the properties of such a system. It follows that an isolated system is incapable of existence and that, if it did exist, we could know nothing about its properties or behavior. In practice, however, the interactions between a particular system and the surroundings may often be made so small that they may be neglected or may be calculated as small corrections to the actual behavior of the system. The concept of the isolated system is therefore an extremely useful one.

Identity of States. When two systems are identical in all their properties, they are said to be in the same *state*. When a system is subjected to influences which change its properties, it is said to have returned to a state identical with its initial one if all its properties are the same after the sequence of changes as they were before the changes. A sequence of changes which returns a system to a state identical with the initial state of the sequence is called a *cyclic process*.

One of the most important generalizations man has made about nature

is that it is possible to determine whether or not two systems are in an identical state by observing a limited number of properties and without undertaking the hopeless task of observing the countless variety of properties which any system possesses. Thus we have absolute confidence that if we start with 1 g of H_2 at 25°C and 1 atm pressure and subject it to the most varied changes, heat it and cool it, liquefy and reevaporate it, burn it to water and recover it by electrolysis, and then return it to 25°C and 1 atm, all of its properties will be the same at the end of this cyclic process as they were at the beginning. This means not merely that it will have the same volume but that its magnetic susceptibility, its index of refraction for light of a particular wavelength, or any other property we might choose to name will be unchanged by a sequence of operations which returns the material unchanged in composition and amount to its original temperature and pressure. We know from the same kind of experience that any other 1-g sample of H_2 at 25° and 1 atm will have the same properties as the first one.

The really important thing about this generalization and indeed about the whole idea of identity of states is the fact that it is possible to have assurance that two systems will have the same volume, the same magnetic susceptibility, the same index of refraction, etc., without actually observing the property in question and merely by observing a sufficient number of other properties. In the illustration given, these determining properties were the mass, the chemical composition, the pressure, and the temperature, but there is nothing unique about this particular set of properties. We could be equally certain that two samples of 1 g of H_2 were in the same state if we showed that both samples possessed the same volume and the same pressure, for we know that, if two samples of 1 g of H_2 have the same volume and pressure, they are necessarily at the same temperature.

Obviously two systems can be identical only if they have the same mass. Identity also requires that the systems contain the same proportions of identical "phases," a term which we have already used, but now attempt to define exactly.

Phases. In some systems, for instance in all gaseous ones, such properties as pressure, temperature, density, and refractive index [these are properties which we shall shortly (page 56) learn to classify as intensive properties] are either constant from point to point throughout the space occupied or vary continuously, as they do, for instance, in the earth's atmosphere in going from one level to another. Such systems are said to consist of a single phase. In other systems there are sharp discontinuities. Thus a system consisting of liquid and gaseous water contains a region of high density, the liquid, and one of low density, the vapor, and

the density and other properties change sharply and very suddenly at the surface of separation. A system is said to contain as many phases as there are kinds of region each of which possesses its own characteristic set of intensive properties. It is not necessary that the portions of a phase form a single undivided portion of matter. Thus a suspension of sand in water contains two phases, a sand phase and a water phase, because all the sand particles have the same set of intensive properties, even though they are not in contact with each other. A system of finely divided rhombic sulfur, monoclinic sulfur, and liquid sulfur (Pauling 360–362, Timm 392) contains three phases, because each particle of rhombic sulfur has the same properties as each other particle of rhombic sulfur but different properties from the liquid and from the particles of monoclinic sulfur.

A system consisting of 1 g of H_2O at 100°C and 1 atm pressure may be entirely liquid, it may be entirely gaseous, or it may consist of a mixture in any proportion of these phases. The volume occupied by the system is greater the greater the proportion of gas; consequently two systems may have different properties—specifically, different volumes—even though they have the same temperature, pressure, mass, and composition. If and only if they contain the same proportions of gas and liquid phases are the volume and other properties found to be identical. This does not mean that in a practical case we must actually measure the mass of liquid and the mass of gas, because the measurement of some other property may suffice to determine the proportions of the phases. Specifically the measurement of the volume of the system composed of 1 g of H_2O at 100°C and 1 atm would necessarily determine the proportions of gas and liquid.

Identity of Chemical Composition. We determine that we have a body of a given chemical composition, *i.e.*, that we have a body chemically identical with another body, which either is at hand or has been previously described, by observing a limited number of physical properties and of changes in physical properties which result from the action of chemical reagents. The techniques of measurement of properties and of carrying out of chemical reactions and observing the properties of the products of the reaction which are employed for this purpose of identification of chemical substances and mixtures of chemical substances make up an extremely important part of the craftsmanship of chemical science. This is analytical chemistry in the broadest possible sense of that term, and it includes the techniques the skilled organic chemist employs to identify an unknown substance or to separate an unknown mixture into identifiable compounds, as well as the techniques which are usually taught in courses of analytical chemistry. As with many skilled opera-

tions it relies much on the experience and judgment of the individual investigator, and its rules of evidence are not written down and universally accepted. Thus an organic chemist will usually have a definite opinion whether a colleague has prepared enough derivatives to surely identify a particular reaction product, but there is no universally accepted rule stating how many derivatives are necessary. And chemists generally had for eighty odd years accepted the identity of nitrogen prepared by removal of oxygen from air with that prepared by the decomposition of ammonium nitrite until Rayleigh's discovery that the two materials differed in density led to the discovery of argon.

We must also recognize that we have not completely and exactly determined whether two samples are chemically identical unless we have proved that the proportions of the isotopes (Pauling 74, Timm 295) of the various elements present are the same in both samples. For most purposes this refinement is unnecessary although small changes in isotopic composition do occur in such processes as distillation or in chemical reactions.

Clearly the problem of determining whether or not two samples of material are chemically identical is not a simple one for which a few set rules can be given, and we shall not attempt any general solution in this discussion of physical chemistry. We shall, however, assume on the basis of the whole record of the science of chemistry that it is possible to solve the problem of identity or nonidentity in any particular case and to solve it from the observation of a limited and humanly possible set of chemical and physical properties.

Definition of Energy. Both logically and historically the concept of energy appears first when idealized systems of moving bodies are considered in which the effects of friction, of viscous resistance to flow, of inelasticity in collisions, and the like, may be neglected. In such systems it is profitable to define a quantity, the mechanical energy, which has the valuable quality of staying constant in an isolated system, no matter what changes the system undergoes. A quantity which has this quality is said to be conserved, hence the phrase the *conservation of energy* (MWM 114–119, Sears I, 120).

When there is friction, or the like, mechanical energy does change with time but it is observed that the regions where the friction occurs get hot. If further we take rise in temperature of a fixed quantity of material of a fixed kind (for example, 1 g of water) as a measure of heat evolved, we find that to a good approximation there is a constant ratio between the amount of heat produced and the amount of mechanical energy which has disappeared. And in a heat engine the same ratio holds between the quantity of mechanical energy produced and the quantity of heat which

disappears. Heat and mechanical energy are therefore equivalent, and it is possible to measure both in terms of a single unit of energy.

This equality between mechanical energy produced and heat lost is valid for mechanical systems; it is not valid for the systems in which a chemist is interested. Consider, for instance, so simple a case as the evaporation of 1 g of water against the pressure of the atmosphere at a temperature of 100°C. The heat absorbed is 538.7 cal; the mechanical energy produced, which is the work used in pushing away the atmosphere, is only 40.5 cal. Suppose, however, we let the vapor produced by the evaporation expand to a lower pressure and temperature in the cylinder of a steam engine and then condense it to liquid and warm it back to its original state of liquid water at 100°C and 1 atm. We then find that the engine has done work, *i.e.*, that mechanical energy has been produced, and that heat has been lost by the surroundings in an amount equivalent to the mechanical energy produced. To meet this situation, we define the internal energy, or for short the energy, e of a system in terms of the change in energy which accompanies a process, as follows

$$\Delta e = q - w \tag{1}$$

The symbol Δe means the difference between the energy of the system at the beginning of the process and at the end of the process, *i.e.*, the increase in energy which accompanies the process. q is the heat absorbed from the surroundings during the process; w is the mechanical energy produced during the process, which is usually called the work done by the system during the process. The quantities Δe, q, and w may be either positive or negative; thus a negative value of Δe means a decrease in the energy of the system, a negative value of q means that heat is given off by the system to the surroundings, and a negative value of w means that work is done on the system by the surroundings.

The Δ symbol is widely used in physical chemistry; it always has the significance of the increase in the value of a property which accompanies the change from some initial to some final state. Here, for instance,

$$\Delta e = e_f - e_i \tag{2}$$

where e_f is the energy of the system after the process is completed and e_i is the energy of the system at the beginning of the process.

First Law of Thermodynamics. What we have said about the behavior of water in the engine offers one example of an extremely important generalization, which is called the *first law of thermodynamics* and which we may put as follows:

When any system is carried through a cyclic process, the heat absorbed q equals the work done w; consequently for a cyclic process, $\Delta e = 0$, that is, the

energy of the system has the same value at the end of the process as it had at the beginning. Note carefully that neither q nor w was zero in the case of the water in the engine; note also that the energy of water does change when it evaporates—it increases by 538.7 − 40.5 = 498.2 cal/g—and that Δe is zero only for the cyclic process which returns the water to its original state.

Energy a Property of a System. It follows that the energy of a system is a property of the system in the sense that two systems of identical composition which are in the same state must possess the same energy. Consequently it is possible to be certain that two systems possess identical energies even though no measurement of energy has been made; it is only necessary to measure the values of enough other properties to make certain that the systems are identical in composition and state. In particular the energy of a system always comes back to its original value after a sequence of changes if the system is returned to its original state, no matter how widely it may have changed during the sequence.

On the other hand we cannot define a "work content" of a system in such a way that its decrease shall be equal to the work done by the system during a process, and which shall therefore be a property of the system, because w is not zero for the cyclic process in the engine. Nor can we define a "heat content" whose change shall be equal to the heat absorbed in a process and which shall be a property of the system. The term heat content is, however, used in a different and specialized sense (page 62).

The quality of being a property of a system has two important features: (1) The increase in the value of a property when a system changes from state a to state b is numerically equal to the decrease when it changes from b to a. This is a necessary corollary of the principle that the total change is zero when the system changes from a to b and then back from b to a. (2) The change in the value of any property which accompanies the change of a system from the state a to the state b is independent of the intermediate states through which the system passes, the rate of the change, and indeed of everything except the nature of the state a and the state b.

These rules seem trivial when we apply them to such a property as the volume. Everybody knows that the increase in volume which accompanies the heating of 1 g of liquid water at 1 atm pressure from 0° to 25°C is numerically equal to the decrease in volume which accompanies its return to 0°. Everybody knows that the increase in volume of 1 g of liquid water in going from 0° to 25°, that is, the difference between the volume at 25° and that at 0°, would be the same if the water were evaporated at 0°, heated in the vapor state, and then condensed to liquid at 25° as it would be if the liquid were heated directly.

In spite of this apparent triviality the most important uses of the principle that energy is a property of a system derive from the fact that this principle makes possible exactly the same kind of pronouncements about the change in energy of a system as those we made about the volume in the last paragraph. The primary reason that this is not so obvious for energy as it is for volume lies in the fact that we measure energy changes only as the difference between heat absorbed and work done, and heat and work are not properties.

In particular work can be done only against an opposing force. If, for instance, we let a gas at moderate pressure expand into an evacuated space, no work is done since there is no opposing force. It is found that only a small amount of heat needs to be absorbed to maintain the temperature constant. The quantity Δe is therefore small and positive for the process consisting of the expansion of a gas at constant temperature. But if the gas is to be returned to its original state, a force must be applied and a relatively very considerable amount of work must be done on the gas by the surroundings, that is, w is large and negative. Since Δe for the compression must be the negative of Δe for the expansion, *i.e.*, must be small and negative, the value of $q = \Delta e + w$ for the compression must be large and negative.

There is one significant difference between the quality of the property energy and that of the property volume. We can unambiguously state that a particular system in a particular state has such and such a volume. We cannot do this for energy except through the purely arbitrary designation of a particular state as having the energy zero, because we cannot measure the energy of a system, we can measure only changes in energy. But so far as changes in energy are concerned, it makes no difference what base line is chosen for the scale of energy. We may take as a parallel the fact that it does not change the height of the Empire State Building, the difference in height between its summit and its ground-floor level, if we measure all heights from mean sea level or from any other arbitrarily fixed base line, instead of from the ground-floor level.

Equation (1) has to be expanded to include electrical, magnetic, and surface energy in the term w and to include energy of radiation in the q term. It has to be further expanded to include Einstein's principle of the interconvertibility of energy and mass, by virtue of which we define the energy change which accompanies a process by the equation

$$\Delta e = q - w + \Delta m \mathbf{c}^2 \tag{3}$$

where $\mathbf{c}$ is the velocity of light and Δm is the change in mass that accompanies the process. It is, however, only in nuclear processes that the mass changes are large enough to make $\Delta m \mathbf{c}^2$ a significant quantity,

in spite of the large value of the factor c^2. Thus extended, the principle that energy is a property of a system is one of the most general and most exact principles of all science.

Definition of Quantity of Heat. More precisely speaking, the first law is exact only if quantity of heat is so defined as to make the law exact. Thus the number of joules of mechanical or electrical energy required to raise the temperature of 1 g of water from 15° to 16°C is 4.1853; the quantity necessary to raise the temperature from 15° to 25°C is 41.8215, which is nearly one-tenth of 1 per cent less than 10 times the quantity necessary for the 1° rise in temperature. If we used the definition which makes rise in temperature of a fixed quantity of a definite substance the measure of heat absorbed, we should have to admit that the first law was an approximation, although a good one. On the other hand, the energy required to raise the temperature of 10 g of water from 15° to 16°C is very exactly 10 times the quantity required for 1 g. Consequently it is entirely reasonable to take the first law to be exact and to make the heat capacity of water, *i.e.*, the quantity of heat required to raise the temperature by 1°, vary with the temperature.

Units of Energy. Since the idea of energy comes originally from mechanical systems the basic unit of energy is either the erg in the centimeter-gram-second (cgs) system or the joule in the meter-kilogram-second (mks) system. There are unfortunately two joules, the absolute joule defined in terms of fundamental units and the international joule (= 1.00017 abs joules) defined in terms of electrical standards. Where it makes any difference, we shall use absolute joules.

The calorie was originally defined as the quantity of heat required to raise the temperature of 1 g of water 1°C. Because heat and mechanical energy are interconvertible, the calorie is a unit of energy, and chemists particularly often measure even purely mechanical energies in calories. Since the calorie as originally defined has different values at different temperatures, a variety of more precise definitions have been employed by different scientists and at different times. The definition we shall employ is a purely numerical one, namely, that

$$1 \text{ cal} = 4.1840 \text{ abs joules}$$

Because the quantities of energy with which we have to deal run to hundreds of thousands of calories and are uncertain to the extent of tens or hundreds of calories, the kilocalorie, or kilogram-calorie, abbreviated kcal, which is 1000 cal, is a convenient and frequently employed unit.

Energy and Mass: Extensive and Intensive Properties. To a close approximation the change in energy which accompanies a process is twice as great when 2 g of material is involved as it is in an otherwise identical

process involving 1 g. The energy of a system is therefore proportional to its mass if all other properties except mass are constant.

The approximation appears in the situation partly because the properties are affected by the surface. Two samples of material of the same mass may have different surface areas if they are of different shape, and even with a constant shape the surface increases with the two-thirds power of the mass and not with the first power. The error involved in the approximation is negligible except with properties which are directly related to the surface area or in systems in which the ratio of surface to volume is large, *i.e.*, in systems in which the material is very finely subdivided. There is a further approximation in that we suppose that the effects of the gravitational, electrical, and magnetic fields, which are inevitably present in the systems with which we terrestrial beings work, may be neglected. This approximation is usually unimportant unless large variations in height above the earth's surface or relatively large and deliberately produced magnetic or electrical fields are present.

Any property of a system, like the energy, whose magnitude is proportional in this way to the mass of the system is called an *extensive property*. Another familiar extensive property is volume. Properties whose magnitude is independent of mass are called *intensive properties*. An example is index of refraction.

If the value of an extensive property for a particular sample of material is divided by the mass of the material, a new property, whose value is independent of mass and which is therefore an intensive property, is obtained. Thus volume divided by mass in grams yields specific volume, whose reciprocal is the more familiar density. Both specific volume and density are intensive properties, properties of a particular kind of matter rather than of a particular sample of matter. Volume divided by number of moles yields molal volume, likewise an intensive property. We shall in general use lower-case letters as symbols for the values of extensive properties and the corresponding capital letters for the intensive properties derived from them, whether these be calculated to the gram or to the mole as unit of mass. Thus if v represents volume and V molal volume we have

$$V = \frac{v}{n} = \frac{vM}{m} = \frac{M}{\rho} \tag{4}$$

where n represents number of moles, m mass in gs, M molecular weight, and ρ density. Similarly if e represents energy and E molal energy,

$$E = \frac{e}{n} = \frac{eM}{m} \tag{5}$$

Kinetic-theory Interpretation. The kinetic theory is of course consistent with the first law; if it were not, we should long ago have abandoned the theory. Indeed the theory furnishes a very satisfactory picture of the equivalence of heat and mechanical energy, for it considers the rise in temperature of a perfect gas, *i.e.*, the absorption of heat, to consist solely in an increase in the kinetic energy of the motion of the molecules. And when we consume heat in the evaporation of water, the theory pictures this heat as going into increased potential energy because the molecules must be separated against the van der Waals attractive forces. In terms of the theory, then, heat is not merely equivalent to mechanical energy—it is mechanical energy on the molecular scale.

REFERENCES

PAUL, "Principles of Chemical Thermodynamics," Chaps. II, III, McGraw-Hill Book Company, Inc., New York, 1951.

PROBLEMS

1. The density of ice at 0°C and 1 atm is 0.9168 g/cc; that of liquid water is 0.9998 at 0° and 0.9584 at 100°C, both at 1 atm. What are the values of the molal volume change ΔV for the following processes: (*a*) ice at 0°C is converted to liquid water at 0°C; (*b*) liquid water at 0°C is converted to liquid water at 100°C; (*c*) liquid water at 100°C is converted to ice at 0°C?

2. To the perfect-gas approximation what are the volume changes of the following processes: (*a*) a mixture of 2 moles of hydrogen and 1 mole of oxygen at 100°C and 1 atm reacts to form water vapor at 100°C and 1 atm; (*b*) the same mixture reacts to form liquid water at 100°C and 1 atm?

3. The density of water vapor at 100°C and 1 atm has been found to be 0.598 g/liter. What is the molar volume change for the evaporation of water at 100°C and 1 atm? What would the value be if steam were a perfect gas?

4. From data given in this chapter compute the molal energy change ΔE for the process consisting in the conversion of liquid water at 100°C and 1 atm to gaseous water at the same temperature and pressure.

5. From the same data compute the value of q for the conversion of 1 mole of water vapor at 100°C and 1 atm to liquid water at the same temperature and pressure.

6. The energy change which accompanies the conversion of 1 mole of H_2 and $\frac{1}{2}$ mole of O_2 to water vapor at 100°C and 1 atm is -57.24 kcal. What is the energy change if the same amounts of H_2 and O_2 react to form liquid water at the same temperature and pressure?

7. When 1 mole of ammonia gas at 25°C and 2 atm expands into an evacuated space large enough so that the pressure drops to 1 atm, 4 cal of energy must be absorbed if the temperature is to be maintained at 25°. If the gas is compressed from 1 atm to 2 atm at 25° by a mechanism which expends 500 cal of mechanical energy in the process, how much heat will be evolved?

8. A battery operates a motor which develops A watts of mechanical energy. The motor heats up to such an extent that B cal/hr of heat must be removed in order to prevent any temperature rise. Heat in the amount C cal/hr must also be removed from the battery if its temperature is to be maintained constant. The process occurring in the battery involves no significant change in volume. By how much does the energy of the battery change in 1 hr?

CHAPTER V

THERMOCHEMISTRY

Heat of Reaction at Constant Volume. What is called the *heat of reaction at constant volume* is measured in the following way: The chemical reaction or other process whose heat is to be measured is allowed to take place in a closed vessel of fixed volume, which because it must often withstand high pressures is usually called a *bomb*. The bomb is contained in a calorimeter, a well-insulated receptacle, which is usually filled with water so that the temperature is constant throughout. A rise or fall of temperature is observed to accompany the process, and its magnitude is corrected for thermal leakage into or out of the calorimeter, thereby computing the temperature change which would have occurred had the calorimeter been perfectly insulated. In a separate experiment, usually by means of an electrical heater contained in the calorimeter, the quantity of energy is determined which is required either (1) to return the calorimeter and reaction products to the initial temperature if the temperature dropped as a result of the reaction, or (2) to produce the same rise in temperature in the system composed of calorimeter and reaction products as that which accompanied the reaction process if the reaction was exothermic. Correction for thermal leakage is made in this experiment also.

In an experiment of this sort or in any other process which occurs at constant volume and in the absence of devices such that weights are lifted, springs compressed, electrical condensers charged, and the like, no work can be done by the system on the surroundings or by the surroundings on the system. For work is force times distance moved against the force. There must be confining forces if the volume is to be constant because without them gases would expand and liquids and solids would evaporate. Hence there is work if there is motion; if there is no motion because the confining vessel is rigid enough to prevent it, there is no work in the absence of special devices of the sort mentioned.

Consider first case 1. The system neither absorbs nor loses any energy during the actual course of the reaction since no work has been done and the small amounts of heat leakage have been corrected for. In the separate experiment with the electrical heater the system is returned to its original temperature, and the total effect of reaction plus subsequent heating is the same as if the reaction had taken place without any change

in temperature. The sole energy taken up or lost by the system in the composite process is that supplied during the electrical heating. This energy must therefore equal the difference in energy between reactants and products, both at the temperature prevailing at the start of the reaction. By virtue of the first law this energy difference must equal the quantity of heat that would have to be absorbed if the reaction were to occur under such conditions that the temperature remained constant. For this reason the quantity is usually called the heat of reaction; because it is an energy change, we shall represent it by the symbol Δe, or by ΔE if it is computed to 1 mole of reactant or to some other standard quantity of material. The subscript v will be appended, as in ΔE_v, if we wish to remind ourselves that the quantity is an energy change at constant volume.

If the temperature of the calorimeter rises as a result of the reaction (case 2), we have no convenient way of determining directly the quantity of energy which must be abstracted from the system after the reaction has occurred in order to return it to its original temperature. But we know that this quantity of energy must be equal in magnitude to the quantity of energy which must be supplied in order to raise the temperature of the calorimeter containing the reaction products from the temperature at which the reaction was initiated to that at which it was completed. Consequently the energy required to raise calorimeter and reaction products from initial to final temperature is the energy change of the reaction at constant volume and at a constant temperature equal to the initial temperature.

Constant-pressure Systems: Enthalpy. Chemists work very frequently with the situation in which there may be volume change and therefore work but in which this occurs against a constant opposing pressure, usually that of the atmosphere. Such systems are called *constant-pressure systems.* It is a considerable convenience to express the work involved in such systems in terms of pressure and volume rather than in terms of force and distance. The relation is obvious for the special case of a gas confined in a cylinder by a piston (*cf.* Fig. 1 of Chap. I). Let the force applied to the piston from outside be F and the area of the piston be A. The quantity $P = F/A$ is a pressure, *i.e.*, a force per unit area. It is the pressure applied from outside upon the system contained in the cylinder; if, but only if, there is balance so that the piston does not move, P thus defined is the pressure of the gas. If now the piston moves through a distance dx, the work w done against the force is given by

$$w = F\,dx = PA\,dx \tag{1}$$

But the quantity $A\,dx$ is the change in volume of the cylinder contents, dv;

hence

$$w = P\,dv \tag{2}$$

(For a generalization of this argument see Sears I, 328).

If the change in volume is finite, the total work will be given by the sum of all the infinitesimal work quantities $P\,dv$, that is, by the integral $\int P\,dv$ taken between the initial volume v_1 and the final volume v_2, that is,

$$w = \int_{v_1}^{v_2} P\,dv \tag{3}$$

By the definition of a constant-pressure system the confining pressure P is constant; hence for such systems Eq. (3) becomes

$$w = P(v_2 - v_1) = P\,\Delta v \qquad (P \text{ constant}) \tag{4}$$

If no other work is involved except that done against the constant confining pressure, Eq. (1) of Chap. IV then yields

$$\Delta e = q - P\,\Delta v \qquad \text{or} \qquad q = \Delta e + P\,\Delta v \qquad (P \text{ constant}) \tag{5}$$

It then becomes useful to define a quantity called the *enthalpy* and symbolized by h as follows:

$$h = e + Pv \tag{6}$$

Since the quantities e, P, and v are properties of a system in the sense of page 49, *i.e.*, since their values are identical in two identical systems and return to their initial values in a cyclic process, enthalpy is also a property of a system in this sense. Since e and v are extensive properties and P is intensive, h also is extensive and $H = h/n$ is intensive.

For any infinitesimal process the enthalpy change is given by simple differentiation of Eq. (6) to be

$$dh = de + P\,dv + v\,dP \tag{7}$$

If, but only if, P is constant, the third term on the right vanishes and

$$dh = de + P\,dv \qquad (P \text{ constant}) \tag{8}$$

This may be immediately integrated to

$$\Delta h = \Delta e + P\,\Delta v \qquad (P \text{ constant}) \tag{9}$$

By Eq. (5) the right side of this equation is equal to q, the heat absorbed in the constant-pressure process; hence

$$\Delta h = q \qquad (P \text{ constant}) \tag{10}$$

Note carefully that, if the pressure changes, $v\,dP$ no longer vanishes and Δh is not equal to q. It is all too easy to think "enthalpy change equals

heat absorbed" and to forget the important qualifications that this is true *if* pressure is constant and *if* no other work than that against the confining pressure is involved. The mistake is particularly easy to make if one calls the enthalpy the *heat content*, as is often done.

Heat of Reaction at Constant Pressure. If a chemical reaction or such a process as vaporization, fusion, or the like, takes place at constant pressure, work will be done if the initial and final volumes of the system differ. By Eq. (4) the quantity of work done is $P\,\Delta v$. If the process occurs in a calorimeter, the quantity of energy, positive or negative, which must be supplied to the system after reaction is complete in order to return it to its initial temperature, the quantity which we call the heat of the reaction, is not equal to the energy change Δe of the process but to this plus the work done, *i.e.*, to $\Delta e + P\,\Delta v$. By Eq. (9) this quantity is, for a constant-pressure process, the value of Δh for the process. Hence the quantity measured in a constant-pressure calorimeter and called the heat of reaction at constant pressure is the value of the enthalpy change Δh or ΔH of the process at constant temperature and pressure.

Sign of the Quantity Heat of Reaction. If we talk about the energy change ΔE or the enthalpy change ΔH in a reaction, there is no ambiguity in sign; there is unfortunately uncertainty about sign if we use the term heat of reaction and the symbol q. For the processes of evaporation and fusion a positive heat q is universally taken to mean heat absorbed, *i.e.*, positive ΔE or ΔH, but many chemists use heat of reaction and q for a chemical reaction in the sense that a positive value means that heat is given out during the process, *i.e.*, that ΔE or ΔH is negative.

Relation between Constant-volume and Constant-pressure Heats of Reaction. The energy change in a reaction carried out at constant pressure is not the same as the energy change at constant volume, because the products of the reaction may occupy different volumes in the two cases, *i.e.*, be in different states. The difference may, however, be neglected to a good precision for any system at moderate pressures (see page 69). Consequently to this precision the molal heat of reaction at constant pressure ΔH_P is related to the molal heat of reaction at constant volume ΔE_V by the equation

$$\Delta H_P = \Delta E_V + P\,\Delta V \tag{11}$$

For systems containing only solids and liquids at moderate pressures $P\,\Delta V$ is of the order of $\frac{1}{10}$ cal or less, whereas the best calorimetric measurements of such quantities as the heats of formation of water have a precision of about 10 cal. If gases are involved, however,

$$P\,\Delta V = P(V_2 - V_1) = \mathbf{R}T(n_2 - n_1) = \Delta n\,\mathbf{R}T \tag{12}$$

to the perfect-gas approximation, n_1 and n_2 being the initial and final number of moles of *gaseous* substances. Since $\mathbf{R}T$ is of the order of 600 cal at room temperature, $\Delta n\ \mathbf{R}T$ cannot be neglected. Hence to a precision as good as most calorimetric measurements

$$\Delta H_P = \Delta E_V + \Delta n\ \mathbf{R}T \tag{13}$$

with Δn the difference between the number of moles of gaseous substance on the right and on the left of the reaction equation.

Indirect Measurement of Heat of Reaction. The heat of a reaction can be measured in practice only if the reaction is very nearly clean and irreversible. Small, but only small, proportions of competing reactions can be tolerated and corrected for if their extent can be determined by analysis and if their reaction heats are known. The ease of measurement and the precision of the result are helped greatly if the reaction is fast, so much so that the precise measurement of the heat of a reaction requiring several hours for completion is a herculean task. This is because calorimeters cannot be completely insulated and the quantity of energy which leaks in or out during the measurement increases directly with the time required.

Reactions which satisfy these requirements are the exception rather than the rule; yet we have need both in chemical theory and in engineering practice for the values of heats of chemical reactions which are not directly measurable. Here the first law comes to the rescue with the rules that the value of ΔE or ΔH for any process in the forward direction is the negative of the value for the reverse direction and that the sum of the ΔE or ΔH values for any sequence of reactions is the value for an over-all reaction which is the resultant of the sequence. These are obvious corollaries of the principle that the energy of a system is a property of the system (page 54).

It is for instance impossible to determine directly the enthalpy change per mole reacted ΔH_1 of the process

$$\mathrm{C} + \tfrac{1}{2}\mathrm{O_2} \rightleftharpoons \mathrm{CO} \tag{I}$$

because this reaction cannot be isolated from the further combustion of carbon monoxide to carbon dioxide. But we can burn either carbon or carbon monoxide cleanly and irreversibly in an excess of oxygen to form carbon dioxide. We thus obtain

$$\mathrm{C} + \mathrm{O_2} \rightleftharpoons \mathrm{CO_2} \qquad \Delta H_{\mathrm{II}} = -94.06 \text{ kcal} \tag{II}$$

$$\mathrm{CO} + \tfrac{1}{2}\mathrm{O_2} \rightleftharpoons \mathrm{CO_2} \qquad \Delta H_{\mathrm{III}} = -67.64 \text{ kcal} \tag{III}$$

The enthalpy change for the reverse reaction

$$\mathrm{CO_2} \rightleftharpoons \mathrm{CO} + \tfrac{1}{2}\mathrm{O_2} \qquad \Delta H_{\mathrm{IV}} = +67.64 \text{ kcal} \tag{IV}$$

must be, as shown, the negative of the change for reaction (III), and the sum of the values for the sequence (II) followed by (IV) must be the desired value for the reaction (I) which is the net effect of the sequence. Consequently $\Delta H_{\text{I}} = -94.06 + 67.64 = -26.42$ kcal.

A generalization of this reasoning leads to the following useful formalization: We may add and subtract chemical equations according to algebraic rules, canceling out common terms on opposite sides of the resulting equation, and transferring terms from one side to the other if the sign is changed. When we perform the corresponding additions and subtractions on the ΔH or ΔE values, the result is the ΔH or ΔE value for the reaction which results from these operations. Thus the calculation of the last paragraph amounts to subtracting reaction (III) from reaction (II), obtaining

$$\text{C} + \tfrac{1}{2}\text{O}_2 - \text{CO} \rightleftharpoons 0$$

and from this

$$\text{C} + \tfrac{1}{2}\text{O}_2 \rightleftharpoons \text{CO}$$

which is reaction (I). Correspondingly

$$\Delta H_{\text{II}} - \Delta H_{\text{III}} = \Delta H_{\text{I}} \tag{14}$$

The procedure may involve multiplying or dividing equations by suitable factors, again following the algebraic rules for eliminating a variable between simultaneous linear equations. Thus if we wrote instead of (III) the reaction

$$2\text{CO} + \text{O}_2 \rightleftharpoons 2\text{CO}_2 \qquad \Delta H_{\text{III}'} = 2(-67.64) \tag{III'}$$

whose ΔH value is twice that of reaction (III) since twice as much material reacts, subtraction of (III') from (II) would not yield any useful result. Subtraction of (III') from the reaction

$$2\text{C} + 2\text{O}_2 \rightleftharpoons 2\text{CO}_2 \qquad \Delta H_{\text{II}'} = 2(-94.06) \tag{II'}$$

would, however, yield

$$2\text{C} + \text{O}_2 \rightleftharpoons 2\text{CO} \tag{I'}$$

whose ΔH value would be $2(-94.06) - 2(-67.64) = 2(-26.42)$.

Heat of Combustion. Any organic compound may be burned in a calorimeter completely and to known products. From the heats of combustion thus obtained the heat of any reaction involving the compounds for which this has been done may be calculated from the simple rule that the heat of any such reaction is equal to the sum of the heats of combustion of the substances on the left side of the chemical-reaction equation minus the corresponding sum for the substances on the right side of the reaction equation. In forming these sums the molal heat of combustion

of a substance must be multiplied by 2 if 2 moles of the substance are involved in the reaction as written, it must be multiplied by 3 if 3 moles are involved, etc.

Thus we may calculate the not directly measurable ΔH value for the polymerization of acetylene to benzene,

$$3C_2H_2(g) \rightleftharpoons C_6H_6(g) \qquad (V)$$

from the heat of combustion of acetylene,

$$C_2H_2(g) + 5/2O_2(g) \rightleftharpoons 2CO_2(g) + H_2O(l) \qquad \Delta H_{IV} = -310.62 \text{ kcal} \qquad (VI)$$

and that of benzene,

$$C_6H_6(g) + 15/2O_2(g) \rightleftharpoons 6CO_2(g) + 3H_2O(l) \qquad \Delta H_{VII} = -789.08 \text{ kcal} \qquad (VII)$$

If we multiply (VI) by 3 and then subtract (VII), the oxygen, the carbon dioxide, and the water cancel and we get

$$3C_2H_2(g) - C_6H_6(g) = 0$$

which is equivalent to V. We therefore conclude that the enthalpy change ΔH_V of reaction (V) is given by

$$\Delta H_V = 3\,\Delta H_{VI} - \Delta H_{VII} \qquad (15)$$

i.e., that $\Delta H_V = 3(-310.62) - (-789.08) = -142.78$ kcal.

The heat of a process is defined only if the initial and final states are defined. The ΔH value of reaction (V) becomes -150.88 if the benzene produced is liquid instead of gaseous, the difference being of course the molal heat of vaporization of benzene. And the ΔH values for reactions (VI) and (VII) would both have different values from those given if the water produced were gaseous rather than liquid. It is usual and desirable to employ, as we have done in these equations, such symbols as (g) for gas, (l) for liquid, (s) for solid and, if necessary, even more specific characterizations to make certain that the states are understood by the reader.

The practice of this method of measuring the heats of reactions of organic compounds is not nearly so pleasant as the principle. Consider so important and so familiar a reaction as the conversion of 1 mole of sucrose to 1 mole each of glucose and fructose. The ΔH of combustion of 1 mole of sucrose at 18°C is reported to be -1349.6 kcal, and the values for glucose and fructose are reported as -673.0 and 675.6 kcal, respectively. From this ΔH for the inversion of sucrose is -1.0 kcal/mole with an uncertainty of several tenths of a kilocalorie. There are two conceivable solutions to this difficulty. Either we must get more precise values

of heats of combustion, or we must learn how to measure directly the heats of reactions which are slow, incomplete, and accompanied by side reactions. Both lines of development are being actively prosecuted and are of the utmost importance for the development of the science of chemistry and for its applications. Table 1 lists a few values of heats of combustion; others may be found in references cited at the end of the chapter.

TABLE 1. ΔH VALUES IN KILOCALORIES AT 25°C FOR COMBUSTION AT CONSTANT PRESSURE*

If water is a product, it is in the liquid state

Hydrogen(g)	−68.317
Graphite(s)	−94 052
Carbon monoxide(g)	−67 636
Methane(g)	−212.80
Ethane(g)	−372.82
Propane(g)	−530.61
n-Butane(g)	−687.98
i-Butane(g)	−686.34
n-Pentane(g)	−845.16
2,2-Dimethylpropane(g)	−840.49
Ethylene(g)	−337.23
Acetylene(g)	−310 62
Benzene(g)	−789 08
Ethanol(l)	−326.71
Acetic acid(l)	−208.5

* Data mostly from Selected Values of the Properties of Hydrocarbons, *Nat'l Bur. Standards* (*U.S.*) *Circ.* C461 (1947); last two items from data in "Chemical Engineers' Handbook."

Heats of Formation. No such general method as that employing heats of combustion is available for the computation of the heats of the reactions of inorganic compounds, and much ingenuity is frequently necessary in order to find a sequence of calorimetrically practicable reactions which sum up to the desired reaction. Thus the ΔH of formation of gaseous hydrogen bromide

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Br_2(g) \rightleftharpoons HBr(g) \qquad \text{(VIII)}$$

has been computed from the experimentally determined values of ΔH for the reactions

$KBr(aq) + \tfrac{1}{2}Cl_2(g) \rightleftharpoons KCl(aq) + \tfrac{1}{2}Br_2(aq)$	$\Delta H = -11.5$ kcal
$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) \rightleftharpoons HCl(g)$	−22.0 kcal
$HCl(g) + aq \rightleftharpoons HCl(aq)$	−17.3
$KOH(aq) + HCl(aq) \rightleftharpoons KCl(aq) + H_2O$	−13.7
$KOH(aq) + HBr(aq) \rightleftharpoons KBr(aq) + H_2O$	−13.7
$\tfrac{1}{2}Br_2(g) + aq \rightleftharpoons \tfrac{1}{2}Br_2(aq)$	−0.5
$HBr(g) + aq \rightleftharpoons HBr(aq)$	−19.9

From these data, all of which are necessary, the enthalpy change ΔH_{VIII} of reaction (VIII) may be calculated to be -8.4 kcal.

The symbol (aq) following the formula of a compound means that the substance is dissolved in so much water that further addition of water would yield only negligible changes in the enthalpy of the system (page 72).

Unfortunately, calorimetrically practicable reactions, *i.e.*, fast, irreversible, and clean reactions, are by their very nature likely to be reactions with large negative values of ΔH, strongly exothermic reactions. As a result the reaction heats which we wish to calculate all too often come out as small differences between large quantities, with a sad loss in precision. The difficulty we noted in computing heats of reactions of organic compounds from heats of combustion is therefore a very general one.

Even with these difficulties, data are available for a vast number of reactions. To tabulate them all would require an inordinate amount of paper and ink, and the problem of indexing would be extremely uncomfortable. This difficulty is generally met by tabulating heats of formation of chemical compounds from the elements. The ΔH value for any reaction involving compounds listed can then be calculated by subtracting the sum of the heats of formation of the substances on the left of the reaction from the corresponding sum for the substances on the right. In forming the sums we multiply the molal heat of formation of a substance by 2 if 2 moles of the substance are involved in the reaction as written, by 3 if 3 moles are involved, etc. In this computation the ΔH value for the formation of an element is obviously zero. The theorem is a direct corollary of the first law.

In this way one may, for instance, compute the enthalpy change for the reaction

$$2Fe_2O_3 + 3C \rightleftharpoons 4Fe + 3CO_2 \qquad \text{(IX)}$$

by subtracting twice the ΔH of formation of Fe_2O_3 from three times the ΔH of formation of CO_2.

Values of heat of formation are ambiguous unless the state both of the compound and of the elements is completely defined. Thus the molal enthalpy of diamond is about 0.5 kcal higher than that of graphite. If diamond is taken as the standard state of carbon, *i.e.*, the state in terms of which heats of formation of carbon compounds are computed, the ΔH of formation of a compound containing n carbon atoms will be $0.5n$ kcal more negative than if graphite is taken as the standard state.

The molal enthalpy change ΔH for the formation of a compound from the elements is frequently called the *molal enthalpy* of the compound.

Table 2 reports a few values of heats of formation of chemical compounds. Tabulations of other data are listed in the references.

TABLE 2. ΔH VALUES IN KILOCALORIES AT 25°C FOR FORMATION OF COMPOUNDS FROM THE ELEMENTS*

HCl(g)	−22.063	CO(g)	−26.416
HI(g)	+6.27	CO_2(g)	−94.052
H_2O(g)	−57.798	NH_3(g)	−10.96
H_2O(l)	−68.317	NO(g)	+21.600
H_2S(g)	−4.77	SO_2(g)	−70 94
CCl_4(l)	−33.8	SO_3(s, α form)	−105.09
C_2H_6(g)	−20 236	CaO(s)	−151 7
C_2H_4(g)	+12 496	$CaCO_3$(s, calcite)	−289 5
C_2H_2(g)	+54.194	NaCl(s)	−98 321

* Data from tabulations in "Chemical Engineers' Handbook."
The standard state of carbon is taken to be graphite.

Effect of Pressure on Energy and Enthalpy. If a gas expands without doing any work, if, for instance, the vessel containing the gas is put into communication with an evacuated container by opening a valve, the average distance between the molecules increases. By the considerations of page 30 the potential energy increases, and if the system is well insulated thermally so that the total energy remains constant, the kinetic energy of the molecules of the gas must decrease. According to the kinetic theory this implies a drop in temperature. Unless the gas is highly compressed, the effect should be small because the forces involved are weak when the average distance between the molecules is large, and its magnitude should tend toward zero as the pressure of the gas decreases.

The effect is in fact so small at moderate pressures that it is difficult to observe and measure. This is particularly so because it requires so little energy per unit volume to change the temperature of a gas and because amounts of heat of this order so easily leak into the gas from the container. Fortunately the magnitude of the drop in temperature on expansion can be calculated from other data of good precision by methods of unimpeachable reliability.

For most problems it is more interesting to consider how much energy must be supplied from the surroundings to return the gas to its original temperature after the expansion and in particular what is the ratio of this quantity of energy to the pressure change. Since the value of this ratio changes with changing pressure, it is necessary to speak of this in terms of the ratio of an infinitesimal increment of energy to the corresponding infinitesimal increment of pressure. This is for the same reason that we start by defining velocity as the ratio of distance x to time t, that is, as $(x_2 - x_1)/(t_2 - t_1) = \Delta x/\Delta t$, but have to refine the definition to dx/dt because the ratio may change during any finite time interval. Since the

change occurs at contant temperature, since, that is, the initial and final temperatures are the same, we use the symbolism of partial derivatives (Appendix A) and write the ratio in the form

$$\left(\frac{\partial E}{\partial P}\right)_T$$

As expected from theory, this quantity is negative, *i.e.*, the energy increases when the pressure decreases, and its magnitude is not very large. The values for gases at moderate pressures lie in the range from -0.1 to -10 cal/mole-atm, which may also be expressed as -0.004 to -0.4 liter/mole. The smaller values apply to gases which are well above the critical temperature.

The value of the quantity $(\partial E/\partial P)_T$ for solids and liquids is likewise difficult to measure directly but is calculable with certainty from other measurements. The values lie in the same range as those quoted for gases. The energy changes in chemical reactions cannot be more sensitive to pressure than the energies of the substances involved in the reaction because the energy changes are merely the differences between the energies of reactants and products. Because it is a rare calorimetric measurement which is reliable to 10 cal/mole, it is therefore unnecessary in most cases to take account of the effect of pressure on the energy change of a reaction unless pressures of many atmospheres are involved. For the same reason the energy change of a reaction which takes place at constant volume differs from the energy change when the same reaction takes place at constant pressure by an amount less than the usual calorimetric error. Equation (11) and its corollary, Eq. (13), are therefore as exact as the data to which they are usually applied.

The molal enthalpy of a substance is defined, following Eq. (6), as the sum of its molal energy and its molal pressure-volume product,

$$H = E + PV \tag{16}$$

Hence

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial E}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T \tag{17}$$

The second term on the right is easily shown from the properties of real gases to have a magnitude of at most a few cal/mole-atm at moderate pressures, so that $(\partial H/\partial P)_T$ is of the same order of magnitude as $(\partial E/\partial P)_T$, that is, not over 10 cal/mole-atm. Because the molal volumes of solids and liquids are small and insensitive to pressure, $(\partial H/\partial P)_T$ is also of the order of a few cal/mole-atm or less for condensed phases at moderate pressures.

The net result of these considerations is that the effect of changes in pressure on heats of reaction, whether at constant volume or at constant pressure, may be neglected unless pressures of many atmospheres or unusually high calorimetric precision is involved. This holds true both for gases and for solids and liquids.

Complete Definition of the Perfect-gas Approximation. As we have now seen, theory makes the equations

$$\left(\frac{\partial E}{\partial P}\right)_T = 0 \tag{18}$$

$$PV = RT \tag{19}$$

inexact for the same reason, namely, because there are forces acting between the molecules of real gases. Further and more significantly the quantity $[\partial(PV)/\partial P]_T$, which measures the deviation from the second of these equations, is of the same order of magnitude as the quantity $(\partial E/\partial P)_T$, which measures the deviation from the first. It is therefore customary and proper to imply by the statement that the perfect-gas approximation is being used in a particular problem that both of these approximations are being employed and not merely the second.

Effect of Concentration on Energy and Enthalpy. When 1000 g of water at 0°C is mixed with m moles of ethanol at the same temperature, the changes in enthalpy observed are those given in the second column of Table 3. The effects, running into the thousands of calories, are con-

TABLE 3. ΔH VALUES IN CALORIES AT 0°C FOR THE FORMATION FROM ETHANOL AND WATER OF AN AMOUNT OF SOLUTION WHICH CONTAINS 1000 G OF WATER*

Molality of ethanol, m	ΔH	$\Delta H/m$
0.329	−1130	−3430
0.443	−1520	−3420
0.555	−1890	−3410
0.890	−3020	−3390
1.109	−3740	−3370
1.328	−4490	−3350
1.67	−5540	−3320
2.22	−7200	−3240

* From work of Pratt as recomputed by him in International Critical Tables, Vol. V, p. 160.

siderable and are consistent with the theory of the energy interactions between solvent and solute (page 38) and the fact that the partial vapor pressure of ethanol from moderately concentrated aqueous solutions differs significantly from that calculated from Raoult's law. The sign

of the heat effect indicates that the energy of interaction of alcohol molecules with water molecules is greater than that of alcohol molecules with alcohol molecules. When the alcohol is added to the water, there is therefore a decrease in potential energy and consequently a rise in kinetic energy, *i.e.*, a rise in temperature. In order to bring the system back to its original temperature, heat must therefore be removed, which means that the enthalpy of mixing is negative.

The ΔH values are plotted against the molality m in Fig. 1. As the plot indicates and as the ratios in the third column of Table 3 show more

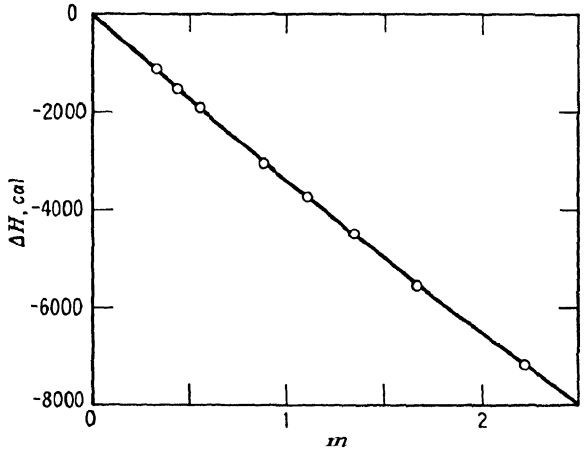


FIG. 1. Enthalpy change ΔH for the process of mixing 1000 g of water with m moles of ethanol at 0°C. (*Data of Table* 3.)

definitely, ΔH is closely proportional to m at low concentrations and deviates significantly from proportionality only at concentrations above 1 m. This again is consistent with theory because in the dilute solutions the alcohol molecules are so far apart that the energy of interaction of alcohol molecule with alcohol molecule is so small that it can be neglected just as the energy of interaction of the molecules of a dilute gas can be neglected. The ratio $\Delta H/m$, which is the heat effect per mole of ethanol, is therefore determined essentially by the large but practically constant energy of interaction of 1 mole of ethanol with the water molecules which are its near neighbors. The constancy disappears in more concentrated solutions; thus $\Delta H/m$ has dropped to -2360 cal/mole in a 6.18 m solution of ethanol.

The proportionality between heat of mixing and molality in dilute solutions has important implications for reactions which involve solutes in dilute solution. The heat of reaction of a process which produces alcohol in dilute solution must, for instance, equal the sum of the heat

of reaction to form pure alcohol and the heat of mixing of the alcohol with the solvent. Since both terms of this sum are proportional to the number of moles of alcohol formed, the sum is also proportional to this number. Consequently the molal heat of reaction to form alcohol in solution, *i.e.*, the heat of reaction per mole of alcohol formed, is independent of the concentration which the alcohol reaches in the solution provided the solution remains dilute. This conclusion may be generalized to the rule that the molal heat of a reaction which produces or consumes a solute in dilute solution is to a good approximation independent of the concentration of the solution. The rule is analogous to the rule that the heat of a reaction involving dilute gases is nearly independent of the pressure and is valid to about the same precision at corresponding concentrations. Both rules are the result of the small magnitude of the energy of interaction of widely separated molecules, whether these be the molecules of a gas or those of a solute in dilute solution.

The heat effect associated with the addition of 1 mole of solvent to a dilute solution is likewise small. Thus it may be calculated from the data of Table 3 that the addition of 1 mole of water to a 1 m solution of ethanol in water is -1.7 cal and that the effect is still smaller in the more dilute solutions. It follows that the molal heat effect of a reaction which produces the solvent water in a dilute solution of ethanol in water is nearly independent of the concentration of the solution. The rule that the heat of a reaction in dilute solution in which the solvent is either a reactant or a reaction product is very nearly independent of the concentration of the solution turns out to be valid generally.

Heat Capacity. The heat capacity of a body originally meant the quantity of heat required to raise its temperature 1°, and early measurements compared the heat capacities of two bodies by determining the drop in temperature of the one and the rise in temperature of the other when the two were brought into thermal contact after being at known and different temperatures. As with many such concepts the sense of this one has undergone a process of refining, modification, and subdivision. We now define *heat capacity at constant volume*, c_v, by the equation

$$c_v = \left(\frac{\partial e}{\partial T}\right)_v \tag{20}$$

Note that this is the ratio of an increase in energy to an increase in temperature, not a ratio of heat absorbed to temperature rise; that it is the ratio of infinitesimal increments of energy and temperature; that the subscript v means that the initial and final volumes are the same. It is still the ratio of heat absorbed to temperature rise for a particular kind of a system, namely, one in which no work is done during the temperature

change either by the system on the surroundings or by the surroundings on the system. By the first law energy increase is equal to heat absorbed under these conditions. The definition in terms of energy is, however, more general because it includes the case that the temperature is changed by the input of electrical, mechanical, or any other kind of energy. The definition is in terms of infinitesimal increments because c_v varies with changing temperature; the condition of constant volume is necessary because the value of the ratio of energy change to temperature change depends upon whether or not the volume changes and, if it changes, upon how large the change is.

We also define heat capacity at constant pressure, c_P, by the equation

$$c_P = \left(\frac{\partial h}{\partial T}\right)_P \tag{21}$$

It is the ratio of heat absorbed to temperature rise in a system subjected to a fixed pressure and in which no work is involved except expansion against this fixed pressure. For, as we have seen [Eq. (10)], change in enthalpy dh is equal to heat absorbed under these conditions. The definition in terms of enthalpy is more general than that in terms of heat.

Measurement of Heat Capacity. The easiest kind of heat capacity to measure experimentally is c_P for a liquid or solid. We need merely place the material in a reasonably well insulated calorimeter vessel at a temperature which we represent by T_0 and arrange that the pressure on the material shall be constant, usually at the pressure of the atmosphere. We then feed in known increments of electrical energy, which may be very accurately measured. After each energy increment we measure the temperature T. We correct for heat leakage into or out of the calorimeter vessel, and we further subtract from the total energy input the amount observed in a separate experiment to be necessary to produce the same temperature rise in the empty calorimeter vessel. The result is a series of values of the electrical energy w_e required to raise the temperature from a fixed starting point T_0 to a series of higher temperatures represented by the variable T. Since we have corrected for thermal leakage, no heat is absorbed or lost and the total energy change Δe is given by

$$\Delta e = w_e - P\,\Delta v \tag{22}$$

the second term on the right being the work done in expanding against the constant pressure P [Eq. (4)]. This is equivalent to

$$w_e = \Delta e + P\,\Delta v \tag{23}$$

and it follows from Eq. (9) that

$$w_e = \Delta h \tag{24}$$

The values of Δh, which represent the quantities of enthalpy which must be supplied to raise the temperature from T_0 to T, may therefore be plotted against T. The slope of this plot s is given by

$$s = \left(\frac{\partial \Delta h}{\partial T}\right)_P = \left(\frac{\partial (h - h_0)}{\partial T}\right)_P \tag{25}$$

h being the enthalpy at temperature T and h_0 being the value at T_0. Since h_0 is a property of the fixed point of reference T_0, its value is independent of T and $\partial h_0/\partial T = 0$. Consequently

$$s = \left(\frac{\partial h}{\partial T}\right)_P = c_P \tag{26}$$

If the plot approximates closely to a straight line, the slope is easily obtained; if it is curved, the estimation of the slope is more difficult and less precise but still entirely possible (Appendix A). In the latter case the slope and hence the value of c_P change with changing temperature, and the investigator naturally endeavors to obtain some kind of functional relationship between c_P and T.

It is much more difficult to determine directly the value of c_v for a solid or liquid than it is to determine the value of c_P, because the pressure required to maintain the volume constant mounts very rapidly with even small increases in temperature. The value of c_v may be calculated by thermodynamic relations from that of c_P if the thermal expansion coefficient and the compressibility of the substance are known.

With gases the problem of determining either heat capacity is more difficult because the calorimeter is necessarily so much heavier and has so much greater a heat capacity than the gas that the energy input into the gas comes out as a small difference between the total input and that which the calorimeter alone would require. A number of indirect but reliable methods of calculating the heat capacity of a gas from other more readily measured properties are available (MWM 265, Sears I, 413).

Molal and Specific Heat Capacities. Both c_P and c_v are extensive properties since e and h are extensive and T is intensive. Molal heat capacities, which we represent by C_P and C_V, are therefore intensive. So also are heat capacities per gram, which are called *specific heat capacities* or merely *specific heats.*

Relation between C_P and C_V. By differentiating the definition of molal enthalpy [see Eq. (16)], we get, provided we restrict ourselves to a system of fixed pressure,

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \tag{27}$$

With gases at low pressures energy is nearly independent of pressure (page 70), and for such materials it therefore makes little difference in the energy required whether the substance is heated at constant pressure or whether the pressure rises, as it does in a constant-volume system. To the perfect-gas approximation, therefore,

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V = C_V \tag{28}$$

The quantity $(\partial V/\partial T)_P$ is easily obtained by differentiating the perfect-gas law, considering P to be a constant in the differentiation

$$P\left(\frac{\partial V}{\partial T}\right)_P = \mathbf{R}$$

Hence, to the perfect-gas approximation,

$$C_P - C_V = \mathbf{R} \tag{29}$$

This equation is not exact for real gases. The error increases roughly proportionally with the pressure and runs to 0.02 to 1 per cent at pressures in the neighborhood of 1 atm.

With solids and liquids the quantity $C_P - C_V$ may be calculated by thermodynamic relationships from measurable quantities. The fractional difference $(C_P - C_V)/C_P$ has the following typical values at room temperature: Ag 0.04, NaCl 0.056, ethyl ether 0.45, water 0.007.

Dependence of Heat Capacity on Temperature. The molal heat capacities at constant pressure of some gases are plotted against temperature in Fig. 2, and values for a few solid elements are similarly plotted in Fig. 3. There are some regularities. The heat capacities of all monoatomic gases are independent of temperature within the precision of the best measurements over the whole range of temperature which has been investigated (20° to 2500°K), and they all agree within this precision with the value

$$C_P = \tfrac{5}{2}\mathbf{R} = 4.97 \text{ cal/mole-deg} \qquad \text{(monoatomic gas)} \tag{30}$$

Except for hydrogen at low temperatures all polyatomic gases have values at least as high as 7 cal/mole-deg, and the values increase with increasing temperature. Both the heat capacity at a given temperature and the temperature coefficient of heat capacity tend to increase with the number of atoms in the molecules, although other factors are important, as the difference between water and carbon dioxide in the plot indicates. Quantum theory accounts for the qualitative features of these plots and can predict them quantitatively from observations on the spectra in the case of the less complicated molecules (page 96).

The S-shaped curves of Fig. 3 are characteristic of crystalline elements and of most crystalline compounds. Fortunately the theoretically inaccessible C_P does not differ a great deal from C_V, for which a highly developed theory is available. The theory is therefore roughly applicable to the practically more important constant-pressure quantity. Both quantities have an upward curvature at low temperatures, an inflection at the point where the heat capacity is about 3 cal/mole-deg, and both rise more rapidly and at a lower temperature the higher the atomic number of the

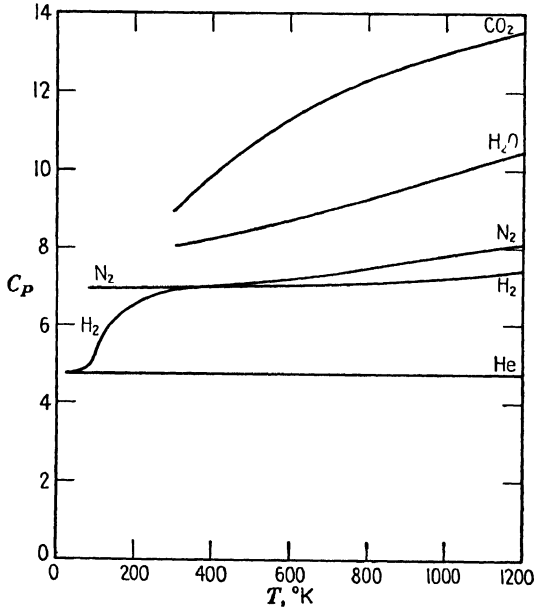


FIG. 2. Molal heat capacities at constant pressure C_P of some gases in cal/mole-deg. [*Based on data in Selected Values of the Properties of Hydrocarbons, Nat'l Bur. Standards (U.S.) Circ. C* 461 (1947), *and for low temperatures from Giauque, J. Am. Chem. Soc.*, **52,** 4816 (1930), *and from Davis and Johnson, ibid.*, **56,** 271 (1934).]

element. They differ chiefly in the fact that C_V usually levels off at a value of $3R = 5.96$ cal/mole-deg instead of rising gradually above this value as does C_P (see plots for lead and aluminum in Fig. 3).

The rule of Dulong and Petit (Pauling 165) that all solid elements have the same molal heat capacity, something like 6.2 cal/mole-deg, is a useful rough approximation for elements of atomic number greater than 10 at room temperature, although silicon has a value of only 4.9 and potassium one of 7.2. The reason for the complete failure of the rule with the lighter elements is illustrated by the case of carbon; with these elements room temperature lies on the steeply rising part of the curve, rather than on the relatively flat upper portion.

The C_P values for crystalline compounds usually follow a curve qualitatively similar to those for the elements. To about the same precision as that of the Dulong and Petit rule the molal heat capacity of a compound at room temperature may be computed as the sum of values for the elements contained in the compound. The actual heat capacities of the elements are employed in these computations when the elements are solids at room temperature and are of high atomic number; in other cases

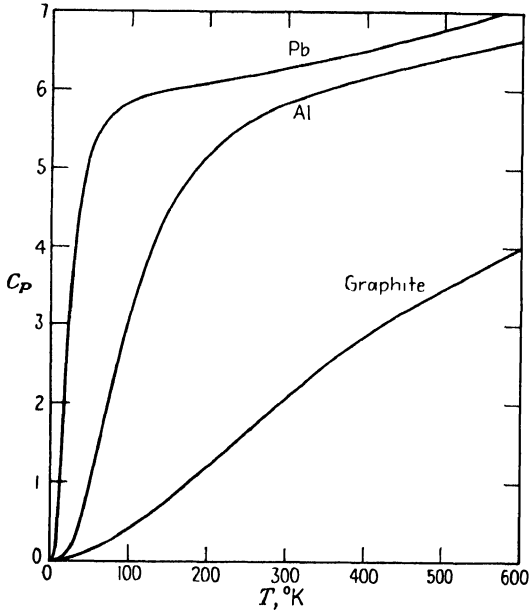


FIG. 3. Molal heat capacities at constant pressure, C_P, of some solid elements in cal/mole-deg. (*Data from International Critical Tables*, Vol. V.)

they are values derived from the behavior of compounds, thus 1.8 for carbon and 4 for oxygen. This very approximate rule of additivity is known as *Kopp's law.*

Nothing of any generality can be said about the heat capacities of liquids.

Even in those cases where heat capacities may be computed theoretically it is not possible to write down C_P as an explicit function of temperature. An explicit function of this sort is very desirable for the important practical problem of calculating the heat of a reaction at one temperature from the known value at another temperature. Recourse is therefore had to purely empirical equations. The normal first resort in such situations, a power series, *e.g.*,

$$C_P = a + bT + cT^2 + \cdots \tag{31}$$

works quite well in many cases, but the equation

$$C_P = a + bT + \frac{c'}{T^2} \tag{32}$$

is a better fit in others. As always with such empirical equations the number of terms which must be included in the equation is greater the greater the precision required, the range to be covered, and the slope and curvature of the plot. For small ranges of temperature a constant value

TABLE 4. C_P VALUES OF DILUTE GASES AS FUNCTIONS OF TEMPERATURE*
According to Eq. (31) or (32)

Substance	Range, °K	Maximum deviation, %	a	10^3b	10^7c	10^9d	$10^{-5}c'$
H_2	298–1500	0.49	6.9469	−0.1999	4 808	0	—
O_2	298–1500	0.65	6.148	3.102	−9.23	0	—
N_2	298–1500	1.15	6.524	1.250	−0 01	0	—
CO	298–1500	1.17	6.420	1.665	−1.96	0	—
HCl	298–1500	0.98	6.7319	0.4325	3.697	0	—
Cl_2	298–1500	0 24	8.764	0.271	—	—	0.656
H_2O	298–1500	0 74	7.256	2 298	2 83	0	—
CO_2	298–1500	0 30	5.152	15.224	−96.81	2 313	—
H_2S	298–1800	0 90	6 864	3.852	7.85	−0.634	—
SO_2	298–1800	3.18	11 895	1 089	—	—	−2.642
CH_4	298–1500	1.03	4 171	14.450	2.67	−1 722	—
C_2H_6	290–1100	0.76	1.375	41 852	−138.27	0	—
C_2H_4	290–1500	1 46	2 706	29.160	−90 59	0	—
n-C_4H_{10}	298–1500	0 44	−0 012	92.506	−479 98	9.706	—
i-C_4H_{10}	298–1500	0.54	2 296	82 407	−287.92	0	—
NH_3	298–1000	0.65	6.189	7.887	−7.28	0	—
S_2	300–1500	—	7.75	0.888	—	—	—

* Data from Spencer *et al.*, *J. Am. Chem. Soc.*, **56**, 2311 (1934); **64**, 2511 (1942), **67**, 1859 (1945).

of C_P may be employed with reasonable precision, but the value to be used is not that of the first term in Eq. (31) or (32). Instead one must calculate the value which the equation yields for a temperature in the middle of the range to be covered. Similarly a linear equation will cover a wider range than the assumption of a constant heat capacity will, but the coefficients in the linear equation will not necessarily be the a and b of Eq. (31) or (32).

Such equations as these have been coerced to fit the data over a limited range of temperature, and the equation may and often does deviate widely from the facts at temperatures only a little outside of this range. It is

therefore necessary to know the range of validity in every case in which such equations are to be used and to avoid scrupulously the temptation to use an equation outside its proper range. Thus the equation for aluminum given in Table 5 fits the facts from 273° to 932°K with a maximum deviation of 1 per cent but leads to a value 60 per cent higher than the observed heat capacity at 100°K.

The values of the coefficients in Eq. (31) or (32) are listed in Table 4 for a few gases. The values are limiting values for zero pressure; the values at moderate pressures do not differ significantly. Table 5 lists the same

TABLE 5. C_P VALUES OF SOLIDS AND LIQUIDS AS FUNCTIONS OF TEMPERATURE*
According to Eq. (32)

Substance	Range, °K	Average deviation, %	a	10^3b	$10^{-5}c'$
Al(s)	273–932	1	4.80	3.22	0
Pb(s)	273–600	2	5.77	2.02	0
Cu(s)	273–1357	1	5.44	1.462	0
NaCl(s)	273–1073	2	10.79	4 20	0
$CaCO_3$(s)	273–1033	3	19.68	11.89	−3 076
CaO(s)	273- 1173	2	10.00	4.84	−1.080
Na(s)	273–371	1.5	5.01	5.63	0
Na(l)	371–451	2	7.50	0	0

* Data from Kelly, *U.S. Bur. Mines Bull.* 371 (1934).

quantities for a few solids and one liquid. Extensive tabulations of this sort are available.

Effect of Temperature upon Heat of Reaction. A heat of reaction ΔH at constant pressure is the difference in the values of the enthalpy of a system in two states, an unreacted one, subscript 1, and a completely reacted one, subscript 2, both at the same pressure and temperature. Thus

$$\Delta H = H_2 - H_1 \tag{33}$$

If the same process occurs at a higher temperature but at the same pressure, both H_1 and H_2 will have new values and so therefore will ΔH. The rate of the change in ΔH per unit change in temperature is $(\partial \Delta H/\partial T)_P$, the partial derivative being written as a reminder that the pressure P is to be invariable. By the usual rule of differentiation applied to the difference in Eq. (33) we get

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = \left(\frac{\partial H_2}{\partial T}\right)_P - \left(\frac{\partial H_1}{\partial T}\right)_P \tag{34}$$

By virtue of the definition of heat capacity [Eq. (21)] we have therefore

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = C_{P2} - C_{P1} = \Delta C_P \tag{35}$$

The relation

$$\left(\frac{\partial \Delta E}{\partial T}\right)_V = \Delta C_V \tag{36}$$

may be derived by similar methods.

The bare mathematics of this derivation may be given a physical sense in the following manner: Consider a reaction occurring isothermally at temperature T and having at that temperature an enthalpy change ΔH. Suppose the reaction products are then heated to temperature $T + dT$, absorbing heat $C_2\,dT$, where C_2 is the constant-pressure heat capacity of the reaction products. Alternatively suppose the reactants are heated to $T + dT$, absorbing heat $C_1\,dT$, where C_1 is the constant pressure heat capacity of the reactants. Then allow the reaction to occur at the higher temperature. The enthalpy change at this temperature will differ from that at T by an infinitesimal amount $d\Delta H$, which may be either positive or negative. Now both of these processes lead from the reactants at T to the products at $T + dT$, that is, they proceed by different paths from the same initial to the same final state. Since enthalpy is a property of the system the total enthalpy change must be the same for the two processes. Hence

$$\Delta H + C_2\,dT = C_1\,dT + \Delta H + d\Delta H \tag{37}$$

From this we have

$$d\Delta H = (C_2 - C_1)\,dT = \Delta C_P\,dT \tag{38}$$

or

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = \Delta C_P \tag{35}$$

Integrated Relations between Heat of Reaction and Temperature. If we wish to calculate the heat of reaction ΔH_2 at temperature T_2 from the known value ΔH_1 at temperature T_1, both being at the same pressure, we may integrate Eq. (38), obtaining

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_P\,dT \tag{39}$$

If the difference $T_2 - T_1$ is small, we may neglect the fact that ΔC_P varies with the temperature because the change will be small over a small range of temperature and we get immediately

$$\Delta H_2 - \Delta H_1 = \Delta C_P(T_2 - T_1) \tag{40}$$

For wider ranges of temperature it is necessary to express ΔC_P as a function of temperature. This may be done readily if empirical expressions of the type of Eq. (31) or (32) are available for the heat capacities of all reactants and reaction products over the temperature range involved. Consider the synthesis of ammonia

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad (X)$$

We find from Table 4 that the heat capacity of 2 moles of ammonia is given by

$$2C_P(NH_3) = 12.378 + 15.774 \times 10^{-3}T - 14.56 \times 10^{-7}T^2$$

Similarly we get for the heat capacity of 1 mole of nitrogen plus 3 moles of hydrogen

$$C_P(N_2) + 3C_P(H_2) = 27.365 + 0.650 \times 10^{-3}T + 14.41 \times 10^{-7}T^2$$

From these

$$\Delta C_P = -14.987 + 15.124 \times 10^{-3}T - 28.97 \times 10^{-7}T^2 \qquad (41)$$

It follows then from Eq. (36) that

$$\begin{aligned}\Delta H_2 - \Delta H_1 &= \int_{T_1}^{T_2} (-14.987 + 15.124 \times 10^{-3}T - 28.97 \times 10^{-7}T^2)\, dT \\ &= -14.987(T_2 - T_1) + 7.562 \times 10^{-3}(T_2^2 - T_1^2) - 9.66 \\ &\qquad \times 10^{-7}(T_2^3 - T_1^3) \qquad (42)\end{aligned}$$

As we have seen, we do not need to measure experimentally the heat of any reaction for which the heats of formation of the substances involved have been determined at the same temperature. We now see that we do not need to know the heats of formation at the temperature of interest if the heat capacities of the substances involved are known as functions of temperature over a suitable temperature range. Consequently the problem of tabulating the multitudinous data of thermochemistry reduces in principle to the much less space-consuming task of tabulating heats of formation at some standard temperature as in Table 2 and coefficients of heat-capacity equations as in Tables 4 and 5. Thus from Table 2 we find the molar heat of formation of ammonia to be $-10{,}930$ cal at 25°C, that is, for $T = 298.2$. For reaction (X) we have therefore $\Delta H = -21{,}860$ cal at $T = 298.2$. Suppose we wish to know the heat of reaction at 500°C. We substitute $-21{,}860$ for ΔH_1, 298.2 for T_1, and 773.2 for T_2 and obtain $-25{,}550$ cal for ΔH_2, which is the enthalpy change for reaction (X) at 500°C.

It is frequently useful to be able to express the heat of a reaction as an explicit function of temperature. For this purpose we integrate Eq. (38)

as an indefinite integral, remembering that this implies an integration constant. Thus for the formation of ammonia we have

$$\Delta H = \Delta H_0 - 14.987T + 7.562 \times 10^{-3}T^2 - 9.66 \times 10^{-7}T^3 \quad (43)$$

We use the customary symbol ΔH_0 for the integration constant although this may be misleading. The quantity is not the heat of reaction at $T = 0$ because the heat-capacity functions used in computing it have no validity at temperatures below 300°K; it is merely a numerical quantity which makes the above equation fit the facts from 300° to 1000°K. To translate the symbol into the proper number, we substitute $T = 298.2$ and $\Delta H = -21.860$ in Eq. (43) and calculate the value of ΔH_0 to be $-18{,}040$. Consequently the general expression for the heat of reaction, valid from 300° to 1000°C, is

$$\Delta H = -18{,}040 - 14.987T + 7.562 \times 10^{-3}T^2 - 9.66 \times 10^{-7}T^3 \quad (44)$$

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BICHOWSKY and ROSSINI, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corporation, New York, 1936. This contains many heats of formation at 18°C.

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PROBLEMS

1. It was found that the combustion of 0.79280 g of benzene in a calorimetric bomb raised the temperature of the calorimeter by 3.097°C. Corrections for heat leakage, stirring heat, etc., reduced the value to a corrected one of 2.974°. In the same calorimeter the combustion of 2.00257 g of sucrose yielded a corrected temperature rise of 2.9660°. If the heat of combustion of sucrose is 3945 cal/g, what is the molal heat of combustion of benzene?

2. A gas contained in a well-insulated cylinder of volume 1 liter is initially at a temperature of 25°C and a pressure of 5 atm. It expands by doing work against an opposing force applied to a piston until its pressure drops to 1 atm. Its volume is found to be 4 liters. Assuming perfect-gas behavior, what is the temperature of the gas after the expansion? Assuming perfect insulation and a heat capacity at constant volume of 5 cal/mole-deg, what is the energy change of the process? What is the enthalpy change?

3. Calculate from data given in Chap. I the value of the quantity $[\partial(PV)/\partial P]_T$ in cal/mole-atm for carbon dioxide at 0°C and pressures of the order of 1 atm.

4. From the data of Table 1 compute the heat of combustion at constant volume of *n*-butane at 25°C, the water formed being in the liquid state.

5. The enthalpy change in the combustion at constant pressure and at 25°C of 1 mole of liquid methanol is −173.64 kcal/mole, the products being gaseous carbon dioxide and liquid water. What is the molal enthalpy of formation of liquid methanol at 25°C?

6. At 20°C the combustion in a bomb calorimeter of 1 mole of solid $(NH_4)_2C_2O_4 \cdot H_2O$ involves an energy change of −189.86 kcal; the corresponding figure for 1 mole of solid $H_2C_2O_4 \cdot 2H_2O$ is −53.10. The solution of 1 mole of the ammonium salt in a large excess of water involves an energy change of +11.47 kcal, that of 1 mole of the acid one of +8.62 kcal. The neutralization of 1 mole of oxalic acid in very dilute aqueous solution by gaseous ammonia involves an enthalpy change of −43.13 kcal. To what value of the enthalpy of formation of gaseous ammonia at 20°C does this information lead?

7. What is the ΔH value for the cracking of 1 mole of *n*-butane to 1 mole each of ethane and ethylene at 25°C?

8. What is the ΔH value for the same process at 500°C?

9. Using the equation $C_P = 1.10 + 4.8 \times 10^{-3}T - 1.2 \times 10^{-6}T^2$ for the molal heat capacity at constant pressure of graphite and any other necessary data contained in this chapter, calculate ΔH for the formation of 1 mole of gaseous methane from graphite and gaseous hydrogen at 500°C.

10. The molal heat of evaporation of water at 100°C is 9705 cal/mole. If the heat capacity of liquid water may be taken as 1 cal/g-deg, what is the molal heat of evaporation of water at 25°C? Check this result against the data of Table 2.

11. The molal heat capacity at constant pressure of liquid ethanol in the region from 0° to 25°C is 26.2 cal/mole-deg. From this datum and others in this chapter compute the value of ΔH at 0°C for the process

$$2C(\text{graphite}) + 3H_2(g) + \tfrac{1}{2}O_2(g) + \text{aq} \rightleftarrows C_2H_5OH(\text{aq})$$

This quantity is usually tabulated as the heat of formation of ethanol in dilute aqueous solution.

12. The quantity $\gamma = C_P/C_V$ is frequently useful in problems involving the behavior of gases. What is its value for argon? Obtain an expression for γ as a power series of the form $\gamma = a + bT + cT^2$ for oxygen between 298° and 1500°K, assuming perfect-gas behavior.

13. The enthalpy of formation of *n*-pentane is reported as −35.04 kcal at 300°K and −40.25 at 600°K. The corresponding values for the isomer 2,2-dimethylpropane are −39.71 and −44.67. Which of these hydrocarbons has the greater value of C_P, and what do you estimate to be the average value of the difference between the heat capacities of the two substances in the temperature range from 300° to 600°K?

14. Calculate the upper limit of temperature possible in a perfectly insulated system in which methane is burned to gaseous CO_2 and H_2O by a 50 per cent excess of air (taken to be 20 per cent O_2, 80 per cent N_2).

15. Justify from the data of Table 3 the conclusion stated on page 72 that the ΔH value associated with the addition of 1 mole of water to a 1 *m* solution of ethanol in water is −1.7 cal.

CHAPTER VI

AN ELEMENTARY DISCUSSION OF QUANTUM PRINCIPLES AND THE USE OF THE BOLTZMANN EQUATION

The Heat-capacity Problem. The very simplicity of the behavior of the heat capacity of the monoatomic gases propounds a puzzling problem. These gases and these alone have a heat capacity which is independent of temperature (page 75). In the limit of zero pressure the values for these gases are $\frac{5}{2}\mathbf{R}$ for C_P and $\frac{3}{2}\mathbf{R}$ for C_V. Except for hydrogen at very low temperatures all other gases have materially higher heat capacities than do the monoatomic gases, and without exception the heat capacities of the polyatomic gases increase with increasing temperature.

The kinetic theory concludes (page 24) that the kinetic energy of the translational motion of the molecules of 1 mole of a perfect gas is $\frac{3}{2}\mathbf{R}T$ and therefore that the total molal energy of the gas is given by

$$E = \tfrac{3}{2}\mathbf{R}T + E_i \tag{1}$$

where E_i is the internal energy of the molecules, the energy which resides in the rotations and vibrations of the molecule and of its atoms. By the definition of heat capacity it follows that

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2}\mathbf{R} + \left(\frac{\partial E_i}{\partial T}\right)_V \tag{2}$$

For monoatomic gases, but for these alone, the quantity $(\partial E_i/\partial T)_V$ must be zero, which means that the internal energy of the molecule is independent of the temperature. For polyatomic molecules, on the other hand, $(\partial E_i/\partial T)_V$ is a positive quantity of considerable magnitude. The latter effect is the one we should expect generally because the increased violence of the collisions between the molecules which accompanies an increase in temperature should increase the intensity of the rotational and vibrational motions of the molecules. Why then should monoatomic gases, which, though simpler than polyatomic ones, are still complex particles composed of a nucleus and surrounding electrons, refuse to take up more internal energy when the temperature increases? This is one of a number of puzzling phenomena which require the adoption of the important generalizations known as *quantum theory.*

Basic Principles of Quantum Theory. The quantum theory proposes, first, that the energy of an atomic or molecular system is not continuously variable but can possess only a series of sharply defined *quantized* values. It proposes, second, that when an atom or a molecule gains energy by the absorption of light, including infrared, ultraviolet, and X-ray radiation, or when it loses energy by the emission of light the frequency ν of the light is related to the energy change $\Delta\epsilon$ by the equation

$$\Delta\epsilon = \mathbf{h}\nu \tag{3}$$

The proportionality constant **h**, *Planck's constant*, has the same value 6.6238×10^{-27} erg-sec for all systems and is a general constant of nature of the same sort of significance as the charge on an electron or the mass of a hydrogen atom.

These principles, which we owe to the genius of Planck, Einstein, and Bohr, are entirely new ones, not derivable from the principles of mechanics as they have been developed from the study of the behavior of bullets or of planets, and they have only reluctantly been accepted by scientists because of the overwhelming evidence of their utility for the understanding and the prediction of natural phenomena. All our experience with macroscopic phenomena and the very mathematics we use to describe these phenomena lead us to expect that the velocities of two moving bodies or of one body at different times may differ by infinitesimal amounts, *i.e.*, amounts smaller than any assignable finite quantity. Since the corresponding kinetic energies are proportional to the squares of the velocities, the energies should also be capable of differing by infinitesimal amounts. The quantum theory on the contrary asserts that an atomic or molecular system can have only certain definite values of energy, say ϵ_0, ϵ_1, ϵ_2, ϵ_3, etc. It cannot therefore possess an energy halfway between ϵ_0 and ϵ_1, that is, $\epsilon_0 + \frac{1}{2}(\epsilon_1 - \epsilon_0)$, or even such an energy as $\epsilon_0 + 10^{-6}(\epsilon_1 - \epsilon_0)$.

Critical Potentials. The most direct evidence for the validity of these principles derives from the study of what are called *critical potentials*. Suppose as indicated in Fig. 1 a filament, a grid, and a plate like those used in radio vacuum tubes are enclosed in a vessel containing sodium vapor at a low pressure and essentially free from other gases. If the filament is heated, it emits electrons, and if a positive potential $\mathcal{E}$ is applied to the grid and a somewhat higher positive potential to the plate, the electrons will be attracted through the grid to the plate. The kinetic energy which an electron attains by the time it passes through the grid will be equal to the electrical work done on it, and this is equal to the product of the potential difference $\mathcal{E}$ by the charge **e** on the electron (MWM 348–349, Sears II, 49–56). If $\mathcal{E}$ is in volts and **e** in coulombs, the product $\mathcal{E}\mathbf{e}$ will be

given in joules. If the grid is close to the filament and the pressure of the sodium vapor is properly adjusted, very few of the electrons will collide with sodium atoms in the space between filament and grid but many collisions will occur between grid and plate. When the potential $\mathcal{E}$ is gradually increased, starting from zero, the tube emits no light up to a sharply defined value, called a *critical potential.* At higher potentials light is emitted, and spectroscopic investigation at potentials just above the critical value shows that the light consists solely of the familiar sodium yellow D lines of frequency 5.08452×10^{14} and $5.08967 \times 10^{14}\,\text{sec}^{-1}$. Only at materially higher potentials do the other lines in the sodium spectrum appear. After correcting for the fact that the electrons leave the filament with some kinetic energy, the value of this critical potential is found to be 2.12 volts. It follows therefore that electrons having a kinetic energy equal to or exceeding 2.12**e**, that is, $2.12 \times 1.602 \times 10^{-19} = 3.40 \times 10^{-19}$ joule or 3.40×10^{-12} erg are capable of producing the emission of the D lines in sodium vapor but of no other sodium frequencies, whereas electrons of less energy produce no light whatsoever.

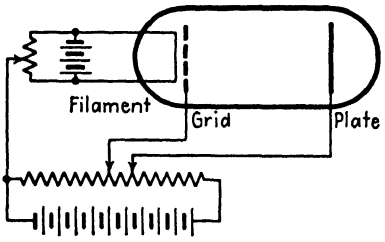


FIG. 1.

The quantum theory interprets these phenomena as follows: The emission of the D lines, which for the present argument may be taken as a single line of frequency $5.09 \times 10^{14}\ \text{sec}^{-1}$, must result from the transition of sodium atoms from a higher quantized level to a lower one, the difference in energy between the levels being given by Eq. (3) as $6.62 \times 10^{-27} \times 5.09 \times 10^{14} = 3.37 \times 10^{-12}$ erg. Now light of the frequency of the D lines is strongly absorbed by sodium vapor at ordinary temperatures and is the lowest frequency that the vapor will absorb. Consequently the absorption corresponds to a transition from a lower level in which many atoms are present to the next higher level which a sodium atom may possess. That is, a sodium atom in the state in which it ordinarily exists, which turns out to be the state of lowest possible energy called the *ground state*, cannot absorb any amount of energy less than 3.37×10^{-12} erg because the atom cannot exist in a state of energy intermediate between the two lowest levels which differ in energy by this amount. Therefore an electron having less energy than this cannot transfer any of its energy to a sodium atom but must bounce off when a collision occurs with practically unchanged energy just as a ping-pong ball would rebound from a collision with a bowling ball. But when the electron possesses a kinetic energy of at least 3.37×10^{-12} erg, some or

all of this energy may be used to transfer the sodium atom to the higher energy level, from which it rapidly returns to the ground level, with emission of the D line.

This picture of the situation may be confirmed by elaborating the apparatus in such a way that the velocity of the electrons which have collided with sodium atoms is measured in terms of the ability of the electrons to reach a plate against an opposing potential. It can be shown in this way that the number of electrons which have high velocities drops sharply just at the point when they have been accelerated through the critical potential.

The agreement between the 3.37×10^{-12} erg calculated from the frequency of the light and the 3.40×10^{-12} found in the critical-potential measurement is as good as can be expected from the precision of the latter datum. Scores of similar experiments on a wide variety of atoms have led to similar agreement between energies calculated from spectral frequencies by the use of Eq. (3), employing a single value 6.624×10^{-27} for **h,** and energies found in critical-potential measurements. The net result represents an overwhelming confirmation of the quantum-theory principles, particularly since this agreement is completely unexpected on the basis of any other theory that scientists have been able to invent.

Energy Levels from Spectra. The principle of equivalence between energy change and frequency once established, the study of the spectrum of an atom or molecule becomes the easiest and most accurate method of determining the spacing of its energy levels. Each line in the spectrum corresponds to a possible change in the energy of the atom or molecule, the energy change being equal to the product of the frequency of the line by the constant **h.** Of course there are more lines in the spectrum than there are energy levels because the atom or molecule can change from one energy level to a variety of other levels, each change corresponding to a line. Consequently the analysis of the spectrum and the assignment of the energy levels may require considerable ingenuity and effort, but this does not alter the principle. Fortunately transitions do not occur between all possible pairs of levels, and the "permitted" transitions obey very definite rules.

Energy Levels of the Hydrogen Atom. This kind of analysis of the spectrum leads to qualitatively similar energy-level diagrams for all atoms, the most characteristic feature being that the levels become more closely spaced the higher the energy content. The simplest case is that of hydrogen, whose atom, containing only one nucleus and one electron, is the simplest possible electrically neutral atomic system. Here the energy values satisfy the equation

$$\epsilon = a - \frac{b}{n^2} \tag{4}$$

where ϵ is energy, a and b are constants, and n is any integer. Each energy level corresponds then to a particular integral value of n. For reasons that will be apparent shortly we write ϵ_∞ for the constant a and $\mathbf{hc}R$ for the constant b. R is called the *Rydberg constant* and has the value 109,677.58 cm^{-1}. We thus obtain

$$\epsilon = \epsilon_\infty - \frac{\mathbf{hc}R}{n^2} \tag{5}$$

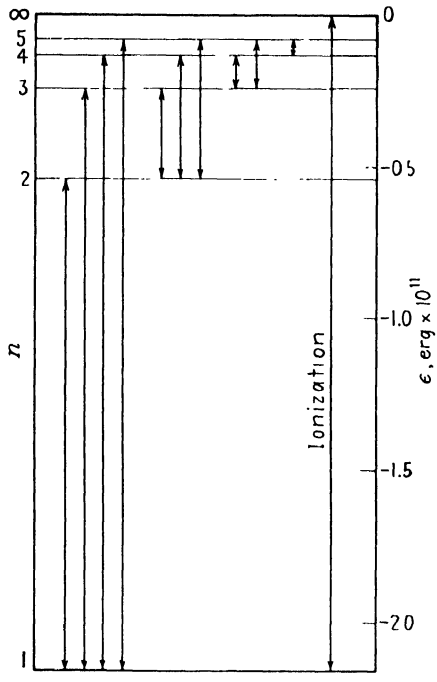


FIG. 2. Energy levels and transitions of the hydrogen atom.

These energies are represented by a sequence of horizontal lines at different levels in Fig. 2, each being labeled on the left by the value of n. It follows from Eq. (5) that the possible energy changes $\Delta\epsilon$ must satisfy the equation

$$\Delta\epsilon = \mathbf{hc}R\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{6}$$

in which n_1 and n_2 are any two integers. Some of these energy changes are indicated by vertical double arrows in Fig. 2. By Eq. (3) the frequencies of the lines in the spectrum of atomic hydrogen are given by the ratio of energy change to **h**, namely, by

$$\nu = \mathbf{c}R\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{7}$$

If we express the frequencies in wave numbers $\tilde{\nu}$ instead of in frequency ν with

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{\mathbf{c}} \tag{8}$$

as is common in spectroscopy, then the wave numbers of the possible lines are given by

$$\tilde{\nu} = R\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{9}$$

These energy levels are contained within a definite range. The highest level cannot be higher than ϵ_∞ since this is the value approached in Eq. (5) when n becomes infinite. The lowest possible energy is given by $\epsilon_\infty - \mathbf{hc}R$, which obtains with $n = 1$. The energy of the atom can therefore range progressively although discontinuously in such a way that each successive energy jump is smaller than the previous one and with a perfectly definite upper limit to the energy. It is reasonable to associate these increases in energy with a progressively increasing removal of the electron to a greater distance from the nucleus, a process which does work against the attraction of the opposite charges of nucleus and electron and therefore increases the internal energy of the atom. If this interpretation is justified, the largest amount of energy which can be absorbed is that required to remove the electron to a practically infinite distance from the nucleus, *i.e.*, to ionize the atom, separating it into a positively and a negatively charged particle. The work required to do this must be the difference between the upper limit of the energy levels ϵ_∞ and the lowest energy $\epsilon_\infty - \mathbf{hc}R$, that is, the energy required to ionize the atom must be $\mathbf{hc}R$. A direct test of this conclusion is not easily carried out with hydrogen because of the difficulty of obtaining pure atomic hydrogen, but critical potentials corresponding to transitions from the level with $n = 1$ to levels with $n = 2$, 3, 4, 5, and 6 have been observed and found to be in good agreement with the spectroscopically predicted values, and a critical potential at 13.54 volts does agree with the value $\mathbf{hc}R$ predicted for ionization.

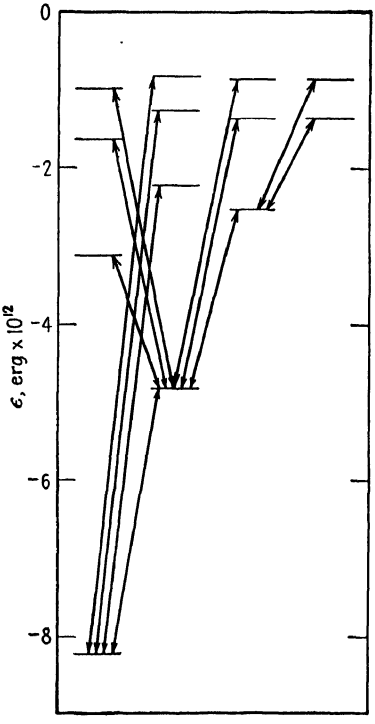


FIG. 3. Energy levels and transitions of the sodium atom.

Energy Levels of Other Atoms. The energy levels of atoms other than hydrogen follow a more complicated pattern. For instance, the horizontal lines in Fig. 3 represent some of the energy levels of the sodium atom, and the double arrows indicate some of the permitted transitions. The levels can be sorted out into a set of series, each of which is indicated by a column of levels in the figure. Within each series the levels march accord-

ing to a definite pattern toward an upper limit, which has the same value for all the series. Transitions occur only between levels which belong to different series. It is entirely reasonable to suppose that the common upper limit of energy of the various series corresponds to the ionization of the atom, just as does the single upper limit in the case of hydrogen. Here also the energy required to ionize the atom should be the difference between the upper limit and the energy of the lowest level. From the spectroscopic data this difference is 8.2306×10^{-12} erg for sodium.

It is possible, although it requires ingenious modification of the apparatus, to determine the potential difference through which electrons must be accelerated in order that their collision with sodium atoms results in ionization of the atoms. The crux of the matter is that the presence of the positively charged sodium ions can be recognized in a system which otherwise contains the negatively charged electrons as the sole charged particles. The potential at which the positive ions appear, called the *ionization potential*, is found to be 5.13 volts for sodium. This means that electrons possessing a kinetic energy of $5.13 \times 1.602 \times 10^{-19} = 8.21 \times 10^{-19}$ joule or 8.21×10^{-12} erg are just capable of ionizing sodium atoms. The agreement between the directly measured energy required for ionization and the value calculated from the study of the spectrum is as good as the precision of the former value. Many similar tests on a wide variety of elements lead to similarly satisfactory agreement and leave no room for doubt of the validity of the argument involved.

Energy Levels of Molecules. The spectrum emitted or absorbed by a molecule containing two or more atoms is much more complicated than the spectrum of hydrogen or of sodium atoms and consists of many closely spaced lines grouped together in bands. It follows that the system of energy levels available to a molecule is more complicated and consists of more closely spaced values of energy than is the case with an atom.

The simplest case is that of a diatomic molecule such as N_2. Here three kinds of spacing of energy levels can be distinguished. There is first a group of closely spaced levels whose separation is of the order of 4×10^{-15} erg, which is equivalent to an energy difference of 50 cal mole. The frequencies due to transitions between adjacent levels of this group are of the order of 5×10^{11} sec^{-1} (wavelength 0.06 cm) and lie in a region of the spectrum which has only recently become accessible to study by the microwave technique. Knowledge of the spacing of the energy levels has, however, been available from the study of transitions which go from one of these groups to another and which lie in a different region of the spectrum. To a good approximation the energies of these levels fit the equation

$$\epsilon = \frac{K(K+1)\mathbf{h}^2}{8\pi^2 I} \tag{10}$$

where K is an integer called a *quantum number* having the values 0, 1, 2, 3, etc., for successive levels and I is the moment of inertia of the molecule in end-over-end rotation given by

$$I = \frac{m_1 m_2 r^2}{m_1 + m_2} \tag{11}$$

with r the distance between the centers of the two atoms and m_1 and m_2 the masses of the two atoms (MWM 141*ff.*, Sears I, 196*ff.*).

Because the moment of inertia I is the determining quantity in the treatment according to classical mechanics of the rotation of the molecule and because of other analogies between these energy levels and the classical energy of rotation of the molecule, these closely spaced levels are called *rotational* energy levels.

Each group of rotational levels is repeated many times with small quantitative modifications at successively higher energies. The energies of the lowest rotational level of these successive groups agree approximately with the equation

$$\epsilon = (n + \tfrac{1}{2})\mathbf{h}\nu \tag{12}$$

in which n is a quantum number, having the values 0, 1, 2, 3, etc., and ν is a quantity of the dimensions of a frequency which is constant for a particular substance. The difference in energy between the adjacent groups is of the order of 10^{-13} to 10^{-12} erg, which is equivalent to several thousand calories per mole. The frequencies corresponding to transitions between adjacent levels are therefore of the order 10^{12} to 10^{13} sec^{-1} (wavelength 10^{-4} to 10^{-3} cm) and lie in the infrared region.

According to classical mechanics the two atoms in the molecule should be capable of vibrating to and from each other much as if they were joined by a spring, and the characteristic frequency ν of the vibration should depend on the mass m of the nitrogen atom and the force constant k operating between them according to the formula (MWM 176, Sears I, 259)

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \tag{13}$$

This frequency turns out to be identical with the ν of Eq. (12), indicating that this series of energy levels is related to the vibrational motion of the molecule. For this and related reasons these are called *vibrational* energy levels.

Finally the whole system of vibrational and rotational levels repeats at a sequence of much higher energies, the differences in energy being of the order of 100,000 cal/mole, *i.e.*, of 10^{-11} erg per molecule. Since the separation of these systems of levels is of the order of the separation of the levels in isolated atoms and since the levels converge toward an upper limit in a manner similar to the levels of atoms, a transition from one to another of these systems is attributed primarily to an increasing separation of one or more electrons from the rest of the molecule. For this reason the levels of these systems are called the *electronic* energy levels of the molecule.

It can be seen from this that the diatomic molecule possesses as many different kinds of quantized energy levels as the number of kinds of motion which the particles making up the molecule would be expected to exhibit if the laws of classical mechanics were valid. Molecules containing more than two atoms would classically possess more kinds of motion than diatomic molecules; it is not therefore surprising that they possess a greater variety of kinds of quantized energy levels. Indeed the pattern of energy levels is so complicated in such cases and the spectrum arising from transitions between them contains so many and so closely spaced lines that it is only in especially favorable cases that the sequence of energy levels has been determined from the study of the spectrum.

Some Quantum-mechanical Principles. Following the discovery of these quantum phenomena there occurred during the twenties and thirties of this century a magnificent outburst of creative thinking on the part of mathematical physicists which led to formulations which describe and predict the observable properties of atomic and molecular systems with remarkable precision and reliability. These formulations, which go under the name of *quantum mechanics*, can be expressed only in rather complicated mathematical terms which go beyond the scope of our present considerations. Some of their corollaries, however, have such wide-ranging applicability to chemical problems that every chemist needs to be familiar with them. These are:

1. *All atomic and molecular motions are quantized*, *i.e.*, only certain discrete levels of energy are possible. This is true even of the translational motion of the molecules of a gas when it is confined to a finite space, but the energy levels are in this case so closely spaced that even the most refined spectroscopic methods fail to separate the frequencies corresponding to the transitions between the levels. The conclusion that the translational energy is quantized is, however, verified completely in terms of properties of gaseous substances which cannot be predicted on any other basis.

2. *The spacing of the energy levels is determined primarily by two factors: the mass of the moving bodies, and the restraints under which they move.* A decrease in mass or an increase in the restraints widens the spacing.

The mass effect has already been encountered. Thus a heavier molecule has a greater moment of inertia, and by Eq. (10) it must have more closely spaced rotational levels; by Eqs. (13) and (12) it must also have more closely spaced vibrational levels. When two molecules differ only by the substitution of one isotope for another, the r of Eq. (11) and the k of Eq. 13 are unaffected by the substitution and the observed effect of the isotopic substitution is found to be quantitatively in agreement with the predictions of these equations.

The effect of the restraints which act on the moving bodies may be illustrated by comparing the spectrum produced by hydrogen atoms with that produced by singly charged helium ions, He^+, a spectrum which may be observed when very intense electric discharges pass through helium. Both the hydrogen atom and the helium ion consist of a single nucleus and a single electron, but the nucleus of the helium ion possesses a positive charge twice as great as that of the hydrogen atom. Consequently the force which acts between the nucleus and the electron and which restrains the relative motion of the two particles is twice as great in the case of the helium ion as it is in the case of the hydrogen atom. The two spectra are identical line for line, except that each frequency in the He^+ spectrum is almost exactly four times as great as the corresponding frequency in the H spectrum. The small deviation of the actual ratio from 4 is that predicted from the difference in the masses in the two cases. It follows that the energy levels of He^+ are four times as widely spaced as those of H.

The close spacing of the energy levels of translational motion is another case of the general principle that decreased restraints decrease the spacing of energy levels, for the motion of atoms is least restrained when they are moving freely in space instead of vibrating with respect to each other in a molecule. It is an important corollary that the translational levels should be more widely spaced the smaller the volume available to the gas, since decreasing the volume involves an increased restraint on the motion.

3. *Energy levels may be multiple, i.e.*, what are essentially different kinds of motion may give rise to the same energy. The multiplicity of an energy level may be decreased but is never increased by the same factors of increased restraint and decreased mass which increase the spacing of the levels. The effect may be interpreted in the sense that, in the absence of any field of force, motion in different directions in space may be fundamentally different kinds of motion, representing what are called different *quantum states* even though they have the same energy. This

interpretation is justified by the fact that in many cases the application of a strong magnetic or electric field will make the energies of these states differ slightly, with the result that what was one line in the spectrum in the absence of the field becomes two or more closely spaced lines in the presence of the field. This splitting of a spectral line into a number of closely spaced lines is called the *Zeeman effect* when it is produced by a magnetic field, the *Stark effect* when it is produced by an electric field.

In terms of the concept of quantum states it may be said that a decrease in the intensity of the restraints acting in a system increases the number of quantum states which lie within a given range of energy both because it makes the energy levels lie closer together and because it may increase the multiplicity of the levels.

4. In a gaseous system at equilibrium the number of molecules N_i whose energy is ϵ_i is given to a useful approximation by the Boltzmann equation

$$N_i = \Lambda g e^{-\epsilon_i/\mathbf{k}T} \tag{14}$$

T is the absolute temperature; $\mathbf{k}$, the Boltzmann constant, or "gas constant per molecule," is given by

$$\mathbf{k} = \frac{\mathbf{R}}{\mathbf{N}} = 1.38026 \times 10^{-16} \text{ erg/deg} \tag{15}$$

where $\mathbf{R}$ is the familiar gas constant per mole and $\mathbf{N}$ is Avogadro's number. g is the multiplicity of the level, the number of quantum states which have the same energy, and Λ is a proportionality constant whose value is characteristic of the substance for which N_i and ϵ_i represent number of molecules and energy. For us, the most important feature of the properties of this constant is that, in any system in which there is chemical reaction, the value of Λ for a compound is the product of the values for the elements contained in the compound, each value for an element being raised to a power equal to the number of atoms of that element contained in the compound. Thus for the compound XY_2

$$\Lambda_{XY_2} = \Lambda_X \Lambda_Y^2 \tag{16}$$

It is shown in Appendix B that the Boltzmann equation, including the properties of the constant Λ, is consistent with considerations of probability theory.

Significance of the Boltzmann Equation. This equation is so widely applicable to chemical problems and we shall have so much occasion to use it that it is particularly important to understand what it means. Consider first the qualification that Eq. (14) applies to a system of molecules *at equilibrium*. A system of gas molecules is continually inter-

changing energy by the collisions between the molecules. After a collision a molecule may have more translational energy than it did before, or it may have less; and its internal energy also may be changed by the collision. Consequently no one molecule remains for long in any one energy state. But there will be a normal or average *distribution* of the molecules among the possible energy levels with, say, N_a molecules in level a, N_b molecules in level b, etc., and if there are many molecules, the actual number in each level will not spontaneously deviate widely from this average value. Moreover, if we were to produce an abnormal distribution by illuminating the gas with light of the proper frequency to raise molecules from level a to level b, the system would rapidly revert to the normal or average distribution as soon as the illumination was discontinued. It is this normal or average distribution which we call the state of equilibrium; it is to this distribution and this one alone that Eq. (14) applies.

One of the most important things we know about nature is indeed the fact that such an equilibrium condition exists in any natural system; that the system will depart significantly from this condition only under the action of some external influence such as the illumination; that it will tend to return, more or less rapidly, to the equilibrium condition if it has been displaced from it. These rules are the essence of the extremely important principle known as the *second law of thermodynamics.*

Some Numerical Applications. Consider the ratio of the numbers of molecules in two energy levels which we distinguish by the subscripts 1 and 2. We have then

$$N_1 = Ag_1 e^{-\epsilon_1/kT} \tag{17}$$

$$N_2 = Ag_2 e^{-\epsilon_2/kT} \tag{18}$$

and consequently

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{(\epsilon_2-\epsilon_1)/kT} \tag{19}$$

If levels 1 and 2 are the two lowest levels of the sodium atom, the quantity $\epsilon_2 - \epsilon_1$ is, as we have seen, 3.37×10^{-12} erg. g_1 and g_2 are known both to have the value 2. Hence

$$\frac{N_2}{N_1} = e^{-(3.37\times 10^{-12})/kT} \tag{20}$$

This leads to the extremely small value of 3×10^{-36} at 298°K and to the materially larger but still very small value of 5×10^{-29} at 373°. Only at temperatures of the order of 20,000° does the proportion of atoms in the higher level become really significant. Of course, the proportion in levels of still higher energy is even smaller.

The case is different with the much more closely spaced levels of a diatomic or more complicated molecule. For two rotational levels spaced 50 cal/mole or 4×10^{-15} erg per molecule apart, the quantity

$$e^{-(\epsilon_2-\epsilon_1)/kT}$$

has a value of 0.91 at 298°K. Since the g value for a higher rotational level is greater than that for a lower level, it is clear that a very significant proportion of the molecules will be in the higher level at moderate temperatures if equilibrium exists.

In general, then, the ratio of the number of molecules in a higher level to the number in a lower one is smaller the greater the difference in energy between the levels and the lower the temperature. The values of the multiplicities have some effect, but this is usually less important than the difference in energy.

The Heat-capacity Problem Again. These results have immediate application, both qualitative and quantitative, to the heat-capacity problem with which we started this chapter. For all monoatomic substances have such widely spaced levels that the case is similar to that of sodium. Practically all of the molecules are in the state of lowest energy except at very high temperatures. A rise in temperature may multiply the number of molecules in a higher energy level by a considerable factor, but the fraction of the *total* number of molecules which absorb energy and are thus raised to a higher level is extremely small. In the sodium case the fraction of the total raised from the lowest to the next highest level by a rise in temperature from 25° to 100°C is $(5 \times 10^{-29}) - (3 \times 10^{-36})$, and the energy required is entirely negligible. Consequently for all practical purposes the internal energy of the sodium molecules is not increased by this rise in temperature, and the total heat capacity of the gas is that due to the increase in the translational energy with temperature, which is $\frac{3}{2}R$ per degree.

But with polyatomic molecules a considerable proportion of the molecules are raised from lower to higher internal energy levels when the temperature rises; a considerable amount of energy is required, and the total heat capacity comes out significantly higher than the $\frac{3}{2}R$ which results from the increase in the translational energy.

With diatomic molecules and with some favorable cases of more complex molecules the values of the energy levels and multiplicities may be completely determined from a study of the spectrum of the substance. This makes it possible to calculate from the Boltzmann equation the fraction of the molecules present in each level at any temperature, and the energy of the system follows immediately by multiplying the energy of each level by the number of molecules in that level. If this is done over a

range of temperatures, the heat capacity can then be obtained as the temperature coefficient of the energy. In Fig. 4 the values of C_V for molecular hydrogen computed in this way are compared with directly measured values. Similarly close agreement has been obtained in a sufficiently large number of cases to verify overwhelmingly the validity of the

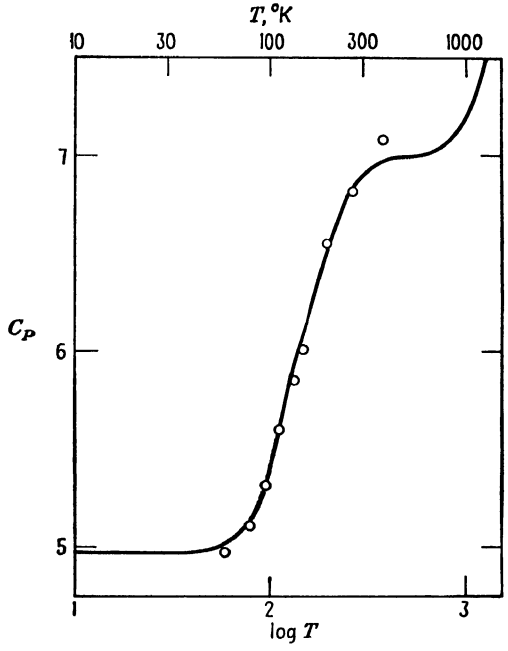


FIG. 4. Heat capacity C_P of hydrogen. The solid line is a plot of values computed from spectroscopic data by Giauque and by Davis and Johnston; the points are representative experimental values from the work of Eucken and of Cornish and Eastman. Although no direct measurements are available for higher temperatures, the temperature rise accompanying the explosion of a mixture of H_2 with O_2 or with Cl_2 shows that the average value of C_P for H_2 in the range from 290° to 2200°K is 7.5.

Boltzmann equation and of the other quantum-mechanical principles involved.

Equivalent Statements of the Boltzmann Equation. The Boltzmann equation may be put into a variety of forms, some of which are instructive. Thus

$$N_i = \Lambda g_i e^{-E_i/\mathbf{R}T} \tag{21}$$

where E_i is the energy possessed by $\mathbf{N}$ molecules all in the ith energy level, $\mathbf{N}$ being Avogadro's number. This follows from Eq. (15) and the relation

$$E_i = \mathbf{N}\epsilon_i \tag{22}$$

Further

$$\ln N_i = \ln \Lambda g_i - \frac{E_i}{\mathbf{R}T} \tag{23}$$

$$\log N_i = \log \Lambda g_i - \frac{E_i}{(2.303\mathbf{R}T)} \tag{24}$$

Since Λg_i and E_i are independent of temperature, a plot of $\ln N_i$ or of $\log N_i$ against the reciprocal of the absolute temperature should be a straight line, whose slope is $-E_i/\mathbf{R}$ or $-E_i/2.303\mathbf{R}$, respectively. Because the Boltzmann equation is so fundamental a relationship, a truly remarkable variety of chemically interesting quantities have the property that the logarithm plots against the reciprocal absolute temperature with approximate linearity. This is true, for instance, of the equilibrium constant and also of the rate constant of a chemical reaction, of the vapor pressure of a liquid or solid, and of the viscosity of a liquid. We shall see later what is the relation between these phenomena and the Boltzmann equation and why the linearity is approximate rather than exact.

Extension to Nonideal Systems. Strictly speaking our discussion of quantization and of the Boltzmann equation applies only to the idealized case of the perfect gas, *i.e.*, to a system of molecules for which the behavior of one molecule is unaffected by the number and behavior of the other molecules present. For real gases in which the intermolecular forces are significant and even more for liquids and solids we must in principle recognize that it is the energy of the whole system which is quantized. It is, however, found that this quantization of the total energy obeys the same rule as the quantization of the energy of a single molecule in that a decrease in the magnitude of the forces restraining the motions of the molecules decreases the spacing of the permitted energy levels and increases the multiplicity of the levels. It is also found that the probability W_i that the system will be in a state of energy ϵ_i and multiplicity g_i is given by

$$W_i = \Lambda g_i e^{-\epsilon_i/\mathbf{k}T} \tag{25}$$

The proportionality constant Λ has the same dependence on the composition of the substance involved as the Λ of the Boltzmann equation [Eq. (14)].

It can be shown that Eq. (25) reduces to the Boltzmann equation for the limiting case of the perfect gas. It is obviously a more difficult equation to apply to a practical case than is the Boltzmann equation, if for no other reason than that we have no direct method for determining the energy levels and multiplicities of the states of a system of molecules analogous to the spectroscopic method for the state of a single molecule. It is therefore necessary to approach such problems by imagining a rea-

sonable theoretical expression for the spacing and multiplicity of the levels and by comparing with experiment the results obtained by combining this expression with Eq. (25). This technique has been applied very successfully in the case of the crystalline elements. Thus Fig. 5 shows the relation between molal heat capacity at constant volume C_V and the logarithm of the absolute temperature for two typical crystalline metals. The points are experimentally observed values; the curves are plots of a function derived by Debye. This function contains a single

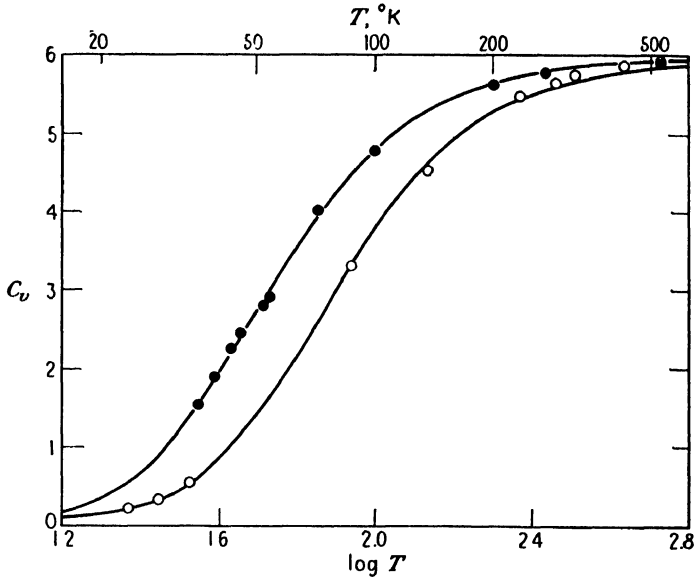


FIG. 5. Plots of heat capacity at constant volume C_V against the logarithm of the absolute temperature T. The points are experimental values, ● for silver, ○ for copper, from the compilation of Nernst and Lindemann, *Z. Elektrochem.*, **17**, 817 (1911). The solid lines represent the theoretical relationship of Debye.

constant whose value is adjusted to the behavior of the individual substance; otherwise the S-shaped course of the variation of C_V with log T is determined completely by the theory. The agreement between experiment and theory is typical of that obtained with a wide variety of crystalline metals. Qualitatively similar plots are obtained for the heat capacity of crystalline compounds.

One of the most important features of these plots is the asymptotic approach of heat capacity to zero as the temperature approaches zero. The explanation is in principle the same as that given for the lack of an internal heat capacity in a gaseous element. No matter how closely spaced the energy levels of a system may be, there must be a temperature

which is still not zero but which is low enough so that the probability is overwhelming that the system lies in the lowest possible energy level. Its energy is therefore negligibly different from that which the same system possesses at a still lower temperature, and the energy which must be supplied to raise the temperature, *i.e.*, the heat capacity, is also negligible.

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PROBLEMS

1. By what amount does the internal energy of 1 mole of gaseous CO_2 increase between 25° and 125°C?

2. Compute the critical potential in volts for the transition of a hydrogen atom from the energy level in which n is 1 to that in which n is 2.

3. To what frequency, wave number, and wavelength does a critical potential of 1 volt correspond?

4. Assuming equal multiplicities in the two levels, what is the equilibrium ratio of the number of molecules in the higher to that in the lower level if (*a*) the difference in energy per mole between the levels is 100 cal; (*b*) the difference in energy per molecule is 10^{-12} erg; (*c*) the wavelength of light absorbed or emitted in the transition between the levels is 4000 A? The temperature in each case is 300°K.

$$1 \text{ angstrom (A)} = 10^{-8} \text{ cm.}$$

5. If the equilibrium ratio of the numbers of molecules of a given substance in two energy levels is 5×10^{-8} at 300°K and if the multiplicities of the two levels are the same, what is the difference in energy between the levels?

6. At what temperature would the ratio of Prob. 5 become 10^{-5}?

7. The plot of Fig. 5 may be represented by the equation $C_V = f(T/\Theta)$, where the constant Θ has different values for different metals but the function f is otherwise the same for all metals. On this basis estimate the temperature at which lead would have a heat capacity at constant volume of 3.00 cal/deg, from the following data alone: heat capacity of lead is 4.00 at 30°K; that of silver is 4.00 at 73°K and 3.00 at 54°K.

CHAPTER VII

THE IDEAL LAW OF CHEMICAL EQUILIBRIUM

Spontaneous Changes. There is an easily recognized quality of being either what we may call uphill or what we may call downhill in all the processes of nature. Water flows downhill unless it is prevented by a dam; heat flows from a hot to a cold body unless it is prevented by insulation. But no dam can make water flow uphill; it must be pumped. No insulation can make heat flow from the cold inside of a refrigerator to the warm outside; this kind of flow of heat can be accomplished only by a refrigerating machine, which in effect pumps heat from a lower to a higher temperature. We call processes of the downhill kind *spontaneous processes*, and we recognize that we may include such phenomena as the flow of electricity from a point of higher to one of lower potential, the solution of a soluble salt in water, and the combustion of coal in this category. Any process which can go spontaneously in one direction can be *forced* to go in the reverse direction, but the force always derives from some other process of the spontaneous, or downhill, kind. Thus we may pump water uphill with a pump driven by a steam or gasoline engine, which exploits the combustion of coal or of gasoline, which is a spontaneous process. Or we may use electric power, which in its turn derives from the spontaneous combustion of coal or from the spontaneous flow of water downhill.

In spontaneous changes water always flows downhill, and heat always flows from a region of higher to one of lower temperature. But chemical processes sometimes run spontaneously in one direction, sometimes in the opposite direction. Consider so simple a process as the evaporation and condensation of a liquid. Even under conditions of fixed temperature and volume the direction of spontaneous change will be evaporation if the pressure of the vapor is less than a certain value, called the *equilibrium value*, but will be condensation if the pressure is greater than this value. Our whole accumulated experience shows that once the pressure of the vapor has reached the equilibrium value no further spontaneous change ever occurs in either direction so long as the temperature and volume remain unchanged.

Much the same situation exists in such a process as the formation and decomposition of hydrogen iodide. If equivalent amounts of hydrogen

and iodine in the gaseous state are brought together at a temperature in the neighborhood of 450°C, combination takes place until a certain proportion of hydrogen iodide is formed. If hydrogen iodide is brought to the same temperature, it decomposes until the fraction left is the same as the fraction formed by the reaction of the hydrogen and iodine. The direction of spontaneous change may be that of formation or that of decomposition of hydrogen iodide, but it is always toward, never away from, a certain definite proportion of hydrogen iodide. And once this proportion, which we call the *equilibrium proportion*, has been attained, our whole experience shows that the system never changes spontaneously away from this proportion either in the direction of formation or in that of decomposition of hydrogen iodide, unless some condition, such as the temperature, is altered.

A system which is in the equilibrium state may be displaced away from that state just as water may be pumped uphill. We shall consider later (page 230) some of the devices which may be used for this purpose and shall see that electrical energy may often be employed. But we get the electrical energy only at the expense of such spontaneous processes as the flow of water downhill, the combustion of coal, or the like.

The Second Law of Thermodynamics. We may therefore state as a generalization from experience the following important law:

For any system under a given set of conditions there exists a state of equilibrium toward which the system may change spontaneously, but away from which it may be displaced only at the expense of the displacement of some other system toward equilibrium.

This is the most general and most immediately useful way of stating what is called the *second law of thermodynamics*.

The Criterion of Equilibrium. One can be sure that a state of equilibrium has been reached only if an identical state has been attained from opposing directions of reaction. Mere failure of any change to occur, even over a considerable period of time, is not sufficient. Thus at room temperature a mixture of hydrogen and iodine does not react measurably over long periods of time. If we took failure to react as a criterion, we should conclude that the equilibrium state at this temperature corresponded to a negligible proportion of hydrogen iodide. But experiment also fails to detect any decomposition of hydrogen iodide under the same conditions, and we have to recognize that experiments at this temperature cannot lead to a determination of the equilibrium state, unless we can find a catalyst which speeds up the process.

In many cases the criterion that an identical state must be reached from opposite directions of reaction can be tested by a suitable temporary change in the conditions. Suppose we are interested in the solubility of

a salt in water, which is defined as the concentration of the solution when it is in equilibrium with the solid salt. We agitate the salt with water at the temperature T of interest until no further change in concentration seems to be taking place. Let the concentration of the solution be A. We then alter the temperature to some value, usually a higher one, at which the concentration becomes greater than A. If we then return the temperature to T and find that the concentration returns to A, we know that a solution of concentration A is in equilibrium with the solid salt at temperature T.

The Ideal Law of Chemical Equilibrium. It is shown in courses in general chemistry (Pauling, Chap. 19, Timm, Chap. 28) that the condition for equilibrium in a homogeneous chemical reaction follows a law which takes the form

$$\frac{[H_2][I_2]}{[HI]^2} = K \tag{1}$$

for the conversion of hydrogen iodide to the elements in the gaseous state, *i.e.*, for the reaction

$$2HI \rightleftharpoons H_2 + I_2 \tag{I}$$

It is shown also that this is consistent with the known laws for the rate of formation of the compound

$$r_1 = k_1[H_2][I_2] \tag{2}$$

and for its decomposition rate

$$r_2 = k_2[HI]^2 \tag{3}$$

At equilibrium the two rates r_1 and r_2 must be equal, and consequently at equilibrium

$$\frac{[H_2][I_2]}{[HI]^2} = \frac{k_2}{k_1} = K \tag{4}$$

The equilibrium constant K is therefore the ratio of the two rate constants. It is also shown that these laws for the rates of reaction are reasonable in the sense that gaseous molecules can react only when they collide and the frequency of collisions between gaseous hydrogen and iodine molecules is proportional to the product of the concentrations of the two substances, while the frequency of collisions between two hydrogen iodide molecules is proportional to the square of the concentration of that substance.

It is true that the rate of a chemical reaction often varies with the concentrations of the reactants in a way which would not be predicted by these rules from the over-all reaction equation, but detailed investigation

has made it overwhelmingly probable that in such cases the reaction proceeds by a sequence of steps, each of which follows the rule that the rate is proportional to the product of the concentrations of the reacting substances (page 179). The ideal law of chemical equilibrium in the form in which we have illustrated it in Eq. (1) emerges in such cases as a necessary consequence of the actual rate laws. The "derivation" of the law as it is given in many elementary texts by way of the rate laws is not therefore in any sense unsound, even though the detailed working out may involve some complications. In any case the important thing is that the law works to a precision which makes it extremely valuable in chemical reasoning. Before examining the evidence that it does work, we emphasize some conventions and point out some variations in the form of statement.

Some Conventions. The symbol $[H_2]$ means the concentration of hydrogen in the system in which the equilibrium exists. It means all the hydrogen which is actually present in the form of molecular hydrogen in unit volume of the system. There is no way in which we can tag some of the hydrogen in a system as hydrogen involved in the equilibrium of hydrogen iodide formation and distinguish it from hydrogen which is not so involved, and, if there were, the distinction would have no bearing on the equilibrium law, in which the symbol has the meaning we have stated.

By a now generally accepted convention the concentrations of the substances whose formulas appear on the right side of the equation for the chemical reaction always appear in the numerator of the expression for the law of equilibrium, and substances whose formulas appear on the left side of the chemical equation appear therefore in the denominator. This is purely a matter of convention, but it is important to reach general agreement on such conventions, since otherwise we either have ambiguity or waste valuable time and space explaining what convention we are using every time we write anything about the matter in question. Of course it was entirely an arbitrary choice that put the hydrogen iodide on the left side of reaction (I). The reaction is reversible, as the symbol indicates, and as in principle all reactions are. Consequently we could equally well have represented the reaction as

$$H_2 + I_2 \rightleftharpoons 2HI \qquad \text{(II)}$$

But our convention now says that the expression for the law of equilibrium must be

$$\frac{[HI]^2}{[H_2][I_2]} = K' \qquad (5)$$

Obviously $K' = 1/K$ if K is the constant of Eq. (1).

If we take the square root of both sides of Eq. (1), we obtain

$$\frac{[H_2]^{1/2}[I_2]^{1/2}}{[HI]} = K'' \tag{6}$$

with

$$K'' = K^{1/2} \tag{7}$$

This is still a valid statement of the conditions for equilibrium in the reaction. By the rule that the coefficients in the chemical equation become the exponents in the statement of the law of equilibrium we see, however, that Eq. (6) is the expression of the equilibrium law for the reaction

$$HI \rightleftharpoons \tfrac{1}{2}H_2 + \tfrac{1}{2}I_2 \tag{III}$$

The Constants K_c and K_P. By the substitutions

$$[H_2] = \frac{P_{H_2}}{RT} \qquad [I_2] = \frac{P_{I_2}}{RT} \tag{8}$$

according to Eq. (16) of Chap. I we can convert Eq. (1) to the form

$$\frac{P_{H_2}P_{I_2}}{P_{HI}^2} = K \tag{9}$$

in which K is identical with the K of Eq. (1). But if we consider the reaction

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \tag{IV}$$

for which

$$\frac{[SO_3]^2}{[SO_2]^2[O_2]} = K_c \tag{10}$$

the same kind of substitution leads to

$$\frac{P_{SO_3}^2}{P_{SO_2}^2 P_{O_2}} = \frac{K_c}{RT} \tag{11}$$

The quantity $K_P = K_c/RT$ is as good a constant at constant temperature as is the constant K_c, and the equation

$$\frac{P_{SO_3}^2}{P_{SO_2}^2 P_{O_2}} = K_P \tag{12}$$

has equal validity with Eq. (10) as a statement of the law of equilibrium for reaction (IV).

In general it follows that the relation between the constant K_P in terms of partial pressures and the constant K_c in terms of concentrations is given by

$$K_P = K_c(RT)^{\Delta n} \tag{13}$$

where Δn is the difference, number of moles of gaseous substance on the right side of the chemical equation minus the number on the left side of the equation. For reaction (IV) the value of Δn is -1; for the hydrogen-iodine reaction, reaction (I), $\Delta n = 0$; consequently for this reaction $(RT)^{\Delta n} = 1$ and $K_P = K_c$.

Because of certain matters involving the different way in which the two constants K_P and K_c vary with temperature (page 144), it is customary and useful to state the ideal law of chemical equilibrium in terms of K_P instead of in terms of K_c for all homogeneous gaseous reactions. It is further customary to use the partial pressure of any gaseous substance taking part in a heterogeneous reaction as a measure of its concentration in the expression of the equilibrium law even though the reaction also involves solutes in solution, whose concentration is measured in moles per liter. We shall follow these conventions consistently and shall express the partial pressures in normal atmospheres unless a specific statement to the contrary is made in the particular case.

Validity of the Ideal Law of Chemical Equilibrium. The most direct way of testing the validity of the law is to measure the partial pressures or concentrations of the substances involved in the reaction, to calculate from these the value of the constant, and to see whether or not this quantity remains constant when the partial pressures of the various substances are varied over a wide range. Table 1 shows the results of a

TABLE 1. EQUILIBRIUM IN THE REACTION $2HI \rightleftharpoons H_2 + I_2$ AT 698.6°K*

Partial pressure, atm			K
H_2	I_2	HI	
0.1645	0.09783	0.9447	0.01803
0.2583	0.04229	0.7763	0 01812
0.1274	0.1339	0.9658	0.01829
0.1034	0.1794	1.0129	0.01808
0.02703	0.02745	0.2024	0.01812
0.06443	0.06540	0.4821	0.01813

* Data from Taylor and Crist, *J. Am. Chem. Soc.*, **63**, 1377 (1941). In the first four entries the equilibrium was approached from the side of formation of HI; in the last two it was approached from the side of decomposition.

particularly careful test of this sort, the reaction being the hydrogen iodide decomposition [reaction (I)]. Although the partial pressures of each substance involved vary widely and although the first four items in the table relate to experiments in which hydrogen and iodine were allowed to react until equilibrium had been attained and the remaining

items relate to experiments in which hydrogen iodide was allowed to decompose until equilibrium was reached, the K of Eq. (1) remains very satisfactorily constant. Many other data could be quoted to show that, provided the pressure is reasonably low, the ideal law of chemical equilibrium is valid to a considerable precision for homogeneous gas reactions, and no cases have been observed in which the law fails seriously under these conditions.

Deviations at High Pressures. If, however, we go to high pressures, we find rather serious deviations. For instance, as Table 2 shows, the

TABLE 2. EQUILIBRIUM CONSTANTS FOR THE REACTION $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$ AT 450°C AT VARIOUS TOTAL PRESSURES P IN ATMOSPHERES*

In each case the equilibrium was approached from a 3:1 mixture of H_2 and N_2

P	10	30	50	100	300	600	1000
K	0.00659	0.00676	0.00690	0.00725	0.00884	0.00895	0.01493

* Data of Larson and Dodge, *J. Am. Chem. Soc.*, **45**, 2918 (1923), and of Larson, *ibid.*, **46**, 367 (1924).

equilibrium constant for the synthesis of ammonia is over twice as large when the total pressure is 1000 atm as it is when the pressure is 10 atm.

We must therefore recognize that the ideal law of chemical equilibrium is an approximate law, which like the perfect-gas law is useful for the description of the equilibrium in the reactions of gases at moderate pressures but has no absolute validity and fails seriously at high pressures.

This result should not be surprising. Our discussion of the properties of gases has shown that there are forces of attraction between the molecules of a gas or a mixture of gases which are of considerable magnitude when the average distance between the molecules is small, as it is when the pressure is high. As we saw in Chap. II the perfect-gas law can be expected to apply only when the pressure is so low, and the average distance between the molecules therefore so large, that these forces can be neglected. By the same kind of reasoning it can be shown that the frequency of collisions between two kinds of molecules should be proportional to the product of the concentrations only to the precision that the attractive forces are of negligible effect. When the forces are significant, the frequency of collision goes up more rapidly than in proportion to the product of the concentrations and the rate of reaction therefore deviates in the same direction from strict proportionality to this product. Equations (2) and (3) can therefore be no better than approximations which approach exactness only as the pressure of the gas approaches zero. Consequently Eq. (1) must be an approximation of the same kind unless we

admit the improbable situation of an exact compensation in the way in which Eqs. (2) and (3) fail. Such a compensation is improbable because the large difference in the magnitude of the deviations from the perfect-gas law observed with different gases (page 6) shows that the magnitude of the intermolecular forces differs greatly with different gases.

It should be emphasized that the failure of the ideal law of chemical equilibrium to be an exact law in no way affects the fundamental principle that there is an equilibrium state in the ammonia reaction or in any reaction which is identical whether approached from the side of synthesis or from that of decomposition. This is the second law of thermodynamics, from which we know no significant deviations What we mean by the failure of the ideal law of chemical equilibrium is that the equation

$$\frac{P_{NH_3}}{P_{N_2}^{1/2} P_{H_2}^{3/2}} = K \tag{14}$$

does not exactly describe the necessary conditions for the state of equilibrium.

Experimental Methods of Determining Equilibrium Constants. The obvious method of determining the equilibrium constant of a reaction is to let the reaction run to equilibrium, using the criterion of page 102 to assure that it is truly at equilibrium, to determine the partial pressures of all the substances involved, and by substitution of these partial pressures in the pertinent equation, to calculate the constant. There are, however, serious limitations. Clearly the reaction must not run so completely either to the right or to the left that the partial pressure of some substance involved in the reaction becomes too small to be measured or even detected. And the rate of reaction must be large enough so that the system comes to the state of equilibrium in a reasonable time; otherwise human patience or human lifetimes become too short. The requirement that the reaction be moderately fast has an important bearing on the kinds of analytical method available. The typical chemical analytical process depends upon the removal of the substance to be determined from the system. Thus we might attempt to determine the concentration of acetic acid in a system in which the esterification of this acid with ethanol has reached equilibrium by titrating the acid with alkali, *i.e.*, by measuring the quantity of sodium hydroxide required to convert the acid to sodium acetate. But if the system was in equilibrium before the titration began, it certainly will not be after the addition of sodium hydroxide has converted some of the acid to the salt. Consequently ester will start reacting with water to form acetic acid and ethanol just as soon as the titration is started, and the observed titer will come out larger than the concentration of acetic acid which actually existed in the equilibrium sys-

tem. How serious the difference between these two quantities will be depends both on the rate of hydrolysis of the ester and on the quickness with which the titration is carried out.

We have in principle three methods of surmounting this difficulty. One is to use a method of analysis which may be carried out rapidly compared with the time required for appreciable reaction of the system whose equilibrium is being investigated. Thus an experienced analyst would have no difficulty in getting a value of good precision for the concentration of acetic acid in the equilibrium state of the ethyl acetate reaction; it might be completely impossible to get the corresponding information in the case of methyl formate, which hydrolyzes much more rapidly.

A second kind of method employs a physical measurement which does not alter the composition of the equilibrium mixture. Thus the concentration of iodine in the hydrogen-iodine reaction can be determined by exploiting the color of iodine vapor, *i.e.*, its property of absorbing strongly light of certain wavelengths which is not appreciably absorbed by hydrogen or by hydrogen iodide. The actual experiment might involve visual comparison of the depth of color of the system under investigation with that of vessels of suitable dimensions containing known partial pressures of iodine, or it might involve more refined techniques of spectrophotometry.

Finally it is often possible to "freeze" the equilibrium. The term derives from a particular application of the general method, in which the system, having reached equilibrium, is suddenly reduced in temperature by an amount so great that the reaction velocity becomes very small. This requires very rapid cooling because the equilibrium composition changes with temperature, and it is necessary to traverse the region in which reaction is moderately fast and equilibrium composition differs from that prevailing at the temperature under investigation so rapidly that there is no appreciable shift of composition. Once the equilibrium is frozen, any suitable method of analysis may be carried out at leisure.

An equilibrium is also said to be frozen if a gaseous or liquid reaction system is removed from a solid catalyst without which the reaction proceeds only at a negligible rate or when, for instance, an acid catalyst is neutralized by the addition of base.

The same situation applies to many heterogeneous reactions. Thus in the reaction

$$\mathrm{FeO(s) + H_2(g) \rightleftharpoons Fe(s) + H_2O(g)} \qquad \text{(V)}$$

removal of the gaseous mixture of H_2 and H_2O from the solids freezes the composition and permits analysis.

Computation of Equilibrium Constants. Physical methods of analysis are rarely if ever available for all the constituents of an equilibrium mix-

ture, and even when chemical methods can be applied, direct determination of some of the substances present is often inaccurate and always tedious. Fortunately we need never make direct determinations of all the partial pressures if we start with a reaction mixture of known composition and if we know qualitatively what substances are present when reaction has occurred until equilibrium has been attained. Knowing the substances produced, we can write reactions for their formation and can then set up material balances which permit the computation of the complete composition from the direct measurement of the amounts of a limited number of substances. Indeed if only one reaction occurs to a significant extent we need measure only one partial pressure or concentration at equilibrium or the value of only one property, such as the density, whose value changes when the reaction takes place. If more than one reaction occurs, as in the practically so important processes of the petroleum industry, a greater number of measurements is necessary. The techniques of infrared spectroscopy offer promise of being helpful in this direction.

Consider, for instance, the decomposition of hydrogen iodide, [reaction (I)], which goes cleanly in one direction or the other when hydrogen, iodine, and hydrogen iodide are introduced into the same space (unless the amounts introduced themselves correspond to the equilibrium composition). Suppose we introduce into a vessel of volume v a mixture of a moles of H_2, b moles of I_2, and c moles of HI. Let the vessel be maintained at the temperature T until equilibrium is reached, and let the *quantity* of iodine present be determined to have the value x moles, either by studying the intensity of the color or by freezing and analyzing the system. If we write n_{H_2} and n_{HI} for the numbers of moles of hydrogen and of hydrogen iodide present at equilibrium, we can state the material balance for iodine in the form

$$2x + n_{HI} = 2b + c \tag{15}$$

That is, we can write that the total number of moles of iodine present at equilibrium either in the form of the element or in the form of the compound must equal the total number of moles initially introduced. Since the other quantities are known, this equation yields a value for n_{HI}. Similarly a material balance for hydrogen

$$2n_{H_2} + n_{HI} = 2a + c \tag{16}$$

yields a value of n_{H_2}. By Eq. (13) of Chap. I

$$P_{I_2} = \frac{x\mathbf{R}T}{v} \qquad P_{HI} = \frac{n_{HI}\mathbf{R}T}{v} \qquad \text{etc.} \tag{17}$$

Substitution of these expressions in Eq. (9) leads to

$$\frac{x(a - b + x)}{(2b + c - 2x)^2} = K \tag{18}$$

by means of which K can be calculated from the known values of a, b, c, and x.

Computations Based on Data from Constant-pressure Systems. Reactions to be studied by the freezing technique are frequently approached by a flow method. Thus a mixture containing known proportions of SO_2 and O_2 may be allowed to flow through a bed of catalyst, and the concentration of SO_3 may then be determined in the exit gases. By making certain that the same equilibrium system is reached by causing to flow through the catalyst a mixture containing more than the equilibrium proportion of SO_3, one may determine whether or not the catalyst bed is thick enough and the flow rate slow enough so that equilibrium is really attained.

In this system the pressure stays constant, but since the reaction is accompanied by a change in the total number of moles, the volume does not. Consider an amount of input which contains a_0 moles of SO_2, b_0 moles of O_2, and c_0 moles of SO_3, no other substances being present. Let a_e, b_e, and c_e represent the numbers of moles of SO_2, O_2, and SO_3 present when this amount of material has reached equilibrium. In such problems as this it is useful to introduce a new variable which represents the change in the number of moles of one of the substances involved. In this case let x be the increase in the number of moles of SO_3, that is, let

$$c_e = c_0 + x \tag{19}$$

Then by inspection from the equation for the chemical reaction (IV) or by solving the material-balance equations for sulfur,

$$a_0 + c_0 = a_e + c_e \tag{20}$$

and for oxygen,

$$2a_0 + 2b_0 + 3c_0 = 2a_e + 2b_e + 3c_e \tag{21}$$

we can get

$$a_e = a_0 - x \tag{22}$$

and

$$b_e = b_0 - \tfrac{1}{2}x \tag{23}$$

Since the total number of moles present at equilibrium, n_e, must equal the sum of the numbers of moles of SO_2, O_2, and SO_3, we find from Eqs. (19), (22), and (23) that

$$n_e = a_0 + b_0 + c_0 - \tfrac{1}{2}x \tag{24}$$

By the definition of partial pressure [Eq. (21) of Chap I], together with Eqs. (19) and (24), we have

$$P_{SO_2} = \frac{a_0 - x}{a_0 + b_0 + c_0 - \frac{1}{2}x} P \tag{25}$$

where P is the total pressure, which is the same in the output as in the input. Similarly we get for the partial pressures of SO_3 and O_2 the relations

$$P_{SO_3} = \frac{c_0 + x}{a_0 + b_0 + c_0 - \frac{1}{2}x} P \tag{26}$$

$$P_{O_2} = \frac{b_0 - \frac{1}{2}x}{a_0 + b_0 + c_0 - \frac{1}{2}x} P \tag{27}$$

Substituting these in Eq. (12), we obtain

$$\frac{(c_0 + x)^2(a_0 + b_0 + c_0 - \frac{1}{2}x)}{(a_0 - x)^2(b_0 - \frac{1}{2}x)P} = K \tag{28}$$

The quantities a_0, a_e, etc., referred to some arbitrarily chosen quantity of input; it can just as well be such that $a_0 + b_0 + c_0 = 1$, in which case a_0 is the mole fraction of SO_2 in the input, etc. The three mole fractions may either be known from the way the mixture of gases was prepared or be determined by analysis of a sample of the input. By Eqs. (19) and (24) the mole fraction of SO_3 in the output is $(c_0 + x)/(a_0 + b_0 + c_0 - \frac{1}{2}x)$. Consequently the value of x may be determined by analysis of the output, and substitution of this value of x together with the known values of a_0, b_0, and c_0 into Eq. (28) leads to the value of K.

Equilibrium Constant from Gas Density. If a reaction is accompanied by a change in the number of moles of gaseous substance and is free from side reactions, the extent to which the reaction has taken place when equilibrium has been reached can be determined under favorable conditions merely by determining the density, the pressure, and the temperature of a sample of the equilibrium system [Eq. (26) of Chap. I]. This information then suffices for the computation of the equilibrium constant. We illustrate the method with the case of phosphorus pentachloride.

This is a solid substance which evaporates completely at temperatures in the neighborhood of 250°C and pressures of 1 atm or so. The gaseous material appears to contain PCl_3 and Cl_2 as well as unreacted PCl_5 and no other substances. We have therefore to deal with the equilibrium in the reaction

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \tag{VI}$$

for which the expression of the equilibrium law is

$$\frac{P_{PCl_3}P_{Cl_2}}{P_{PCl_5}} = K \tag{29}$$

Suppose w g of PCl_5 is evaporated in a vessel of volume v at a temperature T. We can write for n_0, the number of moles of PCl_5 which would be present if the reaction did not occur,

$$n_0 = \frac{w}{M} \tag{30}$$

where M is the molecular weight of PCl_5. If we represent the fraction of the pentachloride which has reacted according to (VI) by x, we have for the numbers of moles of pentachloride, trichloride, and chlorine

$$n_{PCl_5} = n_0(1 - x) \tag{31}$$

$$n_{PCl_3} = n_{Cl_2} = n_0 x \tag{32}$$

The total number of moles present at equilibrium n_e is therefore

$$n_e = n_{PCl_5} + n_{PCl_3} + n_{Cl_2} = n_0(1 + x) \tag{33}$$

and by the argument of page 14 the density ρ is therefore given by

$$\rho = \frac{MP}{(1 + x)\mathbf{R}T} \tag{34}$$

with P the pressure of the equilibrium mixture. If therefore density, pressure, and temperature are measured on the equilibrium system, the fraction reacted, x, can be immediately calculated.

By Eqs. (31) and (33) the mole fraction of PCl_5 at equilibrium is $(1 - x)/(1 + x)$, and we have therefore for its partial pressure

$$P_{PCl_5} = \frac{1 - x}{1 + x} P \tag{35}$$

Similarly

$$P_{PCl_3} = P_{Cl_2} = \frac{x}{1 + x} P \tag{36}$$

Substituting these values in Eq. (29) and simplifying, using the relation $(1 - x)(1 + x) = 1 - x^2$, we get

$$\frac{x^2 P}{1 - x^2} = K \tag{37}$$

Since x and P are known, K can be calculated.

Applications of the Equilibrium Constant. The value of knowing the equilibrium constant of a reaction lies in the possibility of predicting from it the compositions of a wide variety of systems. Thus the degree of dis-

sociation of phosphorus pentachloride at a given temperature, the x of the preceding paragraph, varies widely according to the conditions. It is greater the smaller the total pressure, and it is smaller if either chlorine or phosphorus trichloride is added to the system in addition to the pentachloride. But the equilibrium constant is a constant with respect to these variations, and if its value is known, the composition of the equilibrium mixture can be calculated for all moderate pressures and for all amounts of excess trichloride and chlorine. Such calculations merely reverse those employed in calculating the value of the equilibrium constant from the experimental data on the composition of the equilibrium mixture.

Thus if the equilibrium constant for the hydrogen iodide decomposition [reaction (1)] is known at a certain temperature, Eq. (18) makes it possible to compute x, the number of moles of iodine present when a system initially containing a moles of H_2, b moles of I_2, and c moles of HI has reached equilibrium. Equations (15) and (16) then make it possible to calculate the numbers of moles of hydrogen and hydrogen iodide present.

Similarly the solution of Eq. (28) for x followed by the use of Eqs. (19), (22), and (23) or of Eqs. (25), (26), and (27) makes it possible to determine the equilibrium composition attained in the constant-pressure synthesis of SO_3 from a reaction mixture of any given composition at any temperature for which the equilibrium constant is known. It is true that Eq. (28) is a cubic equation in x and that the corresponding equation in the case of the ammonia synthesis is of the fifth degree. We must therefore recognize that nature does not have the same consideration for human weakness that the writers of algebra textbooks usually do and that equations of higher degree than the second appear frequently in practical problems. Some methods for the numerical solution of such equations are discussed in Appendix A.

Similarly one can calculate from Eq. (37) the equilibrium composition of partly dissociated phosphorus pentachloride under the conditions to which the equation applies if the value of K is known for the temperature in question. This equation is so glib, so easily remembered, and so often quoted that it is easy to overlook the fact that it applies only to a particular case in the general picture of the dissociation of PCl_5, namely, that in which the pentachloride dissociates in the absence of added trichloride or chlorine. Even in this case it is immediately useful only if the pressure P is known.

Consider first the case in which volume rather than pressure is known and no excess of either PCl_3 or Cl_2 is present. Using the symbols of the previous discussion, Eqs. (29) to (33) still apply, but to get the partial pressures of the reactants, we employ Eq. (24) of Chap. I and obtain

$$P_{PCl_3} = P_{Cl_2} = \frac{n_0 x \mathbf{R}T}{v} \tag{38}$$

$$P_{PCl_5} = \frac{n_0(1 - x)\mathbf{R}T}{v} \tag{39}$$

Substituting these in Eq. (29) and simplifying, we get

$$\frac{n_0 x^2}{1 - x} \frac{\mathbf{R}T}{v} = K \tag{40}$$

If we write $c_0 = n_0/v$, we can also put this in the form

$$\frac{c_0 x^2}{1 - x} = \frac{K}{\mathbf{R}T} \tag{41}$$

$K/\mathbf{R}T$ will be recognized [Eq. (13)] as the quantity K_c, the equilibrium constant in terms of concentrations, and c_0 is the concentration of PCl_5 which would have existed if no dissociation had occurred.

Consider further the situation in which n_0 moles of PCl_5 and n_1 moles of Cl_2 are introduced into a vessel of known volume v at the known absolute temperature T. If x represents again the fraction of the pentachloride which has reacted according to (VI), the number of moles of pentachloride present at equilibrium is again given by

$$n_{PCl_5} = n_0(1 - x) \tag{42}$$

Since there is no other source of trichloride than the dissociation, we have also

$$n_{PCl_3} = n_0 x \tag{43}$$

But there are two sources of chlorine, the dissociation and the material added directly. The former supplies $n_0 x$ moles, the latter x_1 moles; consequently

$$n_{Cl_2} = n_0 x + n_1 \tag{44}$$

By way of Eqs. (24) and (29) of Chap. I these lead to

$$\frac{x(n_0 x + n_1)}{1 - x} \frac{\mathbf{R}T}{v} = K \tag{45}$$

This can also be put in the form

$$\frac{c_0 x\{x + (n_1/n_0)\}}{1 - x} = \frac{K}{\mathbf{R}T} \tag{46}$$

It is not a difficult exercise in the differential calculus to prove from the last equation that in a constant-volume system the addition of chlorine

decreases the degree of dissociation of PCl_5 and that the degree of dissociation is smaller the larger the excess of chlorine. It is obvious from the symmetry of the situation that an excess of trichloride would also decrease the dissociation of the pentachloride in a constant-volume system.

Equilibria Involving Solutes in Dilute Solution. As we have seen (page 43) the situation of a solute molecule in a dilute solution is in many respects like that of a molecule in a gas. In particular the average distance between solute molecules is large enough so that the behavior of one solute molecule is negligibly affected by the presence of other solute molecules, and is therefore independent of the concentration of the solution so long as this remains dilute. It is therefore reasonable that the frequency of collisions between solute molecules and consequently the rate of reaction should be proportional to the product of the concentrations of the solute reactants, and that the ideal law of chemical equilibrium should hold for reactions involving solutes in dilute solutions.

That the law is approximately valid is overwhelmingly demonstrated by an immense amount of measurement on equilibria involving electrolytes (page 312). But because the forces between electrically charged molecules are so large and persist to such large distances, the deviations from the law are larger and persist to smaller concentrations than we should expect to be the case with reactions involving only neutral molecules. There can, however, be no doubt that the ideal law does apply to reactions in solution involving nonelectrolytes to a respectable precision and up to considerable concentrations, even though direct experimental checks are meager.

Consider the equilibrium of the reaction $A \rightleftharpoons B$ in a system in which A and B are present simultaneously in the gas phase and in dilute solution in a suitable solvent. The ideal law of chemical equilibrium yields for the equilibrium in the gas phase

$$\frac{P_B}{P_A} = K_1 \tag{47}$$

with P_A and P_B the partial pressures of A and B at equilibrium. Since the solutions are dilute, Henry's law applies in the form

$$\frac{P_A}{c_A} = K_2 \qquad \frac{P_B}{c_B} = K_3 \tag{48}$$

with c_A and c_B the concentrations of A and B in the solution. Eliminating P_A and P_B, we have

$$\frac{c_B}{c_A} = \frac{K_1 K_2}{K_3} \tag{49}$$

Since the quantity K_1K_2/K_3 is constant at constant temperature to the precision of Henry's law and the ideal equilibrium law for the reaction in the gas phase, the ideal law in the usual form must apply to this precision to the reaction in solution.

The generalization of this argument leads to the conclusion that the ideal law of chemical equilibrium applies to the reactions of solutes generally to a precision of the order which applies to Henry's law in solutions of the same concentration range. This conclusion is further supported by much quantitative evidence that rate laws of the form of Eqs. (2) and (3) apply with considerable precision to the reactions of nonelectrolytes in dilute solution. The ideal equilibrium law, because it is a necessary corollary of these rate laws, must apply to the reactions in solution to as good a precision as do the rate laws.

Since the quantity partial pressure has meaning only for gaseous systems, we cannot substitute partial pressure for concentration in writing the equilibrium law for reactions in solution as we did for the reactions of gases. Unless specific statement is made to the contrary, we shall express the concentration of solutes in moles per liter in applications of the equilibrium law. It is obvious from the discussion of page 45 that we could equally well use molalities or mole fractions. With these measures of concentration the numerical values of equilibrium constants would often be different from those applying when the concentration is expressed in moles per liter, but the constants would be equally invariant.

Participation of the Solvent in Equilibria in Solution. Consider the reaction of a solute in dilute solution with the solvent, *e.g.*, the reaction of carbon dioxide dissolved in water to form carbonic acid,

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad \text{(VII)}$$

By the nature of a dilute solution each solute molecule is essentially surrounded by solvent molecules. Consequently the probability, and hence the rate, of reaction between a solute and a solvent molecule is determined entirely by the concentration of solute molecules; with changing concentration of the solution the change in availability for reaction of the solvent molecules is trivial. The rate law for the hydration of CO_2 takes, therefore, the form

$$r_1 = k_1[CO_2] \qquad (50)$$

the more complicated form

$$r_1 = k_1'[CO_2][H_2O] \qquad (51)$$

being unnecessary and indeed no more accurate than Eq. (50). Combining Eq. (50) with the equation

$$r_2 = k_2[H_2CO_3] \qquad (52)$$

for the reverse reaction, we get the equilibrium law in the form

$$\frac{[H_2CO_3]}{[CO_2]} = K_1 \tag{53}$$

We have no precise way of measuring the equilibrium in this reaction although it is known that solutions of CO_2 in water contain two substances, one, presumably H_2CO_3, which reacts almost instantaneously with hydroxyl ion, the other, presumably CO_2, which reacts slowly enough to permit approximate determination of the reaction rate. The proportion of the former can be shown by rate measurements to amount to something less than 1 per cent of the latter. The validity and precision of Eq. (53) may, however, be checked indirectly as follows: Application of the equilibrium law to the ionization of H_2CO_3 leads to

$$\frac{[H^+][HCO_3^-]}{[H_2CO_3]} = K_2 \tag{54}$$

Now let C equal total concentration of dissolved carbon dioxide, hydrated and unhydrated, *i.e.*, let

$$C = [CO_2] + [H_2CO_3] \tag{55}$$

Using Eq. (53), we get from this

$$C = [H_2CO_3]\left(\frac{1}{K_1} + 1\right) \tag{56}$$

and

$$\frac{[H^+][HCO_3^-]}{C} = \frac{K_1K_2}{1 + K_1} \tag{57}$$

As Table 3 shows, the quantity on the left side of this equation is indeed

TABLE 3. EQUILIBRIUM IN THE IONIZATION OF CARBON DIOXIDE IN AQUEOUS SOLUTION AT 25°C*

$C = [CO_2] + [H_2CO_3^-]$; $K = [OH_3^+][HCO_3^-]/C$

C	0.001869	0.010890	0.02140	0.03220
10^7K	4.379	4.400	4.417	4.418

* From conductance measurements of Shedlovsky and MacInnes, *J. Am. Chem. Soc.*, **57**, 1705 (1935).

very nearly constant over a considerable variation in the value of C and this can be true only if K_1 as well as K_2 is essentially constant. The ion concentrations of all these solutions are so small (not over 0.00012) that K_2 should be constant to good precision (page 314).

In general, then, the ideal law of chemical equilibrium applies to reactions in dilute solution which involve the solvent as well as to those which involve solutes only. It is unnecessary to include any factor in the statement of the law which pertains to the concentration of the solvent.

Effect of the Solvent on the Value of the Equilibrium Constant. Because the Henry's law constants of different solutes are differently affected by a change from one solvent to another, because, that is, the constants K_2 and K_3 of Eq. (48) are altered to different extents by such a change, we must expect the equilibrium constant of a reaction in solution to have different values in different solvents, even though the solvents are not directly involved in the reaction. This is in fact the case, as the data of Table 4 show.

TABLE 4. EQUILIBRIUM CONSTANTS FOR THE ISOMERIZATION OF THE KETO FORM OF BENZOYL-CAMPHOR TO THE ENOL FORM IN VARIOUS SOLVENTS AT 0°C*

Solvent	K
Ether	6.81
Ethyl acetate	1.98
Ethanol	1.67
Methanol	0.869
Acetone	0.852

* Data of Dimroth, *Ann.*, **399**, 91 (1913).

Some Heterogeneous Equilibria. Equilibria involving a pure solid phase and a dilute solution or gas or those involving a pure liquid and a gas at low pressure satisfy simple ideal equilibrium laws to the same precision as do the homogeneous reactions which we have been discussing. Thus the solid substance NH_4HS evaporates to form a gas phase consisting of NH_3 and H_2S with no measurable proportion of NH_4HS. As the data of Table 5 show, the condition for equilibrium is the relation

$$P_{NH_3}P_{H_2S} = K \tag{58}$$

The data of this table were of course obtained by allowing the salt to evaporate into a space which except for the seventh entry contained additional NH_3 or H_2S. The evaporation of the salt alone necessarily yields the two gaseous substances in equivalent amounts. In the experiments reported in Table 5 the quantity of solid NH_4HS relative to the volume of the gas space was varied over a wide range. As the results show, this did not affect the validity of Eq. (58). It has been found, and the same conclusion can be derived from general principles (pages 140, 244), that the following rule leads to a statement of the condition for equilibrium in heterogeneous reactions of this sort which has the same kind of precision as the ideal law of chemical equilibrium has for homogeneous reactions: Write the equation for the reaction and form the expression for the ideal

TABLE 5. EQUILIBRIUM CONSTANT IN THE REACTION $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ AT 20°C*

Pressures in atmospheres

P_{NH_3}	P_{H_2S}	$K = P_{NH_3}P_{H_2S}$
0.0424	1.2802	0 0543
0.0509	1.0841	0.0552
0.0609	0.9128	0.0556
0.0867	0.6489	0.0563
0.1153	0.4803	0.0554
0.1397	0.3884	0.0543
0 2335	0.2335	0 0545
0.4518	0.1183	0.0534
0.5306	0.1037	0.0550
0.7106	0.0788	0.0560
0.9239	0.0586	0.0541
1.0812	0.0482	0 0521

* From data of Magnusson, *J. Phys. Chem.*, **11**, 21 (1907).

equilibrium law in the same form as for homogeneous reactions, but omit any factor for a substance which appears as a pure solid or pure liquid phase.

Thus for the reaction

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g) \qquad \text{(VIII)}$$

we have Eq. (58). For the reaction

$$NH_4CO_2NH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g) \qquad \text{(IX)}$$

we must square the pressure of ammonia, obtaining

$$P^2_{NH_3}P_{CO_2} = K \qquad (59)$$

Table 6 shows that Eq. (59) is valid to as high a precision as could be expected from the uncertainties of the data and that the quantity $P_{NH_3}P_{CO_2}$, on the other hand, varies widely.

For the solution of solid barium sulfate in water,

$$BaSO_4(s) \rightleftharpoons Ba^{++} + SO_4^{--} \qquad \text{(X)}$$

the rule leads to the familiar solubility-product equation (Pauling 463 474, Timm 402–410),

$$[Ba^{++}][SO_4^{--}] = K \qquad (60)$$

As with all equilibria involving electrolytes this equation is less precise

TABLE 6. EQUILIBRIUM CONSTANT IN THE REACTION
$NH_4CO_2NH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$
AT 24.9 ± 0.1°C*
Pressures in atmospheres

P_{NH_3}	P_{CO_2}	$10^3 P_{NH_3} P_{CO_2}$	$10^4 P^2_{NH_3} P_{CO_2}$
0 2274	0.0047	1.06	2.40
0.1945	0.0061	1.19	2.31
0.1103	0.0188	2.07	2.28
0.0903	0.0274	2.47	2.23
0.0832	0.0328	2.73	2.27
0.0776	0 0388	3.01	2.34
0.0612	0.0575	3.52	2.15
0.0400	0.1406	5.62	2.24
0.0304	0.2342	7.12	2.16
0.0307	0.2356	7.23	2.22

* From data of Briggs and Migrdichian, *J. Phys. Chem.*, **28**, 1121 (1924).

than similar applications of the ideal equilibrium law to nonelectrolytes. For the reaction

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \qquad \text{(XI)}$$

the rule leads to

$$P_{CO_2} = K \qquad (61)$$

and for the reaction

$$H_2O(l) \rightleftharpoons H_2O(g) \qquad \text{(XII)}$$

i.e., for the evaporation of water, the rule gives the equation

$$P_{H_2O} = K \qquad (62)$$

which is of course nothing but the familiar principle that a pure liquid has a fixed vapor pressure at a given temperature.

The last example makes it especially easy to see why this rule applies. As we have seen (page 41), we may expect the rate of evaporation of water into a gas space to be proportional to the surface A of the interface between liquid and gas but to be essentially dependent of any other influence at a fixed temperature. The probability of a vapor molecule remaining held when it collides with a liquid surface in which it is subject to the attractions of several molecules is much greater than the probability of two vapor molecules sticking together when they collide in the gas phase. Consequently, when a liquid phase is present, the condensation of vapor occurs almost exclusively on the surface of the liquid exposed to the vapor and the rate of condensation is proportional to the area A of the interface, as well as to the pressure of the vapor. We may therefore write for the

rate of condensation

$$r_c = k_c A P \tag{63}$$

and for the rate of evaporation

$$r_e = k_e A \tag{64}$$

At equilibrium the two rates are equal, and consequently

$$k_e A = k_c A P \tag{65}$$

$$P = \frac{k_e}{k_c} \tag{66}$$

This is equivalent to Eq. (62). The general conclusion is that there is no reason to expect the rate of a heterogeneous reaction involving a pure solid or liquid phase to depend on the mass of that phase, and, while the rate should depend on the surface area of the solid or liquid, this effect will be the same for forward and reverse reactions, so that the equilibrium situation is unaffected by the area.

The details of the processes of evaporation and condensation must be more complicated in the case of NH_4HS, in which two different kinds of gas molecules leave the surface of the solid and return to it, so far as we know independently of each other. But there is no reason to doubt that here also the rate of evaporation is proportional to the surface of the solid but independent of its mass and that the rate of condensation shows the same dependence on surface and independence of mass.

Some Forms of Computation for Heterogeneous Equilibria. Computations involving such cases as the evaporative dissociation of NH_4HS necessarily take a different form from those involving a homogeneous dissociation such as that of PCl_5. Thus if a sufficient amount of NH_4HS so that solid is still present when equilibrium is attained is introduced into a vessel of volume v which already contains a moles of NH_3 and b moles of H_2S, and if x moles of solid have evaporated when equilibrium is attained, we have for the numbers of moles of NH_3 and H_2S

$$n_{NH_3} = a + x \qquad n_{H_2S} = b + x \tag{67}$$

and for the total number of moles of gas n_e

$$n_e = a + b + 2x \tag{68}$$

The partial pressures of the two gases may therefore be taken either as

$$P_{NH_3} = (a + x)\frac{RT}{v} \qquad P_{H_2S} = (b + x)\frac{RT}{v} \tag{69}$$

or as

$$P_{NH_3} = \frac{a + x}{a + b + 2x}P \qquad P_{H_2S} = \frac{b + x}{a + b + 2x}P \tag{70}$$

where P is the total pressure. From Eq. (58) we then get either

$$(a + x)(b + x)\left(\frac{RT}{v}\right)^2 = K \tag{71}$$

or

$$\frac{(a + x)(b + x)}{(a + b + 2x)^2} P^2 = K \tag{72}$$

Equation (71) is the form to be used in problems in which the volume is involved as a variable, Eq. (72) in those in which the pressure is involved. These equations serve both for the calculation of the value of the equilibrium constant from experimental data on the reaction and for the computation of the equilibrium composition and pressure when the constant is known. The variable x may be negative as well as positive, a negative value signifying that solid NH_4HS is formed by condensation from the vapor.

In the *special case* that $a = b$, Eq. (72) reduces to

$$\frac{(a + x)(a + x)}{(2a + 2x)^2} P^2 = K$$

i.e., to

$$\frac{P^2}{4} = K \tag{73}$$

This includes the case that a and b are both zero, which applies when NH_4HS evaporates into an empty space.

General Statement of the Ideal Law of Chemical Equilibrium. Considering the various cases of the equilibrium law that we have examined, we may state a general rule for setting up the equilibrium expression for the ideal case, as follows:

Raise the partial pressure of each gaseous substance and the concentration of each solute to a power equal to the coefficient which precedes the symbol of the substance in the reaction equation. Form the product of these quantities for all gases and solutes on the right side of the reaction equation, and divide by the corresponding product for the gases and solutes on the left side of the reaction equation. Do not include any factor which refers to the concentration of a pure solid or liquid phase which is involved in the reaction or to the concentration of the solvent in a dilute solution. To a precision of the same order as that of the perfect-gas and dilute-solution laws the resulting fraction will have a constant value, called the *equilibrium constant*, at constant temperature. If the precision is to be sufficient to be useful, it is necessary that all phases

involved in the reaction be gases at low pressure, dilute solutions, or solid or liquid phases consisting each of a single essentially pure substance.

The Distribution Law. Consider the equilibrium between a solute in dilute solution, *e.g.*, oxygen dissolved in water, and the same substance in the gas phase. The process involved is

$$O_2(aq) \rightleftharpoons O_2(g) \qquad \text{(XIII)}$$

Application of the general rule to this process leads to the expression

$$\frac{P_{O_2}}{[O_2]} = K \qquad (74)$$

for the state of equilibrium, P_{O_2} being the partial pressure of oxygen in the gas phase and $[O_2]$ its concentration in the solution. This is of course Henry's law, which we thus see to be a particular case of the ideal law of chemical equilibrium.

Consider further the case of ammonia present simultaneously as a solute in water and in chloroform. By the general rule the condition for equilibrium in the process

$$NH_3(\text{in } H_2O) \rightleftharpoons NH_3(\text{in } CHCl_3) \qquad \text{(XIV)}$$

is

$$\frac{[NH_3]_{CHCl_3}}{[NH_3]_{H_2O}} = K \qquad (75)$$

TABLE 7. DISTRIBUTION OF AMMONIA BETWEEN WATER AND CHLOROFORM AT 18°C*

$[NH_3]_{H_2O}$†	$[NH_3]_{CHCl_3}$	$K = [NH_3]_{H_2O}/[NH_3]_{CHCl_3}$
0.01941	0 0007057	27.50
0.04823	0.001749	27.58
0.9280	0.03506	26 46
4.333	0.996	21.70

* Data of Abbott and Bray, *J. Am. Chem. Soc.*, **31**, 739 (1909), and of Dawson, *Z. physik. Chem.*, **69**, 120 (1909).

† $[NH_3]_{H_2O}$ is the titer concentration corrected for the ionization of the ammonia, the correction amounting to not over 3 per cent.

The data of Table 7 illustrate the fact that such ratios as this are indeed constant provided the solutions are dilute. At higher concentrations, however, considerable deviations appear, as must be expected.

Catalysts and Equilibrium. The important rule that a catalyst does not alter the equilibrium state of a reacting system is a corollary of the second law of thermodynamics. By definition a catalyst is present in the same amount and in the same state after reaction occurs as it was before.

But a system in equilibrium can be displaced away from that equilibrium only if some other system changes toward equilibrium. Since the catalyst does not so change, the addition of the catalyst cannot shift the state of the reacting system when it is already in equilibrium. Consequently the equilibrium state of the reacting system is the same in the presence as in the absence of the catalyst. The catalyst does greatly affect the rate of the reaction, but it must alter the rates of forward and reverse reactions in the same proportion.

Combination of Equilibria. Consider the two reactions

$$2H_2O \rightleftharpoons 2H_2 + O_2 \tag{XV}$$

and

$$2CO_2 \rightleftharpoons 2CO + O_2 \tag{XVI}$$

and note that if the first is subtracted from the second (*cf.* page 64) and the result divided by 2, we get the reaction

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \tag{XVII}$$

The expressions of the equilibrium law for these reactions are

$$\frac{P_{H_2}^2 P_{O_2}}{P_{H_2O}^2} = K_{XV} \tag{76}$$

$$\frac{P_{CO}^2 P_{O_2}}{P_{CO_2}^2} = K_{XVI} \tag{77}$$

$$\frac{P_{CO} P_{H_2O}}{P_{CO_2} P_{H_2}} = K_{XVII} \tag{78}$$

Now in any system containing H_2O, H_2, CO_2, and CO all three of these reactions may occur, and if the system is completely in equilibrium all three of the equations (76), (77), and (78) must be satisfied. If then we divide Eq. (77) by Eq. (76), getting

$$\frac{P_{CO}^2 P_{H_2O}^2 P_{O_2}}{P_{CO_2}^2 P_{H_2}^2 P_{O_2}} = \frac{K_{XVI}}{K_{XV}} \tag{79}$$

we can cancel out the factor P_{O_2}, obtaining

$$\frac{P_{CO}^2 P_{H_2O}^2}{P_{CO_2}^2 P_{H_2}^2} = \frac{K_{XVI}}{K_{XV}} \tag{80}$$

This step sometimes seems a bit worrisome because of a failure to appreciate the fact that the symbol P_{O_2} represents the total partial pressure of oxygen present in the system and that this quantity cannot have two different values in a single system. Fundamentally this meaning of the symbol goes back to the fact that the equilibrium in reaction (XV) results

from the balance of two opposing rates, and the rate of combination of hydrogen with oxygen will be increased to the same extent by an increase in the concentration of oxygen no matter what the source of the oxygen.

We now recognize that Eqs. (78) and (80) can both be valid only if

$$K_{\text{XVII}} = \sqrt{\frac{K_{\text{XVI}}}{K_{\text{XV}}}} \tag{81}$$

The reasoning may be generalized. If the equations for two reactions may be combined by addition, subtraction, and multiplication or division by suitable factors in such a way as to obtain the equation for a third reaction, the equilibrium constant of the third reaction must be related to the constants of the first two in the following way: Addition of reaction equations leads to multiplication of the corresponding constants; subtraction of reaction equations corresponds to division of the constants; multiplication of the reaction equation by a numerical factor, which may be fractional as well as integral, leads to the appearance of the same numerical factor as an exponent on the corresponding constant.

The three constants involved in Eq. (81) have been measured at temperatures ranging from 1100° to 1550°C, and the results verify the equation as well as can be expected in view of the fact that K_{XV} and K_{XVI} are so small (10^{-13} to 10^{-8}) that high precision in their measurement is extremely difficult. A closer test may be obtained from the series of reactions

$$\text{CoO(s)} + \text{H}_2 \rightleftharpoons \text{Co(s)} + \text{H}_2\text{O} \qquad \text{(XVIII)}$$
$$\text{CoO(s)} + \text{CO} \rightleftharpoons \text{Co(s)} + \text{CO}_2 \qquad \text{(XIX)}$$
$$\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \qquad \text{(XVII)}$$

The expressions of the equilibrium law for these are

$$\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} = K_{\text{XVIII}} \tag{82}$$

$$\frac{P_{\text{CO}_2}}{P_{\text{CO}}} = K_{\text{XIX}} \tag{83}$$

$$\frac{P_{\text{CO}}P_{\text{H}_2\text{O}}}{P_{\text{CO}_2}P_{\text{H}_2}} = K_{\text{XVII}} \tag{84}$$

From the considerations of the last paragraph we have

$$K_{\text{XVII}} = \frac{K_{\text{XVIII}}}{K_{\text{XIX}}} \tag{85}$$

As Table 8 shows, the experimental values of the three equilibrium constants satisfy Eq. (85) to an excellent precision.

TABLE 8. TEST OF THE PRINCIPLE OF COMBINATION OF EQUILIBRIA*

T, °C	K_{XVIII}	K_{XIX}	K_{XVIII}/K_{XIX}	K_{XVII}
450	67	489.6	0.137	0.140
515	57.5	245.9	0.234	0.232
570	50.3	148.4	0.339	0.345

* Data on the cobalt–cobaltous oxide equilibria [reactions (XVIII) and (XIX)], from Emmett and Shultz, *J. Am. Chem. Soc.*, **52**, 2782 (1930). Direct measurements on the water gas equilibrium [reaction(XVII)], from Neumann and Kohler, *Z. Elektrochem.*, **34**, 218 (1928).

REFERENCES

For numerical data on equilibrium constants one must go to the periodical literature; to tabulations of standard free energies of formation, using the relationships reported in Chap. VIII; or to treatises on descriptive chemistry. Some references in the last two categories follow

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PROBLEMS

1. What numerical value of **R** is to be used in Eq. (13) when K_c is in terms of moles per liter and K_P in terms of atmospheres? What value is to be used when K_c is in terms of moles per cubic centimeter and K_P in terms of dynes per square centimeter? In terms of $\mathbf{R}T$ what is the ratio K_P/K_c for reactions (III), (V), (VI), (VII), (VIII), (IX), (XI), (XII), (XVI), (XVII), (XVIII), and (XIX)?

2. A vessel of 500 cc volume at the constant temperature of 50°C held sufficient NOCl to produce a partial pressure of 6.02 cm Hg. On adding a certain amount of CH_3OH the pressure rose to 10.08 cm and remained constant, the content of the vessel being completely gaseous. By using the characteristic absorption of NOCl in the visible spectrum the partial pressure of NOCl in the equilibrium system was found to be 3.44 cm. It appears that the only reaction occurring is $NOCl + CH_3OH \rightleftharpoons CH_3ONO + HCl$. What is the equilibrium constant of this reaction?

3. The equilibrium constant of the homogeneous gaseous reaction $2NO + Br_2 \rightleftharpoons 2NOBr$ is 111 at 25°C, the pressure being in atmospheres. What will be the partial pressure of each of the substances involved if 0.05 mole of NOBr is introduced into a 1-liter flask at 25° and if no other reaction than the one cited takes place?

4. From data of Table 8 calculate the molar ratio in which H_2O vapor and CO must be mixed so that when the mixture is brought to equilibrium at 515°C and 1 atm the partial pressure of CO_2 will be 0.25 atm.

5. A mixture of SO_2 and O_2 in the molar ratio 2.40/1 flows through a catalyst at 1000°K. The pressure throughout is 1.032 atm. The exit gas is found by analysis to contain a mole fraction of SO_2 equal to 0.470. If flow rate and catalyst distribution are such that equilibrium is attained, what is the equilibrium constant of the reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$ at this temperature?

6. It has been found that a mixture of CH_4 and H_2S reaches equilibrium in the process $CH_4 + 2H_2S \rightleftharpoons CS_2 + 4H_2$ over a molybdenum sulfide catalyst at temperatures in the range from 500° to 900°C and that no significant amounts of by-products are formed. If such a mixture whose mole fraction of CH_4 is 0.333 flows through a catalyst bed at 650°C and 1.000 atm in such a way that equilibrium is attained, what will be the composition of the exit gas? At this temperature the equilibrium constant is 1.95×10^{-5} for pressures in atmospheres.

7. At 1000°C a sample of 0.2856 g of iodine exerts a pressure of 447.2 mm when confined in a quartz vessel whose volume is 249.3 cc. Assuming the perfect-gas laws, what is the equilibrium constant for the dissociation of molecular iodine into atoms at this temperature?

8. At 102.1°C the equilibrium constant of the reaction $SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2$ is 2.39 for pressures in atmospheres. Calculate the partial pressure of each substance present when 4.40 g of SO_2Cl_2 in a vessel of 1 liter capacity is brought to equilibrium at this temperature, assuming the perfect-gas laws and no other reaction than the one cited above. What is the degree of dissociation of the SO_2Cl_2 under these conditions?

9. Compute the partial pressures of SO_2, Cl_2, and SO_2Cl_2 in a 1-liter bulb at 102.1°C to which 4.40 g of SO_2Cl_2 and 2.00 of Cl_2 have been added. Make the same assumptions as in Prob. 8.

10. On the same basis compute the total pressure which must exist in a system composed of SO_2Cl_2 and its dissociation products at 102.1° if the partial pressure of Cl_2 is to be 0.5 atm.

11. Show that to the precision of the perfect-gas law the fraction α of the ammonia dissociated to nitrogen and hydrogen at equilibrium is related to the total pressure by the equation $\alpha = \sqrt{1/(1 + (1.30P/K))}$.

12. Starting from Eq. (46), give a general proof that in a constant-volume system the degree of dissociation of PCl_5 is always decreased by the addition of either Cl_2 or PCl_3.

13. Given a system to which the fixed quantity n_0 moles of PCl_5 has been added and which is maintained at the constant pressure P and temperature T, will the addition of Cl_2 increase or decrease the degree of dissociation of the PCl_5?

14. Prove that when PCl_5 evaporates against a fixed pressure which is considerably smaller than K the degree of dissociation may be approximated by $\alpha = 1 - (P/2K)$.

15. Sufficient CO_2 to yield a pressure of 0.0259 atm at 15°C was introduced into an evacuated space of fixed but unknown volume. A small excess of solid ammonium carbamate, $NH_4CO_2NH_2$, was introduced and the pressure was found to be 0.0639 atm when equilibrium was established at the temperature of 15°. Calculate the equilibrium constant at this temperature for the reaction $NH_4CO_2NH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$.

16. At 380°C the equilibrium constant of the process $2HgO(s) \rightleftharpoons 2Hg(g) + O_2(g)$ is 9.5×10^{-4} with pressures in atmospheres. If excess HgO is introduced into a volume of 0.500 liter at 380°C which already contains 0.00100 mole of O_2, what will be the partial pressure of each substance when equilibrium is established?

17. If excess HgO is introduced into a volume of 1.000 liter containing 0.0100 mole of O_2, by what factor will the total pressure differ from that in the case of Prob. 16?

18. At 178°C the pressure resulting from the reaction $2Ag_2O(s) \rightleftharpoons 2Ag(s) + O_2(g)$ when excess silver oxide and silver are present in a volume of 0.500 liter is 0.670 atm. What is the equilibrium constant of this reaction? By what factor will the pressure change if the volume is increased to 1.000 liter?

19. If 0.00500 mole of NH_3 is added to a mixture of 50 cc of water and 25 cc of chloroform at 18°C, what will be the ammonia concentration in each layer?

20. When a solution of c moles of solute C in a cc of solvent A is shaken with b cc of the immiscible solvent B until distribution equilibrium is reached, x moles of C are found in the B layer. What will be the concentration of C in the a cc of solvent A after two successive extractions with b cc of the solvent B?

21. If at a particular temperature the equilibrium constant for the reaction $2NO + 2ICl \rightleftharpoons 2NOCl + I_2$ is K_1 and that for the reaction $2NOCl \rightleftharpoons 2NO + Cl_2$ is K_2, all reactants in both cases being gaseous, what is the equilibrium constant at this temperature of the reaction $2ICl \rightleftharpoons I_2 + Cl_2$? What experimental advantage compared with direct measurement can you perceive in measuring the first two equilibria as a means of determining the constant of the third? None of the three constants is too large or too small to represent a serious difficulty from this source.

22. At 444°C and 1 atm it is found that a mixture of N_2 and H_2 passing through a column of finely divided Fe and Fe_4N attains an equilibrium composition of 0.3 mole of NH_3 to 0.7 mole of H_2. What is the equilibrium constant of the reaction $2Fe_4N + 3H_2 \rightleftharpoons 8Fe + 2NH_3$ at this temperature?

23. At 850°C the pressure of CO_2 in equilibrium with a mixture of $SrCO_3$ and SrO is 0.00325 atm. When a mixture of the finely divided solids $SrCO_3$, SrO, and graphite is heated at this temperature in an evacuated vessel until equilibrium is attained, the total pressure is 0.225 atm and the only gases present are CO_2 and CO. Compute the equilibrium constant at 850°C of the reaction $C(graphite) + CO_2 \rightleftharpoons 2CO$.

24. When HCN is distributed between water and benzene at 15°C, the concentration in benzene c_b and the concentration in water c_w follow closely the relation $c_b/c_w = 0.2458 + 0.0397c_w$ over the range of c_w from 0.01084 to 0.918. Assuming that the solutions are ideal, show that this behavior is consistent with a partial dimerization of HCN in benzene, and calculate the distribution constant of monomeric HCN between benzene and water and the equilibrium constant of the dimerization.

25. When benzoic acid is distributed between water and benzene at 6°C, the ratio $c_w/c_b^{1/2}$ varies by only 2 per cent over the range from $c_b = 0.016$ to 0.20, whereas c_w/c_b varies by a factor of nearly 4. What is the most obvious explanation of this phenomenon?

26. Show that if C is defined by Eq. (55) and P is the partial pressure of gaseous CO_2, then $P/C = K_h(1 + K_1)$, where K_h is the Henry's law constant for CO_2 and K_1 has the same significance as in Eq. (53). Explain why the experimental fact that the ratio P/C is constant within a per cent or two does not serve to establish the validity of Eq. (53).

27. If the probable error in the measurement of a partial pressure is 0.0005 atm, what is the probable error in the value of the quantity $P_{NH_3}^2 P_{CO_2}$ for the first entry in Table 6? What is the probable error of this quantity for the seventh entry?

28. In a certain homogeneous gas reaction the quantity $\Delta H - \Delta E$ at 25°C is 1.19 kcal. What is the value of the ratio K_P/K_c for this reaction?

CHAPTER VIII

THE TEMPERATURE COEFFICIENT OF CHEMICAL EQUILIBRIUM AND RELATED EFFECTS

Theory of an Equilibrium between Isomers. Consider the interconversion of two isomers, specifically of normal and iso butane. The reaction occurs readily on suitable catalysts and is carried out on an enormous scale in the petroleum industry. As the structural formulas of organic chemistry indicate, the two isomers differ in the geometric arrangement of the atoms and in the way in which they are linked together, but these formulas suggest a condition of lifelessness which is far from the picture which our knowledge of these and other molecules forces us to accept. For we have every reason to believe that all molecules are in active motion, with the atoms vibrating with respect to each other and rotating about the bonds which join them, and with the molecule rotating as a whole as well as moving about in space. These motions, like all atomic and molecular motions, are quantized, and the equilibrium with which we have to deal is an equilibrium between a very large number of quantum states, and not merely an equilibrium between two kinds of molecules. These states can be classified as belonging to one or the other of two groups, of which those in one group possess the general characteristics that we recognize as belonging to normal butane and those in the other the characteristics of iso butane. Within each group, transitions from one state to another are so rapid that we cannot isolate molecules belonging to one state from those belonging to another, and we do not therefore recognize any of the states within the group of the normal or of the iso type as constituting a different chemical species from the remainder of the states of the group. The transition from a normal to an iso state is, however, slow enough so that we can separate normal molecules from iso molecules, can study the properties, physical and chemical, of each, and can recognize them as two different chemical species.

In terms of the condition of equilibrium, however, the time required to reach the equilibrium state is irrelevant, and the number of molecules in any state of either group in the condition of equilibrium must be given by the Boltzmann equation. By adding together the numbers in each of the states of one group we may then obtain an expression for the total number

of molecules in that group, and by doing the same for the other group we get an expression for the ratio of the numbers of normal and iso butane molecules at equilibrium.

For this purpose we label the energies and multiplicities of the normal butane states by the subscripts $a0$, $a1$, $a2$, etc., and those of the iso butane states by the subscripts $b0$, $b1$, $b2$, etc. In terms of this nomenclature the number N_{a0} of normal butane molecules in the level of lowest energy available for normal butane is given by

$$N_{a0} = \Lambda g_{a0} e^{\epsilon_{a0}/\mathbf{k}T} \tag{1}$$

the number N_{a1} in the next higher level available for normal butane by

$$N_{a1} = \Lambda g_{a1} e^{-\epsilon_{a1}/\mathbf{k}T} \tag{2}$$

and so on. Consequently the total number N_a of normal butane molecules must be given by the summation

$$N_a = \Lambda \sum_{i=0}^{\infty} g_{ai} e^{-\epsilon_{ai}/\mathbf{k}T} \tag{3}$$

A similar expression may be set up for the total number N_b of iso butane molecules, and the ratio of the numbers of normal and iso molecules is therefore

$$\frac{N_a}{N_b} = \frac{\sum_{i=0}^{\infty} g_{ai} e^{-\epsilon_{ai}/\mathbf{k}T}}{\sum_{i=0}^{\infty} g_{bi} e^{-\epsilon_{bi}/\mathbf{k}T}} \tag{4}$$

The factor Λ has the same value for all states of either group, since these are all states of a set of 4 carbon and 10 hydrogen atoms (page 94), and it vanishes when the ratio is taken. From Eq. (24) of Chap. I and the relation between number of moles n and number of molecules N, for example,

$$N_a = \mathbf{N} n_a \tag{5}$$

we get

$$N_a = \frac{\mathbf{N}v}{\mathbf{R}T} P_a \qquad N_b = \frac{\mathbf{N}v}{\mathbf{R}T} P_b \tag{6}$$

where P_a and P_b are partial pressures of normal and of iso butane. Consequently we have

$$\frac{N_a}{N_b} = \frac{P_a}{P_b} \tag{7}$$

and recognize that the ratio P_a/P_b in a system at equilibrium must be identical with the equilibrium constant K of the reaction

$$i\text{-}C_4H_{10} \rightleftharpoons n\text{-}C_4H_{10} \tag{I}$$

It follows that

$$K = \frac{\sum_{i=0}^{\infty} g_{ai} e^{-\epsilon_{ai}/kT}}{\sum_{i=0}^{\infty} g_{bi} e^{-\epsilon_{bi}/kT}} \tag{8}$$

The significance of this relationship may be illustrated by steplike diagrams of the kind shown in Fig. 1. Here the height of each step measures the energy of a possible state of the molecule and the breadth of the

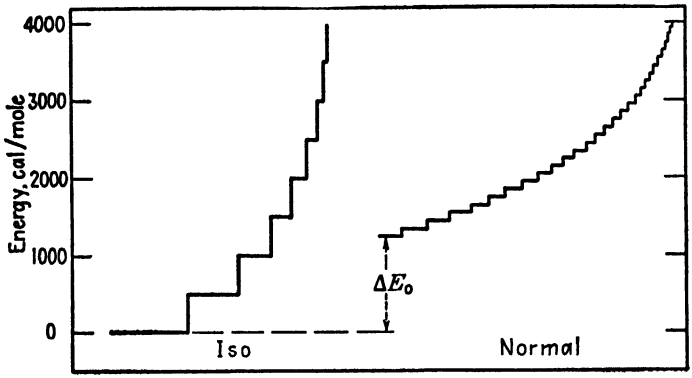


FIG. 1.

step the number of molecules which have that energy in the equilibrium condition. Consequently the breadth of the flight which represents the possible states of the iso butane molecule measures the total number of iso butane molecules in the equilibrium condition, and the breadth of the flight which represents the states available to the normal butane molecule measures the number of normal butane molecules in the equilibrium condition. Because the number of molecules having any given value of energy decreases rapidly as the energy increases, it makes sense to speak of the breadth of the flight even though the number of energy levels is infinite. That is, the series represented by the summations in Eq. (8) are convergent.

In a very schematic way Fig. 1 represents what we know to be the case in the butane isomerization at temperatures in the neighborhood of 300°K. Specifically we know that the lowest energy level for the normal molecule is considerably higher (1270 cal/mole) than the lowest level of

iso butane, and we know that the levels are several times more closely spaced for the normal molecule than for its isomer. As a result the number of molecules in even the lowest normal butane level is considerably smaller than the number in any one of the lower iso butane levels, but the number of normal butane levels is so much greater than the number of iso butane levels that the total number of normal molecules is greater than the total number of iso molecules. This is indicated in the figure by the fact that the breadth of the flight of steps representing normal butane is greater than the breadth of the flight representing iso butane.

Partition Function. In the exploitation of these ideas it is useful to define a quantity Q called a *partition function.* Different scientists use the name for different although closely related quantities; the definition we shall employ is that the partition function Q_a of substance a is given by the summation

$$Q_a = \sum_{i=0}^{\infty} g_{ai} e^{-(\epsilon_{ai} - \epsilon_{a0})/kT} \tag{9}$$

To see how this is related to the summations in Eq. (8), let us multiply the numerator of the right side of that equation by the identity

$$1 = e^{-\epsilon_{a0}/kT} e^{\epsilon_{a0}/kT} \tag{10}$$

getting

$$\sum_{i=0}^{\infty} g_{ai} e^{-\epsilon_{ai}/kT} = e^{-\epsilon_{a0}/kT} \sum_{i=0}^{\infty} g_{ai} e^{\epsilon_{a0}/kT} e^{-\epsilon_{ai}/kT} = e^{-\epsilon_{a0}/kT} \sum_{i=0}^{\infty} g_{ai} e^{-(\epsilon_{ai} - \epsilon_{a0})/kT}$$
$$= e^{-\epsilon_{a0}/kT} Q_a \tag{11}$$

In the light of this relationship Eq. (8) can be written as

$$K = \frac{e^{-\epsilon_{a0}/kT} Q_a}{e^{-\epsilon_{b0}/kT} Q_b} \tag{12}$$

and in terms of the definition

$$\Delta\epsilon_0 = \epsilon_{a0} - \epsilon_{b0} \tag{13}$$

it becomes

$$K = e^{-\Delta\epsilon_0/kT} \frac{Q_a}{Q_b} \tag{14}$$

The quantity $\Delta\epsilon_0$ is the difference in energy between the lowest level of normal butane and the lowest level of iso butane. In view of the discussion of page 97, Eq. (14) can also be written as

$$K = e^{-\Delta E_0/RT} \frac{Q_a}{Q_b} \tag{15}$$

The quantity ΔE_0 is the difference in energy between a mole of normal butane molecules, all in the lowest energy level, and a mole of iso butane molecules, all in the lowest energy level. Its magnitude for the butane isomerization is indicated in Fig. 1.

The definition of the partition function Q involves only differences in energy between particular levels for one kind of molecule and the lowest level for that kind of molecule; hence the magnitude of Q does not depend upon the energy of the lowest level but is determined solely by the way in which the higher levels are spaced above the lowest level and by the multiplicities g. Closer spacing of the levels or larger multiplicities lead to larger values of Q. In terms of the discussion of page 93 this means that the value of the partition function is determined entirely by the molecular motions. It depends primarily upon the freedom of motion of the constituent particles of the molecule, since any restraint which hampers or interferes with the motion increases the spacing of the levels and may also decrease the multiplicities, and both effects decrease the magnitude of the partition function.

The equilibrium constant of a reaction of this type depends therefore fundamentally on two factors. One of these, ΔE_0, is the difference in energy between reactants and products when each substance is in its lowest energy level. Except for the fact that a molecule retains some internal motion, called *zero-point energy*, in its lowest energy state, this energy difference involves the potential energies of the bonds and the other forces of attraction and repulsion between the constituent atoms of the molecule; it is the difference in energy between dead or nearly dead molecules instead of the difference in energy between the actual molecules which are in states of active motion. The other factor, the ratio of the partition functions Q_a/Q_b, depends upon the spacing of the energy levels and the multiplicities and therefore upon the extent to which the molecular motions are hampered or restrained.

The fact that Q is greater for normal butane than for iso butane is on this basis reasonable. In the tighter, more closely knit structure of the branched-chain molecule the constituent atoms get in each other's way and hamper the freedom of motion.

A Dissociation Equilibrium. Consider the dissociation of PCl_5,

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \qquad \text{(II)}$$

which we symbolize by

$$XY \rightleftharpoons X + Y \qquad \text{(II}a\text{)}$$

The number of molecules of each kind is given by a summation analogous to Eq. (1), and consequently

$$\frac{N_X N_Y}{N_{XY}} = \frac{\left(\Lambda_X \sum_{i=0}^{\infty} g_{Xi} e^{-\epsilon_{Xi}/kT}\right)\left(\Lambda_Y \sum_{i=0}^{\infty} g_{Yi} e^{-\epsilon_{Yi}/kT}\right)}{\Lambda_{XY} \sum_{i=0}^{\infty} g_{XYi} e^{-\epsilon_{XYi}/kT}} \tag{16}$$

By virtue of the rule given on page 94 the value of Λ for PCl_3 is the product of the Λ value for phosphorus by the cube of the value for atomic chlorine,

$$\Lambda_{PCl_3} = \Lambda_P \Lambda_{Cl}^3 \tag{17}$$

Similarly

$$\Lambda_{Cl_2} = \Lambda_{Cl}^2 \tag{18}$$

$$\Lambda_{PCl_5} = \Lambda_P \Lambda_{Cl}^5 \tag{19}$$

Consequently

$$\frac{\Lambda_{PCl_3}\Lambda_{Cl_2}}{\Lambda_{PCl_5}} = 1 \tag{20}$$

We see therefore that the Λ factors in Eq. (16) cancel. If we also carry out the substitutions which led from Eq. (8) to Eq. (15), we get

$$\frac{N_X N_Y}{N_{XY}} = e^{-\Delta\epsilon_0/kT} \frac{Q_X Q_Y}{Q_{XY}} \tag{21}$$

with

$$\Delta\epsilon_0 = \epsilon_{X0} + \epsilon_{Y0} - \epsilon_{XY0} \tag{22}$$

The quantity $\Delta\epsilon_0$ is the difference in energy between a molecule of PCl_5 and a molecule each of its dissociation products, all being in the lowest energy level. When we make the further substitutions according to Eq. (6), we get

$$K = e^{-\Delta\epsilon_0/kT} \frac{(Q_X RT/Nv)(Q_Y RT/Nv)}{Q_{XY} RT/Nv} \tag{23}$$

Since the v factors do not cancel, this equation appears to suggest that the equilibrium constant K depends on the volume in which the reaction takes place, whereas it is actually independent of volume to the perfect-gas approximation. The appearance is illusory because the confinement of a gas in a fixed volume constitutes a restraint on its motion which must decrease its partition function, and the detailed working out of the theory (Appendix B) predicts that the multiplicities are so affected by the restraint that the partition function Q is proportional to the volume, *i.e.*, that Q/v is independent of the volume.

The conclusions to be drawn are therefore the same as in the isomerization, namely, that the equilibrium constant depends on two factors, one

determined by the difference in energy between the lowest levels of the reactants and reaction products, the other by a ratio of partition functions, which depend on the freedom of motion of the atoms making up the molecules. In addition we can recognize some special characteristics of a dissociation reaction. Inevitably such reactions break more bonds than they form. Thus there are five P—Cl bonds in PCl_5, whereas the dissociation products contain three P—Cl and one Cl—Cl bond, a total of four. This means almost certainly that the energy in the lowest level of PCl_3 plus that of Cl_2 is greater than the energy in the lowest level of PCl_5 and that the value of $\Delta\epsilon_0$ is positive. The factor

$$e^{-\Delta\epsilon_0/kT}$$

must therefore be less than 1. On the other hand the dissociation loosens the restraints on the atoms, which means that Q_XQ_Y/Q_{XY} is inevitably greater than 1. Actual values of the quantity

$$\frac{(Q_X\mathbf{R}T/\mathbf{N}v)(Q_Y\mathbf{R}T/\mathbf{N}v)}{Q_{XY}\mathbf{R}T/\mathbf{N}v}$$

for typical dissociation reactions at temperatures in the neighborhood of 300°K lie in the region of 10^5 to 10^{11}. This conflict between opposing factors, one tending to make K small, the other to make it large, is highly characteristic of a dissociation reaction and has important implications for the properties of such reactions and particularly of the temperature coefficient.

The conclusions derived from the dissociation and the isomerization may be generalized without difficulty to any homogeneous gas reaction.

The Limitation to Ideal Cases. As we have said before (page 98), we can speak of the quantum state of a molecule only as an approximation which is more exact the more completely the behavior of one molecule is independent of the presence and behavior of other molecules. Consequently the discussion of the last few paragraphs is an approximation which is more nearly exact the more nearly the system approaches the idealized one whose most obvious experimental characteristic is a close approximation to perfect-gas behavior. In other words, the applicability of the ideal law of chemical equilibrium to gaseous systems whose pressure is so low that the perfect-gas law is a close approximation and the serious failure of this equilibrium law at pressures so high that the perfect-gas law is a poor approximation may be taken as confirmation of the statistical-mechanical treatment of the equilibrium in chemical reactions which we have indicated in the last few paragraphs.

Reactions in Solution. Turning the argument in the other direction, we may have considerable confidence that statistical-mechanical equa-

tions of the type of Eqs. (4) and (21) apply to the reactions of solutes in dilute solution, *i.e.*, that our arguments apply to molecules subjected to an essentially constant interaction with solvent molecules as well as to molecules essentially independent of their neighbors. This confidence is strengthened by the fact that the variation of concentration c of a solute with distance x along the direction of a centrifugal field of force f is given by the same application of the Boltzmann equation

$$c = c_0 e^{fx/\mathbf{k}T} \tag{24}$$

as that which determines the decrease in concentration of the earth's atmosphere with increasing height above the earth. In the latter case we substitute minus the height h above the surface of the earth for the x of Eq. (24) and $m\mathbf{g}$ for the f. c_0 is in both cases the concentration when x or h equals zero. Equation (24) is the basis of an important method for determining the molecular weight of high polymers.

For a reaction in solution the convention we have adopted expresses the equilibrium law in terms of concentrations in moles per liter. Consequently, when we have the reaction (IIa) in solution, we substitute the relations

$$N_X = \mathbf{N}c_X v, \text{ etc.} \tag{25}$$

into Eq. (21) instead of using Eq. (6) and obtain

$$K = e^{-\Delta\epsilon_0/\mathbf{k}T} \frac{(Q_X/\mathbf{N}v)(Q_Y/\mathbf{N}v)}{Q_{XY}/\mathbf{N}v} \tag{26}$$

Here also we may expect Q/v to be independent of v in agreement with the fact that K is independent of v to the dilute-solution approximation.

Since the energy of interaction of solute molecule with solvent molecules has different values for a given solute in different solvents, the ϵ_0's and hence the $\Delta\epsilon_0$ of a given reaction will have different values in different solvents; since different solvents may interfere to different extents with the internal motions of the solute molecule, the values of Q may also differ from solvent to solvent.

Factoring of the Partition Function. The energy ϵ of a molecule in a dilute gas can be written as the sum of the energy ϵ^i of its internal motion and the energy ϵ^t of translation of the molecule as a whole. Similarly the multiplicity g can be written as the product of the multiplicity g^i of the internal motion by the multiplicity g^t of the translational motion. For if there is only one kind of internal motion of a given energy, the total multiplicity is the multiplicity of the translational motion; if there are two kinds of internal motion, each of these can be accompanied by the same g^t varieties of translational motion and the

total multiplicity is $2g^t$; and so on. Consequently we can write for any of the multitudinous terms which make up a partition function

$$\begin{aligned} ge^{-(\epsilon-\epsilon_0)/kT} &= g^t g^i e^{-\{(\epsilon^t-\epsilon_0{}^t)+(\epsilon^i-\epsilon_0{}^i)\}/kT} \\ &= (g^t e^{-(\epsilon^t-\epsilon_0{}^t)/kT})(g^i e^{-(\epsilon^i-\epsilon_0{}^i)/kT}) \end{aligned} \tag{27}$$

ϵ_0^t and ϵ_0^i being the energies of the translational motion and of the internal motion, respectively, each being in its lowest energy state. The last expression in Eq. (27) is the product of two factors, one depending only on the translational motion, the other on the internal motion alone. The partition function Q is the sum of all possible products of this kind, *i.e.*, there will be a term for the zero translational state combined with the zero internal state, one for zero translational state and first internal state, one for first translational and zero internal states, and so on. It is shown in Appendix A that a sum of products of this kind is equal to the product of the sums of the possible values of the factors. It follows that

$$Q = \Big(\sum_{j=0}^{\infty} g_j^t e^{-(\epsilon_j{}^t-\epsilon_0{}^t)/kT}\Big)\Big(\sum_{k=0}^{\infty} g_k^i e^{-(\epsilon_k{}^i-\epsilon_0{}^i)/kT}\Big) \tag{28}$$

The first factor on the right is called the translational partition function and written Q_t; the second factor, called the internal partition function, is written Q_i. In terms of these symbols Eq. (28) can be written

$$Q = Q_t Q_i \tag{29}$$

This factoring is possible only because the state of the translational motion of the molecule is unaffected, or almost unaffected, by the state of its internal motion; *i.e.*, it is possible only when the first factor on the right of Eq. (27) has the same value when the second factor refers to the 0, the 1, the 2, or any other internal energy state. But even when two kinds of motion of a molecule are not completely independent of each other, a factoring of the partition function may be a useful approximation. This is true, for instance, of the internal partition function of a diatomic molecule, which may approximately but usefully be further factored into a vibrational and a rotational partition function.

Equilibrium in the Evaporation of a Pure Crystal. The evaporation of a pure crystal is an extreme case of a dissociation or depolymerization process, for it consists in the breaking down of a very large molecular aggregate into a great many identical fragments. In the case of quartz the forces that hold the crystal together are the same kind of chemical valence forces that hold together the Si and O atoms in a gaseous SiO_2 molecule; in the case of naphthalene the forces that hold the crystal together are the van der Waals forces, weak compared with the valence

forces that hold the $C_{10}H_8$ molecule together. But this alters nothing in the essential nature of the process of evaporation, which can be symbolized in both cases by the equation

$$X_n = nX \tag{III}$$

Consequently the equilibrium in the process should be given by

$$\frac{N_g^n}{N_c} = e^{-n\,\Delta\epsilon_0/kT}\frac{Q_g^n}{Q_c} \tag{30}$$

Here N_g is the number of molecules of the gaseous substance X, N_c is the number of the giant molecules which we call the crystal, n is the number of X units in the crystal, $\Delta\epsilon_0$ is the energy required to remove an X unit from the crystal to the vapor, both crystal and vapor molecule being in the lowest energy state, Q_g is the partition function of gaseous X, and Q_c the partition function of the crystal.

The energy of the crystal in any state is the sum of the energies of the X units, and the energy of an X unit must be to a large extent independent of its position in the structure of the crystal and even of the size of the crystal. This follows from the fact that forces between atoms die out very rapidly with increasing distance; consequently the forces which act on any one unit and determine the energy of its motion are essentially the same as those which act on any other unit, except for the small proportion of the units which are within a distance of 10^{-7} cm or less from the exterior of the crystal. Consequently it should be possible to factor the partition function Q_c for the crystal into n nearly identical partition functions Q_u, one for each unit in the polymer. To a good approximation, then,

$$Q_c = Q_u^n \tag{31}$$

the error arising from the small number of units which lie near the surface. Q_u must be considerably smaller than Q_g because the X units are subjected to strong constraints in the crystal and have much less freedom of motion than in the gas. Substituting Eq. (31) in Eq. (30), we have

$$\frac{N_g^n}{N_c} = \left(e^{-\Delta\epsilon_0/kT}\frac{Q_g}{Q_u}\right)^n \tag{32}$$

Consider first the case that only one crystal is present in equilibrium with the vapor; then the quantity $N_c = 1$, and we have

$$N_g = e^{-\Delta\epsilon_0/kT}\frac{Q_g}{Q_u} \tag{33}$$

$$P = e^{-\Delta\epsilon_0/kT}\frac{Q_g RT/\mathbf{N}v}{Q_u} \tag{34}$$

with P the partial pressure of gaseous X. Since Q_0/v is independent of the volume, and since the quantity n, which measures the size of the crystal, has dropped out, we have the result that the partial pressure of the vapor in equilibrium with a single crystal is independent of the size of the container and of the size of the crystal. If therefore the pressure of the vapor is such that it is in equilibrium with a crystal of one size, it is in equilibrium with a crystal of any size or with any assembly of crystals of any size. These conclusions are of course in agreement with experiment except that measurable deviations occur when the crystals are so small that the fraction of the total number of units which lie near the exterior becomes appreciable.

These considerations may be extended without too much difficulty to any heterogeneous equilibrium involving pure or nearly pure solids or liquids on the one hand and gaseous substances and solutes in dilute solutions on the other. The result justifies in a sense the general statement of the ideal law of chemical equilibrium for heterogeneous reactions as it was reported on page 119. It also supplies a basis for the theoretical prediction of the dependence of the equilibrium constant on temperature and on other influences.

A Generalized Statement. We define a quantity Q° by the following equations:

For a perfect gas or a constituent of a perfect-gas mixture

$$Q^\circ = \frac{Q\mathbf{R}T}{\mathbf{N}v} \tag{35}$$

For a solute in dilute solution

$$Q^\circ = \frac{Q}{\mathbf{N}v} \tag{36}$$

For a pure or nearly pure solid or liquid

$$Q^\circ = Q^{1/n} \tag{37}$$

where n is the number of identical units from which the crystal or drop of liquid is constructed.

Unlike Q itself, Q° is, to the perfect-gas and dilute-solution approximation, independent of the partial pressure of a gas or the concentration of a solute; for a pure solid or liquid it is independent of the size of the crystal or body of liquid.

Then for any situation in which the ideal law of chemical equilibrium is valid to a reasonable precision for a reaction which we may represent in general terms as

$$aA + bB + \cdots \rightleftharpoons mM + nN + \cdots \tag{IV}$$

the equilibrium constant K will be given by

$$K = e^{-\Delta\epsilon_0/kT} \frac{(Q_M^\circ)^m (Q_N^\circ)^n \cdots}{(Q_A^\circ)^a (Q_B^\circ)^b \cdots} \tag{38}$$

By virtue of Eq. (35) the K of this equation will have a value consistent with the convention that in writing the expression for the equilibrium law we shall use partial pressure as a measure of concentration for gaseous reactants; by virtue of Eq. (36) it is consistent with the convention that concentrations of solutes shall be expressed in moles per liter; by virtue of

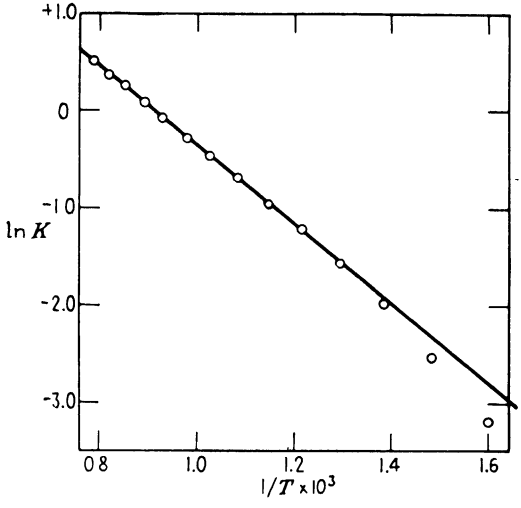


FIG. 2. Dependence of the equilibrium constant K for the reaction $CO_2 + H_2 \rightleftharpoons CO + H_2O$ on the absolute temperature T.

our discussion of heterogeneous reactions we see that it is consistent with the rule that no factor will be included in the expression of the equilibrium law to represent substances present as pure or nearly pure solids and liquids.

Temperature Dependence of the Equilibrium Constant. It is a thoroughly verified rule, which historically was first derived from thermodynamics (page 360) that the slope of a plot of the natural logarithm of the equilibrium constant of a reaction against the reciprocal of the absolute temperature is equal to $-\Delta H/R$ where ΔH is the enthalpy change of the reaction. Thus the ordinates of the points in Fig. 2 are experimental values of ln K for the water-gas reaction

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \tag{V}$$

and the abscissas are the corresponding values of $1/T$. Over this wide range of temperature (350° to 1000°C) the plot deviates appreciably but

not widely from a straight line. The line drawn has a slope of -4080, that is, it corresponds to a value of ΔH of $+4080\mathrm{R}$ or 8100 cal. This is the value of ΔH at 1100°K, that is, at $1/T = 0.909 \times 10^{-3}$ as computed from thermochemical data by the methods of Chap. V. The deviation of the points from the line at high values of $1/T$, that is, at low temperatures, is in the direction expected from the known value of ΔC_P for the reaction.

The proof of this rule from equations of the type of Eq. (38) requires a certain amount of mathematical complication but no difficult or advanced principles. Taking the logarithm of both sides of this equation, we get

$$\ln K = -\frac{\Delta\epsilon_0}{\mathbf{k}T} + m \ln Q_M^\circ + n \ln Q_N^\circ \cdots - a \ln Q_A^\circ - b \ln Q_B^\circ \cdots \quad (39)$$

If we then differentiate with respect to T, the first term on the right becomes $\Delta\epsilon_0/kT^2$ since $\Delta\epsilon_0$ is independent of temperature, and the remaining terms are converted to quantities of the type of $m(d \ln Q_M^\circ/dT)$. If the substance concerned is a pure solid or liquid,

$$\ln Q^\circ = \frac{1}{n} \ln Q \quad (40)$$

and

$$\frac{d \ln Q^\circ}{dT} = \frac{1}{n} \frac{d \ln Q}{dT} \quad (41)$$

If the substance is a solute in dilute solution,

$$\ln Q^\circ = \ln Q - \ln \mathbf{N} - \ln v \quad (42)$$

and

$$\frac{d \ln Q^\circ}{dT} = \frac{d \ln Q}{dT} \quad (43)$$

To make this exact, a term $-d \ln v/dT$ should be added to the right side, but this is so small with liquid solutions that it can be neglected. If the substance is a gas,

$$\ln Q^\circ = \ln \frac{Q}{v} + \ln T + \frac{\ln \mathbf{R}}{\mathbf{N}} \quad (44)$$

and

$$\frac{d \ln Q^\circ}{dT} = \frac{d \ln (Q/v)}{dT} + \frac{1}{T} \quad (45)$$

The whole problem therefore reduces to that of obtaining values of the quantity $d \ln Q/dT$ for a pure solid or liquid or for a solute and of the quantity $d \ln (Q/v)/dt$ for a gas. For the first of these cases we get, by

straightforward differentiation of each term in the summation which defines the partition function,

$$\frac{d \ln Q}{dT} = \frac{dQ/dT}{Q} = \frac{\sum_{i=0}^{\infty} \frac{\epsilon_i - \epsilon_0}{\mathbf{k}T^2} g_i e^{-(\epsilon_i - \epsilon_0)/\mathbf{k}T}}{\sum_{i=0}^{\infty} g_i e^{-(\epsilon_i - \epsilon_0)/\mathbf{k}T}} \tag{46}$$

If we now multiply numerator and denominator of the last expression by Λ, take the constant factor $1/\mathbf{k}T^2$ outside the summation in the numerator, and substitute $\mathbf{R}/\mathbf{N}$ for $\mathbf{k}$, we get

$$\frac{d \ln Q}{dT} = \frac{1}{\mathbf{R}T^2} \frac{\mathbf{N} \sum_i (\epsilon_i - \epsilon_0) \Lambda g_i e^{-(\epsilon_i - \epsilon_0)/\mathbf{k}T}}{\sum_i \Lambda g_i e^{-(\epsilon_i - \epsilon_0)/\mathbf{k}T}} \tag{47}$$

Each term in the summation in the numerator consists of the product of the excess energy of a particular level of the molecule over the energy of the lowest level, namely, $\epsilon_i - \epsilon_0$, by a factor which equals the number of molecules which possess that energy. The product is therefore equal to the excess energy possessed by all the molecules in that level, and the summation must consequently equal the excess energy of all the molecules in all the levels. Each term in the denominator, on the other hand, equals the number of molecules in a particular level, and the summation must therefore equal the total number of molecules. The last factor in the equation is therefore equal to the excess energy of all the molecules divided by the number of molecules and multiplied by Avogadro's number, and this is the excess energy of 1 mole of the substance, that is, $E - E_0$, where E is the actual energy of 1 mole and E_0 the energy 1 mole would have if all the molecules were in the lowest energy level. From these considerations we have

$$\frac{d \ln Q}{dT} = \frac{E - E_0}{\mathbf{R}T^2} \tag{48}$$

For the pure solid or liquid E is the energy of 1 mole of the giant molecules which constitute the crystal or the liquid drop. If we divide by n, the number of monomer units in the crystal or drop, we convert this to the energy of 1 mole of the unit. Consequently by Eq. (41)

$$\frac{d \ln Q^\circ}{dT} = \frac{E - E_0}{\mathbf{R}T^2} \tag{49}$$

where E and E_0 are now molal energies in the sense in which we represent the molecular weight of crystalline quartz by the formula SiO_2. By Eq. (43) we may substitute Q° for Q without further ado for a solute in liquid solution. Equation (49) therefore applies to this case also. To the precision of our present considerations the enthalpy and the energy of a solid or liquid system are identical (page 62), and we may therefore substitute H for E, obtaining

$$\frac{d \ln Q^\circ}{dT} = \frac{H - E_0}{RT^2} \tag{50}$$

We have already mentioned that the partition function of a gaseous substance is, to the perfect-gas approximation, proportional to the volume (page 135). Consequently the Q/v of Eq. (45) is independent of the volume. Fundamentally this proportionality goes back to a proportionality of the multiplicities g to volume. If therefore we carry through the argument which led from Eqs. (46) to (48) except that we substitute the volume-independent and therefore temperature-independent quantity g_i/v for the g_i of Eq. (46), we arrive at a similar result, namely,

$$\frac{d \ln (Q/v)}{dT} = \frac{E - E_0}{RT^2} \tag{51}$$

By Eq. (45) we have therefore for a gaseous substance

$$\frac{d \ln Q^\circ}{dT} = \frac{E - E_0}{RT^2} + \frac{1}{T} = \frac{(E + RT) - E_0}{RT^2} \tag{52}$$

Since $H = E + PV$ and $PV = RT$ to the perfect-gas approximation, we have finally for the gaseous system the same equation as for the condensed phases,

$$\frac{d \ln Q^\circ}{dT} = \frac{H - E_0}{RT^2} \tag{50}$$

With this value of the quantity $d \ln Q^\circ/dT$ we return to the differentiation of Eq. (39). Writing E_0/R for ϵ_0/k, we get

$$\frac{d \ln K}{dT} = \frac{\Delta E_0}{RT^2} + m \frac{H_M - E_{M0}}{RT^2} + n \frac{H_N - E_{N0}}{RT^2} + \cdots - a \frac{H_A - E_{A0}}{RT^2} - b \frac{H_B - E_{B0}}{RT^2} - \cdots \tag{53}$$

By virtue of the definitions of energy change and enthalpy change in a reaction we have

$$\Delta E_0 = mE_{M0} + nE_{N0} + \cdots - aE_{A0} - bE_{B0} - \cdots \tag{54}$$

$$\Delta H = mH_M + nH_N + \cdots - aH_A - bH_B - \cdots \tag{55}$$

Therefore

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \tag{56}$$

Finally since

$$\frac{d \ln K}{dT} = \frac{d(1/T)}{dT} \frac{d \ln K}{d(1/T)} = -\frac{1}{T^2} \frac{d \ln K}{d(1/T)} \tag{57}$$

we have

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta H}{R} \tag{58}$$

which is the rule we set out to prove.

Integration of the Relation between Equilibrium Constant and Temperature. Except for reactions which involve the formation or disappearance of ions in solution the plot of $\ln K$ against $1/T$ is usually reasonably close to a straight line over a moderate range of temperature. For such ranges Eq. (58) may be integrated immediately on the basis that ΔH is constant. If the form of the definite integral between temperatures T_1 and T_2 is used, the result is

$$\int_{K_1}^{K_2} d \ln K = -\frac{\Delta H}{R} \int_{T_1}^{T_2} d \frac{1}{T}$$

i.e.

$$\ln K_2 - \ln K_1 = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \tag{59}$$

which may also be put in the form

$$\ln \frac{K_2}{K_1} = \frac{\Delta H (T_2 - T_1)}{R T_1 T_2} \tag{60}$$

If the form of the indefinite integral is used, the equations become

$$\ln K = -\frac{\Delta H}{RT} + \text{constant} \tag{61}$$

For a wider range of temperature or for cases where ΔH is especially sensitive to temperature it is necessary to express ΔH as a function of temperature before integrating. If the heat capacities of all the substances involved in the reaction are known in the form of equations of the type of Eq. (31) of Chap. V, we have by virtue of Eq. (35) of Chap. V

$$\frac{d\Delta H}{dT} = \Delta C_p = \Delta a + \Delta b T + \Delta c T^2 + \cdots \tag{62}$$

The quantities Δa, Δb, etc., are to be computed from the a, b, etc., values of the substances involved in the reaction in the way illustrated on page

81. By integration of Eq. (62) we get the desired expression of ΔH as a function of temperature.

$$\Delta H = \Delta H_0 + \Delta a T + \tfrac{1}{2}\Delta b T^2 + \tfrac{1}{3}\Delta c T^3 + \cdots \qquad (63)$$

The integration constant ΔH_0 has the significance discussed on page 82. Substituting this value of ΔH in Eq. (56) and separating variables, we have

$$d \ln K = \left(\frac{\Delta H_0}{\mathrm{R}T^2} + \frac{\Delta a}{\mathrm{R}T} + \frac{1}{2}\frac{\Delta b}{\mathrm{R}} + \frac{1}{3}\frac{\Delta c}{\mathrm{R}} T + \cdots\right) dT \qquad (64)$$

Integration of this leads to

$$\ln K = -\frac{\Delta H_0}{\mathrm{R}T} + \frac{\Delta a}{\mathrm{R}} \ln T + \frac{1}{2}\frac{\Delta b}{\mathrm{R}} T + \frac{1}{6}\frac{\Delta c}{\mathrm{R}} T^2 + \cdots + I \qquad (65)$$

If the heat capacities are expressed in forms other than that of Eq. (31) of Chap. V, the value of $\ln K$ will have a different form of dependence on temperature from Eq. (65) but the principle by which the proper equation may be derived is the same. It must be emphasized that Eq. (65) or any similarly derived equation can be valid only for the temperature range for which the heat-capacity equation employed is valid and that ΔH_0 is not the heat of reaction at 0°K (*cf.* page 82).

Equation (65) is extremely useful for the calculation of equilibrium constants at temperatures widely separated from those at which values can be determined by direct experiment and particularly for the calculation of the equilibrium constant at a temperature at which the reaction is too slow, too complete in the one direction or the other, or too confused by competing reactions to permit direct measurement. If the heat capacities of the substances involved in the reaction are known as functions of temperature, Eq. (65) contains two unknown quantities ΔH_0 and I, both of which came into the situation as integration constants. Two determinations of K at two temperatures which are not too close together suffice to calculate these two quantities, after which the value of K at any temperature within the range of validity of the heat-capacity equations follows by simple substitution. Alternatively a measurement of the heat of reaction at any temperature within the range of validity of the heat-capacity equation permits the calculation of the value of ΔH_0 by way of Eq. (63), after which a measurement of K at a single temperature suffices to determine the value of I. In either case the heat of reaction at any temperature within the range may be calculated from Eq. (63), once ΔH_0 is known. If a series of values of K over a range of temperatures have been obtained experimentally, the best values of ΔH_0 and I will be

obtained by plotting the quantity

$$\ln K - \frac{\Delta a}{\mathrm{R}} \ln T - \frac{1}{2}\frac{\Delta b}{\mathrm{R}} T - \frac{1}{6}\frac{\Delta c}{\mathrm{R}} T^2 - \cdots$$

against $1/T$. The slope of the resulting straight line will then be $-\Delta H_0/\mathrm{R}$, and the intercept for $1/T = 0$ will be the value of I.

Dependence of Vapor Pressure on Temperature. A frequent application of Eq. (56) or (58) is to the temperature dependence of the vapor pressure of a solid or liquid. By Eq. (34) the vapor pressure depends upon energies and partition functions in the same way as any equilibrium constant (*cf.* page 142), and Eqs. (56) and (58) therefore apply merely by substituting the vapor pressure P for K in these equations. Consequently

$$\frac{d \ln P}{dT} = \frac{\Delta H}{\mathrm{R}T^2} \tag{66}$$

$$\frac{d \ln P}{d(1/T)} = -\frac{\Delta H}{\mathrm{R}} \tag{67}$$

Equation (66) is usually known as the *Clausius-Clapeyron equation.* The integration of Eq. (66) for either narrow or wide ranges of temperature takes the same course as that of Eq. (56) and leads to equations of the type of Eq. (60), (61), or (65) with P substituted for K.

The Boiling-point Law for Dilute Solution. Equation (67) is valid for the vapor pressure of the solvent from a dilute solution, and the value of ΔH for the evaporation from the dilute solution must be essentially the same as it is for the pure solvent (page 71). By Eq. (67), therefore, a plot against reciprocal temperature of the vapor pressures of solvent from a solution and from the pure solvent over a small range of temperature must have the character of Fig. 3. Because the temperature range is small, the plots are essentially straight lines; because the values of ΔH for solution and for pure solvent are essentially the same, they are parallel lines. By Eq. (67) their slope is $-\Delta H/\mathrm{R}$. Raoult's law, $P = P^\circ N_a$ can be put in the form

$$\ln P = \ln P^\circ + \ln N_a \tag{68}$$

where P is vapor pressure of solvent from dilute solution, P° is vapor pressure from pure solvent, and N_a is mole fraction of solvent in the solution. Since any point on the solvent line of Fig. 3 has for ordinate the value of $\ln P^\circ$ at a temperature whose reciprocal is given by the abscissa and any point on the solution line has for ordinate the value of $\ln P$ at the same temperature, the constant vertical difference between the parallel lines, represented for instance by the length AB, represents the value of $\ln N_a$ for the solution.

If the solute is nonvolatile, the total pressure from the solution is equal to the vapor pressure of the solvent, the P of Eq. (68). The horizontal line OCA of the figure, which is drawn for an ordinate of $\ln P = 0$, that is, for $P = 1$, must therefore intersect the vapor-pressure lines at points C and A, whose abscissas are the reciprocals of the boiling points under a pressure of 1 atm of the solution and of the pure solvent. This is because by definition the boiling point of a solution is the temperature at which its vapor pressure equals the external pressure. Let the boiling point of the pure solvent be T_0 and that of the solution be T. Then the distance CA represents the quantity $(1/T_0) - (1/T)$. The ratio of lengths AB/CA is

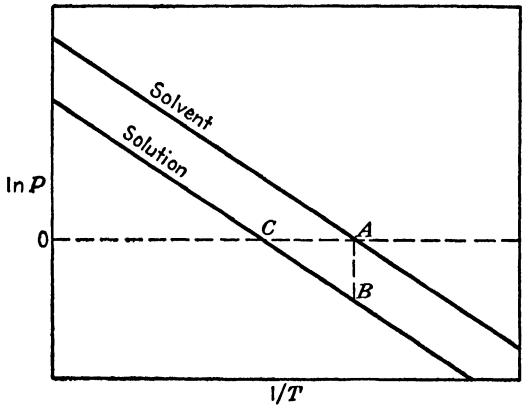


FIG. 3.

obviously the slope of the vapor-pressure lines of the figure, and this, as we have seen, is $-\Delta H/\mathbf{R}$. Consequently

$$\frac{\ln N_a}{(1/T_0) - (1/T)} = -\frac{\Delta H}{\mathbf{R}} \tag{69}$$

To a precision which is determined by the use of Raoult's law for any but ideal solutions, this equation may be considerably simplified. If N_b is the mole fraction of the solute, we have

$$\ln N_a = \ln (1 - N_b) = -N_b - \tfrac{1}{2}N_b^2 - \tfrac{1}{3}N_b^3 - \cdots \tag{70}$$

When $N_b = 0.1$, the term $\frac{1}{2}N_b^2$ is only 0.005 and the higher terms in the series are relatively very small. The relation

$$\ln N_a = -N_b \tag{71}$$

is therefore good to 5 per cent when $N_b = 0.1$ and is good to a better precision the smaller the value of N_b, that is, the more dilute the solution. Except for very nearly ideal solutions Raoult's law, upon which Eq. (69)

is based, is hardly likely to be good to a precision as high as this; consequently we are unlikely to lose any precision by substituting $-N_b$ for $\ln N_a$. The replacement of N_b by $mM_a/1000$, where m is molality and M_a is molecular weight of solvent, likewise involves negligible error in dilute solutions (page 45). We have therefore to the precision of the dilute-solution laws

$$\ln N_a = -\frac{mM_a}{1000} \tag{72}$$

The quantity $(1/T_0) - (1/T)$ can be written $\Delta T/TT_0$, where

$$\Delta T = T - T_0$$

is the increase in boiling point produced by the presence of the solute. If T_0 is of the order of 300° or more and ΔT of the order of a few degrees or less, we can replace TT_0 by T_0^2 with negligible error. Hence

$$\frac{1}{T_0} - \frac{1}{T} = \frac{\Delta T}{T_0^2} \tag{73}$$

From Eqs. (69), (72), and (73) we have finally

$$\Delta T = \frac{M_a \mathbf{R} T_0^2}{1000\,\Delta H}\, m \tag{74}$$

To the precision of the dilute-solution laws, then, the elevation of the boiling point, ΔT, is proportional to the molality of the solution. The proportionality constant

$$K_b = \frac{M_a \mathbf{R} T_0^2}{1000\,\Delta H} \tag{75}$$

is called the *boiling-point constant* or the *ebullioscopic constant.* A few values are reported in Table 1. The constant for a given solvent may be

TABLE 1. BOILING-POINT AND FREEZING-POINT CONSTANTS
Boiling point T_b and freezing point T_f are in degrees centigrade

Solvent	T_b	K_b	T_f	K_f
Water	100.0	0.515	0 0	1.86
Benzene	80.2	2.57	5.5	5.12
Acetic acid	118.5	3.07	17.0	3.9
Ethylene bromide	130 0	6.43	9.975	12.5
Camphor	.....	.....	172	40

determined either by direct measurement of the boiling-point elevation of a solution of known molality in that solvent or by calculation from the measured heat of evaporation of the solvent.

Measurements of boiling-point elevation are often used for the determination of the molecular weight of a nonvolatile solute. If a solution of known weight concentration is prepared and the boiling-point elevation is measured, then Eq. (74) makes it possible to calculate the molality, and the ratio of concentration in grams solute per 1000 g solvent to the molality is the molecular weight of the solute.

The Freezing-point Law for Dilute Solutions. We may derive a law for the effect of a solute in dilute solution upon the freezing point of the solution for the particular but rather common case that the solid solvent does not dissolve any significant amount of the solute, *i.e.*, for the case where solid solutions of solute in solvent are not formed. For such a solution the freezing point is the temperature at which pure solid solvent is in equilibrium with the liquid solution, just as the freezing point of the pure solvent is the temperature at which the pure solid and liquid solvents are in equilibrium. This equilibrium between solid and liquid can exist only if the partial vapor pressure of the solvent from the liquid is identical with the partial vapor pressure from the solid. If the two pressures were not identical, a distillation process would occur when both phases are present by which solvent would evaporate from the phase of higher vapor pressure and condense into the phase of lower vapor pressure. This would amount to a spontaneous change in a system which is already in equilibrium, and by the second law of thermodynamics this is impossible.

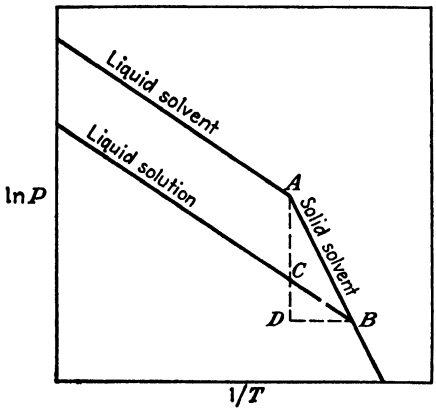


FIG. 4.

We may therefore plot against reciprocal temperature the logarithm of the partial vapor pressures of the solvent from the pure liquid, the pure solid, and the liquid solution as shown in Fig. 4. Point A, at which the plots for pure liquid and solid solvents intersect, must then have as abscissa the reciprocal temperature of the freezing point of the pure solvent, and point B must have the same relationship to the freezing point of the solution. As in the boiling-point case the plots for the two liquid systems will be essentially parallel for dilute solutions, and the slope will be $-\Delta H_l/\mathbf{R}$, where ΔH_l is the heat of evaporation of the liquid solvent. The slope of the plot for the solid will be $-\Delta H_s/\mathbf{R}$, where ΔH_s is the heat of sublimation of the solid solvent. By the geometry of the figure the

ratio of lengths DA/DB must equal the slope of the line AB, which we have just seen to be $-\Delta H_s/\mathbf{R}$; the ratio of the lengths DC/DB must be the slope of CB, which is $-\Delta H_l/\mathbf{R}$. Consequently we can write

$$\frac{DA - DC}{DB} = -\frac{\Delta H_s - \Delta H_l}{\mathbf{R}} \tag{76}$$

By the application of Raoult's law as in the boiling-point case we have

$$DA - DC = \ln N_a \tag{77}$$

and as in that case we have

$$DB = \frac{1}{T} - \frac{1}{T_0} \tag{78}$$

where T_0 is freezing point of pure solvent and T is freezing point of solution. Consequently

$$\frac{\ln N_a}{(1/T) - (1/T_0)} = -\frac{\Delta H_s - \Delta H_l}{\mathbf{R}} \tag{79}$$

The quantity ΔH_s is the enthalpy change for the process solid $\rightleftharpoons$ gas, and the quantity ΔH_l is the enthalpy change for the process liquid $\rightleftharpoons$ gas; the difference $\Delta H_s - \Delta H_l$ is therefore the enthalpy change for the process solid $\rightleftharpoons$ liquid. This enthalpy change is the heat of fusion of the solvent, which we represent by ΔH_f. Consequently

$$\frac{\ln N_a}{(1/T) - (1/T_0)} = -\frac{\Delta H_f}{\mathbf{R}} \tag{80}$$

By operations identical with those which led from Eq. (69) to Eq. (74), except that we define the freezing-point depression ΔT as the decrease in freezing point produced by the solute, *i.e.*, as $T_0 - T$, we obtain finally

$$\Delta T = \frac{M_a \mathbf{R} T_0^2}{1000\, \Delta H_f} m \tag{81}$$

This is of course valid only to the dilute-solution precision. Table 2 illustrates how good this precision is in very dilute solutions. The proportionality constant

$$K_f = \frac{M_a \mathbf{R} T_0^2}{1000\, \Delta H_f} \tag{82}$$

is called the *freezing-point constant* or the *cryoscopic constant.* Values for a few solvents are listed in Table 1. As with the boiling-point constant, values of the freezing-point constant may be derived either from measurements of the freezing point of solutions of known molality or from

TABLE 2. FREEZING POINTS OF DILUTE SOLUTIONS OF MANNITOL IN WATER*

m	T (obs)	T (calc)	T/m
0.00402	0.0075	0.0075	1.86
0.00842	0.0157	0.0156	1.86
0.01404	0.0260	0.0261	1.852
0.02829	0.0525	0.0525	1.856
0.06259	0.1162	0.1162	1.857

* From data of Adams, *J. Am. Chem. Soc.*, **37**, 481 (1915).

thermochemical data. Measurements of freezing-point depression are even more commonly used than measurements of boiling-point elevation for the determination of the molecular weights of solutes.

Standard Free Energy. Many important chemical, biological, and industrial problems can be solved only through a knowledge of equilibrium constants which we do not know how to measure directly at any temperature. We now consider the means available for the calculation of such constants from other measurements. For this purpose it is convenient to define a quantity called the *standard free energy* of a substance and represented by the symbol $\bar{F}^\circ$. For the present we define it by the equation

$$\bar{F}^\circ = E_0 - \mathrm{R}T \ln Q^\circ \tag{83}$$

in which Q° has the meaning of Eqs. (35), (36), and (37) and E_0 is the energy 1 mole of the substance would have if all the molecules were in the lowest energy state. This definition of standard free energy is adequate for all cases in which the ideal law of chemical equilibrium is applicable; a more general and more exact definition will be given later in terms of thermodynamics. For the general chemical reaction [reaction (IV)], the change in standard free energy which accompanies the reaction, and which according to the usual convention we represent by $\Delta\bar{F}^\circ$, is given by

$$\Delta\bar{F}^\circ = m\bar{F}^\circ_M + n\bar{F}^\circ_N \cdots - a\bar{F}^\circ_A - b\bar{F}^\circ_B \cdots \tag{84}$$

Thus in the reaction

$$\mathrm{N_2} + 3\mathrm{H_2} \rightleftharpoons 2\mathrm{NH_3} \tag{VI}$$

the standard free-energy change is given by

$$\Delta\bar{F}^\circ = 2\bar{F}^\circ_{\mathrm{NH_3}} - \bar{F}^\circ_{\mathrm{N_2}} - 3\bar{F}^\circ_{\mathrm{H_2}} \tag{85}$$

Substituting the proper values of Eq. (83) in Eq. (84), we have

$$\Delta\bar{F}^\circ = \Delta E_0 - m\mathrm{R}T \ln Q^\circ_M - n\mathrm{R}T \ln Q^\circ_N + a\mathrm{R}T \ln Q^\circ_A + b\mathrm{R}T \ln Q^\circ_B \tag{86}$$

Comparing this with Eq. (39), we see that

$$\Delta\bar{F}^\circ = -\mathrm{R}T \ln K \tag{87}$$

We can write a pair of important equations which parallel Eqs. (83) and (86) from the following considerations: Equation (50) may be rearranged to

$$H = E_0 + \mathrm{R}T^2 \frac{d \ln Q^\circ}{dT} \tag{88}$$

Substitution of the proper values of this equation in Eq. (53), followed by the replacement of $d \ln K/dt$ by $\Delta H/\mathrm{R}T^2$ according to Eq. (56), leads to

$$\Delta H = \Delta E_0 + m\mathrm{R}T^2 \frac{d \ln Q^\circ_M}{dT} + nRT^2 \frac{d \ln Q^\circ_N}{dT} \cdots - a\mathrm{R}T^2 \frac{d \ln Q^\circ_A}{dT} - b\mathrm{R}T^2 \frac{d \ln Q^\circ_B}{dT} \cdots \tag{89}$$

Spectroscopic Approach to the Value of an Equilibrium Constant. For many simple molecules it is possible through the study of the spectrum in the gaseous state, combined with the application of general quantum-mechanical principles, to derive values of the energy levels and the multiplicities. From these we can by substitution in Eq. (9) obtain values of the partition function at any temperature and through Eq. (35) can convert these values to values of the quantity Q°. From a series of such values over a range of temperatures we can by empirical or analytical differentiation obtain values of the quantity $d \ln Q^\circ/dT$. By Eqs. (83) and (88) we may then compute values of the quantities $\bar{F}^\circ - E_0$ and $H - E_0$ at any desired temperature or temperatures. Figure 5 shows the results of such a computation for nitric oxide. By the nature of the computations the E_0 involved is a somewhat fictitious quantity, namely, the energy which 1 mole of nitric oxide would have if it were gaseous and all the molecules were in the lowest energy state. In fact the only way a large proportion of the molecules can be got into the lowest level is to go to extremely low temperatures, and at these temperatures neither nitric oxide nor any other substance is gaseous.

If such computations have been made for all the substances involved in a particular reaction and if the ΔH value for the reaction has been measured calorimetrically at some temperature in the range of the calculations, substitution of the value of ΔH and of the values of the $d \ln Q^\circ/dT$ quantities for the substances involved in the reaction into Eq. (89) leads immediately to the value of ΔE_0. This quantity is therefore an experimentally well defined entity. Using this value of ΔE_0 together with the appropriate values of the $\ln Q^\circ$ quantities for the substances involved in Eq. (86), the value of $\Delta \bar{F}^\circ$ for the reaction follows and the value of the equilibrium constant can then be gotten from Eq. (87).

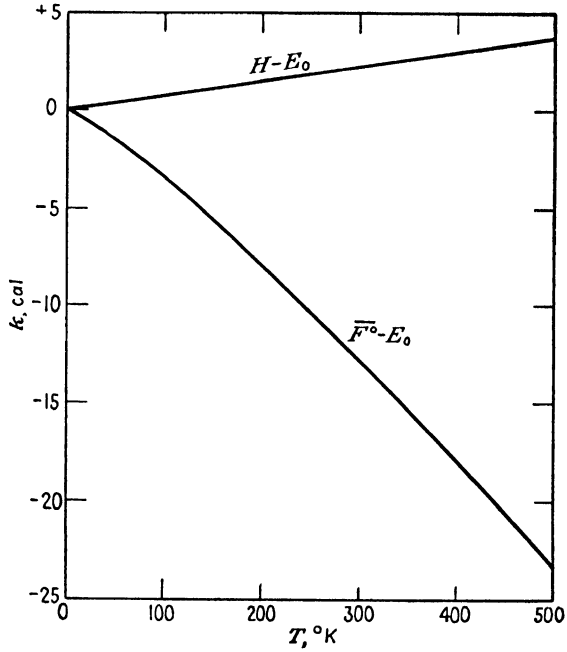


FIG. 5. Enthalpies and standard free energies of gaseous nitric oxide computed from the spectrum. [*Johnston and Chapman, J. Am. Chem. Soc.*, **55**, 153 (1940).]

Table 3 illustrates the kind of results that may be obtained by this method, the reaction being

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad (V)$$

Many other verifications of this sort have been obtained. Such data emphasize the validity of the Boltzmann equation and the other quantum-

TABLE 3. COMPARISON OF OBSERVED AND SPECTROSCOPICALLY COMPUTED VALUES OF THE EQUILIBIRUM CONSTANT OF THE WATER-GAS REACTION, $CO_2 + H_2 \rightleftharpoons CO + H_2O$*

T, °C	K (obs)	K (calc)
400	0.080	0.087
600	0.410	0.380
800	0.93	0.95
1000	1.66	1.70

* Observed values from Neumann and Köhler, *Z. Elektrochem*, **34**, 218 (1928); computed values from Kassel, *J. Am. Chem. Soc.*, **56**, 1838 (1934).

mechanical principles and justify the use of this method for computing equilibrium constants which are not accessible to direct measurement.

Unfortunately the method can be used only with relatively simple molecules because the spectra become too complicated and the spectral lines too closely spaced to permit the necessary analysis with more complicated ones.

The Third-law Approach. In the limit of very low temperatures the term $\mathbf{R}T \ln Q^\circ$ must vanish unless Q° becomes infinite. To check on this, we write the first few terms in the definition of the partition function [Eq. (9)],

$$Q = g_0 + g_1 e^{-(\epsilon_1 - \epsilon_0)/\mathbf{k}T} + g_2 e^{-(\epsilon_2 - \epsilon_0)/\mathbf{k}T} + \cdots \tag{90}$$

The first term might have been written out as

$$g_0 e^{-(\epsilon_0 - \epsilon_0)/\mathbf{k}T}$$

but this reduces to g_0 because $e^0 = 1$. This term is independent of temperature, but all the other terms decrease in magnitude as the temperature decreases and approach zero as the temperature approaches zero. This is because in the limit $(\epsilon_i - \epsilon_0)/\mathbf{k}T \to \infty$ and $e^{-\infty} = 0$. We have therefore

$$\lim_{T \to 0} Q = g_0 \tag{91}$$

and by Eq. (37), which applies since all substances are solid or liquid in the limit of low temperatures,

$$\lim_{T \to 0} Q^\circ = g_0^{1/n} \tag{92}$$

and

$$\lim_{T \to 0} \ln Q^\circ = \frac{1}{n} \ln g_0 \tag{93}$$

Since the multiplicity cannot be either zero or infinite, its logarithm cannot be infinite in either direction. Consequently

$$\lim_{T \to 0} (RT \ln Q^\circ) = 0 \tag{94}$$

and

$$\lim_{T \to 0} \bar{F}^\circ = E_0 \tag{95}$$

It can be shown by simple manipulation of Eq. (46) that the quantity $\mathbf{R}T^2(d \ln Q^\circ/dT)$ of Eq. (88) consists of a summation of the following kind:

$$\mathbf{R}T^2 \frac{d \ln Q^\circ}{dt} = \frac{\mathbf{N}(\epsilon_1 - \epsilon_0) g_1 e^{-(\epsilon_1 - \epsilon_0)/\mathbf{k}T}}{nQ} + \frac{\mathbf{N}(\epsilon_2 - \epsilon_0) g_2 e^{-(\epsilon_2 - \epsilon_0)/\mathbf{k}T}}{nQ} + \cdots \tag{96}$$

For reasons which we have just discussed the exponential factor in each of these terms approaches zero as the temperature approaches zero. The factor Q does not approach zero, and the other factors are independent of temperature and finite. Consequently each term in the summation approaches zero, and we have

$$\lim_{T\to 0} \mathbf{R}T^2 \frac{d \ln Q^\circ}{dT} = 0 \tag{97}$$

By Eq. (88) then

$$\lim_{T\to 0} H = E_0 \tag{98}$$

With the knowledge represented by Eq. (98) we are in a position to integrate the equation [cf Eq. (21) of Chap. V]

$$dH = C_P\, dT \tag{99}$$

with 0°K as the lower limit of the integration. We obtain

$$\int_{E_0}^{H_\tau} dH = \int_0^\tau C_P\, dT \tag{100}$$

Hence

$$H_\tau - E_0 = \int_0^\tau C_P\, dT \tag{101}$$

H_τ being the value of H at the temperature τ which is the upper limit of the integration. Using τ to represent the temperature, we now rearrange Eq. (88) and integrate over the temperature range from 0 to Φ, getting

$$\mathbf{R} \int_0^\Phi \frac{d \ln Q^\circ}{d\tau}\, d\tau = \int_0^\Phi \frac{H_\tau - E_0}{\tau^2}\, d\tau \tag{102}$$

In the light of Eq. (93) the left side of this equation may be evaluated as $(\mathbf{R} \ln Q^\circ) - (\mathbf{R} \ln g_0^{1/n})$. Using the value of $\ln Q^\circ$ given by Eq. (83), Eq. (102) is then easily transformed into

$$\bar{F}_\Phi^\circ - E_0 = -\mathbf{R}\Phi \ln g_0^{1/n} - \Phi \int_0^\Phi \frac{H_\tau - E_0}{\tau^2}\, d\tau \tag{103}$$

The determination of the value of the integral on the right side of Eq. (101) amounts to the determination of the area included between a curve of the type of those illustrated in Fig. 3 of Chap. V, the horizontal axis, and the ordinate for the temperature τ. The only difficulty is that of getting experimental values of heat capacity at temperatures low enough so that C_P is very close to zero and may be expected to remain essentially zero at all lower temperatures. These are not insurmountable. So long as fusion, evaporation, or other change of state does not occur, this integral yields the value of $H_\tau - E_0$ without further ado. Where these

occur, one takes the value of the heat-capacity integral up to the temperature of the transition, adds the enthalpy change for the transition, and continues the integration of the heat capacity up to the temperature of interest or to the next transition.

With values of the quantity $H_T - E_0$ determined in this way for the temperature range from zero to the temperature of interest, the integral which forms the last term of Eq. (103) may be evaluated either graphically or by equivalent methods. If then the value of $g_0^{1/n}$, the multiplicity of the lowest energy level, can be estimated, the value of the quantity $\bar{F}^\circ - E_0$ can be estimated for any temperature within the range. If such measurements are made for all the substances involved in a reaction, the problem of computing $\Delta\bar{F}^\circ$ values and equilibrium constants would then become the same as it was in the spectroscopic approach of the last section.

Fortunately the problem is a bit simpler than that of obtaining the g_0 values of individual substances, for the quantity we wish ultimately to obtain is a $\Delta\bar{F}^\circ$ value, not the individual $\bar{F}^\circ$ values. Thus for the reaction $XY \rightleftharpoons X + Y$ we need only know the difference

$$\ln (g_0^{1/n})_X + \ln (g_0^{1/n})_Y - \ln (g_0^{1/n})_{XY}$$

Theory predicts that many of the factors that determine the $g_0^{1/n}$ values affect reactants and products in the same way; consequently the difference tends to be more nearly zero than any individual $\ln g_0^{1/n}$ value. And even before the theory developed, it had been found empirically that there is considerable justification for a rule, often called the *third law of thermodynamics*, which is equivalent to the hypothesis that such differences in $\ln g_0^{1/n}$ are always zero. It is therefore customary to assume that the term $\mathbf{R}\Phi \ln g_0^{1/n}$ of Eq. (103) can be omitted. This seems to be justified in most cases. Thus a survey of the available data involving reactions of organic compounds by Parks and Huffman in 1932 showed that in seven different reactions the average deviation between the experimental value of the equilibrium constant and the value calculated by the third-law method was of the order of 30 per cent. This apparently large difference was in no case larger than could be expected from the uncertainty of the experimental data available, the most serious uncertainty arising from the calorimetric values of the heats of reaction. Since moreover we have no other method than this for estimating even the order of magnitude of the equilibrium constants of many reactions of great practical importance, an estimate of the value of an equilibrium constant of even this precision is extremely valuable. This is the justification for the large amount of work that currently goes on in the difficult and expensive field of the measurement of heat capacities at temperatures down to the liquid-

hydrogen range and in the effort to refine and improve the precision of calorimetric measurements.

In Fig. 6 we have plotted the values of $H - E_0$ and of $\bar{F}^\circ - E_0$ obtained in this way from heat-capacity measurements on carbon disulfide. The sharp increase in H at $T = 161$ is the heat of fusion of the crystalline substance, this temperature being the melting point. The E_0 of this plot and of the third-law treatment generally is the energy of 1 mole of the substance in the form in which it exists as the temperature approaches zero. In this case the form is that of a crystalline solid; in no case will it be gaseous.

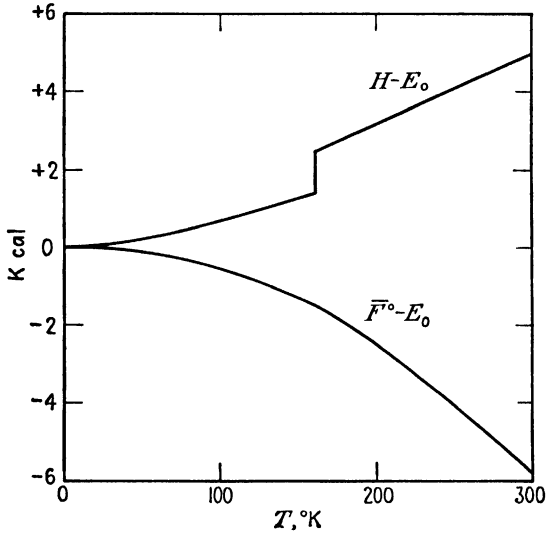


FIG. 6. Enthalpy and standard free energy of solid and liquid carbon disulfide from third-law calculations. [*Brown and Manov, J. Am. Chem. Soc.*, **59**, 500 (1937).]

Combination of Standard Free-energy Changes. A considerable virtue of the treatment of equilibria in terms of standard free-energy changes is that it involves only the sums and differences of quantities, the values of reactants and products, each of which is a characteristic property of a single substance [*cf.* Eqs. (84) and (85)], independent of the particular reaction in which it is involved. Thus for the reaction $A \rightleftharpoons B$ the standard free-energy change is $\Delta\bar{F}^\circ_{AB} = \bar{F}^\circ_B - \bar{F}^\circ_A$, and for the reaction $A \rightleftharpoons C$ it is $\Delta\bar{F}^\circ_{AC} = \bar{F}^\circ_C - \bar{F}^\circ_A$. Consequently for the reaction $B \rightleftharpoons C$ we have $\Delta\bar{F}^\circ_{BC} = \bar{F}^\circ_C - \bar{F}^\circ_B = \bar{F}^\circ_C - \bar{F}^\circ_A - (\bar{F}^\circ_B - \bar{F}^\circ_A) = \Delta\bar{F}^\circ_{AC} - \Delta\bar{F}^\circ_{AB}$. Generalizing this conclusion, we obtain a formalization identical with that we met earlier with respect to enthalpy changes in reactions (page 64): we may add and subtract chemical equations according to algebraic rules, canceling out common terms on opposite sides of the resulting equations, and

transferring terms from one side to the other if the sign is changed. When we perform the same additions and subtractions on the $\Delta\bar{F}^\circ$ values for the reactions, the result is the $\Delta\bar{F}^\circ$ value for the reaction which results from the operations on the equations.

In view of the relation between $\Delta\bar{F}^\circ$ and K [Eq. (87)] this procedure of combining $\Delta\bar{F}^\circ$ values by addition and subtraction is equivalent to that of combining equilibrium constants by multiplication and division (page 125).

Standard Free Energy of Formation. In the light of the rule just formulated it is possible, just as it was in the case of enthalpy changes, to condense a large number of data on the standard free-energy change of reactions into the smaller compass of a table of the standard free-energy changes for the formation of compounds from the elements. From such a table the standard free-energy change for any reaction involving the compounds listed and their elements can then be calculated in the same simple way that is used for the calculation of the enthalpy change of a reaction from a table of enthalpies of formation of compounds. Table 4

TABLE 4. STANDARD FREE ENERGIES OF FORMATION AT 25°C IN KILOCALORIES PER MOLE*

HCl(g)	−22.778
HI(g)	+0.365
H_2O(g)	−54.6351
H_2O(1)	−56.6899
H_2S(g)	−7.85
C_2H_6(g)	−7.860
C_2H_4(g)	+16.282
C_2H_2(g)	+50.000
CO(g)	−32.808
CO_2(g)	−94.260
NH_3(g)	−3.903
NO(g)	+20.719
SO_2(g)	−71.68
SO_3(s, α form)	−88.22
CaO(s)	−144.3
$CaCO_3$(s)	−270.8
NaCl(s)	−91.894

* From "Chemical Engineers' Handbook."

contains a selection of values of the standard free energy of formation of compounds from the elements. The quantity is often listed in reference and textbooks as the *molal free energy* of the compound.

In principle one might accomplish the same result by tabulating equilibrium constants for the formation of compounds from the elements, and at first sight this might seem a more direct approach. A good case can, however, be made against this procedure because of the extremely large

and small values of K involved. Thus the equilibrium constant at 25°C for the formation of water,

$$K = \frac{P_{H_2O}}{P_{H_2} P_{O_2}^{1/2}} \tag{104}$$

would have the value 1.01×10^{40}. Since we define the equilibrium constant in terms of the ratios of partial pressures, such a value of K implies a serious belief that the partial pressure of oxygen in equilibrium with water vapor at 25° and 1 atm is 8.5×10^{-28} atm and that its concentration is 3.5×10^{-29} mole/liter. In view of the atomic nature of matter and the known value of the Avogadro constant such a concentration has no physical meaning. This deprives K of physical meaning in terms of the original definition but would not do so if one defined K by Eq. (87), *i.e.*, in terms of standard free-energy changes. The definition of $\Delta\bar{F}°$ in terms of Eqs. (83) and (84) leads to no difficulties of this sort because the $Q°$ quantities are physically meaningful properties of the substances involved, no matter how large or small $\Delta\bar{F}°$ may be. However, the temptation to give the same name to quantities which are defined by different physical operations of measurement is one of the greatest logical perils to which the scientist is subject, and it is safer to employ the free-energy treatment and to reserve the use of the equilibrium constant for cases where it is physically meaningful as a ratio of concentrations.

Standard Entropy. Text- and reference books frequently tabulate values of the standard entropies of elements and compounds, usually at 25°C. The standard entropy $\bar{S}°$ is defined by the equation

$$\bar{S}° = \frac{H - \bar{F}°}{T} \tag{105}$$

and the standard entropy change in a reaction is taken as the sum and difference of the standard entropy values of the reacting substances in the same way as is done in the case of standard free-energy change or standard enthalpy change. Consequently

$$\Delta\bar{S}° = \frac{\Delta H - \Delta\bar{F}°}{T} \tag{106}$$

A table of $\bar{S}°$ values therefore enables one to calculate the $\Delta\bar{S}°$ value for the formation of any compound, and from a table of enthalpies of formation and Eq. (106) one can then calculate the standard free energy of formation of the compound. A table of standard entropies plus a table of enthalpies of formation is therefore equivalent to a table of standard free energies of formation and one of enthalpies of formation; it may be

used for the same purposes, and the values it contains may be obtained by the same methods.

A useful equation is obtained by substituting the value of $\Delta\bar{F}^\circ$ in terms of the equilibrium constant [Eq. (87)] in Eq. (106), getting

$$\Delta\bar{S}^\circ = \frac{\Delta H + \mathbf{R}T \ln K}{T} \tag{107}$$

This may be rearranged to

$$K = e^{\Delta\bar{S}^\circ/\mathbf{R}} e^{-\Delta H/\mathbf{R}T} \tag{108}$$

Further Remarks on the Temperature Dependence of Equilibrium Constant and Heat of Reaction. As we have shown, the partition function of a substance at a given temperature is larger the more closely spaced the energy levels and the greater the multiplicity of the levels of the substance. By Eq. (83), therefore, the negative quantity $\bar{F}^\circ - E_0$ has a greater magnitude the closer the spacing and the greater the multiplicity. It is also true that the quantity $H - E_0$ has a greater magnitude the closer the spacing of the energy levels. This can be appreciated from the discussion of page 95. We saw there that with wide spacing practically all the molecules might be in the lowest level at a given temperature. Under such conditions H would equal E_0. With closer spacing many of the molecules would be in higher levels at the same temperature, and H would be larger than E_0. It follows that the plot of $\bar{F}^\circ - E_0$ in Fig. 5 or 6 must drop more sharply the closer the spacing of the energy levels and that the plot of $H - E_0$ must rise more sharply the closer the spacing. It follows also that the entropy, which measures the divergence of the two plots, must increase with increased closeness of spacing.

Consider now three reactions of the type $A \rightleftharpoons B$ for all of which ΔE_0 is positive. In case 1 let the energy levels of B be more closely spaced than those of A. Plots of H_B and $\bar{F}^\circ_B$ must then diverge more widely from their common initial value E_{0B} than do plots of H_A and $\bar{F}^\circ_A$. We shall therefore have the sort of situation shown in Fig. 7. In this case $\Delta\bar{F}^\circ$ is positive at low temperatures, which means by Eq. (87) that K is less than 1. As the temperature rises, the two $\bar{F}^\circ$ plots come nearer together and K increases, both because of the decrease in $\Delta\bar{F}^\circ$ and because of the increase in temperature, since

$$\ln K = -\frac{\Delta\bar{F}^\circ}{\mathbf{R}T} \tag{109}$$

At the temperature at which the two $\bar{F}^\circ$ curves intersect, $K = 1$, and at higher temperature K is greater than 1. Meanwhile the enthalpy change of the reaction, which was positive at $T = 0$, remains positive and

indeed increases with increasing temperature. All dissociation reactions are of this type.

In case 2 let the energy levels be less closely spaced for B than for A. The H_B and $\bar{F}_B^\circ$ plots then diverge less widely than the H_A and $\bar{F}_A^\circ$ plots, and we have the kind of situation shown in Fig. 8. Here $\Delta\bar{F}^\circ$ is positive at all temperatures and increases in magnitude with increase in temperature. K is therefore always less than 1, and its magnitude depends on the opposing effects of the variation in $\Delta\bar{F}^\circ$ and in T in Eq. (109). ΔH, initially positive, decreases with increasing temperature and eventually goes through zero and becomes positive. By virtue of Eq. (56), K must

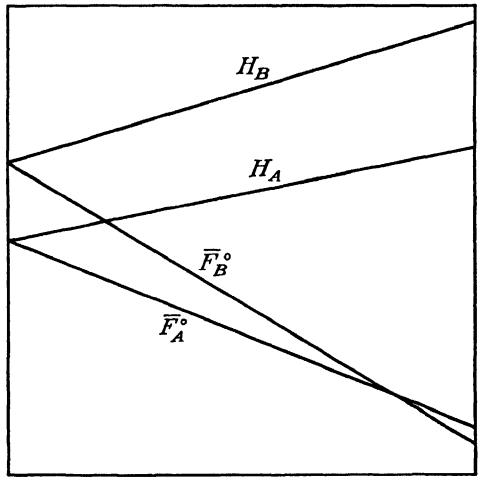


FIG. 7.

increase with increasing temperature at low temperatures, go through a maximum at the temperature at which $\Delta H = 0$, and decrease at higher temperatures. The ionization of acetic acid and other carboxylic acids in water (page 344) is an example of this case, the temperature for which $\Delta H = 0$ being in the region of room temperature.

Finally it may happen that the divergence of the H_B and $\bar{F}_B^\circ$ plots is essentially identical with the divergence of the H_A and $\bar{F}_A^\circ$ plots as shown in Fig. 9. ΔH and $\Delta\bar{F}^\circ$ are both independent of temperature and are equal to each other and to ΔE_0. K is small at low temperatures but increases with increasing temperature, approaching g_{0B}/g_{0A} as the temperature becomes infinite.

Conclusions on the Determination of Equilibrium Constants. We possess the following methods for obtaining the equilibrium constant, or,

what amounts to the same thing, the value of the standard free-energy change of a reaction:

1. Direct determination.
2. Calculation of the constant of one equilibrium from the equilibrium constants of other reactions.
3. Calculation of the equilibrium constant at one temperature from a measurement at another.
4. Analysis of the spectra of the reacting substances, calculation from these results of the partition functions, and the use of a calorimetric determination of ΔH at some temperature.

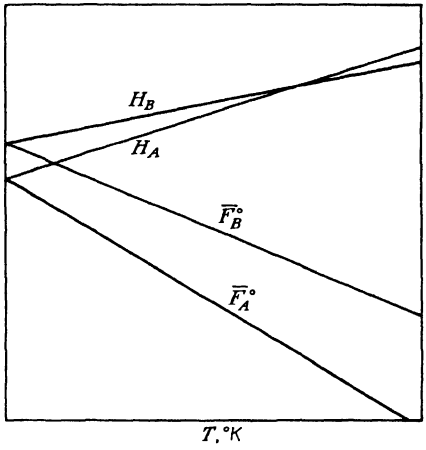


FIG. 8.

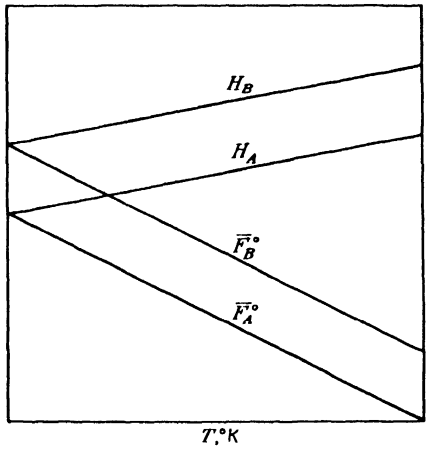


FIG. 9.

5. Calculation of $\Delta\bar{F}^\circ$ values by integration of heat capacities from very low temperatures combined with a calorimetric heat of reaction at some temperature.
6. A method, to be discussed later (Chap. X), in which standard free-energy changes are computed from measurements on galvanic cells in which the reaction involved takes place.

The ultimate aim of work in this field is to tabulate standard free energies of formation or standard entropies of formation at 25°C, heats of formation at the same temperature, and heat capacities as functions of temperature for all substances. From such tabulations equilibrium constants at any temperature within the range of the heat-capacity equations may be computed for any reaction involving the substances tabulated.

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PROBLEMS

1. If the energy levels of a molecule A are given by $\epsilon = 1 \times 10^{-13}n$, where ϵ is energy per molecule in ergs and n is 0, 1, 2, 3, etc., calculate to four significant figures the value of the partition function of the substance at 350° and at 500°K. Take the multiplicities to be 1 in all levels.

2. Calculate the partition function at 350°K for a molecule B whose energy levels are given by $\epsilon = (0.7 \times 10^{-13}n) + (0.1 \times 10^{-13})$.

3. What is the equilibrium constant at 350°K of the reaction $A \rightleftharpoons B$?

4. What is the value of ΔH for this reaction at 350°K?

5. Using data from the tables in this text calculate the equilibrium constant of the reaction $C_2H_6 \rightleftharpoons C_2H_4 + H_2$ at 25°C. Calculate also the fraction to which ethane will be dissociated according to this reaction at 25°C and 1 atm total pressure.

6. Calculate the equilibrium constant for this dissociation of ethane and the degree of dissociation at 500°K, assuming ΔH independent of temperature.

7. Calculate the same equilibrium constant and degree of dissociation, taking into account the dependence of ΔH on the temperature.

8. Compute the temperature at which the degree of dissociation of ethane at 1 atm will be 1 per cent.

9. It has been found experimentally that log K for the reaction $H_2(g) + \frac{1}{2}S_2(g) \rightleftharpoons H_2S(g)$ is 2.205 at 1023°K and 0.964 at 1338°K. Calculate the value of log K and of $\Delta\bar{F}°$ at 298.2°K. Explain why the value of $\Delta\bar{F}°$ differs from the standard free energy of formation of H_2S given in Table 4.

10. Calculate from data in the tables the degree of dissociation of HCl into H_2 and Cl_2 at 1800°K.

11. Derive expressions analogous to Eqs. (63) and (65) for the dependence of ΔH and of ln K on temperature for the case that $\Delta C_P = a + bT - cT^{-2}$.

12. At 100°C the heat of evaporation of water is 538.7 cal/g. Assuming the specific heat of liquid water is 1 cal/g-deg and using other data from this text, calculate the heat of evaporation of water at 0°C. What is the value of the quantity $d \ln P/dT$, where P is vapor pressure of water when the temperature is 100°C? What is the value at 0°C?

13. The pressure P of water vapor over a mixture of $CuSO_4 \cdot 5H_2O$ and $CuSO_4 \cdot 3H_2O$ is 8.07 mm at 26.30°C and 21.73 mm at 39.70°C. What is the value of ΔH for the process $CuSO_4 \cdot 5H_2O \rightleftharpoons CuSO_4 \cdot 3H_2O + 2H_2O$ in this range of temperature?

14. Perrin found that the number of particles per unit volume of a suspension of resin droplets in water varies with height according to the equation $N = ae^{-bh}$, where a and b are constants for a given sample, h is height, and N is number of droplets per cubic centimeter. It is possible experimentally to determine the values of a and b in this equation in a suspension whose particles are small enough to prevent complete settling out but large enough so that the particle size can be measured under the

microscope. The density ρ of the resin is known. Show how a value of Avogadro's number **N** can be obtained from this experiment.

15. A certain aqueous solution freezes at -0.186°C. What is its vapor pressure at 25°C?

16. If the molecular weight of the solute in Prob. 15 is to be calculated to a precision of 5 per cent, what error is permissible in the vapor-pressure measurement? What error in temperature is permissible in the freezing-point measurement?

17. The quantity $d \ln P/dT$, P being vapor pressure, has the value of 0.0132 deg^{-1} for chloroform in the neighborhood of 61°C, its boiling point at 1 atm. By how much will the boiling point of chloroform be increased by a nonvolatile solute present at a molality of 0.1?

18. If the freezing-point constant of diphenyl is 8.0 and the freezing point is 70.2°C, what is the heat of fusion of diphenyl?

19. Explain why Eq. (74) cannot be used to determine the molecular weight M_a of the solvent in a dilute solution through measurements of the boiling-point elevation produced by a solute of known molality even though M_a appears in the equation.

20. A solution of 2.28 g of phenol in 100 g of $CHBr_3$ freezes 1.191° lower than pure $CHBr_3$, whose freezing point is 8°C. What fraction of the phenol is associated into double molecules, assuming that dimerization is the only reaction occurring? The freezing-point constant is 14.1.

21. From Fig. 3 of Chap. V estimate graphically the values of the quantities $H - E_0$ and $\bar{F}^\circ - E_0$ for aluminum at 25°C.

22. Show from Eqs. (83), (88), and (105) that $\bar{S}^\circ = -d\bar{F}^\circ/dT$ and hence that $\Delta\bar{S}^\circ = d(\mathbf{R}T \ln K)/dT$.

23. Show from the result of Prob. 22 that $d\bar{S}^\circ/dT = C_P/T$.

24. Prove that the slope of a plot of $\bar{F}^\circ$ against T, such as that of Fig. 6, must change discontinuously at a melting point or at any other temperature at which heat is absorbed at constant temperature.

25. At 75°C and 1 atm total pressure N_2O_4 is 74.1 per cent dissociated into NO_2; at 15°C and 1 atm the per cent dissociated is 12.2. If a sample of N_2O_4 is sealed in a vessel at 75°C and 1 atm, what will be the pressure when the temperature reaches 15°C?

CHAPTER IX

THE RATE OF CHEMICAL REACTION IN HOMOGENEOUS SYSTEMS

Definitions. The term *rate of reaction* is sometimes used for the quantity of material reacting or produced by reaction per unit time. If, then, n is moles of reacting material and t is time, rate of reaction is $-dn/dt$; if n is moles of reaction product, rate of reaction is $+dn/dt$. Rather more frequently the term rate of reaction is applied to the quantity of material reacting or produced per unit time in unit volume, *i.e.*, rate r is given by

$$r = \pm \frac{1}{v}\frac{dn}{dt} \tag{1}$$

where v is volume. If the volume is constant, as will be true to sufficient precision for any reaction in dilute solution but may or may not be true for a reaction in the gas phase,

$$r = \pm \frac{dc}{dt} \qquad (v \text{ constant}) \tag{2}$$

since

$$\frac{dc}{dt} = \frac{d(n/v)}{dt} = \frac{1}{v}\frac{dn}{dt} \tag{3}$$

if v varies, however,

$$\frac{dc}{dt} = \frac{v\dfrac{dn}{dt} - n\dfrac{dv}{dt}}{v^2}$$

$$= \pm r - \frac{c}{v}\frac{dv}{dt} \tag{4}$$

$$r = \pm \left(\frac{dc}{dt} + \frac{c}{v}\frac{dv}{dt}\right) \qquad (v \text{ variable}) \tag{5}$$

First Principle of Chemical-reaction Kinetics. It is a basic assumption of all work in this field, an assumption which we shall call the *first principle of chemical-reaction kinetics*, that, within the precision of the perfect-gas and dilute-solution approximations, the rate of a chemical reaction is proportional to the product of the concentrations of the reacting substances and depends on no other concentrations than those of the

actually reacting substances. The phrase "product of concentrations" is to be interpreted in the sense that the rate of a reaction involving two molecules of the same kind is proportional to the square of the concentration of that kind of molecule. This principle is partly generalization from experience and partly a reasonable conclusion from the kinetic theory, involving the assumption that at a given temperature a fixed fraction of the molecules which collide react. At first sight it appears to be a difficult principle to uphold, for the apparent exceptions are at least as numerous as the verifications. Before considering these complications, we shall discuss the behavior of some cases which are in obvious agreement.

Specific Rate and Order of Reaction. If the empirically observed rate of a reaction involving the substances A, B, C, etc., is given at constant temperature by an equation of a form consistent with the first principle, such as

$$r = k[A] \tag{6}$$
$$r = k[A]^2 \tag{7}$$
$$r = k[A][B] \tag{8}$$
$$r = k[A][B][C] \tag{9}$$

the proportionality constant k is called the *specific rate* or the *rate constant.* The former term, which is more descriptive than the latter, follows from the fact that k is the actual rate divided by the product of the concentrations of the reacting substances. It is sometimes useful to recognize that it is the rate when the concentrations of all reactants are unity.

The *order of the reaction* is the sum of the exponents of the concentration factors which appear in the rate equation. The order is 1 if Eq. (6) applies, 2 if Eq. (7) or (8) fits the data, 3 if Eq. (9) is applicable. The *order of the reaction with respect to* A is 1 in the cases represented by Eqs. (6), (8), and (9), 2 in that represented by Eq. (7).

Methods of Measurement. Although there are ways of measuring a reaction rate directly, it is a more common procedure to measure the change in the concentration of reactant or of reaction product in a finite time interval. The experimental problem is much the same as that involved in measuring the concentrations of the substances present in a system at equilibrium, and we have the same resources: (1) We may be lucky enough to be working with a slow reaction and to have methods of analysis fast enough so that the analysis can be completed within a time interval in which the amount of reaction is negligible, (2) We may use some physical property whose instantaneous value can be measured without disturbing the system, (3) We may be able to freeze the system by a sudden drop in temperature or by neutralization or removal of a catalyst. In many cases we measure a concentration other

than the one we want and compute the desired value from material-balance considerations as illustrated on page 176.

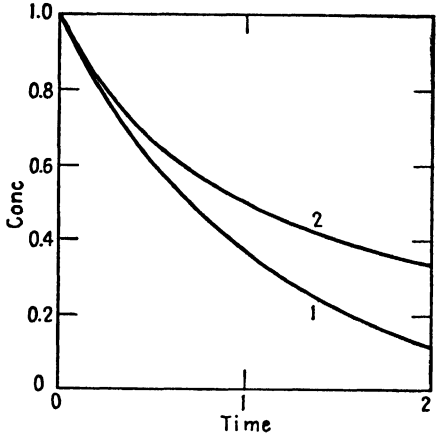


FIG. 1. Plots of concentration of reactant against time for (1) a first-order and (2) a second-order reaction. $k = 1$ and $c_0 = 1$ in both cases.

Having thus obtained values of the concentration at a series of time intervals, we might then plot these against time and attempt to obtain the slope of the curve, which is the desired rate, either graphically or analytically. Such a plot is inherently a rather sharply curved one as is shown in Fig. 1, and empirical differentiation of data which plot in this way is never a very precise procedure. Consequently we generally attempt to apply an integrated form of a relationship of the type of Eqs. (6) to (9) in such a way that the specific rate can be obtained from the slope of a linear or nearly linear plot.

First-order Reaction. For a first-order reaction in a system of constant volume we have from Eqs. (2) and (6)

$$-\frac{dc}{dt} = kc \tag{10}$$

with c the concentration of the reactant A. Separating the variables and integrating (ST 230), we get

$$-\int \frac{dc}{c} = k \int dt + X \tag{11}$$

from which

$$-\ln c = kt + X \tag{12}$$

If we choose the time scale so that $t = 0$ at the beginning of the reaction and represent the concentration at the beginning by c_0, the integration constant X is seen to equal $-\ln c_0$ and we get

$$\ln c_0 - \ln c = kt \tag{13}$$

or

$$\ln \frac{c_0}{c} = kt \tag{14}$$

Consequently a plot of ln c against t will be a straight line whose easily determined slope is the value of k. Since

$$\log c_0 - \log c = \frac{kt}{2.303} \tag{15}$$

plot of log c against t will have a slope of $k/2.303$.

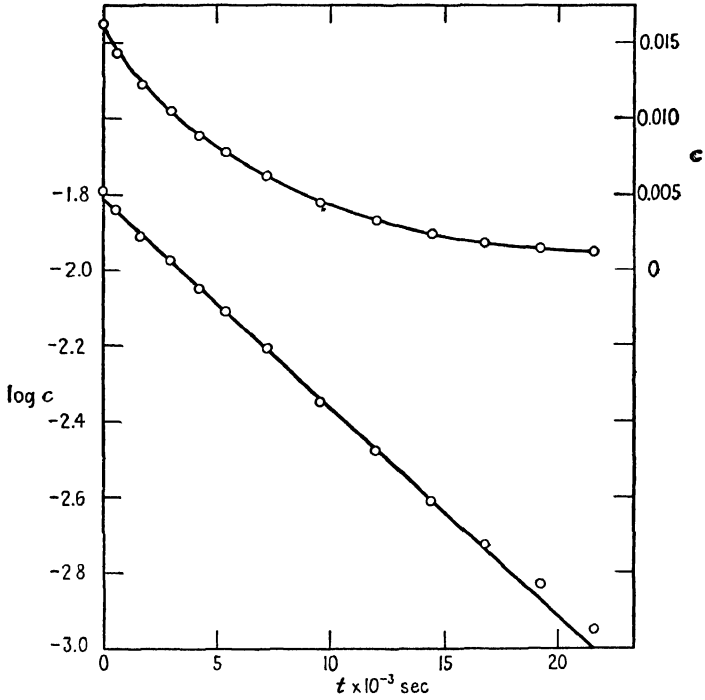


FIG. 2. Decomposition of N_2O_5 in the gas phase. Plots of c, the concentration of N_2O_5, and of log c against time t. [*Data of Daniels and Johnston, J. Am. Chem. Soc.*, **43**, 53 (1921).] Some of the experimental points omitted to avoid crowding.

Figure 2 presents data on the decomposition of nitrogen pentoxide,

$$2N_2O_5 \rightarrow 2N_2O_4 + O_2 \tag{I}$$
$$N_2O_4 \rightleftharpoons 2NO_2 \tag{II}$$

a reaction which has been very thoroughly and carefully studied. The figure includes a plot of the concentration of nitrogen pentoxide against time and also one of the logarithm of the concentration against time. Except for the last few points, for which the concentration is so low that the uncertainty in its measurement is large, the points in the logarithmic plot lie closely along a straight line, whose slope, -5.48×10^{-5}, corre-

sponds to a rate constant 2.303 times larger, *i.e.*, to 1.257×10^{-4} sec^{-1}. The actual measurement of the concentration of reactant in this case derived from a measurement of total pressure, and the computation was considerably complicated by the reversible reaction (II). This reaction in both directions is known to be very rapid compared with reaction (I), and the equilibrium constant has been measured over a wide range of temperatures. It is further known that the only substances present in the system formed by the partial decomposition of N_2O_5 are N_2O_5, N_2O_4, NO_2, and O_2. With this information and a knowledge of the volume of the vessel in which the reaction takes place and the reaction temperature, two measurements, one of the total pressure at time t, the other of the total pressure when the decomposition of the N_2O_5 is practically complete, suffice for the computation of the concentration of N_2O_5 at time t. The principles involved are those employed in many of the calculations of Chap. VII; we shall not discuss their application to the present case in detail but shall consider a simpler case.

Suppose the reaction

$$A \rightarrow 2B \tag{III}$$

occurs cleanly in the gas phase. If we start with A alone at partial pressure P° in a vessel of fixed volume, then at time t when the partial pressure of A has dropped to P_A the partial pressure of B will be $2(P_A^\circ - P_A)$ and the total pressure $P = P_A + P_B$ will equal $2P^\circ - P_A$. Consequently

$$P_A = 2P^\circ - P \tag{16}$$

and the concentration of A, which we represent by c, will be given by

$$c = \frac{2P^\circ - P}{\mathbf{R}T} \tag{17}$$

Substituting in Eq. (14), we get

$$\ln \frac{P^\circ}{2P^\circ - P} = kt \tag{18}$$

or

$$\ln P^\circ - \ln (2P^\circ - P) = kt \tag{19}$$

The value of k may therefore be obtained from a plot of $\log (2P^\circ - P)$ against time without actually computing the concentration of the reactant A.

It frequently happens in such investigations as this that it is difficult to determine the quantity P° directly by measurement of the pressure before any reaction has occurred or to compute it from a weight or a volume measurement on the substance A. It is therefore convenient to make use

of the fact that the final pressure P^∞ which prevails when the reaction is essentially complete is equal to $2P^\circ$. Consequently we have

$$\ln \frac{P^\infty}{2} - \ln (P^\infty - P) = kt \tag{20}$$

and it follows that the value of k can also be obtained from the slope of a plot of $\ln (P^\infty - P)$ against time.

In the study of reactions in solution it rather frequently happens that the available method of analysis determines the product of the reaction rather than the reactant. Thus in the first-order alcoholysis of benzhydryl chloride in ethanol solution,

$$(C_6H_5)_2CHCl + C_2H_5OH \rightarrow (C_6H_5)_2CHOC_2H_5 + H^+ + Cl^- \tag{IV}$$

it is easy to determine either the H^+ ion by an acidimetric titration or the Cl^- by a Volhard titration. Let x equal the concentration of hydrogen or of chloride ion determined in this way, and let a equal the concentration of benzhydryl chloride initially present. Then the c_0 of Eq. (13) is given by a and the c by $a - x$, and the equation takes the form

$$\ln a - \ln (a - x) = kt \tag{21}$$

By the stoichiometry of the reaction the concentration of hydrogen or chloride ion must equal a after reaction is essentially complete. Consequently, we may represent this concentration by x_∞ and write

$$\ln x_\infty - \ln (x_\infty - x) = kt \tag{22}$$

The development involving Eqs. (16) to (20) illustrated one way in which a reaction rate could be measured by the determination of a physical property. As another case we consider the hydrolysis of sucrose to an equimolal mixture of glucose and fructose. Representing sucrose by S, glucose by G, and fructose by F, we may write the reaction as

$$S + H_2O \rightarrow G + F \tag{V}$$

The reaction is of the first order, and the integrated rate equation is therefore

$$\ln \frac{[S]_0}{[S]} = kt \tag{23}$$

The quantity $[S]_0$ is the concentration of sucrose at the time zero at which the reaction starts and only sucrose and solvent are present. The reaction is conveniently followed by observing the rotation of the plane of polarized light. In dilute solutions of a single active solute the rotation

is proportional to the concentration; in solutions containing more than one active solute the rotation α is the sum of the rotations which each solute alone would produce. In this case therefore

$$\alpha = m[S] + n[G] + p[F] \tag{24}$$

m, n, and p being proportionality constants. From the stoichiometry of the reaction

$$[G] = [F] = [S]_0 - [S] \tag{25}$$

From Eqs. (24) and (25) we get

$$\alpha = (m - n - p)[S] + (n + p)[S]_0 \tag{26}$$

Instead of determining the three quantities m, $n + p$, and $[S]_0$ in this relation between rotation and concentration of sucrose at time t, it is experimentally easier to measure the rotation α_0 at the beginning and the rotation α_∞ when the reaction is essentially complete. Substituting $\alpha = \alpha_0$ and $[S] = [S]_0$ in Eq. (26), we have

$$\alpha_0 = m[S]_0 \tag{27}$$

and similarly

$$\alpha_\infty = (n + p)[S]_0 \tag{28}$$

Hence by eliminating m and $n + p$ between Eqs. (26), (27), and (28)

$$\alpha = (\alpha_0 - \alpha_\infty)\frac{[S]}{[S]_0} + \alpha_\infty \tag{29}$$

from which

$$\frac{[S]_0}{[S]} = \frac{\alpha_0 - \alpha_\infty}{\alpha - \alpha_\infty} \tag{30}$$

Setting this value of $[S]_0/[S]$ in Eq. (23), we have

$$\ln \frac{\alpha_0 - \alpha_\infty}{\alpha - \alpha_\infty} = kt \tag{31}$$

This can be written either as

$$\ln (\alpha_0 - \alpha_\infty) - \ln (\alpha - \alpha_\infty) = kt$$

or as

$$\ln (\alpha_\infty - \alpha_0) - \ln (\alpha_\infty - \alpha) = kt \tag{32}$$

The value of k can therefore be obtained from the slope of a plot of $\ln(\alpha - \alpha_\infty)$ or $\ln (\alpha_\infty - \alpha)$ against time. It is not necessary to make any direct measurement of any concentration or to know the relationship between concentration and rotation. It is not even necessary to know the initial rotation α_0.

A similar result is obtained for any other physical property of a system undergoing a first-order reaction in which the value of the physical property changes linearly with change in concentration of reactants and products, *i.e.*, according to an equation of the type of Eq. (24). Thus many reactions in solution are accompanied by small volume changes, and the total volume of a dilute solution is related to the concentrations of the solutes present by a linear equation of the type of Eq. (24). If the reaction takes place in a dilatometer, which is a vessel provided with a

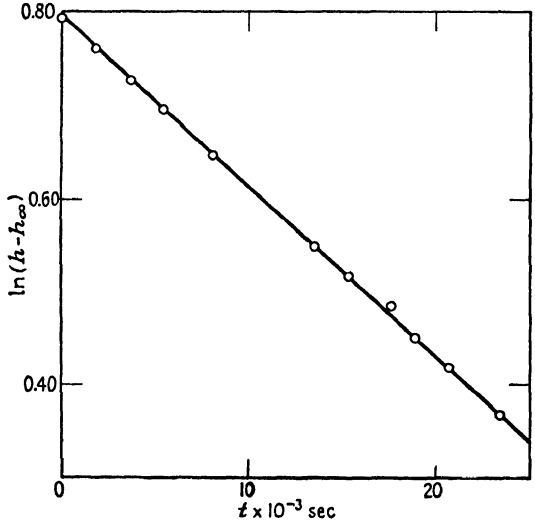


FIG. 3. Hydration of ethylene oxide [reaction (VI)] in aqueous solution. Plot against time t of ln $(h - h_\infty)$, where h is dilatometer reading and h_∞ is reading for $t \rightarrow \infty$. [*Data of Brønsted, Kilpatrick, and Kilpatrick, J. Am. Chem. Soc.*, **51**, 428 (1929).] Some of the experimental points omitted.

stem like an overgrown thermometer, these small changes in volume are translated into easily measurable displacements of the liquid level in the stem. It can be shown by an argument identical with that which leads from Eq. (23) to Eq. (32) that the height h of the liquid in the stem must follow the equation

$$\ln (h_0 - h_\infty) - \ln (h - h_\infty) = kt \tag{33}$$

if the volume decreases during the reaction and to the equation

$$\ln (h_\infty - h_0) - \ln (h_\infty - h) = kt \tag{34}$$

if the volume increases. In either case k is easily obtained from the slope of a linear plot. Figure 3 shows a plot of this sort resulting from a dilatometer investigation of the rate of the hydration of ethylene oxide to

glycol in aqueous solution,

$$C_2H_4O + H_2O \rightleftharpoons C_2H_4(OH)_2 \qquad \text{(VI)}$$

The excellent agreement of the experimental points with the straight line shows how well Eq. (33) applies.

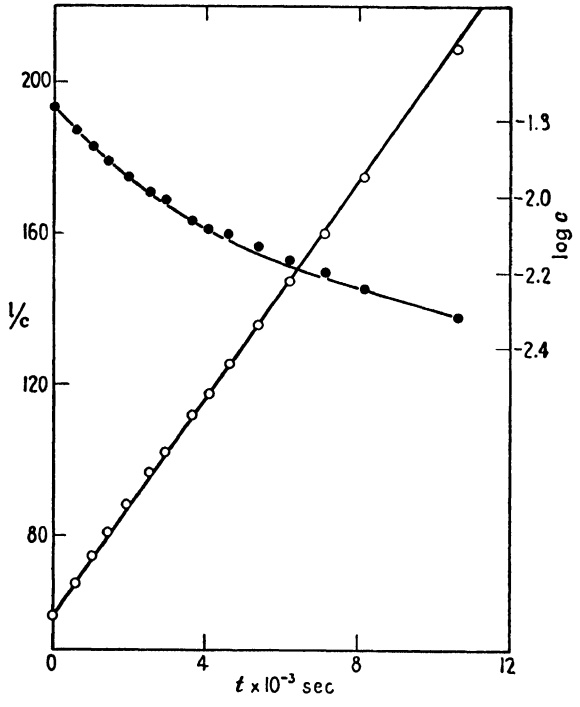


FIG. 4. Dimerization of butadiene [reaction (VII)] in the gas phase. Plots against time t of : ○ $1/c$, the reciprocal concentration of butadiene in liters per mole; ● $\log c$. [*Data of Vaughan, J. Am. Chem. Soc.*, **54**, 3863 (1932).] Some of the experimental points omitted.

Second-order Reactions. In a second-order reaction according to Eq. (7) in a constant-volume system we have

$$-\frac{dc}{dt} = kc^2 \qquad (35)$$

where c is concentration of reactant. This is easily integrated to

$$\frac{1}{c} - \frac{1}{c_0} = kt \qquad (36)$$

It follows that a plot of the reciprocal of the concentration of reactant against time should be linear and that the slope is the specific rate k.

The open circles of Fig. 4 illustrate this situation for the dimerization of butadiene,

$$2C_4H_6 \rightarrow C_8H_{12} \tag{VII}$$

in the gas phase. The reaction was followed by the change in pressure. If c_m is the concentration of monomeric butadiene in moles per liter, c_d that of the dimer, and c_0 the concentration of butadiene at time zero when butadiene alone was present, then by the stoichiometry of the reaction

$$c_m + 2c_d = c_0 \tag{37}$$

from which

$$c_d = \frac{c_0 - c_m}{2} \tag{38}$$

The total number of moles of gas present will be given by

$$c_m + c_d = \frac{c_0 + c_m}{2} \tag{39}$$

and the pressure by

$$P = \mathbf{R}T\frac{c_0 + c_m}{2} \tag{40}$$

From this

$$c_m = \frac{2P}{\mathbf{R}T} - c_0 \tag{41}$$

At time zero $c_m = c_0$, and if P_0 is the pressure at that time, substitution in Eq. (41) leads to

$$2c_0 = \frac{2P_0}{\mathbf{R}T} \tag{42}$$

From Eqs. (41) and (42)

$$c_m = \frac{2P - P_0}{\mathbf{R}T} \tag{43}$$

The reciprocal of this value of c_m is plotted in Fig. 4. It is a matter of considerable practical importance that in such cases as this it is necessary to know the pressure P_0 at a time when no reaction has yet occurred, but at which the system is at reaction temperature, and to measure the reaction time from this point as zero.

If a reaction of the type $A + B \rightarrow$ products has a rate proportional to the product of the concentrations of the reactants according to Eq. (8), then

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B] \tag{44}$$

In the particular case that the initial concentrations of A and B are identical, $[A]$ must equal $[B]$ at all times since the rates of change of the two concentrations are the same. Consequently we can write

$$-\frac{d[A]}{dt} = k[A]^2 \tag{45}$$

This is identical with Eq. (35) and integrates to the same forms.

The more general case in which the initial concentrations of A and B are not identical can be worked out by the following substitutions:

$$\begin{aligned} a &= \text{initial concentration of A} \\ b &= \text{initial concentration of B} \\ a - x &= \text{concentration of A at time } t \\ b - x &= \text{concentration of B at time } t \end{aligned}$$

With these Eq. (44) becomes

$$\frac{dx}{dt} = k(a - x)(b - x) \tag{46}$$

The integral

$$\int \frac{dx}{(a - x)(b - x)} = \frac{1}{b - a} \ln \frac{b - x}{a - x} \tag{47}$$

is listed in the usual tables of integrals or may be worked out by the method of partial fractions. After introducing the condition that $t = 0$ when $x = 0$, we get

$$\frac{1}{b - a} \ln \frac{a(b - x)}{b(a - x)} = kt \tag{48}$$

Table 1 illustrates the application of this equation to the reaction of normal propyl bromide with thiosulfate ion,

$$C_3H_7Br + S_2O_3^{--} \rightarrow C_3H_7S_2O_3^- + Br^- \tag{VIII}$$

The reaction was followed by titration with iodine of samples of the reaction mixture taken at suitable time intervals. The iodine reacts with thiosulfate ion but with no other constituent of the mixture, and the concentration of this reactant follows therefore directly from the titer. Since the thiosulfate was in excess and one propyl bromide molecule reacts for each thiosulfate ion, the difference between the thiosulfate-ion concentration at time t and that at infinite time must equal the concentration of alkyl bromide at time t. The mixture was prepared at time zero by mixing solutions of the two reactants, and the concentrations of the two reactants at this time represent, therefore, the a and b of Eq. (46).

TABLE 1. REACTION OF *n*-PROPYL BROMIDE WITH THIOSULFATE ION AT 37.50°C IN AQUEOUS-ALCOHOLIC SOLUTION*

t, sec	$[S_2O_3^{--}]$	$[RBr]$	10^3k†
0	0.09660	0.03951	—
1,110	0.09036	0.03327	1.658
2,010	0.08633	0.02924	1.644
3,192	0.08189	0.02480	1.649
5,052	0.07665	0.01956	1 636
7,380	0.07198	0.01489	1.618
11,232	0.06677	0.00968	1.618
∞	0.05709	0.0	—

* Data of Crowell and Hammett, *J. Am. Chem. Soc.*, **70,** 3444 (1948).

† Average value of k 1.637 × 10^{-3} liter/mole-sec, probable error 0.6 per cent.

The concentrations at subsequent times represent the $a - x$ and $b - x$ of this equation. The values of specific rate k listed were obtained by substitution of these data in Eq. (46), and since they are constant to a probable error of 0.6 per cent, the equation is valid to excellent precision for this reaction under these conditions.

Determination of Reaction Order. The fact that one of these integrated forms fits the data over a moderate range of amounts of reaction does not suffice to prove that the reaction is of the order which the equation represents. Thus the solid circles in Fig. 4 exhibit in a plot of log c against time the same data for which the open circles represent a plot of $1/c$ against time. The log c plot shows a definite curvature over the range plotted, but if one had only the data between 0 and 2 × 10^3 sec, the curvature would be neither obvious nor certain. Before he draws conclusions, the careful worker therefore always determines not only that the form for a particular order fits the data but also that the forms for other orders do not. It is always wise, also, to make a series of measurements at differing initial concentrations because cases occur in which a reaction product affects the rate in such a way that data obtained from a single initial concentration fit a particular order but data obtained at different initial concentrations lead to different values of the specific rate.

Reaction Mechanisms. When acetone, which we represent by A, is brominated in alkaline aqueous solution, the over-all reaction is

$$CH_3COCH_3 + 3OBr^- \rightarrow CH_3COO^- + CHBr_3 + 2OH^- \qquad \text{(IX)}$$

yet the rate is found experimentally to follow the law

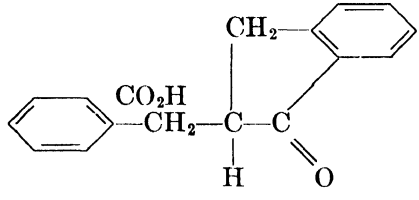
$$-\frac{d[A]}{dt} = k[A][OH^-] \qquad (49)$$

Although hypobromite ion is a reactant, the rate of reaction does not depend on the concentration of this ion and the rate is directly proportional to the concentration of hydroxyl ion, which is not a reactant but a product of the reaction. To explain this, we suppose that reaction (IX) consists of the process

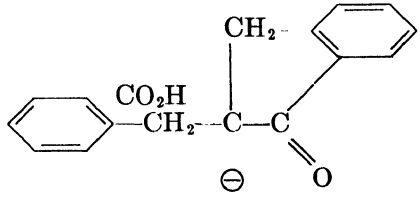
$$CH_3COCH_3 + OH^- \rightarrow CH_3COCH_2^- + H_2O \qquad (X)$$

followed by reactions of the ion $CH_3COCH_2^-$ with hypobromite ion or bromine which are of high specific rate and lead to the observed reaction products. Reaction (X) is then a bottleneck for the whole reaction; every ion formed reacts practically instantaneously, and the rate of the whole process becomes the rate of formation of this ion, *i.e.*, the rate of reaction (X). According to the first principle the rate of reaction (X) should be given by Eq. (49).

So far this is what is called an *ad hoc hypothesis.* It is a not unreasonable guess about the mechanism of the reaction which fits the facts of the particular case. The hypothesis has, however, been overwhelmingly verified by the following facts: First, the rate of reaction of acetone with iodine is identical with its rate of reaction with bromine under similar conditions, *i.e.*, the rate of reaction is independent not merely of the concentration of halogen but also of the kind of halogen. Second, the rate of racemization of the optically active ketone

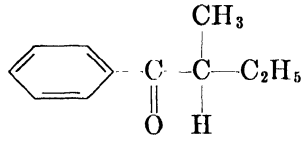


is identical with its rate of bromination under the same conditions, the specific rates being 0.0471 for the bromination and 0.0438 for the racemization. This is consistent with our hypothesis since the ion



produced by a reaction corresponding to reaction (X) has only three groups attached to the originally asymmetric carbon and cannot be

optically active. We know that the ion must return rapidly to the form of the neutral ketone, because the concentration of the ion is never large enough to be detected and measured directly. When it does return, it has equal probability of forming dextro and levo ketone, *i.e.*, the regenerated ketone will be racemic. The rate of formation of the ion will therefore be the bottleneck or rate-determining step for the racemization as it is for the bromination. Third, the rate at which the ketone



exchanges hydrogen for deuterium in alkaline D_2O is very nearly the same as the rate of racemization of its optically active form under the same conditions and is probable identical if corrected for minor complications. The rate of exchange is again that of the ionization, but a D^+ ion instead of an H^+ ion is added when the ion reverts to the ketone.

This is one of the most completely verified cases of a sequence of reactions which leads to a rate law different from that expected from the stoichiometric equation for the over-all reaction. Many other examples could be quoted, however, in which such a complex mechanism accounts for a large variety of facts and may be taken to have a high degree of validity. As a result we accept without reservation and as a general law of complete validity within the precision of the perfect-gas and dilute-solution laws the rule that reaction rate is proportional to the product of the concentrations of the actual reactants (page 166).

This investigation of ketone halogenation has not only verified the first principle of chemical-reaction kinetics, it has furnished valuable information on the mechanism of the reaction, *i.e.*, on the details of the process by which the reaction takes place. Even without such elaborate investigations the study of the rate of a reaction is a powerful tool for the interpretation of reaction mechanisms. This tool does not often give an unambiguous positive answer; it rarely says, "This is the mechanism." But it frequently says unambiguously, "This is not the mechanism," and the conclusion is important even though sometimes unpalatable.

It was, for instance, a dogma beyond dispute of the predominant school of physical chemists of a few decades ago that ionization reactions are instantaneous. Many of them are in fact so fast that we have found no means of catching them on the way, which is necessary if the rate is to be measured. It is true that scientists must make generalizations from limited data, but it is unfortunate when they become closed-minded about

the validity of such generalizations. In the light of this dogma the organic chemists who discovered that the neutralization of certain weak acids, such as nitromethane, is a relatively slow process were forced to conclude that nitromethane is not really an acid but that it rearranges slowly into a true acid whose neutralization is instantaneous. This conclusion had a wide-reaching and unhelpful influence on theoretical organic chemistry. Yet it has been known for a long time that the rate of the neutralization is proportional to the concentration of hydroxyl ion. This fact is irreconcilable with a mechanism consisting of a slow internal rearrangement which does not involve hydroxyl ion followed by a rapid reaction with hydroxyl ion.

Mathematics of Consecutive Reactions. It is not difficult to set up the differential equations which apply to a sequence of consecutive reactions. Thus if we consider only the first two steps in the bromination of acetone,

$$CH_3COCH_3 + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3COCH_2^- + H_2O \qquad (X)$$

$$CH_3COCH_2^- + Br_2 \xrightarrow{k_2} CH_3COCH_2Br + Br^- \qquad (XI)$$

supposing that the later steps leading to the observed products have such high specific rates that they have no influence on these processes, we can write

$$\frac{d[A]}{dt} = -k_1[A][OH^-] + k_{-1}[I] \qquad (50)$$

$$\frac{d[I]}{dt} = k_1[A][OH^-] - k_{-1}[I] - k_2[I][Br_2] \qquad (51)$$

The symbols A and I are used for acetone and the ion $CH_3COCH_2^-$, respectively. In these equations the constant concentration of the solvent water is absorbed into the constant k_{-1} for reasons which will be discussed later (page 188).

The integration of such a system of equations is in general a difficult problem in mathematics. It has been solved for the case that all the reactions follow a first-order course. The solution holds not only for two but for any number of successive steps, but its form is complicated and difficult to apply to experimental data. An approximate solution, which is of high precision in such cases as the one under discussion, may be derived by a method which is called the *method of the stationary state* or the *method of the unstable intermediate.* This may be applied whenever all the reaction intermediates are present only in small concentrations.

In the present case the concentration of the ion I is always extremely small, too small to permit direct demonstration of its presence, much less

determination of its concentration. This means that the quantity $d[I]/dt$ of Eq. (51) must be a small quantity; otherwise the accumulation of I over any considerable period of time would be appreciable. On the other hand, I is being formed at a rate at least as great as the over-all rate of reaction, since the reaction products are formed only by way of the ion. Consequently the term $d[I]/dt$ in Eq. (51) is a small difference between the relatively large quantities $k_1[A][OH^-]$ and $k_{-1}[I] + k_2[I][Br_2]$, and it may be neglected compared with them. That is to say, Eq. (51) is closely approximated by the equation

$$0 = k_1[A][OH^-] - k_{-1}[I] - k_2[I][Br_2] \tag{52}$$

from which we have

$$[I] = \frac{k_1[A][OH^-]}{k_{-1} + k_2[Br_2]} \tag{53}$$

Introducing this value of $[I]$ into Eq. (50), we get

$$-\frac{d[A]}{dt} = k_1[A][OH^-]\frac{k_2[Br_2]}{k_{-1} + k_2[Br_2]} \tag{54}$$

Equation (54) is valid only for the situation in which $[I]$ is always very small, which we may describe by the inequality

$$k_{-1}[I] \gg k_1[A][OH^-] \tag{55}$$

If in addition the inequality

$$k_2[Br_2] \gg k_{-1} \tag{56}$$

holds, *i.e.*, if the rate of reaction of the ion with bromine, $k_2[Br_2][I]$, is much greater than the rate, $k_{-1}[I]$, at which it reverts to acetone, the term k_{-1} in Eq. (54) may be neglected compared with the term $k_2[Br_2]$ and the latter then cancels the same term in the numerator and the equation reduces to

$$-\frac{d[A]}{dt} = k_1[A][OH^-] \tag{57}$$

which is the observed situation. The result is the same as that given by our previous qualitative discussion, namely, that the over-all rate is the rate of the first step.

When the opposite extreme applies, namely, when

$$k_2[Br_2] \ll k_{-1} \tag{58}$$

Eq. (54) reduces to

$$-\frac{d[A]}{dt} = \frac{k_1k_2}{k_{-1}}[Br_2][A][OH^-] \tag{59}$$

Consider the situation which would exist if there were equilibrium in reaction (X) uncomplicated by the effect of reaction (XI). By the usual equilibrium law we have

$$\frac{[I]}{[A][OH^-]} = K \tag{60}$$

and by a rule which we have already used (page 103) and whose validity we shall discuss later (page 183) we have

$$K = \frac{k_1}{k_{-1}} \tag{61}$$

Combining Eqs. (59), (60), and (61), we get

$$-\frac{d[A]}{dt} = k_2[I][Br_2] \tag{62}$$

The over-all rate of reaction under these conditions is therefore the rate of the second step [reaction (XI)], with the concentration of the ion I given by the application of the equilibrium law to reaction (X). In this case reaction (XI) is said to be the *rate-determining step* in the over-all reaction; when Eq. (57) holds, reaction (X) is called the rate-determining step.

When neither the approximation of Eq. (56) nor that of Eq. (58) holds, the general equation [Eq. (54)] applies and the reaction shows no simple order with respect to bromine, *i.e.*, its rate is not proportional to an integral power of the bromine concentration. The reaction is still first order in acetone and first order in hydroxyl ion. This situation has been observed in the alkaline chlorination of acetone.

Reversible Reactions. It is an important corollary of the first principle that the rate of one reaction in a given system is unaffected by the presence or absence of other reactions. This rule is implicit in our discussion of the bromination of acetone, for we have assumed that the rate $k_1[A][OH^-]$ at which acetone reacts with hydroxyl ion to form the ion I is not altered by the reverse reaction which converts I to acetone and that the total rate of change of acetone concentration is the sum of the effects of the processes by which it reacts and by which it is formed, each undisturbed by the presence of the other.

This corollary and hence the first principle itself have been given an especially critical test in the study of reversible reactions which come to a measurable equilibrium. For the reaction, first order in both directions

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \tag{XII}$$

the rate should be given by

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = k_1[A] - k_{-1}[B] \tag{63}$$

By the definition of equilibrium, $d[A]/dt = 0$ when the system is at equilibrium; hence at equilibrium

$$0 = k_1[A]_e - k_1[B]_e \tag{64}$$

the subscript e indicating that these are concentrations in an equilibrium system. From this

$$\frac{[B]_e}{[A]_e} = \frac{k_1}{k_{-1}} \tag{65}$$

Since we know from Chap. VII that

$$\frac{[B]_e}{[A]_e} = K \tag{66}$$

where K is the equilibrium constant of the reaction, we have

$$\frac{k_1}{k_{-1}} = K \tag{67}$$

This important relationship is not limited to the particular case for which we have derived it but is easily shown to be valid for any reversible reaction no matter what the reaction order may be.

If the system initially contains only A at the concentration a, and if x equals the concentration of B at time t, Eq. (63) becomes

$$\frac{dx}{dt} = k_1(a - x) - k_{-1}x \tag{68}$$

The algebra of such problems as this is considerably simplified by introducing the quantity x_e, the value of x attained when the system reaches equilibrium. Since at equilibrium $dx/dt = 0$, we have

$$0 = k_1(a - x_e) - k_{-1}x_e \tag{69}$$

Eliminating the quantity a between Eqs. (69) and (68), we get

$$\frac{dx}{dt} = (k_1 + k_{-1})(x_e - x) \tag{70}$$

This integrates to

$$-\ln (x_e - x) = (k_1 + k_{-1})t + X \tag{71}$$

Since $x = 0$ when $t = 0$, the integration constant X has the value $-\ln x_e$ and we get finally

$$\ln x_e - \ln (x_e - x) = (k_1 + k_{-1})t \tag{72}$$

Consequently a plot of $\ln (x_e - x)$ against time is linear for a reversible reaction, first order in both directions. Since x_e is the value which x attains in the limit of infinite time, this equation is closely analogous to Eq. (22) for an irreversible first-order reaction. In the reversible case the slope of the plot is not a single specific rate but the sum of the specific rates for forward and reverse reactions. If the equilibrium constant is known, Eq. (67) gives another relation between these two specific rates and each can then be calculated.

In this case also it is not necessary to measure directly any concentration if a suitable physical property is available. Suppose, for instance, that the substances A and B of reaction (XII) rotate the plane of polarized light and that the rotation α of a solution containing them is given by

$$\alpha = m[A] + n[B] \tag{73}$$

where m and n are proportionality constants. For the case in which no B is present at time zero this becomes

$$\alpha = m(a - x) + nx = ma + (n - m)x \tag{74}$$

The initial rotation α_0 is given by

$$\alpha_0 = ma \tag{75}$$

and the rotation at equilibrium α_e by

$$\alpha_e = ma + (n - m)x_e \tag{76}$$

Eliminating m, n, and a between Eqs. (72), (74), (75), and (76), we obtain

$$\ln (\alpha_e - \alpha_0) - \ln (\alpha_e - \alpha) = (k_1 + k_{-1})t \tag{77}$$

The sum $k_1 + k_{-1}$ may therefore be obtained from the slope of a plot of $\log (\alpha_e - \alpha)$ against time. In order to compute the equilibrium constant and the individual values of k_1 and k_{-1}, it is necessary to measure the rotation of a solution containing a known concentration of B either alone or in mixture with a known amount of A.

In Fig. 5 the quantity $\log (\alpha - \alpha_e)$ is plotted against time for a reaction which is called the mutarotation of α-glucose. The reaction consists in the reversible conversion of one stereoisomer into another, called β-glucose, which has a different specific rotation; it conforms therefore to the situation we have been considering. The linearity of the plot confirms the assumptions involved in the derivation of Eq. (77), including the corollary

of the first principle that the rate of the forward reaction is unaffected by the presence of the reverse reaction. Further substantiation is obtained from the fact that similar experiments starting with β-glucose lead to a value of 3.96×10^{-4} sec^{-1} for the quantity $k_1 + k_{-1}$, whereas the data from experiments starting with α-glucose, which are plotted in Fig. 5, lead to the essentially identical value 4.03×10^{-4} for the same quantity.

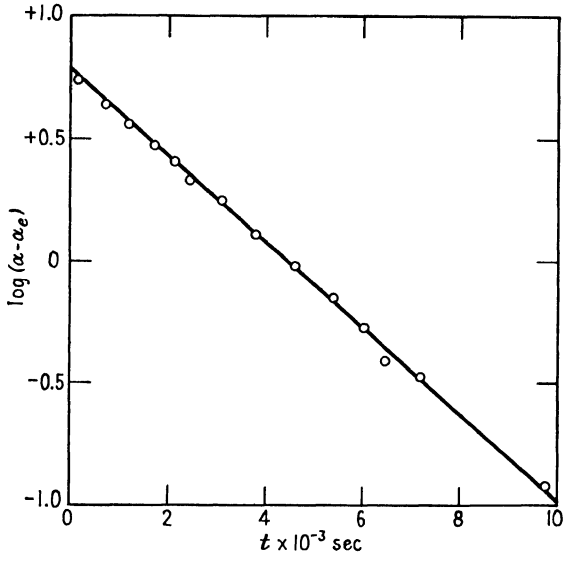


FIG. 5. Mutarotation of α-glucose in very dilute aqueous HCl. Plot of the quantity log $(\alpha - \alpha_e)$ against time. α is rotation, and α_e is rotation at equilibrium. [*Data of Nelson and Beagle, J. Am. Chem. Soc.*, **41**, 559 (1919).]

The differential equations for a reversible reaction can also be integrated if the reaction is of the second order in both directions, although the algebra gets more complicated. The reaction

$$2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2 \qquad \text{(XIII)}$$

has been carefully investigated by Bodenstein and found to agree completely with the equations developed in this way on the assumption that the rate is given by

$$-\frac{d[\text{HI}]}{dt} = 2\frac{d[\text{I}_2]}{dt} = k_1[\text{HI}]^2 - 2k_{-1}[\text{H}_2][\text{I}_2] \qquad (78)$$

Catalysis. The definition of a catalyst, a substance which accelerates a reaction although it is present unchanged in amount and state at the end of the reaction, does not in any sense require that the catalyst take no part in the reaction. Indeed the rate of a catalyzed reaction in a

homogeneous system is characteristically proportional to an integral power of the concentration of the catalyst, usually the first. The first principle requires therefore that the rate-determining step of the reaction is one in which the catalyst takes part. The situation is clear in such cases as the racemization of an optically active ketone (page 178). This is a reversible reaction by which dextrorotatory ketone dK is converted to levorotatory ketone lK. Since the specific rate has the same value for the two opposed reactions, the equilibrium constant is 1 and the final rotation is 0. In view of our previous discussion we recognize that the process goes through the steps

$$dK + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I + H_2O \qquad \text{(XIV)}$$

$$I + H_2O \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} lK + OH^- \qquad \text{(XV)}$$

Since the concentration of the intermediate ion I is at all times extremely small, as much hydroxyl ion is formed by reaction (XV) as is consumed by reaction (XIV) and the concentration of hydroxyl ion remains unchanged. The rate equations

$$-\frac{d[dK]}{dt} = k_1[dK][OH^-] - k_{-1}[I] \qquad (79)$$

$$\frac{d[I]}{dt} = k_1[dK][OH^-] + k_1[lK][OH^-] - 2k_{-1}[I] \qquad (80)$$

$$-\frac{d[lK]}{dt} = k_1[lK][OH^-] - k_{-1}[I] \qquad (81)$$

may be simplified as in the discussion on page 180 by recognizing that the quantity $d[I]/dt$ is a small difference between large quantities. On this basis Eq. (80) yields

$$[I] = \frac{k_1[OH^-]}{2k_{-1}}\{[dK] + [lK]\} \qquad (82)$$

Substituting this in Eqs. (79) and (81), we get

$$-\frac{d[dK]}{dt} = \frac{1}{2}k_1[OH^-]\{[dK] - [lK]\} \qquad (83)$$

$$-\frac{d[lK]}{dt} = \frac{1}{2}k_1[OH^-]\{[lK] - [dK]\} \qquad (84)$$

By subtraction

$$-\frac{d\{[dK] - [lK]\}}{dt} = k_1[OH^-]\{[dK] - [lK]\} \qquad (85)$$

The observed rotation α is proportional to the difference in the concentrations of the d and l forms, *i.e.*,

$$\alpha = m\{[dK] - [lK]\} \tag{86}$$

from which, with Eq. (85), we have

$$-\frac{d\alpha}{dt} = k_1[OH^-]\alpha \tag{87}$$

This may be integrated, since $[OH^-]$ is independent of time, to

$$\ln \alpha_0 - \ln \alpha = k_1[OH^-]t \tag{88}$$

A plot of log α against time is therefore linear as in a simple first-order reaction, but the value of the slope $k_1[OH^-]$ is proportional to the concentration of the catalyzing hydroxyl ion.

There is no reason to doubt that all cases of catalysis in homogeneous systems involve sequences of this sort in which the catalyst enters into the reaction to form intermediates which are present only in minute concentrations, the catalyst being regenerated in the later steps of the process. The racemization of an optically active ketone in alkaline solution is a catalysis because the hydroxyl ion used in the first step is regenerated; the bromination of the ketone in the same medium is not a catalysis by hydroxyl ion because there is more hydroxyl ion present after the reaction than before. Yet both reactions have the same initial and rate-determining step.

Pseudo First-order Reactions. The rate of the racemization discussed in the last section is proportional to the product of two concentrations, that of ketone and that of hydroxyl ion. The reaction is therefore of the second order. Yet the integrated form of the relation between rotation and time is that of a first-order not that of a second-order reaction. However the slope of the plot of ln c against t, which would be the specific rate if the reaction were first order, is itself proportional to the concentration of the reactant hydroxyl ion, which remains constant during the reaction. Much the same result is obtained in a second-order reaction between reactants A and B when the concentration of A is much greater than that of B. The total change in the concentration of A cannot be greater than the change in the concentration of B and must therefore be a small fraction of the amount of A present. That is, x in Eq. (46), which cannot be greater than b, can be neglected compared with a, and the equation becomes

$$\frac{dx}{dt} = ka(b - x) \tag{89}$$

This integrates to

$$\ln b - \ln (b - x) = kat \tag{90}$$

Here again the form of the equation is that of a first-order reaction except that the first-order specific rate is replaced by the product of the second-order specific rate by the concentration of a reactant, in this case the reactant present in large excess. All reactions to which equations of this form apply are said to "follow a first-order course" or to be pseudo first order.

Participation of the Solvent. We cannot determine whether or not the solvent takes part in the rate-determining step of a reaction because our only method of answering such questions is to observe whether or not the rate changes when the concentration of reactant is changed. Thus we know that bromine is not involved in the rate-determining step of the acetone bromination because a change in the concentration of bromine has no effect on the rate of the reaction. But if we change the concentration of the solvent, for example, by mixing it with another solvent, we change the nature of the medium in which the reaction occurs and therefore the energy of the solute molecules (page 44), and we must expect a change in rate even if the solvent does not participate in the rate-determining step. That a change in the nature of the solvent must generally alter the reaction rate follows from the fact that such a change alters the equilibrium constant of a reaction (page 119). Since the equilibrium constant is the ratio of the specific rates for forward and reverse reactions, a change in the medium which alters the equilibrium constant must change at least one of the two rate constants. Such effects of solvent on reaction rate are often large. Thus Norris and Prentiss found that the reaction of pyridine with ethyl iodide,

$$C_5H_5N + C_2H_5I \rightarrow C_5H_5NC_2H_5^+ + I^- \tag{XVI}$$

is 25 times faster in nitrobenzene solution than it is in benzene solution.

Temperature Coefficient of Reaction Rate. Chemical reactions whose rates lie in a measurable range show rates which increase rapidly with increasing temperature, and plots of specific rate against temperature show pronounced positive curvature. A rule of thumb says that the rate increases by a factor of 2 to 3 for every 10° increase in temperature. This behavior suggests an exponential relationship, and it is a fact, first observed by Arrhenius, that a plot of the logarithm of the specific rate k against the reciprocal temperature is to a considerable precision a straight line. That is

$$\frac{d \ln k}{d(1/T)} = \text{constant} \tag{91}$$

This relationship is illustrated in Fig. 6 by means of data on the rate of decomposition of nitrogen pentoxide [reaction (I)]. Equation (91) is immediately reminiscent of the temperature dependence of the equilibrium constant K of a reaction

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta H}{\mathbf{R}} \qquad (92)$$

It is therefore natural to write the constant of Eq. (91) in a similar form, *i.e.*, to write

$$\frac{d \ln k}{d(1/T)} = -\frac{E}{\mathbf{R}} \qquad (93)$$

This equation is in fact the definition of a quantity E called the *energy of activation* of the reaction. The definition can also be put in the forms

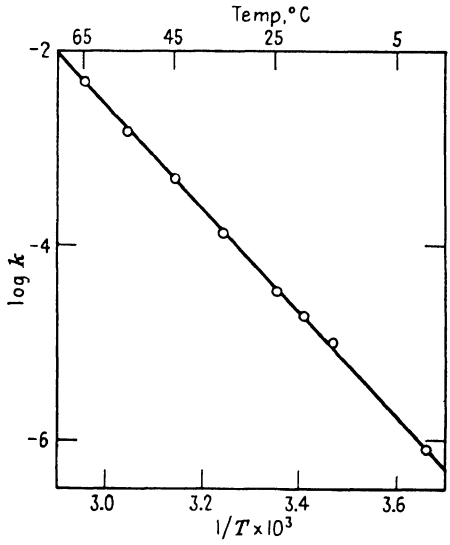


FIG. 6. Plot against reciprocal temperature of the logarithm of the specific rate of the decomposition of nitrogen pentoxide. (*Data of Daniels and Johnston.*)

$$E = -\mathbf{R} \frac{d \ln k}{d(1/T)} \qquad (94)$$

and

$$E = \mathbf{R}T^2 \frac{d \ln k}{dT} \qquad (95)$$

The energy of activation E_1 for a reaction from left to right of the reaction equation and that E_{-1} for the reaction from right to left are necessarily related to the heat of the reaction ΔH. From Eq. (67)

$$\ln K = \ln k_1 - \ln k_{-1} \qquad (96)$$

Differentiating this with respect to $1/T$, we have

$$\frac{d \ln K}{d(1/T)} = \frac{d \ln k_1}{d(1/T)} - \frac{d \ln k_{-1}}{d(1/T)} \qquad (97)$$

and comparing this with Eqs. (92) and (93), we see that

$$\Delta H = E_1 - E_{-1} \qquad (98)$$

Since ΔH varies with temperature, the apparent constancy of the energy of activation and hence of the slope of the plot of $\ln k$ against $1/T$ depends

upon the fact that the range of temperatures over which a reaction rate may be measured with precision is limited by the impossibility of measuring the rates of very fast reactions and the impracticality of measuring the rates of very slow ones. In those cases in which ΔH is known to be most largely dependent on the temperature, namely, in reactions involving ions in solution, it has been shown beyond question that the energy of activation is also a function of temperature.

The Collision Theory. There have been two important theoretical approaches to the interpretation of the phenomena of reaction kinetics. Both have their usefulness and their weakness. The earlier one historically, the collision theory, starts out from the consideration of the frequency of collisions between reacting molecules. Obviously molecules can react only when they come in contact with each other. Gas kinetic theory gives for Z, the number of collisions per unit time in a volume of 1 cc between the spherical molecules of the substances A and B, the diameters of which are σ_A and σ_B and the masses m_A and m_B, the value

$$Z = N_A N_B \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \sqrt{8\pi \mathbf{k} T \left(\frac{1}{m_A} + \frac{1}{m_B}\right)} \tag{99}$$

where N_A and N_B are the numbers of molecules of each kind in 1 cc. If every collision resulted in reaction, the quantity Z would be the number of molecules reacting in 1 sec in 1 cc and the number of moles reacting in 1 sec in 1 liter would be $1000/\mathbf{N}$ times this. Using the relation $N_A = \mathbf{N}c_A/1000$ and remembering that specific rate equals rate divided by the product of reactant concentrations, we get for $k°$, the specific rate which would prevail if all collisions resulted in reaction,

$$k° = \frac{\mathbf{N}}{1000}\left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \sqrt{8\pi \mathbf{k} T \left(\frac{1}{m_A} + \frac{1}{m_B}\right)} \tag{100}$$

With the representative values of 4×10^{-8} for σ and a molecular weight of 50 this leads to a value of $k°$ at 300°K of 1.5×10^{11} liter/mole-sec. The specific rates of second-order reactions which are neither so fast nor so slow that measurement is impossible lie in the region around 10^{-1} to 10^{-4} liter/mole-sec, and we must conclude that only a fraction of the intermolecular collisions in such cases result in reaction. Since both collision frequency and reaction rate are directly proportional to the product of the concentrations, the fraction of the collisions which result in reaction must be independent of the concentrations. The fraction is, however, sharply dependent on temperature, as the following considerations show:

Logarithmic differentiation of Eq. (100) leads to

$$\frac{1}{k^\circ}\frac{dk^\circ}{dT} = \frac{1}{2T} \tag{101}$$

and this implies that if all collisions resulted in reaction the temperature coefficient of the rates of all reactions would be the same and would amount to only 0.16 per cent per degree at room temperature. Observed temperature coefficients differ considerably from reaction to reaction but are often of the order of 10 per cent per degree for reactions of measurable rate.

The collision theory assumes that the effective collisions are those in which an especially large amount of energy is available. This might mean that one or both of the reacting molecules possess a large amount of internal energy, or it might mean that one or both are moving so rapidly that the collision is an especially violent one. In either case it is assumed that the fraction of collisions of sufficient energy is given by $e^{-E/\mathbf{R}T}$, where E is the extra energy required for an effective collision. This is obviously a Boltzmann sort of expression. Its exact applicability to the problem in question is not entirely clear, and this uncertainty is one of the major weaknesses of the collision theory. Even more serious is the fact that any serious consideration of structural chemistry shows that only a fraction of the collisions between two molecules, and a very small fraction in the case of complicated molecules, brings the molecules together in such a way that their reactive portions are in contact and in contact in the right orientation to permit the formation of a stable bond. If one overlooks these difficulties, the collision theory then leads to the equation

$$k = k^\circ e^{-E/\mathbf{R}T} \tag{102}$$

from which

$$\frac{d \ln k}{d(1/T)} = -\frac{1}{2}T - \frac{E}{\mathbf{R}} \tag{103}$$

The $\frac{1}{2}T$ term results from the temperature dependence of k° [*cf.* Eq. (101)]. It is usually trivial compared with the term $E/\mathbf{R}$, and if it is neglected, the E of the collision theory is identical with the experimental energy of activation defined by Eq. (93).

For the reactions in the gas phase of such simple molecules as H_2, I_2, and HI, Eq. (102) with k° calculated from Eq. (100) is in reasonable agreement with experiment. Indeed the agreement is perhaps too good in view of the assumption that all collisions having sufficient energy result in reaction, whereas we know that only those collisions in which the molecules come together in the right way spatially can be effective no matter what the energy. With more complicated molecules the observed rates

of reactions in the gas phase are considerably slower than those predicted by this equation, sometimes as much as 10^5 times slower. It is difficult to predict the frequency of collisions between solute molecules in solution, but if one assumes the frequency to be the same as that between similar molecules at the same concentration in the gas phase, predictions are in even worse agreement with experiment, discrepancies of as much as a factor of 10^8 in either direction being common.

The Transition-state Theory. The transition-state theory shares with the collision theory the idea of an energy of activation. Indeed this idea predominates to such an extent that the theory does not explicitly consider the molecular collisions which form a coordinate feature of the collision theory and which must in fact be a necessary part of the process of reaction. Both theories are abstractions of a sort that are frequently necessary in the development of science; whereas the collision theory oversimplifies the concept of activation, the other glosses over the necessity of collision.

The theory starts from the idea that a molecule or group of molecules can react only if it gets into a state in which it contains much more than the usual amount of energy. It must, according to a frequently used phrase, cross an energy "hill" or "barrier." Just as a hill has a summit from which it is possible without further expenditure of energy to roll down on either side, so a reacting system must go through a state, the transition state, from which it may advance to form the reaction products or return to form the reactants without in either case requiring any further supply of energy. The transition state is the half-reacted state; in view of its high energy content and in the light of the Boltzmann principle it must be a relatively improbable state, one in which only a small fraction of the molecules exist at any time.

The theory endows this transition state with many of the properties of a stable substance. In particular it attempts to calculate the concentration of molecules in the transition state by methods which are closely patterned on those used to calculate those of any stable molecular species involved in an equilibrium. We can most easily appreciate the justification for this approach if we think of a reversible reaction, *e.g.*,

$$A + B \rightleftharpoons M + N \qquad \text{(XVII)}$$

under such conditions that the whole system is in a state of equilibrium. The number of molecules in the transition state, or rather in the total set of quantized states which represent various possible ways of getting over the energy barrier, must then be calculable in essentially the same form in which the number of molecules in any state or set of states in any sys-

tem at equilibrium may be calculated, *i.e.*, by the methods of Chap. VIII. On this basis we may write

$$\frac{c_t}{[A][B]} = K_t \tag{104}$$

where c_t is the concentration of molecules in the transition state and K_t is an equilibrium constant which is given by

$$K_t = \frac{Q_t^\circ}{Q_A^\circ Q_B^\circ} e^{-\Delta E_0^\ddagger/RT} \tag{105}$$

Q_t is the partition function of the transition state, *i.e.*, a sum of exponential terms involving the quantized energies of the transition state, and $E_0^\ddagger$ is the difference in energy between 1 mole of the transition state and 1 mole each of the reactants A and B, all being in the lowest energy levels.

Because the rates of the forward and reverse reactions are equal in the equilibrium system, just half of the molecules in the transition state must be in the process of reacting to form M and N, the other half in the process of reacting to form A and B. If then r_t is the specific rate of reaction in the direction from A, B to M, N of the transition state, *i.e.*, the fraction of the transition-state molecules which react in this direction per second, it will also be the specific rate in the direction from M, N to A, B. By Eq. (104) the concentration of molecules in the transition state is given by $K_t[A][B]$. Consequently the rate of reaction in the direction from A, B to M, N must be $\frac{1}{2}r_tK_t[A][B]$. Dividing by $[A][B]$ to get the specific rate k, we have

$$k = \tfrac{1}{2}r_tK_t \tag{106}$$

Our whole accumulated experience in the field of reaction kinetics makes us feel that the reaction in the direction from A, B to M, N is not influenced by the reaction in the reverse direction (*cf.* page 182). We therefore argue that, even though we have derived Eq. (106) on the basis that the two reactions were occurring at equal rates, the equation must still apply to the reaction in the direction from A, B to M, N if the reverse reaction is suppressed by decreasing the concentrations of M and N to a negligible value.

The theory then proposes that a factor corresponding to motion in the direction in which reaction occurs be taken out of Q_t° and combined with the factor $\frac{1}{2}r_t$. By an ingenious argument it concludes that the resulting product is given by $\mathbf{k}T/\mathbf{h}$. If we represent the residue of Q_t° from which the factor has been removed by $Q^\ddagger$ we have from Eqs. (105) and (106)

$$k = \frac{\mathbf{k}T}{\mathbf{h}} \frac{Q^\ddagger}{Q_A^\circ Q_B^\circ} e^{-\Delta E_0^\ddagger/RT} \tag{107}$$

If we define a "quasi-equilibrium constant" $K^\ddagger$ by the relation

$$K^\ddagger = \frac{Q^\ddagger}{Q_A^\circ Q_B^\circ} e^{-\Delta E_0^\ddagger/RT} \tag{108}$$

we may also write

$$k = \frac{\mathbf{k}T}{h} K^\ddagger \tag{109}$$

The rate given by Eqs. (108) and (109) represents what may be called the *normal* rate. The theory admits that the actual rate may be smaller than this by a factor which it expects not to differ largely from unity except in very special cases.

Equation (108) cannot be verified by comparison with experiment as the corresponding relationship [Eq. (38) of Chap. VIII] for an equilibrium constant can be, for it is impossible to observe, much less to analyze, the spectrum of an entity so fugitive as a transition state or to integrate its heat capacity from temperatures which approach absolute zero. For molecules of very simple structure it is, however, possible to make reasonable guesses about the kinds of motion which the transition-state system can undergo and through these to estimate the magnitude and temperature coefficient of the quantity $Q^\ddagger$. The results of such tests are in respectable agreement with experimental observation.

The theory has been useful in the sense that it leads to the application to problems of reaction rate of the same kind of qualitative or semiquantitative arguments involving the structure of the reactants, and the effects of solvation and of the electrical interactions of ions that are also successfully used for the problems of chemical equilibrium.

Enthalpy and Entropy of Activation. In spite of the somewhat special properties of $Q^\ddagger$ it is still a sum of Boltzmann terms, and by the argument which led to Eq. (50) of Chap. VIII its temperature coefficient must be given by

$$\frac{d \ln Q^\ddagger}{dT} = \frac{H^\ddagger - E_0}{\mathbf{R}T^2} \tag{110}$$

where $H^\ddagger$ is the enthalpy of 1 mole of the transition state. It follows by the argument which led to Eq. (56) of Chap. VIII that

$$\frac{d \ln K^\ddagger}{dT} = \frac{\Delta H^\ddagger}{\mathbf{R}T^2} \tag{111}$$

where $\Delta H^\ddagger$ is the enthalpy change involved in the formation of 1 mole of transition state from the reactants. $\Delta H^\ddagger$ is usually called the *enthalpy of activation*. From Eq. (109)

$$\Delta H^{\ddagger} = \mathbf{R}T^2 \frac{d \ln k}{dT} - \mathbf{R}T \tag{112}$$

Except for the relatively unimportant term $\mathbf{R}T$ the enthalpy of activation is identical with the energy of activation defined experimentally by Eq. (95).

It is convenient to define a free energy of activation $\Delta F^{\ddagger}$ by the equation

$$\Delta F^{\ddagger} = -\mathbf{R}T \ln K^{\ddagger} = -RT \ln k + RT \ln \frac{\mathbf{k}T}{\mathbf{h}} \tag{113}$$

and an entropy of activation $\Delta S^{\ddagger}$ by the equation

$$\Delta S^{\ddagger} = \frac{\Delta H^{\ddagger} - \Delta F^{\ddagger}}{T} \tag{114}$$

Combining Eqs. (113) and (114) and rearranging, we have

$$k = \frac{\mathbf{k}T}{\mathbf{h}} e^{\Delta S^{\ddagger}/\mathbf{R}} e^{-\Delta H^{\ddagger}/\mathbf{R}T} \tag{115}$$

The equation bears a close analogy to Eq. (108) of Chap. VIII. If the rate of reaction has been measured over a range of temperatures, the enthalpy of activation can be obtained by Eq. (112). The value of $\Delta S^{\ddagger}$ may then be obtained by substitution in Eq. (115). The entropy of activation may be obtained more directly through the relationship of Prob. 22 of Chap. VIII,

$$\Delta S^{\ddagger} = \frac{d(\mathbf{R}T \ln K^{\ddagger})}{dT} \tag{116}$$

from which

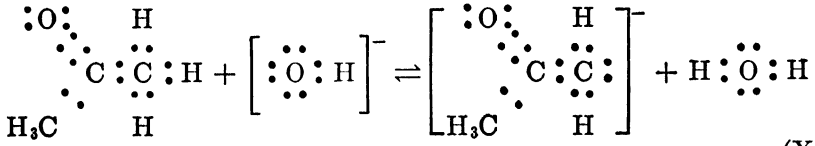
$$\Delta S^{\ddagger} = \frac{d(\mathbf{R}T \ln k)}{dT} - \mathbf{R} \ln \frac{\mathbf{k}T}{\mathbf{h}} - \mathbf{R} \tag{117}$$

Nature of Chemical Reactions. Chemical reactions involve the rupture of bonds in the reactants and the formation of new bonds in the reaction products. Very characteristically the energies of activation for reactions of measurable rate come out in the range of 10 to 30 kcal/mole for reactions in which the energy required to break the bonds is known to be of the order of 80 to 100 kcal/mole. This can only be because the new bonds are being formed at the same time that the old ones are being broken, giving the transition state a lower energy than that of a system in which the old bonds had been broken but the new ones had not yet begun to form. A transition state of this sort can easily arise in a bimolecular reaction, which we define as one which depends upon the direct and immediate reaction of two molecules without the intervention of catalysts

or solvent molecules and in a single step rather than in a succession of steps. It is much less probable in a unimolecular reaction, *i.e.*, the decomposition or rearrangement of a single molecule. This probably has much to do with the observed fact that unimolecularity is a rare phenomenon in ordinary chemical reactions. First-order reactions are common, but most of them involve complicated sequences of steps, and a system of this sort is not unimolecular.

Except for the unimolecular reaction the formation of the transition state involves an association. As we saw in Chap. VIII, an association necessarily involves a partition-function ratio less than unity and a negative entropy change. Observed entropies of activation in the gas phase run from -10 cal/mole-deg for reactions of very simple molecules to -30 cal/mole-deg for reactions of more complicated molecules. In solution, values run from -50 to $+30$, but the positive values appear only with reactions between oppositely charged ions. In such cases many of the solvent molecules attached to the ions have been set free in the transition state so that there is actually more, rather than less, freedom of motion in the transition state than in the reactants. For the few reactions which we may take confidently to be unimolecular the entropy of activation lies in the range between 0 and 10 cal/deg; for termolecular reactions it is even more negative than for bimolecular reactions involving molecules of similar complexity. Thus for the third-order reaction $2NO + O_2 \rightarrow 2NO_2$, $\Delta S^{\ddagger}$ is -47.3 at 350°K. When a reaction has so negative an entropy of activation as this, it can have a measurable rate only if the enthalpy of activation is also low [*cf.* Eq. (115)]. For the formation of NO_2 the latter value is nearly zero. This requirement probably accounts for the infrequence of observable termolecular reactions.

A large proportion of the reactions in solution and especially in solution in polar solvents, about whose mechanism we have assured knowledge, are of a type, often called *heterolytic*, in which the electrons go by twos. Thus the attack on acetone by hydroxyl ion [reaction (X)] involves the use of a pair of electrons from the hydroxyl ion to form the new bond in the water molecule and leaves the pair of electrons which formerly bonded the hydrogen to carbon attached to the carbon as an unshared pair



(XVIII)

Radical Chain Reactions. An even larger proportion of the reactions in the gas phase about which we have detailed knowledge involve what

are called *radical reaction chains*, sequences in each step of which the electrons go one by one. Such processes are called *homolytic*. Thus a mixture of hydrogen and chlorine fails to react measurably in the absence of an external stimulus, but the absorption of light of suitable wavelength or of X rays, the action of gaseous ions, or the introduction of a minute amount of sodium atoms leads to the formation of hydrogen chloride in an amount that seems out of all proportion to the magnitude of the stimulus. One light quantum or one sodium atom may induce the formation of as many as 1000 molecules of hydrogen chloride. Apparently the light quantum, which we represent by $h\nu$, or the sodium atom produces atomic chlorine by the homolytic process

$$: \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}} : \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}} : + h\nu \rightleftharpoons : \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}} \cdot + \cdot \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}} : \qquad \text{(XIX)}$$

or

$$\mathrm{Na} \cdot + : \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}} : \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}} : \rightleftharpoons [\mathrm{Na}]^+ [: \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}} :]^- + \cdot \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}} : \qquad \text{(XX)}$$

and the chlorine atoms react as follows:

$$: \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}} \cdot + \mathrm{H} : \mathrm{H} \rightleftharpoons : \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}} : \mathrm{H} + \cdot \mathrm{H} \qquad \text{(XXI)}$$

$$\mathrm{H} \cdot + : \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}} : \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}} : \rightleftharpoons \mathrm{H} : \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}} : + \cdot \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}} : \qquad \text{(XXII)}$$

The sequence of these last two reactions produces two molecules of hydrogen chloride and regenerates a chlorine atom ready to repeat the sequence. The atomic chlorine and hydrogen are called the *chain carriers*. Obviously the chain, whose links are reactions (XXI) and (XXII), can continue until something happens to a carrier which does not produce a carrier to take its place. If such chain-breaking reactions are sufficiently rare, the large number of hydrogen chloride molecules produced by the initial formation of one chlorine atom is immediately accounted for.

Possible chain-breaking reactions are

$$\mathrm{H} \cdot + \cdot \mathrm{H} \rightleftharpoons \mathrm{H} : \mathrm{H} \qquad \text{(XXIII)}$$

$$: \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}} \cdot + \cdot \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}} : \rightleftharpoons : \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}} : \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}} : \qquad \text{(XXIV)}$$

$$\mathrm{H} \cdot + \cdot \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}} : \rightleftharpoons \mathrm{H} : \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}} : \qquad \text{(XXV)}$$

Even if these reactions had large specific rates, their actual rates would be small because they are second-order reactions involving two reactants present in minute concentrations, whereas the chain-carrying reactions involve one reactant present in large concentration. In addition the chain-breaking reactions in this case, although not necessarily in cases where the radicals are complex structures, are impeded by the fact that two atoms can combine on collision only if a simultaneous collision with a third body dissipates the energy of the reaction of combination. The chain may also be broken by adsorption of a carrier on the wall of the container, a process which lowers its energy to the point where it can no longer carry on the chain. The chain may finally be broken by the reaction of a carrier with an impurity to form products which, even though they are still odd-electron substances, are incapable of attacking hydrogen or chlorine in such a way that the chain continues. Since the concentration of the carriers is minute, the concentration of chain-breaking impurity need only be small to exert a profound effect on the rate of reaction. If one carrier atom may produce 1000 molecules of hydrogen chloride, the removal of one carrier atom may inhibit the formation of 1000 molecules. Such an inhibition is in fact produced by traces of oxygen in the hydrogen-chlorine reaction. When the formation of carriers is continued by steady illumination with light of suitable frequency, the inhibiting oxygen is eventually removed by reaction with the carriers and the reaction then speeds up greatly. The reaction under these conditions shows a "period of inhibition," a period of slow or negligible reaction during which the inhibiting impurity is destroyed, after which a rapid reaction takes place.

Such radical chain processes are therefore characterized by an extreme sensitivity to traces of impurities or of deliberately added material, which react, some as reaction initiators by virtue of an easy decomposition into radicals, some as inhibitors. Some of the most familiar reactions, notably all gaseous combustion, and many reactions of industrial importance such as the polymerizations which lead to synthetic rubber and to many plastics, belong in this category. Although the reaction systems are complex, the equations for the rate of reaction may often be worked out by application of the method of the steady state (page 180).

Diffusion in Liquids. A solute particle in a dilute liquid solution is surrounded by solvent molecules which interfere with its mobility. If it is to move from such a position of equilibrium, it must push aside these molecules, and this requires energy. It then arrives at a new position of equilibrium. This is a process analogous in many ways to a chemical reaction with the extra energy required to push aside the surrounding molecules playing the part of an activation energy. The new position of equilibrium may be more or less distant from the old one; it is reasonable

to suppose that there is some average distance l which we may use in our considerations. We may expect then that the frequency r with which a solute molecule moves this characteristic distance l is proportional to the concentration of solute molecules

$$r = kc \tag{118}$$

where c is concentration and

$$k = \frac{\mathbf{k}T}{\mathbf{h}} \frac{Q^{\ddagger}}{Q^{\circ}} e^{-\Delta E_0^{\ddagger}/RT} \tag{119}$$

with the Q°'s and ΔE_0 having their usual significance in rate theory.

Consider now a slab of solution of thickness l and area A in a concentration gradient such that the concentration of solute is c on the left side of the slab and $c + dc$ on the right side. Then the number of molecules which traverse the slab from right to left in unit time will be given by $kA(c + dc)$ and the number which traverse the slab from left to right by kAc. The net result is a transfer of $kA\ dc$ molecules from right to left in unit time. This would also be the transfer through two such slabs in series if the concentration difference were dc across each slab or 2 dc in all, but it would be $\frac{1}{2}kA\ dc$ if the total concentration difference were dc. It follows that the number of molecules transferred through a distance dx is inversely proportional to dx. If we represent the number of moles transferred in unit time by dn/dt, then

$$\frac{dn}{dt} = DA \frac{dc}{dx} \tag{120}$$

The proportionality constant D, called the *diffusion constant*, is equal to the k of Eq. (118) divided by **N**.

The same equation may be shown to apply to diffusion in a mixture of gases, although for different reasons.

In view of Eq. (119) we see that a plot of log D against $1/T$ should be linear and that the slope of this plot should yield a value of the "activation energy for diffusion." The observed values are of the order of 1 to 10 kcal/mole, that is, considerably lower than the activation energies of most chemical reactions of measurable rate.

Viscosity of Liquids. The phenomena of viscosity and the techniques for studying it are described in texts on physics (MWM 219–220, Sears I 335–343). The flow of a liquid under an applied force requires the same kind of shift of a molecule from one position to another as does diffusion. In diffusion there is a net transfer in one direction because a concentration gradient makes the rate of transfer in one direction exceed that in the opposite direction. In viscous flow the net transfer of molecules results because the applied force makes flow in one direction exceed that in the

other. It is not surprising therefore that the logarithm of the coefficient of viscosity of a liquid plots linearly against reciprocal temperature, as is illustrated in Fig. 7, and that the "activation energy for viscous flow"

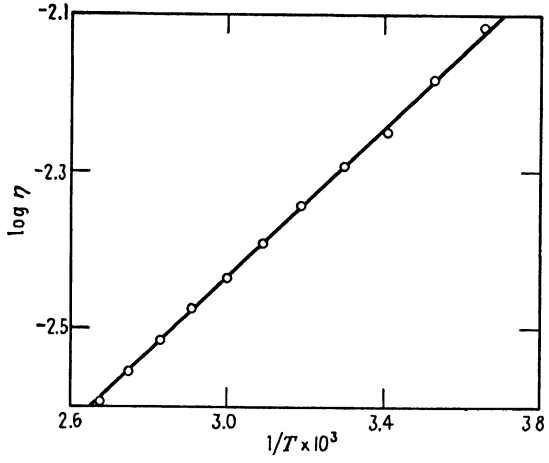


FIG. 7. Plot of the logarithm of η, the coefficient of viscosity of methyl butyrate, against reciprocal temperature. [*Data of Arrhenius, Medd. Vetenskapsakad. Nobelinst.*, **3**, (20) (1916).]

calculated from this plot is of the same order of magnitude as the activation energy for diffusion.

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PROBLEMS

1. In the first-order reaction of $(C_6H_5)_2CHCl$ with ethanol [reaction (IV)] at 25°C a solution containing 0.09798 *M* benzhydryl chloride was allowed to react, and 10-cc samples were titrated at intervals with 0.0484 *M* sodium ethylate. The following data were obtained:

Time, sec	480	1080	1980	2880	3840	5520	16080
Titer, cc	0.55	1.23	2.17	3.07	3.97	5.47	12.11

What is the specific rate?

2. The observed rotations α of a sucrose solution in 2.5 *M* formic acid at 30°C were found to be

Time, hr	2	5	10	15	20	26	30	39	45	59	73	94	133	∞
α	20.30	17.85	14.15	11	10	8 65	6 00	4 50	1 90	0.35	−1.80	−3.20	−4.30	−5.10	−5.50

What is the specific rate of the reaction?

3. At temperatures in the neighborhood of 950°K the decomposition of phosphine is first order and goes cleanly according to the reaction $4PH_3 \rightarrow P_4 + 6H_2$. Express the pressure of a system in which this reaction is occurring as an integrated function of time in a system of fixed volume.

4. In the reaction of ethyl acetate with sodium hydroxide in aqueous solution at 24.9°C a mixture was prepared containing 8.072×10^{-3} *M* ethyl acetate and 0.01001*M* sodium hydroxide. Samples were removed at intervals and the concentration of sodium hydroxide determined by titration. The following values were found:

t, min	2.27	3.01	5.85	6.83	8.02	8.92	10.05	10.96	11.93
$[NaOH] \times 10^3$	8 934	8 630	7 669	7.392	7.085	6.872	6.632	6 441	6.258

What is the specific rate of the reaction?

5. When the mutarotation of α-glucose catalyzed by a certain toluic acid buffer took place in a dilatometer, the following readings of the height h on the stem were obtained:

Time, min	0	18	40	70	120	∞
h	4 40	5 00	5.53	6.02	6.50	6.90

What is the specific rate?

6. What is the ratio of the time required for the reaction of three-fourths of the material initially present in a reaction mixture to that required for the reaction of one-half of the material initially present if the reaction is first order? What is the value of the ratio for the reaction $2A \rightarrow$ products?

7. Show that the time required for the reaction of any given fraction of the material initially present is independent of the initial concentration for a first-order reaction but varies inversely with the initial concentration for a second-order reaction.

8. What is the time for reaction of one-half the material initially present in Probs. 1 and 2?

9. When a dilute solution of benzene in nitromethane is nitrated by a considerable excess of nitric acid, a plot of dilatometer readings against time is found to be linear. What can you say about order and mechanism of this reaction?

10. It has been found experimentally that the rate of the reaction $CO + Cl_2 \rightleftharpoons COCl_2$ in the gas phase is proportional to the quantity $[Cl_2]^{\frac{1}{2}}[CO]$. What are some of the possible equations for the dependence on concentrations of the rate of the reverse reaction, the dissociation of phosgene?

11. In an aqueous-alcoholic solution of isopropyl bromide (RBr) and $S_2O_3^{--}$ two reactions occur, one of them of the first order forming ROH, the other of the second order forming $RS_2O_3^-$. If the specific rates of these reactions are k_1 and k_2, respec-

tively, what fraction of the molecules of RBr which react in any time interval dt form isopropyl alcohol?

12. The reaction of stilbene, $C_6H_5CH{=}CHC_6H_5$, with bromine in methanol solution yields two products, a dibromide, $C_6H_5CHBrCHBrC_6H_5$ and a methoxy-bromide, $C_6H_5CHBrCH(OCH_3)C_6H_5$. Assuming that the initial and rate-determining step is the reaction

$$C_6H_5CH{=}CHC_6H_5 + Br_2 \rightleftharpoons C_6H_5\overset{Br^{\oplus}}{C}HCHC_6H_5 + Br^-$$

followed by the reaction of the positive ion thus produced either with bromide ion or with the solvent, obtain expressions for the measured rate of reaction $-d[Br_2]/dt$ and for the proportion of the stilbene which is converted to the dibromide.

13. The reaction of persulfate and iodide ions follows the equation

$$2I^- + S_2O_8^{--} \rightleftharpoons 2SO_4^{--} + I_2.$$

Provided the solution is kept saturated with iodine to avoid complications associated with the rapid reversible process $I_2 + I^- \rightleftharpoons I_3^-$, the rate follows the law

$$r = k[I^-][S_2O_8^{--}].$$

In a solution containing initially 0.01 M potassium iodide and 0.005 M potassium persulfate the quantity x of iodine in moles per liter produced at time t was observed as follows:

t, min	150	290	425	490	640	720	1185	2070
10^3x	0.631	1.088	1.431	1.618	1.900	2.047	2.644	3.345

Show that these data are consistent with the rate law cited.

14. The reaction $3S_2O_8^{--} + 2Cr^{3+} + 7H_2O \rightarrow 6SO_4^{--} + Cr_2O_7^{--} + 14H^+$ is catalyzed by silver ion. In a series of experiments with the initial concentrations listed the initial slopes r of plots of persulfate ion concentration against time were found to have the following values:

$[S_2O_8^{--}]$	$[Cr^{+++}]$	$[Ag^+]$	$[H^+]$	10^4r, moles/liter-min
0.0311	0.02	0.01178	0.1	1.25
0.0311	0.01	0.01178	0.1	1.23
0.01556	0.01	0.01178	0.1	0.60
0.0311	0.01	0.00589	0.1	0.57
0.01556	0.01	0.01178	0.2	0.56

What is the order of the reaction with respect to each substance involved? What conclusions can be drawn about the reaction mechanism?

15. In terms of the information reported in Prob. 10 obtain an integrated expression for the concentration of chlorine as a function of time in a system of fixed volume in which phosgene is being formed by reaction of chlorine with a large excess of carbon monoxide.

16. Will the rate from left to right of an endothermic reaction increase with temperature more or less rapidly than the rate from right to left?

17. Chemists often assume that lowering the temperature at which a reaction is carried out will increase the proportion of the main reaction product and decrease the proportion of by-products. Show that this assumption is justified if the reaction which forms the chief product has the same entropy of activation as the reactions which form the byproducts but may not be true if the reactions have different entropies of activation.

18. It is often stated that the rates of chemical reactions are increased by a factor of 2 to 3 for every 10° rise in temperature. What activation energy corresponds to a factor of 2? What to a factor of 3?

19. The specific rates of the reaction in aqueous-alcoholic solution

$$C_2H_5Br + S_2O_3^{--} \rightarrow C_2H_5SSO_3^- + Br^-$$

are: at 12.50°C, 2.43×10^{-4} liter/mole-sec; at 25.00°, 9.53×10^{-4}; at 37.50°, 33.3×10^{-4}. Calculate energy of activation, enthalpy of activation, and entropy of activation.

20. What would be the specific rate of the reaction of Prob. 19 at 50°C? How much time would be required for half reaction in a system initially containing 0.05 mole/liter of each reactant at this temperature?

21. The reaction of butadiene and acrolein in the gas phase is second order, and its temperature dependence in the region of 80° to 150°C is given by

$$k = 10^6 e^{-16{,}700/RT}$$

with R in cal/mole-deg. If the collision theory were to apply to this reaction, what molecular diameters would be calculated? How do these compare with real molecular diameters for such molecules?

22. Explain why the slope of a plot of the logarithm of the viscosity coefficient against $1/T$ is positive. Would the corresponding plot for diffusion coefficient have a positive or a negative slope?

CHAPTER X

A FIRST APPROXIMATION TO THE PROPERTIES OF THE GALVANIC CELL

Nature of the Electric Current. A metal behaves as if it contains electrons which are relatively free to move, and the flow of electric current in a metal has all the properties to be expected of a flow of electrons (MWM 330). A few other substances, notably graphite and Fe_3O_4, have similar properties and are classed with metals as *metallic conductors.* A solution of salt or of sulfuric acid in water, on the other hand, contains no detectable concentration of electrons, and the flow of current is indissolubly associated with the motion of ions whose mass is several orders of magnitude greater than that of the electron. When current traverses the boundary between a metallic and an electrolytic conductor, it does so by virtue of electrons becoming attached to or being removed from an atom or group of atoms. Since we call chemical reactions which consist in the removal of electrons from the atoms or molecules of a substance *oxidations* and those which consist in the addition of electrons *reductions,* we may also say that flow of current across the boundary is accompanied by an oxidation or a reduction. By Faraday's *laws of electrolysis* (Pauling 303, Timm 342) the ratio of the quantity of electricity transferred to the quantity of chemical change is the constant quantity, 96,493 coulombs/equiv (23,062 cal/volt-equiv) regardless of the reaction involved.

Equilibrium at an Inert Electrode. Suppose an electrical potential difference is applied to a pair of gold, platinum, or carbon electrodes immersed in a solution containing ferric and ferrous ions. Electrodes of such materials as these, being chemically inert toward the solution, act merely as a means of bringing electrons in contact with the constituents of the solution and are said to be *inert electrodes.* The flow of current that results will involve the oxidation of ferrous ions to ferric ions at one electrode and the reduction of ferric ions to ferrous ions at the other. There exists therefore a reversible chemical process

$$Fe^{++} \rightleftharpoons Fe^{3+} + e \qquad \text{(I)}$$

which takes place at the surface of an electrode in contact with a solution containing these ions. This is forced from right to left by the presence of a relatively high concentration of electrons in the conductor, the *cathode,* to

which the *negative* side of the potential is applied, and is forced from left to right by the relatively low concentration of electrons in the other electrode, the *anode*.

By virtue of all that we have learned about the nature of reversible chemical processes we must suppose that reaction (I) takes place even in the absence of an external potential, but takes place in such a way that the rates in the two opposite directions are equal. It follows that Fe^{3+} or any other oxidant must always react in such a way as to remove electrons from an inert electrode and that ferrous ion or any other reductant must always transfer electrons to such an electrode. But the removal of electrons by the action of the oxidant sets up a potential difference between solution and electrode which opposes the further removal of electrons from the electrode and also makes it easier for the electrode to take electrons away from the solution. Consequently the rate of reaction of oxidant with electrode slows down, while that of the reaction of reductant accelerates. The eventual result is an equilibrium in which the rates of the two processes have become equal. It can be shown by chemical analysis of the solution or by the study of the electrical capacity (the ratio of charge transferred to potential change) of the electrode-solution system that the total quantity of reaction required to reach this state of equilibrium is extremely small. In any practical case we may therefore take the concentrations of oxidant and reductant in the solution and of electrons in the electrode to be essentially the same after equilibrium is attained as they were at the beginning of the process.

Potential Difference at an Electrode. In so far as the ideal law of chemical equilibrium is satisfactory, we have therefore for the state of equilibrium

$$\frac{[Fe^{3+}][e]}{[Fe^{++}]} = K \tag{1}$$

with

$$K = \frac{Q^{\circ}_{Fe^{3+}} Q^{\circ}_{e}}{Q^{\circ}_{Fe^{++}}} e^{-\Delta\epsilon_0/kT} = \frac{Q^{\circ}_{Fe^{3+}} Q^{\circ}_{e}}{Q^{\circ}_{Fe^{++}}} e^{-\Delta E_0/RT} \tag{2}$$

In contrast to the other cases we have considered, $\Delta\epsilon_0$ is not a constant with respect to the extent of reaction but depends on the difference in electrical potential between the solution and the electrode. Thus it requires more energy to transfer an electric charge, namely, the electron, from solution to electrode, *i.e.*, to make reaction (I) go toward the right, if the solution is at a positive potential relative to the electrode than it does if it is at a negative potential. Consequently we may write

$$\Delta\epsilon_0 = \Delta\epsilon_0^{\circ} + \mathcal{E}e \tag{3}$$

or, since $\mathbf{F} = \mathbf{Ne}$,

$$\Delta E_0 = \Delta E_0^\circ + \varepsilon\mathbf{F} \tag{4}$$

The quantity ε is the potential difference between solution and electrode. $\Delta\epsilon_0^\circ$ is the energy required to transfer an electron from a ferrous ion in solution to the inert electrode, leaving a ferric ion, under the following conditions: (1) both ions and the electron are in the lowest quantized energy level; (2) the potential difference between electrode and solution is zero. ΔE_0° is the corresponding quantity of energy for the transfer of 1 faraday to the electrode from 1 mole of ferrous ion. We may therefore replace the quantity $e^{-\Delta E_0/RT}$ in Eq. (2) by the product $e^{-\Delta E^\circ_0/RT}e^{-\varepsilon\mathbf{F}/RT}$. Since the changes in electron concentration involved in the approach to equilibrium are extremely small, we may take the quantity $[e]$ in Eq. (1) to be constant. From these considerations we get

$$\frac{[Fe^{3+}]}{[Fe^{++}]} = K'e^{-\varepsilon\mathbf{F}/RT} \tag{5}$$

with

$$K' = \frac{1}{[e]}\frac{Q^\circ_{Fe^{3+}}Q^\circ_e}{Q^\circ_{Fe^{++}}}e^{-\Delta E^\circ_0/RT} \tag{6}$$

The quantity K' is a constant with respect to the concentrations of oxidant and reductant and with respect to the potential difference ε. A more familiar form for Eq. (5) is

$$\varepsilon = \varepsilon^\circ - \frac{\mathbf{R}T}{\mathbf{F}}\ln\frac{[Fe^{3+}]}{[Fe^{++}]} \tag{7}$$

The quantity ε° of this equation is related to the K' of Eq. (5) by the relation

$$\varepsilon^\circ = \frac{\mathbf{R}T}{\mathbf{F}}\ln K' \tag{8}$$

ε° is called the *standard oxidation potential* of the Fe^{++}-Fe^{3+} system. It has the important quality of being the value of the solution-electrode potential when each of the concentrations involved is unity.

The extension of this argument to other electrode processes is straightforward. If the reaction involves two electrons, as in

$$Sn^{++} \rightleftharpoons Sn^{4+} + 2e \tag{II}$$

Eq. (4) becomes

$$\Delta E_0 = \Delta E_0^\circ + 2\varepsilon\mathbf{F} \tag{9}$$

since two electrons are transferred for each atom reacting and the energy change is twice as great as with one electron. Hence

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{2F} \ln \frac{[Sn^{4+}]}{[Sn^{++}]} \tag{10}$$

with a factor 2 in the denominator of the second term. The value of K' will be given by an equation analogous to Eq. (6). In place of Eq. (8) we have

$$\mathcal{E}^\circ = \frac{RT}{2F} \ln K' \tag{11}$$

again with the factor 2 in the denominator.

If the electrode process is more complicated than a simple electron transfer, all the concentrations which would appear in the statement of the ideal law of chemical equilibrium for the electrode reaction must appear in the equation for the potential difference. Thus for the oxidation of hydroquinone to quinone

$$C_6H_4(OH)_2 + 2H_2O \rightleftharpoons C_6H_4O_2 + 2OH_3^+ + 2e \tag{III}$$

which we abbreviate as

$$H_2Q \rightleftharpoons Q + 2H^+ + 2e$$

the equilibrium at the electrode is given by

$$\frac{[Q][H^+]^2[e]^2}{[H_2Q]} = K \tag{12}$$

and it follows that

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{2F} \ln \frac{[Q][H^+]^2}{[H_2Q]} \tag{13}$$

with $\mathcal{E}^\circ$ given by

$$\mathcal{E}^\circ = \frac{RT}{2F} \ln \frac{Q_Q^\circ Q_{H^+}^{\circ 2} Q_e^{\circ 2}}{[e]^2 Q_{H_2Q}^\circ Q_{H_2O}^{\circ 2}} - \frac{\Delta E_0^\circ}{2F} \tag{14}$$

An important special case occurs when the metal of the electrode is the reductant involved, as when a silver electrode is immersed in a solution containing silver ion. As we do with any equilibrium involving a pure solid phase, we omit any factor involving that phase; hence for the reaction

$$Ag \rightleftharpoons Ag^+ + e \tag{IV}$$

we have at equilibrium

$$[Ag^+][e] = K \tag{15}$$

and from this

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{F} \ln [Ag^+] \tag{16}$$

The standard oxidation potential $\mathcal{E}^\circ$ is given by

$$\mathcal{E}^\circ = \frac{\mathbf{R}T}{\mathbf{F}} \ln \frac{Q^\circ_{Ag^+} Q^\circ_e}{[e] Q^\circ_{Ag}} - \frac{\Delta E^\circ_0}{\mathbf{F}} \tag{17}$$

Another important special case is exemplified by what is called a *calomel* electrode. This consists of mercury immersed in a solution of some soluble chloride, such as KCl or HCl, which is carefully saturated with calomel Hg_2Cl_2 and contains an excess of solid calomel. The oxidation process $2Hg \rightleftharpoons Hg_2^{++} + 2e$ will be immediately followed by the precipitation of more calomel since the solution is already saturated. Similarly the reduction of mercurous ion to mercury will make the solution unsaturated and lead to the solution of calomel. The net electrode reaction is therefore

$$2Hg(l) + 2Cl^- \rightleftharpoons Hg_2Cl_2(s) + 2e \tag{V}$$

The condition for equilibrium is simply

$$\frac{[e]^2}{[Cl^-]^2} = K \tag{18}$$

since both mercury and calomel are pure phases. Consequently

$$\mathcal{E} = \mathcal{E}^\circ - \frac{\mathbf{R}T}{2\mathbf{F}} \ln \frac{1}{[Cl^-]^2} \tag{19}$$

This can also be written

$$\mathcal{E} = \mathcal{E}^\circ - \frac{\mathbf{R}T}{\mathbf{F}} \ln \frac{1}{[Cl^-]} \tag{20}$$

since $\frac{1}{2} \ln x^2 = \ln x$.

The $\mathcal{E}^\circ$ in this equation is the solution-electrode potential for the mercury–mercurous chloride–chloride-ion system when the chloride-ion concentration is 1. Because of the low solubility product of calomel the mercurous-ion concentration of such a solution is low. This $\mathcal{E}^\circ$ is therefore not identical with the $\mathcal{E}^\circ$ of the equation,

$$\mathcal{E} = \mathcal{E}^\circ - \frac{\mathbf{R}T}{2\mathbf{F}} \ln [Hg_2^{++}] \tag{21}$$

which is called the *standard oxidation potential* of the mercury–mercurous-ion system and is the potential against metallic mercury of a solution whose mercurous-ion concentration is 1.

In the light of this discussion we can formulate the general rule for writing the equation for the solution-electrode potential difference $\mathcal{E}$ as follows: Write down the same ratio of concentrations that appears in the

expression of the law of chemical equilibrium for the electrode reaction but omitting the concentration of electrons. Call this Π. Then

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT'}{n\mathbf{F}} \ln \Pi \tag{22}$$

The quantity n is the number of electrons which appears in the equation for the electrode reaction.

Conventions about Electrode Potentials. It is necessary to adhere rigidly to a definite set of conventions if hopeless confusion between positive and negative quantities is to be avoided. The conventions we shall use are the following:

1. The reaction equation for an electrode process is written so that the electrons appear on the right side.
2. The potential difference $\mathcal{E}$ is the potential of the solution relative to that of the electrode, that is, $\mathcal{E}$ is positive when the solution is more positive than the electrode.

It is a necessary consequence of these and of the usual convention about the formulation of the equilibrium law that the ratio Π of Eq. (22) contains the oxidant in the numerator and the reductant in the denominator and further that the last term in Eq. (22) is always preceded by the negative sign.*

The Junction-potential Problem. There is no method of measuring the potential difference between solution and electrode about which we have been talking. Indeed the concept is a fiction convenient for argument but canceling out in every conclusion involving observable phenomena. This is because the measurement of potential difference requires a closed circuit, which means another metallic conductor immersed either in the same solution or in another solution in contact with it. If two identical inert electrodes are immersed in the same solution, the two solution-electrode potential differences are necessarily equal in magnitude and opposite in sign and the observed potential difference between the two electrodes is therefore zero no matter what the nature of the solution.

* These conventions agree with the weight of current American usage among physical chemists. Most European chemists and most American analytical and biological chemists use a convention which formulates the electrode process with the electrons on the left and defines $\mathcal{E}$ as the potential of the electrode relative to the solution. On the basis of this convention one replaces Eq. (22) by the equation

$$\mathcal{E} = \mathcal{E}^\circ + \frac{RT'}{n\mathbf{F}} \ln \Pi$$

in which $\mathcal{E}^\circ$ is equal in magnitude but opposite in sign to the $\mathcal{E}^\circ$ of Eq. (22).

The same thing is true in a practical sense, though not in theory, even when the two inert electrodes are of different metals. It must be true because, if there were a potential difference, current would flow when the electrodes are connected and work could be obtained from the flow of current. Since the process at one electrode is the exact reverse of that at the other, the composition of the solution would remain unchanged and the process could go on forever. The system would therefore constitute a perpetual motion, and one of the surest principles we have learned from experience is that nature is so constructed that a perpetual motion is impossible.

Because, however, different metals bind electrons with different degrees of firmness, the $\Delta\epsilon_0^\circ$ of Eq. (3) is certainly different for different inert metals in contact with the same oxidant-reductant system. As a result the equilibrium potential difference has different values for different metals and the same solution. But for the same reason there is a potential difference where the two metals are in contact with each other. The two effects exactly cancel out, and the net potential which we measure is zero. As a result of this situation it makes no difference what metal we use for electrode in investigating electrode potentials so long as it either is chemically inert or is the metal involved in the reaction under consideration.

In order to make measurements of any chemical consequence or even to verify the equations we have derived, we must therefore operate with two different solutions in contact with each other, and this introduces a new and serious complication. When two solutions are brought in contact, they immediately begin to interdiffuse. If the cation of solution A is more diffusible than the anion of solution A, it diffuses more rapidly into solution B, with which A is in contact, and tends to make solution B more positive than solution A, that is, to set up a potential difference across the boundary between the two solutions. When we measure the potential of a cell in which one electrode is immersed in solution A, the other in solution B, the measured potential of the cell will then be the algebraic sum of the two potential differences at the solution-electrode boundary and the potential difference at the liquid junction. Although we can thus predict the existence of what is called a *liquid-junction potential* and can make some qualitative predictions about its magnitude, we have no quantitative theory by which its exact magnitude can be calculated except in special cases. Indeed experiment shows that the magnitude of the potential difference at the junction of two liquids which contain different electrolytes may vary by several millivolts depending on the way in which the two liquids are brought in contact with each other and the length of time during which they have been in contact.

Suppression of the Liquid-junction Potential. A detailed consideration, which we shall not attempt to carry through, of the phenomena at the boundary between two electrolyte solutions shows that the junction potential must be smaller the more nearly alike the two liquids are in concentrations and kinds of ions present. Suppose, for instance, we have one solution containing 1.975 *M* KNO_3 and 0.025 *M* $AgNO_3$ and another containing 1.9875 *M* KNO_3 and 0.0125 *M* $AgNO_3$. The total ion concentration of the two solutions is the same, 2.000 *M*, and a very large proportion of the ions in both consists of K^+ and NO_3^-. Under such conditions the theory predicts that the junction potential will be very small. This conclusion can be verified to a better precision than is often the case in reactions involving ions because the conditions of a large and constant

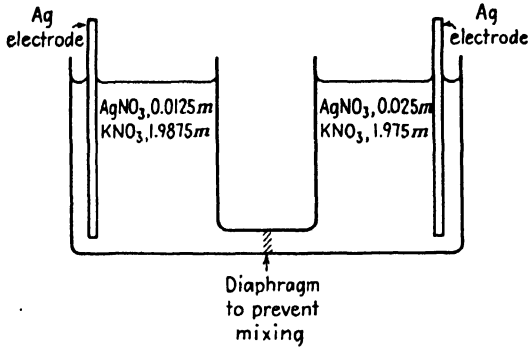


FIG. 1. A silver concentration cell.

concentration of ions not involved in the reaction (K^+ and NO_3^-) and a small concentration of ions involved (Ag^+) are just those which give the ideal law of chemical equilibrium high precision in reactions involving ions (page 324). In a cell such as that indicated in Fig. 1 we should therefore expect the potentials between the solution and the electrode to be given very closely by

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{F} \ln [Ag^+] \tag{23}$$

with $\mathcal{E}^\circ$ exactly instead of approximately independent of silver-ion concentration. At 20°C the quantity $(RT/F) \ln x = 0.05816 \log x$; consequently at this temperature the potential difference between solution and left-hand electrode in this call should be $\mathcal{E}^\circ - 0.05816 \log 0.0125$, and the corresponding value for the right-hand electrode should be $\mathcal{E}^\circ - 0.05816 \log 0.025$. If the junction potential is negligible, the total potential difference between the two electrodes must be the difference between these two quantities, the difference because the solution-electrode bounda-

ries face in opposite directions. The total potential difference $\mathcal{E}$ is therefore given by

$$\begin{aligned}\mathcal{E} &= \mathcal{E}^\circ - 0.05816 \log 0.0125 - (\mathcal{E}^\circ - 0.05816 \log 0.025) \\ &= -0.05816 \log 0.0125 + 0.05816 \log 0.025 \\ &= 0.05816 \log \frac{0.025}{0.0125} = 0.0175\end{aligned}$$

The observed potential of the cell of Fig. 1 is in fact 0.0175, confirming the assumptions.

Similar results have been obtained from a number of other cells of this type, as indicated in Table 1. The column headed $\mathcal{E}$(calc) contains values

TABLE 1. POTENTIALS AT 20°C OF SILVER CONCENTRATION CELLS*

c_1	c_2	$\mathcal{E}$(obs)	$\mathcal{E}$(calc)
a. Cells containing silver nitrate at c_1 and c_2 molar with *ca* 2 *M* potassium nitrate			
0.2000	0.1000	0.01781	0.0175
0 1000	0.0500	0.01762	0.0175
0.0500	0 0250	0.01783	0.0175
0 0250	0.0125	0.01749	0 0175
b. Cells containing silver sulfate at c_1 and c_2 molar with *ca* 4 *M* magnesium sulfate			
0.0400	0.0160	0.0229	0.0231
0 0160	0.0020	0.0528	0 0525

* From data of Brønsted, *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.*, **3**, (9) (1920).

calculated in the way we have just indicated; the column headed $\mathcal{E}$(obs) contains the experimentally observed values. The data of Table I*a* refer to cells with silver electrodes in which the solution on the left side contains c_2 molar silver nitrate and $2 - c_2$ molar potassium nitrate, while that on the right contains c_1 molar silver nitrate and $2 - c_1$ molar potassium nitrate. The data of Table I*b* refer to cells in which the solution on the left side contains c_2 molar silver sulfate and $4 - c_2$ molar magnesium sulfate, while the solution on the right contains c_1 molar silver sulfate and $4 - c_1$ molar magnesium sulfate.

Measurement of Cell Potentials. The potential of a cell cannot be measured reliably by so simple a means as that of connecting the electrodes to a voltmeter. The indications of a voltmeter depend upon a flow of current, and the potentials we have been discussing are the potentials which exist when there is equilibrium at the boundary between solution

and electrode. If there is equilibrium, there is no reaction, and if there is no reaction, there is no flow of current. The potential difference across the terminals of a galvanic cell is in fact observed to change when current is drawn from the cell by an amount which is greater the greater the current. This is partly because of the potential drop associated with the resistance of the cell, partly because the reaction at the electrodes which accompanies the current changes the concentrations in the neighborhood of the electrodes (page 291), and partly because the actual electrode processes are sometimes so sluggish that a material change in electron concentration and hence in potential is necessary to drive them at an appreciable rate. The difficulty can be minimized by making the current needed to yield an indication very small, for instance by connecting the electrodes to grid and filament of a vacuum tube and using the resulting plate current as a measure of the potential difference between the electrodes.

The problem is completely solved by the use of a potentiometer (MWM 384, Sears II, 122). Figure 2 is a conventionalized representation of this method of measuring the potential of a cell. Current from a source B flows through a resistance R. The sliding contact P is adjusted until the galvanometer G indicates that no current is flowing through the cell. Under these conditions there is balance between the potential of the cell and an opposing potential which is equal to the product of the current flowing through R and the resistance of the portion of R included between A and P. The potential of the cell under equilibrium conditions is therefore equal in magnitude and opposite in sign to this product. Both factors in the product can be measured directly, or the value of the product can be obtained by equivalent methods.

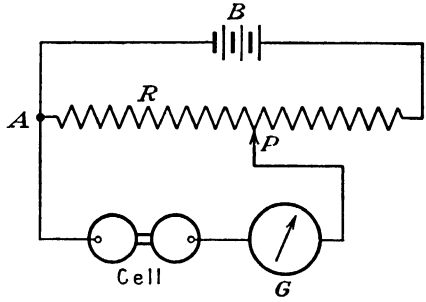


FIG. 2. Schematic representation of the measurement of the potential of a cell by means of a potentiometer.

Conventions about Cells. We use as a conventional representation of a galvanic cell a symbolism which we illustrate by the following formulation of the cell of Fig. 1:

$$\text{Ag: } KNO_3(1.9875\ M),\ AgNO_3(0.0125\ M);\ KNO_3(1.975\ M),\ AgNO_3(0.025\ M)\text{: Ag} \quad (A)$$

We use colons to indicate the boundaries between electrode and solution, semicolons for the boundaries between solutions of different composition,

while commas separate the formulas for the constituents of a single homogeneous solution.

The sign of the cell potential is taken as the sign of the *right-hand electrode.* That is, if the positive side of the opposing potential from the potentiometer must be applied to the right-hand electrode to obtain balance, the potential of the cell is said to be positive; if the negative side of the opposing potential must be applied to the right-hand electrode to obtain balance, the potential of the cell is said to be negative.

The potential of the whole cell is then the sum of individual potential differences, each taken from left to right. Thus in the case of cell (*A*) and Fig. 1 the cell potential is the solution-electrode potential difference $\mathcal{E}^\circ - 0.05816 \log 0.0125$ at the left-hand electrode plus the electrode-solution potential difference for the right-hand electrode. The latter is equal in magnitude but opposite in sign to the solution-electrode potential difference and is therefore given by $-(\mathcal{E}^\circ - 0.05816 \log 0.025)$. By adding these expressions we obtain the value given on page 212 for the cell potential. If there were a liquid junction potential, this would have to be added, its sign being positive if the right side of the junction is positive, negative if the right side is negative.

Provided the processes which occur at the liquid junction can be neglected, the cell process is described by a chemical-reaction equation which can be written as the difference between the reactions at the two electrodes, each being multiplied by such a factor that the electrons cancel in the resulting equation. Thus for the cell

$$\text{Au}: Q, H_2Q, HNO_3(c_1); HNO_3(c_1), AgNO_3(c_2): \text{Ag} \qquad (B)$$

Q being quinone and H_2Q hydroquinone, the electrode reaction on the left is (III), that on the right is (IV). If c_1 is considerably larger than c_2, the process at the liquid junction consists almost entirely in the transfer of H^+ across the boundary in one direction and the transfer of NO_3^- in the opposite direction. The former go from one solution to another of identical concentration, the latter from one solution to another of nearly identical concentration, and we take both these processes to be trivial. To cancel the electrons we must multiply reaction (IV) by 2, getting

$$2Ag \rightleftharpoons 2Ag^+ + 2e \qquad (VI)$$

If we then subtract (VI) from (III), we have

$$H_2Q + 2Ag^+ \rightleftharpoons Q + 2H^+ + 2Ag \qquad (VII)$$

We could also subtract (III) from (VI), getting

$$Q + 2H^+ + 2Ag \rightleftharpoons H_2Q + 2Ag^+ \qquad (VIII)$$

We cannot by any principle say that one of these is correct and the other wrong, for the cell reaction can always be made to go either in the one direction or in the opposite direction merely by adjusting the opposing potential. By an important convention, however, we decide that the cell process shall always be written in such a way that the reductant in the right half of the cell appears on the right side of the reaction for the cell process. The reductant in the right half of cell B is Ag; consequently reaction (VII) is a proper formulation, and reaction (VIII) is contrary to convention. The italic r's in the statement of the convention offer a possible mnemonic device.

By this procedure the cell reaction for cell A comes out

$$Ag^+(0.025\ M) + Ag(s) \rightleftharpoons Ag^+(0.0125\ M) + Ag(s)$$

which we simplify to

$$Ag^+(0.025\ M) \rightleftharpoons Ag^+(0.0125\ M) \qquad \text{(IX)}$$

since the transfer of silver metal from one piece to another is a trivial process.

Salt-bridge Device. It is an important generalization from experience that the potential difference at the junction between a concentrated aqueous solution of a salt whose cation and anion have nearly the same mobilities (page 306) and any dilute aqueous solution is to a useful approximation independent of the composition of the latter. Saturated potassium chloride is usually employed as the concentrated solution for this purpose, but ammonium nitrate and other salts are also useful in some cases. This generalization is not unreasonable theoretically because the diffusibilities of potassium and chloride ions are nearly the same and neither should get ahead of the other to set up a potential difference, while the high concentration of the potassium chloride tends to swamp out differences in diffusibility of the ions of the dilute solution. This is, however, far from a proof that the potential is zero. The experimental justification for accepting the generalization will be discussed later. Meanwhile we shall proceed to use it.

On this basis the potential of the cell

$$\text{Metal } X\text{: solution } X\text{; satd KCl; solution } Y\text{: metal } Y \qquad (C)$$

equals the difference between the two solution-electrode potential differences X and Y because the two liquid-junction potential differences are equal and opposed and hence cancel.

Hydrogen Electrode. The electrode process

$$H_2 + 2H_2O \rightleftharpoons 2OH_3^+ + 2e \qquad \text{(X)}$$

can take place on an electrode in any aqueous solution containing dissolved molecular hydrogen. In the absence of a catalyst the reaction is so sluggish that electromotively active impurities in solution or electrode have a serious effect on the potential. A fresh deposit of finely divided platinum on the electrode is an adequate catalyst. We write for the solution-electrode potential difference of this "hydrogen electrode"

$$\mathcal{E} = \mathcal{E}^\circ - \frac{\mathbf{R}T}{2\mathbf{F}} \ln \frac{[OH_3^+]^2}{P_{H_2}} \tag{24}$$

The use of the partial pressure of gaseous hydrogen with which the dissolved hydrogen is in equilibrium in place of the concentration of dissolved hydrogen has the same reason and the same justification as the corresponding procedure in the formulation of statements of the ideal law of chemical equilibrium.

Standard Oxidation Potentials. In order to establish a base line for the numerical statement of the values of solution-electrode potential differences, we now adopt the completely arbitrary convention that the value of $\mathcal{E}^\circ$ in Eq. (24) shall be 0, the pressure of hydrogen being measured in atmospheres and the concentration of OH_3^+ in moles per liter. This statement is sufficient if we are satisfied with the not very high precision to which the ideal laws apply to ions in solution. To a higher precision than this the quantity $\mathcal{E} + (\mathbf{R}T/2\mathbf{F}) \ln [OH_3^+]^2/P_{H_2}$, which must equal $\mathcal{E}^\circ$, is not constant but varies with the total ion concentration of the solution. A precise statement of the convention is that we accept the relationship

$$\lim \left\{ \mathcal{E} + \frac{\mathbf{R}T}{2\mathbf{F}} \ln \frac{[OH_3^+]^2}{P_{H_2}} \right\} = 0 \tag{25}$$

when $P_{H_2} = 1$, the limit being taken for an approach toward zero of the total ion concentration of the solution.

On this basis there are two ways in which we may establish the value of the standard oxidation potential of an electrode reaction. One of these is approximate but easy, the other precise but more difficult. For the approximate method consider the cell

Metal X: solution X; satd KCl; $OH_3^+(c$ molar), H_2(1 atm): Pt (*D*)

If the concentration of OH_3^+ and of other electrolytes in the hydrogen half cell is small enough so that the ideal laws have respectable precision, the solution-electrode potential difference at the right hand electrode will be given from Eq. (24) by

$$\mathcal{E} = -\frac{\mathbf{R}T}{\mathbf{F}} \ln [OH_3^+] \tag{26}$$

since $P_{H_2} = 1$, $\frac{1}{2} \ln x^2 = \ln x$, and, by convention $\mathcal{E}^\circ = 0$. The potential of cell (D) is therefore given by

$$\mathcal{E} = \mathcal{E}_X + \frac{\mathbf{R}T}{\mathbf{F}} \ln [OH_3^+] \tag{27}$$

with $\mathcal{E}_X$ the desired potential difference between metal X and solution X. If $\mathcal{E}$ is measured and $[OH_3^+]$ is known, the value of $\mathcal{E}_X$ then follows by substitution in Eq. (27). To the precision to which ideal laws may be applied to solution X the $\mathcal{E}^\circ$ value for metal X–solution X follows from Eq. (22) if the electrode process is known.

To appreciate the precise method, consider the cell

$$\text{Ag: AgCl(s), HCl}(m \text{ molal}); \text{HCl}(m \text{ molal}), H_2(1 \text{ atm}): \text{Pt} \qquad (E)$$

The two solutions which meet at the liquid junction differ only by the presence of a minute concentration of dissolved silver chloride on the left and of a small concentration of dissolved hydrogen on the right. Even with small concentrations of HCl the junction potential should therefore be negligible. Since HCl is a strong acid, $[OH_3^+] = [Cl^-] = m$. The potential difference $\mathcal{E}_l$ at the left electrode is given to the precision of the ideal laws by [*cf.* Eq. (20)]

$$\mathcal{E}_l = \mathcal{E}^\circ_{AgCl} - \frac{\mathbf{R}T}{\mathbf{F}} \ln \frac{1}{m} \tag{28}$$

with $\mathcal{E}^\circ_{AgCl}$ the standard oxidation potential of the electrode reaction

$$Ag(s) + 2Cl^- \rightleftharpoons AgCl(s) + 2e \tag{XI}$$

To the same precision the potential difference $\mathcal{E}_r$ at the right electrode will be given by substitution of m for $[OH_3^+]$ in Eq. (26), namely, by

$$\mathcal{E}_r = -\frac{\mathbf{R}T}{\mathbf{F}} \ln m \tag{29}$$

The potential $\mathcal{E}$ of the cell is therefore

$$\mathcal{E} = \mathcal{E}^\circ_{AgCl} - \frac{\mathbf{R}T}{\mathbf{F}} \ln \frac{1}{m} - \left(-\frac{\mathbf{R}T}{\mathbf{F}} \ln m \right) = \mathcal{E}^\circ_{AgCl} + \frac{\mathbf{R}T}{\mathbf{F}} \ln m^2 \tag{30}$$

If the solutions were ideal, we could obtain the value of $\mathcal{E}^\circ_{AgCl}$ by measuring the potential of a single cell with a known concentration m of HCl. But because deviations from ideality are relatively large with ions, we find a somewhat different value of $\mathcal{E}^\circ_{AgCl}$ for each value of m. Thus if m is 0.1238, $\mathcal{E}^\circ_{AgCl}$ comes out as -0.2347; if m is 0.009138, it comes out as -0.2274. For purposes of tabulation it is generally agreed that the value of the standard oxidation potential to be recorded for any electrode

process shall be the limit approached by the values of $\mathcal{E}^\circ$ obtained in a series of measurements of this sort when the total ion concentration of the solution approaches zero. In this case the limit is -0.2225, and this is the value which is entered in tables of standard oxidation potentials like Table 2.

TABLE 2. STANDARD OXIDATION POTENTIALS AT 25°C

Electrode Reaction	
$Li \rightleftharpoons Li^+ + e$	+3.025
$K \rightleftharpoons K^+ + e$	+2.922
$Ca \rightleftharpoons Ca^{++} + 2e$	+2.87
$Na \rightleftharpoons Na^+ + e$	+2.713
$Mg \rightleftharpoons Mg^{++} + 2e$	+2.40
$Zn \rightleftharpoons Zn^{++} + 2e$	+0.758
$Fe \rightleftharpoons Fe^{++} + 2e$	+0.44
$Cr^{++} \rightleftharpoons Cr^{3+} + e$	+0.40
$Cd \rightleftharpoons Cd^{++} + 2e$	+0.398
$Pb + SO_4^{--} \rightleftharpoons PbSO_4 + 2e$	+0.355
$Sn \rightleftharpoons Sn^{++} + 2e$	+0.14
$Pb \rightleftharpoons Pb^{++} + 2e$	+0.12
$H_2 + 2H_2O \rightleftharpoons 2OH_3^+ + 2e$	Zero
$Ti^{3+} \rightleftharpoons Ti^{4+} + e$	0.0
$Ag + Br^- \rightleftharpoons AgBr + e$	−0.073
$Cu + Cl^- \rightleftharpoons CuCl + e$	−0.129
$Ag + Cl^- \rightleftharpoons AgCl + e$	−0.2225
$2Hg + 2Cl^- \rightleftharpoons Hg_2Cl_2 + 2e$	−0.2675
$Cu \rightleftharpoons Cu^{++} + 2e$	−0.344
$MEBH_2 + 2H_2O \rightleftharpoons MEB + 2OH_3^+ + 2e$*	−0.53
$Fe(CN)_6^{-4} \rightleftharpoons Fe(CN)_6^{3-} + e$	−0.48
$3I^- \rightleftharpoons I_3^- + 2e$	−0.54
$MnO_4^{--} \rightleftharpoons MnO_4^- + e$	−0.66
$H_2O_2 + 2H_2O \rightleftharpoons O_2 + 2OH_3^+ + 2e$	−0.68
$H_2Q + 2H_2O \rightleftharpoons Q + 2OH_3^+ + 2e$†	−0.6996
$Fe^{++} \rightleftharpoons Fe^{3+} + e$	−0.771
$2Hg \rightleftharpoons Hg_2^{++} + 2e$	−0.799
$Ag \rightleftharpoons Ag^+ + e$	−0.800
$Hg_2^{++} \rightleftharpoons 2Hg^{++} + 2e$	−0.901
$Au + 4Cl^- \rightleftharpoons AuCl_4^- + 3e$	−1.00
$2Br^- \rightleftharpoons Br_2 + 2e$	−1.066
$Mn^{++} + 6H_2O \rightleftharpoons MnO_2 + 4OH_3^+ + 2e$	−1.33
$2Cl^- \rightleftharpoons Cl_2 + 2e$	−1.359
$Co^{3+} \rightleftharpoons Ce^{4+} + e$	−1.61
$PbSO_4 + 6H_2O \rightleftharpoons PbO_2 + SO_4^{--} + 4OH_3^+ + 2e$	−1.68
$Co^{++} \rightleftharpoons Co^{3+} + e$	−1.82

* *MEB* is methylene blue; $MEBH_2$ is leuco methylene blue.

† Q is quinone; H_2Q is hydroquinone.

In principle, standard oxidation potentials should always be determined by an extrapolation procedure of this sort, but this is sometimes difficult. Thus a dilute solution of ferric salt in the presence of a low concentration

of acid may be largely hydrolyzed, and this kind of phenomena complicates the extrapolation in the case of the ferrous-ferric potential. And complex-ion formation may be a serious and unrecognized factor in electrode reactions involving the ions of heavy metals. In view of these difficulties and the fact that many older measurements derive from measurements on cells with large and unknown liquid-junction potentials, the standard oxidation potentials tabulated in Table 2 are of widely varying reliability. Some, like the silver–silver chloride potential just discussed, are of a precision to be measured in 10^{-5} volt; others cannot be trusted to 0.1 volt. Nevertheless the tabulation has great practical value, as we shall see, provided one recognizes these limitations on its precision.

Calomel Reference Electrode. The hydrogen electrode is a somewhat inconvenient system in practice. Most measurements for which the precision supplied by the salt-bridge device is sufficient use therefore some other fixed half-cell or electrode system of reference. The commonest of these is what is called a *saturated calomel half cell*, but calomel cells of other compositions and half cells involving the silver–silver chloride electrode are also used. The saturated calomel half cell consists of liquid mercury in contact with an aqueous solution saturated both with solid calomel and with solid potassium chloride. The electrode process is

$$\mathrm{Hg(l) + KCl(s) \rightleftharpoons \tfrac{1}{2}Hg_2Cl_2(s) + K^+ + } e \qquad \text{(XII)}$$

If we use this system for the metal X: solution X of cell (D), we can calculate the potential difference between electrode and solution of the calomel half cell as the $\mathcal{E}_X$ of Eq. (27). The value found at 25°C ranges from -0.244 to -0.246 depending on the nature of the solution in the right half of cell (D). This vagueness arises from the approximate nature of the whole theory. We shall arbitrarily adopt for this quantity, which we represent by $\mathcal{E}_{cal}$, the value

$$\mathcal{E}_{cal} = -0.246 \qquad (25°\mathrm{C}) \qquad (31)$$

If we now set up a cell

$$\text{Metal } Z\text{: solution } Z\text{; KCl(satd), } \mathrm{Hg_2Cl_2(s)}\text{: Hg} \qquad (F)$$

its potential $\mathcal{E}$ will be given by

$$\mathcal{E} = \mathcal{E}_Z - \mathcal{E}_{cal} \qquad (32)$$

where $\mathcal{E}_Z$ is the potential difference between metal Z and solution Z. If $\mathcal{E}$ is measured, $\mathcal{E}_Z$ is then known to the precision permitted by the salt-bridge device.

Measurement of Electrometric pH. The potential $\mathcal{E}$ of the cell

$$\text{Pt: } H_2(1 \text{ atm}), \text{ solution } X; \text{ KCl(satd)}, Hg_2Cl_2(s): Hg \qquad (G)$$

is given by

$$\mathcal{E} = -\frac{RT}{F} \ln [OH_3^+] - \mathcal{E}_{cal} \qquad (33)$$

to the precision permitted by the salt-bridge device. If $\mathcal{E}$ is measured, substitution in this equation leads to a value for the concentration $[OH_3^+]$ in solution X valid to this precision. If we define the pH of the solution by

$$pH = -\log [OH_3^+] \qquad (34)$$

Eq. (33) simplifies to

$$pH = \frac{\mathcal{E} + \mathcal{E}_{cal}}{2.303RT/F} \qquad (35)$$

At 25°C, $2.303RT/F = 0.05915$, and $\mathcal{E}_{cal} = -0.246$; hence

$$pH = \frac{(\mathcal{E} - 0.246)}{0.05915}$$

Validity of Electrometric pH Measurements. In so far as these equations are valid, they are obviously of great utility. The concentration of $[OH_3^+]$ in an aqueous solution is one of the most important factors affecting the equilibrium and the rate of reactions occurring in the solution, and other solvated hydrogen ions are equally important in other solutions. No one who has ever run an electrometric titration curve or who has looked carefully at such curves as they are presented in texts on quantitative analysis (RNN, Chaps. IX, X) can doubt that the electrometric pH computed from a cell of type (*G*) by Eq. (35) bears at least a good qualitative correspondence to the actual value of the quantity $-\log [OH_3^+]$ in the solution. Nor can anyone who has used such measurements for the control of biological or engineering processes hesitate about accepting the same conclusion.

When, however, the quantitative data are scrutinized carefully, it becomes apparent that the correspondence is not by any means exact. Table 3 lists the values of pH computed by Eq. (35) from careful electrometric measurements on a series of dilute aqueous solutions at 25°C and also the actual values of the quantity $-\log [OH_3^+]$ for the same solutions. The latter are calculated by completely reliable methods from the results of conductance measurements (Chap. XIII).

Such differences as those exhibited in this table have been very irritating. We have a measurement, that of electrometric pH, which is

TABLE 3. COMPARISON OF THE QUANTITY $-\log [OH_3^+]$ WITH ELECTROMETRIC pH AT 25°C*

Solution	$-\log [OH_3^+]$	pH
0.1 *m* HCl	1.00	1.12
0.00868 *m* chloracetic acid, 0.01143 *m* sodium chloracetate	2.98	2.91
0.00107 *m* chloracetic acid, 0.001900 *m* sodium chloracetate	3.10	3.08
0.1000 *m* acetic acid, 0.1000 *m* sodium acetate	4.76	4.70
0.00900 *m* acetic acid, 0.00100 *m* sodium acetate	3.80	3.86

* Data on acetate and chloracetate buffers from MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corporation, New York, 1939, and from MacInnes, Belcher, and Shedlovsky, *J. Am. Chem. Soc.*, **60**, 1094 (1938). Data on HCl from Clark, "The Determination of Hydrogen Ions," 3d ed., The Williams & Wilkins Company, Baltimore, 1928.

clearly valid qualitatively and which is enormously useful in a practical sense. We have an electrical measuring instrument which is easily capable of a precision of 0.0001 volt, which corresponds to an uncertainty of 0.002 in the value of pH; yet we have discrepancies between real and electrometric values of $-\log [OH_3^+]$ as large as 0.1. One effort that has been made to circumvent this unpleasant situation has involved the definition of pH as $-\log a_{H^+}$, where a_{H^+} is the activity of hydrogen ion. This definition is a safe one since we have no way of measuring a_{H^+}, and this avoids the uncomfortable necessity of comparing actual values with those computed from the potential measurement. The only sensible conclusion is to recognize that the concept of pH is somewhat more fuzzy than most of the concepts with which we work, to use the pH measurement in the very many situations in which it is extremely valuable, and to recognize the futility of enforcing on the concept a precision of which it is not capable.

Relation between Equilibrium Constants and Oxidation Potentials. Consider cell (*B*) for which the cell reaction is (VII). The potential difference at the left-hand electrode is given by Eq. (13), that at the right-hand electrode by Eq. (16). The cell potential $\mathcal{E}$ is therefore

$$\mathcal{E} = \mathcal{E}_Q^\circ - \frac{RT}{2F} \ln \frac{[Q][H^+]^2}{[H_2Q]} - \left(\mathcal{E}_{Ag}^\circ - \frac{RT}{F} \ln [Ag^+] \right) \tag{36}$$

where $\mathcal{E}_Q^\circ$ is the standard oxidation potential for the hydroquinone-quinone system and $\mathcal{E}_{Ag}^\circ$ that for the silver–silver-ion system. This can be condensed to

$$\mathcal{E} = \mathcal{E}_Q^\circ - \mathcal{E}_{Ag}^\circ - \frac{RT}{2F} \ln \frac{[Q][H^+]^2}{[H_2Q][Ag^+]^2} \tag{37}$$

Note that we have changed (RT/F) ln $[Ag^+]$ to $(RT/2F)$ ln $[Ag]^2$ in order to combine it with the other logarithm, which is also preceded by the factor $RT/2F$. Substituting the standard oxidation potentials from Table 2 for 25°C and making other substitutions appropriate to this temperature, we have

$$\mathcal{E} = 0.100 - 0.0296 \log \frac{[Q][H^+]^2}{[H_2Q][Ag^+]^2} \qquad (38)$$

It follows from this equation that when the ratio $[Q][H]^2/[H_2Q][Ag^+]^2$ is large the last term of Eq. (38) will be greater than 0.100 and $\mathcal{E}$ will be negative. This means that the silver electrode is negative relative to the quinone electrode; consequently, if the circuit is closed by a metallic conductor between these electrodes, negative current will flow through the circuit external to the cell from the silver electrode to the quinone electrode. The process at the silver electrode will therefore be $Ag \rightleftharpoons Ag^+ + e$, and the course of reaction (VII) will be from right to left. If the ratio $[Q][H^+]^2/[H_2Q][Ag^+]^2$ is small, everything will be reversed, the silver electrode will be positive, and on short circuit reaction (VII) will run from left to right.

There must then be a value of the concentration ratio which makes the last term of Eq. (37) just equal to 0.100 and which therefore confers on the cell potential $\mathcal{E}$ the value 0. On closing the circuit in this case no current will flow, and no reaction will occur; hence we must conclude that the system is at equilibrium. We can best appreciate that this satisfies the criteria of a state of equilibrium from the following considerations: If the circuit is closed in a system for which $\mathcal{E}$ is negative, reaction (VII) running from right to left will use up quinone and hydrogen and will therefore decrease the concentrations of these substances. It will likewise increase the concentrations of hydroquinone and of silver ion. Both effects decrease the magnitude of the concentration ratio in the last term of Eq. (38). Since $\mathcal{E}$ was negative because the negative last term overbalanced the positive quantity 0.100, $\mathcal{E}$ will become less negative as this process continues. If on the other hand the value of the concentration ratio is such that $\mathcal{E}$ is positive, closing the circuit will run reaction (VII) from left to right, which will increase the value of the concentration ratio and make $\mathcal{E}$ less positive. We see therefore that the direction of reaction is always such as to make $\mathcal{E}$ more nearly zero. The condition that $\mathcal{E} = 0$ is therefore the condition that prevails when reaction has gone as far as it can, no matter whether it is approached from the side of excess quinone and hydrogen ion or from the side of excess hydroquinone and silver ion. These are the properties possessed by a true state of equilibrium (page 102).

We may therefore predict that, subject to the uncertainties arising from the neglect of the junction potential and the use of the ideal-solution approximation, the condition for equilibrium in the reaction

$$H_2Q + 2Ag^+ \rightleftharpoons Q + 2H^+ + 2Ag \qquad \text{(VII)}$$

is that

$$0 = \mathcal{E}^\circ_Q - \mathcal{E}^\circ_{Ag} - \frac{RT}{2F} \ln \frac{[Q][H^+]^2}{[H_2Q][Ag^+]^2} \qquad (39)$$

We have previously defined the equilibrium constant K of a reaction in such a way that for reaction (VII)

$$K = \frac{[Q][H^+]^2}{[H_2Q][Ag^+]^2} \qquad (40)$$

when the concentrations are such that the system is in equilibrium. It follows from Eqs. (39) and (40) that

$$\mathcal{E}^\circ_Q - \mathcal{E}^\circ_{Ag} = \frac{RT}{2F} \ln K \qquad (41)$$

The equilibrium constant of reaction (VII) may also be determined by mixing finely divided silver with a solution containing silver ion, quinone, and hydroquinone and determining the composition of the resulting solution after it has reached the state of equilibrium. The average value of a number of experiments of this sort obtained at 25°C by Livingstone and Lingane, *J. Chem. Education*, **15**, 320 (1938), is 2.0×10^3; the value computed from Eq. (41) and the standard oxidation potentials of Table 2 is 2.24×10^3. The agreement is probably better than can be expected in the general case, but it illustrates the essential correctness of the method used and the possibility of estimating equilibrium constants which are much too large or too small for direct measurement.

That this is a favorable case may be seen by comparing the actual value -0.0232 volt at 25°C of the cell

Pt: quinhydrone(satd), HNO_3(0.1227 *M*); HNO_3(0.1227 *M*), $AgNO_3$(0.00100 *M*): Ag

with that calculated from Eq. (38), which is -0.0243. The net effect of the junction potential and the deviations from ideality is therefore small.

Generalization of the Relation. Any oxidation-reduction reaction is the difference between two electrode processes. One of these, which we shall call the *direct process*, is written in the same order in the electrode reaction as it is in the total reaction. Thus in reaction (VII) the direct process is $H_2Q \rightleftharpoons Q + 2H^+ + 2e$, because when it is written according

to the accepted convention with the electrons on the right, H_2Q appears on the left side and Q on the right, and this is the order in which these symbols appear in Eq. (VII). The other electrode process we shall call the *reverse process.* We represent the standard oxidation potential of the direct process by $\mathcal{E}_d^\circ$, that of the reverse process by $\mathcal{E}_r^\circ$. An argument parallel to that which led to Eq. (41) then demonstrates that

$$\mathcal{E}_d^\circ - \mathcal{E}_r^\circ = \frac{\mathbf{R}T}{n\mathbf{F}} \ln K \tag{42}$$

K is the equilibrium constant of the total oxidation-reduction reaction. n is the number of electrons transferred from one oxidant to the other reductant when the reaction proceeds; its value is 2 in reaction (VII).

Standard Free-energy Change and Standard Oxidation Potentials. The standard free-energy change of a reaction $\Delta\bar{F}^\circ$ is related to the equilibrium constant by the equation [Eq. (87) of Chap. VIII]

$$\Delta\bar{F}^\circ = -\mathbf{R}T \ln K \tag{43}$$

It follows that for an oxidation-reduction reaction

$$\Delta\bar{F}^\circ = -n\mathbf{F}(\mathcal{E}_d^\circ - \mathcal{E}_r^\circ) \tag{44}$$

pH Measurement by the Quinhydrone Electrode. Quinone and hydroquinone form a 1:1 compound quinhydrone, which is difficultly soluble in water. Saturation of an aqueous solution with the compound provides small and equal concentrations of quinone and of hydroquinone. For such a solution the factors $[Q]$ and $[H_2Q]$ in Eq. (13) cancel, and the equation becomes

$$\mathcal{E}_Q = \mathcal{E}_Q^\circ - \frac{\mathbf{R}T}{\mathbf{F}} \ln [OH_3^+] \tag{45}$$

Consequently the potential of the cell

Au: solution X satd with quinhydrone; KCl(satd), Hg_2Cl_2(s): Hg *(H)*

is given by

$$\mathcal{E} = \mathcal{E}_Q^\circ - \frac{\mathbf{R}T}{\mathbf{F}} \ln [OH_3^+] - \mathcal{E}_{cal} \tag{46}$$

Substituting the numerical values for 25°C, this becomes

$$\mathcal{E} = -0.6996 - 0.05915 \log [OH_3^+] + 0.246 \qquad (25°C) \tag{47}$$

from which

$$\text{pH} = \frac{\mathcal{E} + 0.454}{0.05915} \qquad (25°C) \tag{48}$$

The quinhydrone electrode is not satisfactory in solutions of pH greater than 7, partly because hydroquinone is a weak acid and changes the pH of the solution and partly because quinone decomposes rapidly in alkaline media.

Glass Electrode. Because both the hydrogen electrode and the quinhydrone electrode depend upon mobile oxidation-reduction reactions at the electrode, they cannot be employed for pH measurements in solutions which contain active oxidants or reductants. The active reagents in solution would react directly either with the hydrogen–hydronium-ion system or with the hydroquinone-quinone system in such a way as to alter the composition of the solution. The "glass electrode" does not possess this disadvantage, and it has in consequence become the most widely used device for pH measurement. The method depends upon the empirical observation, for which reasonable but complicated theoretical interpretations can be given, that a potential difference exists between an aqueous solution and a glass surface which is independent of the presence or absence of oxidation-reduction systems and which follows the law

$$\mathcal{E} = \mathcal{E}^\circ - \frac{\mathbf{R}T}{\mathbf{F}} \ln [OH_3^+] \tag{49}$$

except in the presence of considerable alkali concentrations in alkaline solution. Consequently the cell

Calomel electrode; solution of unknown pH: glass diaphragm: solution of fixed pH; calomel electrode (*I*)

possesses a potential which is a measure of the pH of the unknown solution. There are six potential differences in this cell, two electrode-solution boundaries involving mercury and the solutions of the calomel half cells, two at liquid junctions, and two between glass and aqueous solutions. Only one depends on the acidity of the unknown solution. Lumping the others together with the $\mathcal{E}^\circ$ of Eq. (49), we have

$$\text{pH} = \frac{\mathcal{E} - \mathcal{E}^{\circ\prime}}{2.303\mathbf{R}T/\mathbf{F}} \tag{50}$$

The value of $\mathcal{E}^{\circ\prime}$ is determined by inserting a solution of known pH in place of the unknown in cell (*I*).

Determination of Other Ion Concentrations. The principle of the pH measurement may be applied to the determination of unknown ion concentrations other than that of hydronium ion. Thus the potential of the cell

Ag: KNO_3(1.98 *M*), $AgNO_3$(0.02 *M*); KNO_3(1.98 *M*), KCl(0.02 *M*), AgCl(s): Ag (*J*)

in which the right-hand solution is saturated with silver chloride, was found by Brønsted, *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.*, **3** (9) (1920), to be −0.3705 volt at 20°C. Junction potentials should be negligible (page 211). Assuming that silver chloride is a strong electrolyte, its solubility s equals the quantity $[Ag^+]$ in the right half of the cell. By the standard rules the potential is given by

$$\mathcal{E} = \mathcal{E}^\circ_{Ag} - \frac{RT}{F} \ln 0.02 - \left(\mathcal{E}^\circ_{Ag} - \frac{RT}{F} \ln s\right) \qquad (51)$$

Substituting the above value of the potential, we get $s = 1.092 \times 10^{-8}$. If we multiply this silver-ion concentration by the concentration of chloride ion, which is 0.02, we obtain the value 2.184×10^{-10} for the solubility-product constant (page 313). This is the value of the solubility-product constant in the presence of a large concentration of potassium nitrate and is considerably larger than the value for a saturated solution of silver chloride in pure water. But because the large concentration of potassium nitrate makes the junction potential and the deviations from ideality negligible, it is a value possessing high precision. A value for the solubility-product constant in more dilute solutions may be obtained from measurements of such a cell as

$$Ag: AgNO_3(c_1); NH_4NO_3(satd); KCl(c_2), AgCl(s): Ag \qquad (K)$$

in which c_1 and c_2 are small. While the result thus obtained is useful because other methods of measuring the solubility equilibrium are difficult or impossible with such slightly soluble substances as silver chloride, the value cannot be expected to have high precision because of the junction-potential difficulty.

A similar method may be employed for investigating the equilibrium of the formation of such stable complex ions as $Ag(NH_3)_2^+$ and $Ag(CN)_2^-$.

Conditions Required for the Determination of the Oxidation-Reduction Potential. It is in principle impossible to remove oxygen *completely* from a solution; it is in fact impossible to obtain completely inert electrodes, for the purest platinum and gold contain traces of reducing metals. Such impurities as these tend to establish a solution-electrode potential, and it is only when the system under investigation is highly mobile with respect to the transfer of electrons to or from the electrode that the effect of the impurities is completely overcome. Thus a gold electrode immersed in a solution containing hydrogen and hydronium ion does not take up the potential corresponding to equilibrium in the process $H_2 + 2H_2O \rightleftharpoons 2OH_3^+ + 2e$, whereas a platinum electrode so treated as to have high catalytic activity for this reaction does. Consequently it is possible to determine the potentials of oxidation-reduction reactions only when these

either inherently or in the presence of a catalyst have a high rate of reaction.

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Further study:

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PROBLEMS

1. To the dilute-solution approximation a tenfold increase in the concentration of Fe^{3+} decreases the potential of a solution containing Fe^{++} and Fe^{3+} relative to an inert electrode by 0.059 volt at 25°C. Make similar predictions for: (*a*) an increase in the concentration of Tl^+ in a system containing Tl^+ and Tl^{3+} and an inert electrode, (*b*) an increase in the concentration of $Fe(CN)_6^{3-}$ in a system containing $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ and an inert electrode; (*c*) an increase in the concentration of sodium sulfate in a system consisting of a solution of sodium sulfate saturated with lead sulfate and a lead electrode; (*d*) an increase in the concentration of acid in a system consisting of a strong acid, hydrazobenzene, $C_6H_5NHNHC_6H_5$, azobenzene, $C_6H_5N{=}NC_6H_5$, and an inert electrode.

2. Write the cell reactions for the following cells, and predict from Table 2 the value of the potential in both sign and magnitude:

a. Pt: H_2(1 atm), NaOH(0.01 *M*); NaOH(0.01 *M*), HgO(s): Hg

b. Pb: $PbSO_4$(s), H_2SO_4(0.01 *M*); H_2SO_4(0.01*M*), PbO_2(s): Pb

c. Pt: quinhydrone(s), $HClO_4$(0.01 *M*); $HClO_4$(0.01 *M*), $MnClO_4$(0.001 *M*), MnO_2(s): Pt

3. By how much and in what direction will the potential of the cell of Prob. 2*a* change if the concentration of alkali is multiplied by 10? What would be the effect upon this cell if the hydrogen pressure were reduced to 0.1 atm? What would be the effect upon the potentials of the cells of Prob. 2*b* and 2*c* of increasing the acid concentration by a factor of 10?

4. Write cell reactions for the following cells, and predict whether the potential will be positive or negative

a. Tl amalgam 10% Tl: Tl_2SO_4(0.01 *M*): Tl amalgam 5% Tl

b. Pt: O_2(1 atm), H_2O_2(0.1 *M*), $HClO_4$(0.01 *M*); KCl(satd);$K_3Fe(CN)_6$(0.01 *M*), $K_4Fe(CN)_6$(0.01 *M*): Pt

5. Set up schematic representations of cells in which the following reactions occur, and estimate the cell potentials at 25°C to the dilute-solution approximation, assuming that junction potentials can be eliminated by the salt-bridge device:

a. $2Ag^+$(0.01 *M*) + Cu(s) $\rightleftharpoons$ 2Ag(s) + Cu^{++}(0.01 *M*)

b. $PbSO_4$(s) + Zn(s) $\rightleftharpoons$ Pb(s) + SO_4^{--}(0.01 *M*) + Zn^{++}(0.01 *M*)

c. $2OH_3^+$(0.01 *M*) + MnO_2(s) + H_2O_2(0.01 *M*) $\rightleftharpoons$ Mn^{++}(0.01 *M*) + O_2(1 atm) + $4H_2O$

6. Obtain a formula for the dependence on the pH of solution *X* of the potential at 25°C of the cell

Pt: H_2(1 atm), solution *X*; KCl(satd), AgCl(s): Ag

7. Estimate the equilibrium constants and the standard free-energy changes, both at 25°C, for the reactions of Prob. 5 and for the reactions occurring in the cells of Prob. 2.

8. Compute the pH of solutions having the following values of $[OH_3^+]$: 0.1, 2.0×10^{-5}, 6×10^{-12}.

9. If the potential of cell (*G*) is 0.300 volt at 25°C, what is the pH of solution *X*? What is the pH if the potential is 0.500 volt? What if it is 0.750 volt?

10. The observed potential at 25°C in the system

$$Hg: Hg_2Cl_2(s), KCl(satd); \text{solution } X: \text{glass: } HCl(0.1\ M)\ AgCl(s): Ag$$

is found to be −0.3510 with a certain glass diaphragm. When a buffer solution which is known to have a pH of 6.49 is substituted for solution *X*, the potential becomes −0.2916. What is the pH of solution *X*?

11. In connection with a potentiometric titration of NaCl with $AgNO_3$ a potential of −0.017 volts was observed at 25°C in the cell

$$Ag: AgCl(s), NaCl(0.064\ M); KNO_3(satd); KCl(1\ M), Hg_2Cl_2(s): Hg$$

The potential of the electrode system on the right, which is called the *normal calomel electrode*, is known to be −0.281 volt. To what value of the solubility-product constant of silver chloride does this datum lead?

12. Calculate a value of the standard free-energy change of the reaction $H_2 + O_2 \rightleftharpoons H_2O_2$ from the data of Table 2.

13. From data of Table 2 estimate the solubility-product constant of lead sulfate.

14. From data of Table 2 estimate the equilibrium constant of the reaction $Hg + Hg^{++} \rightleftharpoons Hg_2^{++}$.

15. The cell

$$Cd: Cd(ClO_4)_2(0.00972\ M), NaClO_4(2.99\ M); NaClO_4(2.90\ M), Cd(ClO_4)_2(0.00972\ M), NaCN(0.094\ M): Cd$$

has a potential of −0.4127 volt at 25°C. If the only reaction of significance between Cd^{++} and CN^- is the formation of $Cd(CN)_4^{--}$, what is the equilibrium constant for the formation of this complex ion? If you could set up a series of cells of this sort differing only in the concentration of sodium cyanide added to the right side, how could you determine whether or not the assumption that only $Cd(CN)_4^{--}$ is present is justified?

16. Solution *X* was prepared by adding 10 cc of a solution containing 0.2050 *N* $K_2Cr_2O_7$ and 0.2000 *M* HCl to 75 cc of a solution containing 0.00484 *N* hydroquinone and 0.2 *M* HCl. The cell Au: solution *X*; KCl(satd), $Hg_2Cl_2(s)$: Hg showed a potential of −0.4115 at 25°C. What would be the potential of a similar cell in which solution *X* was replaced by a solution made by adding 1 cc of the dichromate solution to 75 cc of the hydroquinone solution? The oxidation of hydroquinone to quinone by dichromate at this acidity is essentially complete.

CHAPTER XI

AN INTRODUCTION TO THE THERMODYNAMIC CONCEPT OF FREE ENERGY AND ITS APPLICATION TO CHEMICAL PROBLEMS

Necessity of the Thermodynamic Approach. In our study of physical chemistry we have now encountered a considerable variety of approximate but very useful relationships, the perfect-gas and dilute-solution laws, the ideal law of chemical equilibrium, the reaction-rate equations, and the equations for the potentials of cells, which have in common the property that the precision with which they agree with the actual behavior of nature increases with increasing dilution. We have recognized qualitatively that the difference between the behavior of real substances and that predicted by these ideal or limiting laws arises in every case from the same source, the existence of forces of attraction between gas molecules or between solute molecules whose magnitude decreases with increasing distance between the molecules of the gas or of the solute. We have not, however, attempted to set up quantitative relations between the magnitude of the deviations from one of these laws and that of the deviations from another. It is primarily for the purpose of studying such quantitative relationships that we now approach the further application to chemical problems of the science of thermodynamics.

Relation between Useful Work and the Approach to Equilibrium. We have previously (page 102) had occasion to state the extremely important generalization from experience known as the second law of thermodynamics in the form that a given system may be displaced away from equilibrium only at the expense of some other system which moves toward equilibrium. We now wish to make the qualitative idea of displacement away from or toward equilibrium quantitative, *i.e.*, we wish to be able to say that the displacement of system A toward equilibrium by some definite amount which may be expressed by a number is competent to displace system B away from equilibrium by a definite quantitative amount. In this connection we find the concept of the *reversible useful work* of a process helpful.

By sufficient ingenuity we can always use the displacement of any system toward equilibrium as a source of what we call useful work, which we may think of as the raising of a weight, the compressing of a spring,

or the like. Likewise we can always use the fall of a weight or the expansion of a spring as the displacement toward equilibrium required to force any system in which we may be interested away from equilibrium. Thus the chemical reaction in a storage battery driving a motor can raise a weight, and the flow of heat from the higher temperature of the boiler to the lower temperature of the condenser of a steam engine can furnish the same kind of useful work. On the other hand the fall of a weight can be employed to drive a generator which can charge the storage battery and thereby displace the chemical system in the battery away from equilibrium. And the falling weight can drive a refrigerating machine which forces heat from the cool inside to the warmer outside of a refrigerator.

Now it is clearly true that the work y that must be supplied to displace a system from a state B to a state A which is further removed than B from the equilibrium state must be at least as great as the work x that can be gained by the displacement of the same system from state A to state B. The mechanism by which the weight is raised and by which the weight acts on other systems when it falls must involve some friction as do all mechanisms. A certain amount of the effort put into raising the weight is therefore wasted in overcoming friction, and a certain amount of the accomplishment that might be gained from the fall of the weight is wasted in the same way; consequently the effort is always greater than the accomplishment.

More generally we see that x cannot be greater than y because if it were we could use the displacement of the system from A to B to raise a weight of mass m to a height $x/m\mathbf{g}$, then allow the fall of the weight through a distance $y/m\mathbf{g}$ to return the system from B to A. The weight would be higher than at the beginning of the process by the distance $(x - y)/m\mathbf{g}$, that is, would have been displaced away from equilibrium, while the system in state A has not progressed toward equilibrium. Such a result is contrary to the second law, and it follows that x cannot be greater than y. It is in fact one of the surest conclusions about the behavior of nature which the human race has reached that a perpetual motion is impossible, and the device we have been talking about would be a perpetual motion if x were greater than y.

Reversible Work. In any practical case quite a bit can be done to reduce the difference $y - x$. One can refine the mechanisms to reduce friction; one can reduce the electrical inefficiencies represented by the RI^2 effect and polarization at the electrodes by operating at a low rate. It is possible therefore to imagine an ideal case in which the difference has become infinitesimal, *i.e.*, smaller than any assigned finite quantity. In this idealized case the magnitudes of x and y become identical, and either may be taken as the measure of what is called the *reversible work* of the

$A \rightleftharpoons B$ process. The reversible work is then the ideal upper limit of the work x that may be obtained from the spontaneous process $A \rightarrow B$, and it is also the idealized lower limit to the work y that must be expended to carry out the reverse process $B \rightarrow A$.

According to the convention that work done by a system on the surroundings is positive, the reversible work of the spontaneous process is a positive number, and the reversible work of the reverse process is a negative number of the same magnitude.

The concept of reversible work is closely parallel to a number of familiar ideas. Thus the pressure of a gas is a quantity which can be defined only as lying between an upper and a lower limit (page 2). In terms of a sample of gas confined in a cylinder (Fig. 1 of Chap. I) provided with a piston of area A on which a weight of mass m acts there will inevitably be a range of weights within which the piston moves in neither direction. Let the lower limit of this range be m_1, that is, let m_1 be the smallest weight which will prevent the piston from rising, and let m_2 be the upper limit, the largest weight that can be placed on the piston without making it fall. We can then define the pressure by the inequality

$$\frac{m_2 \mathbf{g}}{A} > P > \frac{m_1 \mathbf{g}}{A} \tag{1}$$

By improving our instrumentation we can reduce the breadth of the range between m_1 and m_2, but we cannot make it zero. Consequently we can define the pressure of the gas only in terms of an idealized limit in which m_1 and m_2 have come to differ only infinitesimally.

If the weight has a value slightly less than m_1, say $m_1 - dm$, the piston will rise and the expansion of the gas, a spontaneous process, will therefore have done work by raising the weight. If the increase in volume is dv the work done by the gas on the weight will be $(\mathbf{g}/A)m_1\, dv - (\mathbf{g}/A)\, dm\, dv$. This is positive work from the point of view of the gas. Similarly, if the weight has a value slightly greater than m_2, say $m_2 + dm$, the piston will fall, and the work $(\mathbf{g}/A)m_2\, dv + (\mathbf{g}/A)\, dm\, dv$ will be done on the gas by the weight. This is negative work from the point of view of the gas according to the convention, and the quantity is in fact negative because dv is negative. By the definition of reversible work we have therefore for the reversible work w_r associated with the expansion of the gas by the amount dv

$$-\frac{\mathbf{g}}{A} m_2\, dv > w_r > \frac{\mathbf{g}}{A} m_1\, dv \tag{2}$$

We have justifiably neglected the small quantity of the second order $dm\, dv$. Comparing Eqs. (1) and (2), we see that

$$w_r = P\, dv \tag{3}$$

within any precision to which either w_r or P can be defined. There is therefore just as much but just as little uncertainty and indefiniteness about the pressure of the gas as there is about the reversible work of its expansion.

A similar situation is involved in the definition of the potential of a galvanic cell. This is measured by balancing the cell potential against a known opposing potential. We thereby bracket the value of the cell potential between $\mathcal{E}_1$, the numerically smallest opposing potential which will prevent the flow of current in the sense of discharge of the cell, and $\mathcal{E}_2$, the numerically largest opposing potential which fails to cause a flow of current in the opposite direction. We may visualize the opposing potential as derived from a mechanism which can act as a motor to raise a weight or can be driven as a generator by the fall of the weight. Then the maximum work that can be done by the cell on the weight when dq coulombs flow in the sense of discharge of the cell is $\mathcal{E}_1\, dq$, and the minimum quantity of work done on the cell by the fall of the weight is $\mathcal{E}_2\, dq$ for every dq coulombs. The reversible work associated with the reaction in the cell of the quantity of material corresponding to dq coulombs is therefore bracketed between the quantities $|\mathcal{E}_1\, dq|$ and $|\mathcal{E}_2\, dq|$. The reversible work is known to the same precision and with the same definiteness that the potential of the cell is known.

Devices for Obtaining Work from a Process. Work may be derived from a given process by a variety of mechanisms or devices. Thus work can be obtained from the process consisting in the flow of heat from a boiler to a condenser by means of a reciprocating steam engine, by means of a mercury turbine, or by means of a number of other devices. Each of these devices may in principle be refined so that the actual work obtained from the spontaneous process approaches the reversible work of the process. The reversible work of the process $A \rightarrow B$, which is the upper limit of the actual work, must have the same value for all these devices. If this were not so, if the reversible work w_k for the device k were greater than the reversible work w_j for the device j, we could couple the two devices in such a way that the system proceeds from A to B by the device k and is returned to its original state by the device j. The net quantity of work $w_k - w_j$ would then have been done by the system on the surroundings without the system having been displaced toward equilibrium. This is contrary to the second law; indeed such a combination of devices would constitute a perpetual motion.

Work and Equilibrium. If a system is already at equilibrium, it cannot be displaced further toward equilibrium, and it cannot therefore act in such a way as to displace another system away from equilibrium. Specifically it cannot raise a weight or do any other useful work. It

follows that a system which is at equilibrium is incapable of doing useful work. In view of the relation between work and electrical potential discussed on page 232 this conclusion includes the finding of page 222 that the potential of a cell must be zero if the reaction which constitutes the cell process is at equilibrium. The converse conclusion, namely, the rule that a system which is incapable of doing useful work is at equilibrium, may be derived from the following *reductio ad absurdum:* Suppose that a cell has a potential of zero but that the cell reaction is not at equilibrium. The materials involved in the cell at the concentrations which yield a potential of zero could therefore be allowed to react toward equilibrium independently of the cell. They could then be returned to the cell, whose potential would not now be zero. The potential might not be given exactly by the equations of the last chapter, but the change in concentration would inevitably result in a change in potential. Since the changed potential is not zero, the cell could operate to do useful work until the resulting changes in concentration (*cf.* page 222) brought the potential back to zero. This cycle could be repeated indefinitely, producing useful work without a permanent displacement of the cell reaction toward equilibrium. By the second law this is impossible; therefore the situation in which the potential is zero but the cell reaction not at equilibrium is impossible. This argument may be generalized to all the ways in which a chemical reaction or other process can do work, thus justifying the proposition that a system incapable of doing work is necessarily at equilibrium.

Another Convention about Signs. The conclusion that the reversible work associated with the flow of dq coulombs of electricity through a cell is given by $\pm|\mathcal{E}\ dq|$, the quantity being positive if the flow of current is in such a direction that the system moves toward equilibrium and negative if it moves away from equilibrium, needs to be supplemented by a convention about signs. We shall use the convention that dq shall be positive if the cell reaction as written goes from left to right when this quantity of electricity flows and that dq shall be negative if the reaction runs from right to left.

Let us consider the results of this convention in terms of a particular case, the cell

$$\text{Au: } Q,\ \text{H}_2Q,\ \text{HNO}_3;\ \text{HNO}_3,\ \text{AgNO}_3\text{: Ag} \qquad (A)$$

This may be set up (page 214) in such a way that the effects at the liquid junction are trivial and the cell reaction consists in

$$\text{H}_2Q + 2\text{Ag}^+ \rightleftharpoons Q + 2\text{H}^+ + 2\text{Ag} \qquad (\text{I})$$

Suppose the concentrations in this cell are such that the potential is positive. By convention this means that the right-hand electrode is positive

relative to the left-hand electrode. If the circuit is closed, positive current will therefore flow through the connecting wire from the silver electrode to the quinhydrone electrode. The electrode reaction

$$Ag \rightleftharpoons Ag^+ + 2e \qquad (II)$$

must then run from right to left, because positive current *out* from the silver electrode is equivalent to negative current, *i.e.*, to a flow of electrons, *into* the electrode. It follows that reaction (I) runs from left to right. This spontaneous flow of current could be used to do work against the surroundings; hence by convention w_r is positive. $\mathcal{E}$ is positive, and by the convention we have just adopted dq is positive; consequently

$$w_r = \mathcal{E}\, dq \qquad (4)$$

By considering all possible cases, including those in which $\mathcal{E}$ is negative and those in which current is forced through a cell by an opposing potential in the direction opposite to that of the spontaneous process, it can be shown that Eq. (4) is valid no matter what the signs of the three quantities involved, provided they are all defined in terms of the conventions we have adopted.

Useful Work in a System at Constant Pressure. The chemist is especially interested in systems which are maintained at a fixed temperature and a fixed pressure. That is, he is likely to thermostat the system he is working with and to expose it to the pressure of the atmosphere. If the process under consideration is accompanied by a change in volume, a complete balance sheet on the work accompanying the process must include the quantity $P\,\Delta v$, which represents positive or negative work done by the system against the confining pressure P. So long as the system is restricted to the fixed pressure P, this pressure-volume work is not useful work in the sense that it is available for the raising of weights and the like. It is work that is committed to operation against the confining pressure and which is not therefore available for any other purpose. If we represent the total reversible work of a process by w_r and the useful reversible work by w_r', we have therefore

$$w_r' = w_r - P\,\Delta v \qquad (P \text{ constant}) \qquad (5)$$

For a system maintained at fixed pressure, everything we have said about the relation between work and equilibrium applies to the useful reversible work thus defined and not to the total reversible work.

The difference between total work and useful work may be considerable when gases are involved. Consider the cell

$$Pt: H_2(1\ atm),\ HCl(c);\ HCl(c),\ Hg_2Cl_2(s): Hg \qquad (B)$$

for which the cell reaction is

$$H_2(1 \text{ atm}) + Hg_2Cl_2(s) \rightleftharpoons 2HCl(c) + 2Hg(l) \qquad \text{(III)}$$

For the amount of reaction represented by the quantity of electricity dq and the volume change dv the useful work w_r' is the work which may be obtained from the flow of current, *i.e.*,

$$w_r' = \mathcal{E}\, dq \tag{6}$$

and the total work w_r is given by

$$w_r = \mathcal{E}\, dq + P\, dv \tag{7}$$

Since the flow of dq coulombs is by Faraday's laws accompanied by the reaction of $\frac{1}{2}\, dq/\mathbf{F}$ moles of hydrogen and the volume of 1 mole of hydrogen is $\mathbf{R}T/P$, we have

$$dv = -\frac{\mathbf{R}T}{2\mathbf{F}P}\, dq \tag{8}$$

The sign is negative because hydrogen is consumed, *i.e.*, the volume decreases when dq is positive, *i.e.*, when reaction runs from left to right. We may therefore write

$$\frac{w_r}{dq} = \mathcal{E} - \frac{\mathbf{R}T}{2\mathbf{F}} \tag{9}$$

$$\frac{w_r'}{dq} = \mathcal{E} \tag{10}$$

For reaction (III) $\mathcal{E}$ is in the neighborhood of $+0.27$ volt, the exact value depending on the HCl concentration; the quantity $\mathbf{R}T/2\mathbf{F}$ is 0.0128 volt.

Free Energy. We now introduce an incomplete but exact definition of the free energy of a system, incomplete because restricted to a system maintained at a fixed temperature and pressure, as follows: The free-energy change accompanying any process in a system maintained at constant pressure and temperature equals the reversible useful work of the process, *i.e.*,

$$\Delta f = -w_r' \qquad (T \text{ and } P \text{ constant}) \tag{11}$$

where f is free energy.

We further define the *quantity of reaction* dx as equal to the change in the number of moles of any substance divided by the stoichiometric coefficient which precedes the symbol of that substance in the equation. We understand that the stoichiometric coefficient is to be positive for substances which appear on the right side of the equation and negative for substances which appear on the left side. Thus for reaction (III) dx equals one-half the increase in the number of moles of HCl or of Hg and

one times the decrease in the number of moles of H_2 or of Hg_2Cl_2. Any reaction may in principle go either from left to right or from right to left; we have defined dx so that it is positive when the reaction goes from left to right and negative when it goes in the opposite direction. We have already (page 209) defined a quantity n, which we shall call the *electrochemical equivalent of a reaction*, as the number of electrons transferred from reductant to oxidant when the reaction occurs. n is always a positive number. In the case of reaction (III) its value is 2 since two electrons are transferred from the one hydrogen molecule to the two mercury atoms in Hg_2Cl_2.

It follows from these definitions and the convention about the sign of quantity of electricity dq by way of Faraday's laws that

$$dx = \frac{dq}{n\mathbf{F}} \tag{12}$$

By Eq. (6) the useful work which accompanies the flow of dq coulombs is $+\mathcal{E}\ dq$; hence by Eq. (11) the free-energy change df is given by

$$df = -\mathcal{E}\ dq \tag{13}$$

and by Eq. (12)

$$df = -n\mathbf{F}\mathcal{E}\ dx \tag{14}$$

Although the galvanic cell offers an easy way to visualize the possibility of obtaining work from a chemical reaction and is frequently a useful method of measuring the reversible work and hence the free-energy change accompanying the process, it is extremely important to realize that, so far as the free-energy change is concerned, the cell is merely a device for obtaining work from the reaction. As we have seen, the reversible work of the process must be the same if any other device is used to obtain work from the process. In a constant-pressure system the quantity $P\ \Delta v$ depends only on the initial and the final state of the system. It follows therefore from Eqs. (5) and (11) that the free-energy change in a given process is independent of the device by which work may be obtained from the process.

Free Energy as a Property of a System. What this amounts to is that the free energy of a system is a property of the system (page 54). Considering first a system of constant temperature and pressure, we know that the reversible work of the spontaneous process $A \rightarrow B$ must be equal in magnitude and opposite in sign to the reversible work of the process $B \leftarrow A$. The cycle $A \rightarrow B \rightarrow A$ leads therefore to a net work of zero. The volume change is necessarily zero since the system returns to its original state. Δf is therefore zero for the cyclic process at constant temperature and pressure. By the considerations of the last paragraph this conclusion is valid no matter what device or mechanism may have been

employed to get work from the spontaneous process or to do work in forcing the process in the opposite direction. This quality of having a value which is completely determined by the state of a system and independent of the way in which the system has attained that state is just the characteristic of what we have defined as the nature of a property of the system.

Although we have not yet learned to define the change in free energy which accompanies a process in which temperature or pressure changes, we can see that the principle that free energy is a property of a system is valid even if such processes are involved. Consider two states A and A' which differ in temperature or pressure or in both properties, and suppose that the free energy of the system in state A' depended on the rate at which the system was brought from A to A' or on the intermediate stages through which it had passed in the same process. Then we should be able to convert two identical systems at A to two systems of different free energy at the temperature and pressure of A'. These two systems would therefore undergo different changes in free energy if they were now transformed to some state B' at the temperature and pressure of A'. But if this were true, it would be possible to couple the two processes in such a way as to have a perpetual motion. We must therefore conclude that the free energy of the system in state A' does not depend upon the path or the rate of the process by which it attained that state but is determined only by the properties of the state itself.

Free-energy Change in an Irreversible Process. A system may react in such a way that it does no work or less work than the reversible work. The process is then said to be *irreversible*. The word is a bit confusing because it tends to carry the implication that the process cannot be driven in the reverse direction, whereas it can be so driven by the expenditure of a quantity of work greater than that gained from the spontaneous process. As an example, consider a galvanic cell which has been short-circuited for a period during which reaction occurs but no work is done. The system will thereby have lost in ability to do work just as much as if the same amount of reaction had been accompanied by the performance of reversible work. Since therefore the work that can be performed by further reversible reaction has been decreased by the short circuit, the free energy has also been decreased by an amount equal to the useful work that might have been done if the reaction which occurred during the short circuit had taken place reversibly. Indeed it is just because we wish to measure the ability to do work, rather than to describe the actual quantity which has been done in the past, that we define the quantity free energy. There is also a loss in ability to do work and therefore in free energy if we mix silver metal and an acid solution of quinone and let reaction (I) run from right to left, and this loss must be as great as it would be if the materials

had been set up in the form of cell A and allowed to do work as they reacted.

Absolute Value of Free Energy Not Defined. We have not defined the absolute value of the free energy of a system, but only the change which accompanies a process. This causes just as much and just as little difficulty as the fact that we do not define the absolute value of the energy of a system.

Free Energy and Equilibrium. It follows from the definition of free energy and what we have said about the relation between useful reversible work and the approach toward equilibrium that the spontaneous displacement toward equilibrium of a system maintained at constant temperature and pressure must be accompanied by a decrease in free energy; that the forced displacement away from equilibrium of a system of this kind must be accompanied by an increase in free energy; that the condition in which the system possesses the lowest value of free energy compatible with the prevailing temperature and pressure corresponds exactly to the condition of equilibrium for that temperature and pressure.

Consider what this means in terms of a reversible chemical reaction, specifically in terms of reaction (I). As we have seen (page 222), it is possible to prepare a mixture of the materials involved in this reaction of such a composition that the reaction proceeds spontaneously from left to right. In terms of the definition of page 235 the quantity x increases; because this is a spontaneous progression toward equilibrium, f must decrease. When the materials are merely mixed together, the reaction can proceed only until the composition becomes such that a state of equilibrium exists, but if they are set up in the form of cell (A), reaction can be forced past the point of equilibrium by the imposition of a potential from outside. A plot of f against x must then have the character of Fig. 1. Reaction from left to right is at first spontaneous, and f decreases as x increases; in the region of high x values, x can increase only if the reaction is forced from outside, and f increases as x increases; the value of f must therefore go through a minimum, and when f has its minimum value, the reaction is at equilibrium.

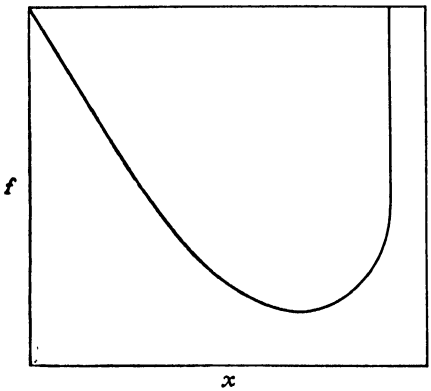


FIG. 1. Schematic plot of the relation between free energy f and quantity of reaction x.

Since the mathematical condition for the minimum is that

$$\frac{df}{dx} = 0 \tag{15}$$

we have reached the very general and exact conclusion that equilibrium exists in a system maintained at constant temperature and pressure only when Eq. (15) applies to the reactions of which the system is capable. The conclusion is general and exact because the only assumptions we have used in reaching it are that the second law is universally valid and exact and that a chemical reaction is capable of doing work when it proceeds toward equilibrium and may be forced away from equilibrium by work done on the system from outside. Whether the conclusion is useful depends upon the success we can attain in relating the value of the quantity df/dx to the composition of systems of chemical interest. In order to investigate this, we introduce a new quantity.

Molal Free Energy, or Chemical Potential. It is shown in Appendix A that, if the free energy of a system of fixed temperature and pressure is determined by the amounts n_A, n_B, and n_C of three substances which can interact according to the process

$$A + B \rightleftharpoons 2C \tag{IV}$$

then for an amount dx of reaction according to this equation

$$df = -\left(\frac{\partial f}{\partial n_A}\right)_{T,P,n_B,n_C} dx - \left(\frac{\partial f}{\partial n_B}\right)_{T,P,n_A,n_C} dx + 2\left(\frac{\partial f}{\partial n_C}\right)_{T,P\ n_A,n_B} dx \tag{16}$$

The quantity $(\partial f/\partial n_A)_{T,P,n_B,n_C}$ is the rate at which the total free energy of the system changes with changing number of moles of A, *under such conditions that the number of moles of all other substances in the system, as well as the temperature and pressure are constant.* We call this quantity the *molal free energy* or the *chemical potential* of the substance A and represent it by the symbol $\bar{F}_A$,* that is, we define

$$\bar{F}_A = \left(\frac{\partial f}{\partial n_A}\right)_{T,P\ n_B,n_C} \tag{17}$$

* Nomenclature and symbolism in this area are not standardized. Gibbs, who invented chemical thermodynamics, called the quantity defined by Eq. (17) the *potential of substance A* and used the symbol μ for it. Lewis, who taught chemists how to use exact thermodynamics, called the quantity *molal free energy* and represented it by F when A forms a pure phase but called it *partial molal free energy* and represented it by $\bar{F}$ when A is a constituent of a gaseous, liquid, or solid solution. The terms *chemical potential* and *thermodynamic potential* have also come to be widely used.

With this definition we can abbreviate Eq. (16) to

$$\left(\frac{\partial f}{\partial x}\right)_{T,P} = -\bar{F}_A - \bar{F}_B + 2\bar{F}_C \tag{18}$$

We further define a quantity $\Delta\bar{F}$, which we call the *free-energy change of the reaction*, by the relation

$$\Delta\bar{F} = \left(\frac{\partial f}{\partial x}\right)_{T,P} \tag{19}$$

and have therefore for reaction (IV)

$$\Delta\bar{F} = -\bar{F}_A - \bar{F}_B + 2\bar{F}_C \tag{20}$$

For reaction (I) the corresponding equation is

$$\Delta\bar{F} = -\bar{F}_{H_2O} - 2\bar{F}_{Ag^+} + \bar{F}_Q + 2\bar{F}_{Ag} + 2\bar{F}_{H^+} \tag{21}$$

The general rule for writing the relationship for a reaction is the following: Multiply the molal free energy $\bar{F}$ of each substance by the number which precedes the symbol of that substance in the chemical-reaction equation, giving the number a negative sign for substances on the left side of the equation and a positive sign for substances on the right side. Form the sum of these quantities, and equate it to the free-energy change of the reaction $\Delta\bar{F}$. This rule exactly parallels the rule which relates the energy change in a reaction to the molal energies of the reactants and the similar rule for the enthalpy change.

By Eqs. (15) and (19) the condition for equilibrium in a system of constant temperature and pressure may be expressed in the form

$$\Delta\bar{F} = 0 \tag{22}$$

Potential of a Cell and Free Energy Change of the Cell Reaction. We have by Eq. (19) for any infinitesimal amount of reaction at constant temperature and pressure

$$df = \Delta\bar{F}\, dx \tag{23}$$

Comparing this with Eq. (14), we have

$$\Delta\bar{F} = -nF\mathcal{E} \tag{24}$$

where $\mathcal{E}$ is the potential of a cell involving the reaction.

Molal Free Energy as Intensive Property. The value of $\Delta\bar{F}$ for any process remains unchanged if the total amount of material present is altered provided there is no change in concentration of any phase. Thus it would be obviously absurd to suppose that the potential of cell (B) and hence the work that can be obtained by allowing the cell to discharge

would be altered if the quantity of mercury available for the cell process were changed by closing a stopcock so arranged as to isolate part of the mercury from the cell. Indeed it can be shown that if there were a change in potential it would be possible to set up a perpetual motion, the only assumption being that the work required to open and close the stopcock can be neglected. Since mercury can take part in many reactions, the value of $\Delta\bar{F}$ can be independent of the quantity of mercury in all of them only if the molal free energy of mercury $\bar{F}_{Hg}$ is independent of the quantity of mercury. It follows therefore that the molal free energy of a substance is an intensive property, *i.e.*, a property which, like density or molal energy, depends upon the kind of matter but is independent of the total quantity of matter of a given kind and composition which is present in a given system. Since by Eq. (17) molal free energy is the ratio of a free energy f to a quantity of substance n, the free energy must be an extensive property.

General Conclusions. We have now reached the following conclusions: (1) We may define for any substance A a quantity $\bar{F}_A$, which is an intensive property of any system containing that substance. (2) The quantity $\Delta\bar{F}$, which is the difference between the $\bar{F}$ values for the reactants and the products in any process, has the property that $\Delta\bar{F}\ dx$ equals the negative of the useful reversible work which may be obtained from the quantity of reaction dx at constant temperature and pressure. (3) If $\Delta\bar{F}$ is zero for a certain process under given conditions, the system is at equilibrium with respect to that process under those conditions, and if the system is at equilibrium, the value of $\Delta\bar{F}$ is zero. (4) The value of $\Delta\bar{F}$ for a process may be obtained from measurements of the reversible potential of a galvanic cell whose operation consists in that process or by any other method by which the process may be made to do work in something which approaches a reversible fashion.

These are extremely general and rigidly exact statements about the reversible work and the equilibrium of a process. They permit exact and completely reliable predictions to be made both about matters such as cell potentials which are related to reversible work and also about equilibrium conditions provided exact relationships can be learned which describe the relation between the composition of a material and the $\bar{F}$ values of the constituents of the material.

Molal Free Energy of a Pure Phase. In the particular case of a pure phase composed of a single pure substance maintained at a fixed temperature and pressure, $\bar{F}$ is constant. For, as we have seen, the value is independent of the total quantity of the phase, and the composition is unalterable. In such cases we use the symbol $\bar{F}^\circ$ instead of $\bar{F}$, the $^\circ$ superscript implying constancy at constant temperature and pressure.

Molal Free Energies of Solutes in Dilute Solution. The potential of the cell

$$\text{Ag: } AgNO_3(c_2),\ KNO_3(2 - c_2);\ AgNO_3(c_1),\ KNO_3(2 - c_1)\text{: Ag} \qquad (C)$$

is well approximated by the formula (page 211)

$$\mathcal{E} = \frac{\mathbf{R}T}{\mathbf{F}} \ln \frac{c_1}{c_2} \qquad (25)$$

By Eq. (24) therefore

$$\Delta\bar{F} = -\mathbf{R}T \ln \frac{c_1}{c_2} \qquad (26)$$

The cell reaction is

$$Ag^+(c_1) + Ag_s \rightleftharpoons Ag^+(c_2) + Ag_d \qquad (V)$$

the symbol Ag_d representing silver in the right-hand electrode and Ag_s silver in the left-hand electrode. The free-energy change is therefore given by

$$\Delta\bar{F} = \bar{F}_2 - \bar{F}_1 + \bar{F}_d - \bar{F}_s \qquad (27)$$

$\bar{F}_1$ and $\bar{F}_2$ being the molal free energies of silver ion in solutions of concentration c_1 and c_2, respectively, and $\bar{F}_d$ and $\bar{F}_s$ being the molal free energies of metallic silver on the right-hand and left-hand electrodes, respectively. By the considerations of the last paragraph the molal free energy of the pure phase metallic silver is a characteristic property of the substance which has a constant value at any given temperature and pressure. Consequently $\bar{F}_d = \bar{F}_s$, and Eq. (27) reduces to

$$\Delta\bar{F} = \bar{F}_2 - \bar{F}_1 \qquad (28)$$

Comparing Eqs. (26) and (28), we have

$$\bar{F}_2 - \bar{F}_1 = \mathbf{R}T \ln c_2 - \mathbf{R}T \ln c_1 \qquad (29)$$

This can be true for all value of c_1 and c_2 only if for all values of the concentration c of silver ion the molal free energy is given by

$$\bar{F} = \bar{F}^\circ + \mathbf{R}T \ln c \qquad (30)$$

The quantity $\bar{F}^\circ$ is a constant at constant temperature and pressure and is called the *standard free energy of the substance whose concentration is c.*

Two points require especial attention. First, Eq. (30) is an approximate relationship, which is more nearly valid the more nearly the conditions approach those of the ideal solution. This follows from the fact that Eq. (25) is an approximation of the same kind. Second, the coefficient $\mathbf{R}T$ in front of the logarithm has come into the picture in the devel-

opment we have followed by way of the Boltzmann equation (page 205). We can justify the value by the impressive sum total of verification of that expression and more immediately by the validity of Eq. (25) as a close approximation under favorable conditions. We shall learn later that a purely thermodynamic argument can be given for the coefficient $\mathbf{R}T$.

The form of Eq. (30) is further verified by the validity of the ideal law of chemical equilibrium as a close approximation under favorable conditions. Consider reaction (IV),

$$A + B \rightleftharpoons 2C \tag{IV}$$

By the ideal law of chemical equilibrium the condition for equilibrium in this reaction is

$$\frac{[C]^2}{[A][B]} = K \tag{31}$$

By Eqs. (20) and (22) the exact condition for equilibrium is

$$\Delta\bar{F} = -\bar{F}_A - \bar{F}_B + 2\bar{F}_C = 0 \tag{32}$$

If relations of the type of Eq. (30) apply to A, B, and C, Eq. (32) becomes

$$-\bar{F}_A^\circ - \mathbf{R}T \ln [A] - \bar{F}_B^\circ - \mathbf{R}T \ln [B] + 2\bar{F}_C^\circ + 2\mathbf{R}T \ln [C] = 0 \tag{33}$$

which may be rearranged to

$$-\bar{F}_A^\circ - \bar{F}_B^\circ + 2\bar{F}_C^\circ = -\mathbf{R}T \ln \frac{[C]^2}{[A][B]} \tag{34}$$

The left side of this equation is a constant at constant temperature and pressure by virtue of the definition of the standard free energy $\bar{F}^\circ$. We may set it equal to a quantity $\Delta\bar{F}^\circ$, which we call the *standard free-energy change of the reaction.* This standard free-energy change is related to the standard free energies of the reactants and products in the same way that the molal free-energy change, $\bar{F}$ without the $^\circ$ superscript, is related to the molal free energies $\bar{F}$ (Eq. 20). With this definition Eq. (34) may be rearranged to

$$\frac{[C]^2}{[A][B]} = e^{-\Delta\bar{F}^\circ/\mathbf{R}T} \tag{35}$$

Since the right side of this equation is constant at constant temperature and pressure, Eq. (35) is consistent with the ideal law of chemical equilibrium [Eq. (31)]. This consistency with respect to a single reaction does not prove that Eq. (30) must be valid for each reactant. But if the same consistency is to be obtained for all reactions involving a solute A, this

can only be because $\bar{F}_A$ is equal to one constant plus another constant multiplied by ln $[A]$.

Molal Free Energy of a Constituent of a Gaseous Mixture. The same argument applied to a reaction in the gas phase with the ideal law of chemical equilibrium written in terms of the partial pressures of the reactants leads to the conclusion that the molal free energy of substance X in a gaseous mixture is given by

$$\bar{F}_X = \bar{F}^\circ_X + \mathbf{R}T \ln P_X \tag{36}$$

to the precision to which the ideal equilibrium law applies to reactions in that mixture. The standard free energy $\bar{F}^\circ_X$ in this equation is not equal to the value of $(\bar{F}^\circ_X)_c$ in the likewise valid equation

$$\bar{F}_X = (\bar{F}^\circ_X)_c + \mathbf{R}T \ln [X] \tag{37}$$

For if we substitute $[X] = P_X/\mathbf{R}T$ in Eq. (37), we get

$$\bar{F}_X = \{(\bar{F}^\circ_X)_c - \mathbf{R}T \ln (\mathbf{R}T)\} + \mathbf{R}T \ln P_X \tag{38}$$

The quantity in braces is a constant at constant temperature and pressure if $(\bar{F}^\circ_X)_c$ is constant and is equal to the $\bar{F}^\circ_X$ of Eq. (36).

If we use Eq. (36), we see that $\bar{F}^\circ_X$ is the value of $\bar{F}_X$ when the partial pressure of X is unity. If the pressure is measured in atmospheres, we say in this case that we have chosen the "standard state" of substance as that of gaseous X at 1 atm. If we use Eq. (37), we say that we have chosen the standard state of X as a concentration of unity. If we measure concentration in moles per liter $(\bar{F}^\circ_X)_c$ is the value of $\bar{F}_X$ when the concentration is 1 mole/liter.

Thermodynamic Justification of Some Familiar Formulas. By virtue of the rule of page 240, Eq. (32) involves twice the molal free energy of substance C because the factor 2 appears before the symbol of this substance in reaction (IV). This leads to a factor 2 in front of the term $\mathbf{R}T$ ln $[C]$ in Eq. (33), and this in turn leads to a squaring of the concentration of C in the equation for the ideal law of chemical equilibrium [Eq. (35)]. The familiar rule that the concentration of a substance must carry as exponent in the expression for the ideal law of chemical equilibrium the number which precedes its formula in the equation for the chemical reaction is therefore a necessary result of the thermodynamic rules for the condition of equilibrium.

If substance C in reaction (IV) is a pure solid while A and B are solutes or gases, the molal free energy of C is a constant $\bar{F}^\circ_C$. In this case we would replace Eq. (33) by

$$-\bar{F}^\circ_A - \mathbf{R}T \ln [A] - \bar{F}^\circ_B - \mathbf{R}T \ln [B] + 2\bar{F}^\circ_C = 0 \tag{39}$$

from which the expression for the ideal law of chemical equilibrium would become

$$\frac{1}{[A][B]} = e^{-\Delta\bar{F}^\circ/RT} \tag{40}$$

This justifies on the basis of thermodynamics the familiar rule that the expression for the equilibrium law includes no factor related to substances present as pure solid or liquid phases. $\Delta\bar{F}^\circ$, however, continues to include the term $2\bar{F}_c^\circ$.

Relation to Statistical-mechanical Ideas. We have now defined for ideal systems a quantity $\bar{F}^\circ$, the standard free energy of a substance, in two different ways. In Chap. VIII it was defined in terms of the microscopic properties of the substance, specifically in terms of the energy of the lowest quantized energy level and the spacing of the other levels above the lowest one. In the present chapter we have given the same name and symbol to a quantity defined in terms of macroscopic properties, specifically in terms of the reversible useful work of processes involving the substance. In terms of the first definition we found in Eq. (87) of Chap. VIII that $\Delta\bar{F}^\circ$, the difference in $\bar{F}^\circ$ values between reactants and products in a reaction, is related to the constant K of the ideal law of chemical equilibrium by the relation

$$\Delta\bar{F}^\circ = -RT \ln K \tag{41}$$

Comparing Eqs. (31) and (35) of this chapter, we now see that Eq. (41) is equally valid when molal free energy is defined in the second way. It follows that the two very different approaches define an identical quantity $\Delta\bar{F}^\circ$, at least to the precision of the ideal laws. This can be true for all the reactions into which a particular substance may enter only if for any given substance the two definitions of $\bar{F}^\circ$ for that substance are also identical within this precision.

Activity and Fugacity Coefficients. The great virtue of the ideas which have been developed in this chapter is that they make it possible to describe the behavior of a system, and in particular to state the conditions for the state of equilibrium in the system, even when the perfect-gas and dilute-solution laws are not sufficiently precise. For this purpose it has proved useful to define a quantity γ_X. For a gaseous substance the definition may be written

$$\bar{F}_X = \bar{F}_X^\circ + RT \ln P_X + RT \ln \gamma_X \tag{42}$$

P_X is the partial pressure of X, and $\bar{F}_X^\circ$ is independent of the partial pressure of X and of the partial pressures of other gases which may be present. Defined in this way, γ_X is called a *fugacity coefficient.* This may seem an

unnecessarily complicated form of definition, but chemists seem to prefer it to the equivalent explicit form

$$\gamma_X = \frac{1}{P_X} e^{(\bar{F}_X - \bar{F}_X^\circ)/RT} \tag{43}$$

If X is a solute in liquid solution, the definition is

$$\bar{F}_X = \bar{F}_X^\circ + RT \ln [X] + RT \ln \gamma_X \tag{44}$$

or some similar form involving molality or mole fraction instead of concentration in moles per liter. Defined in any of these ways, γ_X is called an *activity coefficient.*

If $\gamma_X = 1$, $RT \ln \gamma_X = 0$ and Eqs. (42) and (44) reduce to the ideal equations

$$\bar{F}_X = \bar{F}_X^\circ + RT \ln P_X \tag{45}$$

for the gas and

$$\bar{F}_X = \bar{F}_X^\circ + RT \ln [X] \tag{46}$$

for the solute. It must therefore be possible to make the extent to which the value of γ_X deviates from a constant value of 1 a direct measure of the extent to which the substance X deviates from ideal behavior. Since the ideal behavior is a limiting behavior approached by dilute solutions or gases, this requires for the gas case that

$$\lim_{P \to 0} \bar{F}_X = \bar{F}_X^\circ + \lim_{P \to 0} (RT \ln P_X) \tag{47}$$

because in this limit $\gamma_X = 1$ and $RT \ln \gamma_X = 0$. Now the definition of γ_X imposed no restrictions on the numerical value of $\bar{F}_X^\circ$, merely requiring that it be constant with respect to changes in partial pressures; consequently we may define it in any way consistent with these restrictions, and we choose the definition

$$\bar{F}_X^\circ = \lim_{P \to 0} (\bar{F}_X - RT \ln P_X) \tag{48}$$

which is merely a rearrangement of Eq. (47). If this value of $\bar{F}_X^\circ$ is substituted in Eq. (42), it becomes clear that $\lim (RT \ln \gamma_X) = 0$ and $\lim \gamma_X = 1$. By defining $\bar{F}_X^\circ$ in this way we have therefore provided that γ_X shall approach unity as P_X approaches zero and the behavior of X approaches the ideal. This advantage is partially balanced by the disadvantage that numerical values can be given to $\bar{F}_X^\circ$ and γ_X only by making measurements in systems so dilute that the approximation to ideality is close and further that no simple physical meaning can be given to the concept of the standard state, *i.e.*, to the state in which $\bar{F}_X = \bar{F}_X^\circ$.

For a solute we define $\bar{F}^\circ_X$ by the relation

$$\bar{F}^\circ_X = \lim_{[X]\to 0} \{\bar{F}_X - \mathbf{R}T \ln [X]\} \tag{49}$$

We thereby provide in this case also that γ_X shall approach unity as the concentration of X approaches zero and its behavior approaches ideality.

Chemical Equilibrium in Nonideal Systems. Consider the chemical reaction in a homogeneous gas or liquid system

$$A \rightleftharpoons B \tag{VI}$$

without making any assumptions of the validity of the perfect-gas or dilute-solution laws. The condition for equilibrium

$$\bar{F}_B - \bar{F}_A = 0 \tag{50}$$

becomes

$$\bar{F}^\circ_B - \bar{F}^\circ_A + \mathbf{R}T \ln \frac{[B]}{[A]} + \mathbf{R}T \ln \frac{\gamma_B}{\gamma_A} = 0 \tag{51}$$

in the light of Eq. (44). A corresponding equation involving partial pressures and fugacity coefficients instead of concentrations and activity coefficients will be obtained for the case of a reaction in the gas phase. From this we have

$$\frac{[B]}{[A]} = K \frac{\gamma_A}{\gamma_B} \tag{52}$$

K being a constant at constant temperature and pressure, whose value is given by

$$K = e^{-(\bar{F}_B^\circ - \bar{F}_A^\circ)/\mathbf{R}T} = e^{-\Delta \bar{F}^\circ/\mathbf{R}T} \tag{53}$$

We see therefore that (1) the quantity $[B]/[A]$, which would be constant if the ideal law of chemical equilibrium were exactly valid, varies when the composition of the system changes because the γ's vary; (2) the ratio is approximately constant, *i.e.*, the ideal law works, if the system is sufficiently dilute so that γ's may be taken to be unity; (3) the variation of the ratio with composition can be quantitatively predicted if the dependence of the γ's on the composition of the system is known quantitatively.

We have thus developed techniques by which we can approach the problem of the condition for equilibrium in an ammonia synthesis mixture at 1000 atm, in which the ratio

$$\frac{P^2_{\mathrm{NH_3}}}{P_{\mathrm{N_2}} P^3_{\mathrm{H_2}}}$$

is far from constant even at constant temperature and pressure, or the problem of the condition for equilibrium in the third ionization of phos-

phoric acid in which the ratio

$$\frac{[OH_3^+][PO_4^{3-}]}{[HPO_4^{--}]}$$

is extremely sensitive to any change in the concentration and kind of ions present in the solution.

Exact Treatment of Galvanic Cells. Consider the cell

$$\text{Ag: AgCl(s), HCl}(m)\text{; HCl}(m)\text{, H}_2(1\text{ atm})\text{: Pt} \qquad (D)$$

in which the molality of HCl is m in both halves of the cell. The cell reaction is

$$2\text{Ag(s)} + 2\text{H}^+ + 2\text{Cl}^- \rightleftharpoons \text{H}_2 + 2\text{AgCl(s)} \qquad \text{(VII)}$$

and the free-energy change $\Delta\bar{F}$ is therefore given by

$$\Delta\bar{F} = \bar{F}_{H_2} + 2\bar{F}_{AgCl} - 2\bar{F}_{Ag} - 2\bar{F}_{H^+} - 2\bar{F}_{Cl^-} \qquad (54)$$

If we are meticulous, we shall note that some free-energy change is involved in the transfer of hydrogen ion from the left side of the cell, in which silver ion is present, to the right side, in which it is absent, and in the transfer of chloride ion in the opposite direction. But silver chloride is so insoluble that these effects are negligible unless the molality of HCl is unusually small. This is another way of saying that the liquid-junction potential is negligible.

By Eq. (24) the potential of the cell is given by

$$\mathcal{E} = -\frac{1}{2\mathbf{F}}(\bar{F}_{H_2} + 2\bar{F}_{AgCl} - 2\bar{F}_{Ag} - 2\bar{F}_{H^+} - 2\bar{F}_{Cl^-}) \qquad (55)$$

The silver and the silver chloride are pure phases for which $\bar{F}$ has the constant value $\bar{F}°$. Using Eq. (42) for the molal free energy of the hydrogen and Eq. (44) for the ions, we get

$$\mathcal{E} = -\frac{\Delta\bar{F}°}{2\mathbf{F}} + \frac{\mathbf{R}T}{2\mathbf{F}}\ln\frac{[H^+]^2[Cl^-]^2}{P_{H_2}} + \frac{\mathbf{R}T}{2\mathbf{F}}\ln\frac{\gamma_{H^+}^2\gamma_{Cl^-}^2}{\gamma_{H_2}} \qquad (56)$$

with

$$\Delta\bar{F}° = \bar{F}°_{H_2} + 2\bar{F}°_{AgCl} - 2\bar{F}°_{Ag} - 2\bar{F}°_{H^+} - 2\bar{F}°_{Cl^-} \qquad (57)$$

This equation completely and exactly describes the way in which the potential of such a cell varies with the molalities of hydrogen and chloride and the partial pressure of hydrogen. For the case that P_{H_2} is constant we may define a quantity $\mathcal{E}°$ by the relation

$$\mathcal{E}° = -\frac{\Delta\bar{F}°}{2\mathbf{F}} - \frac{\mathbf{R}T}{2\mathbf{F}}\ln P_{H_2} - \frac{\mathbf{R}T}{2\mathbf{F}}\ln\gamma_{H_2} \qquad (58)$$

Since HCl is a strong electrolyte, we can write $[H^+] = [Cl^-] = m$. Changing the numerical coefficient before the logarithm and the exponent inside, we have

$$\mathcal{E} = \mathcal{E}^\circ + \frac{RT}{F} \ln m^2 + \frac{RT}{F} \ln \gamma_{H^+}\gamma_{Cl^-} \tag{59}$$

This may also be put in the form

$$\mathcal{E} - \frac{RT}{F} \ln m^2 = \mathcal{E}^\circ + \frac{RT}{F} \ln \gamma_{H^+}\gamma_{Cl^-} \tag{60}$$

All the quantities involved in the left-hand member of this equation may be fixed or determined in an actual experiment. Both in theory and in

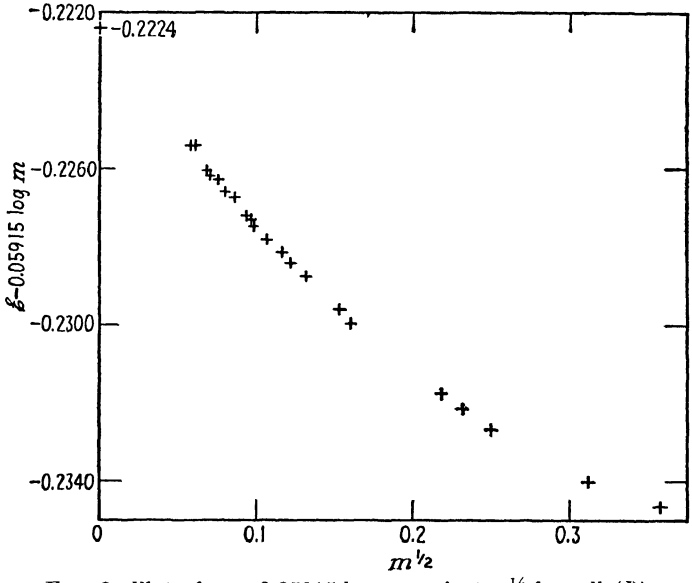


FIG. 2. Plot of $\mathcal{E} - 0.05915 \log m$ against $m^{1/2}$ for cell (*D*).

practice the dependence of the γ's on the molality of HCl is of such a nature that a plot of this left-hand member against $m^{1/2}$ approaches linearity in dilute solutions. Such a plot is shown in Fig. 2. As m approaches 0, the term in Eq. (60) involving the γ's approaches 0; consequently the intercept on the axis of ordinates is the value of $\mathcal{E}^\circ$. For the case plotted in Fig. 2 this turns out to be -0.2224. If this is substituted for $\mathcal{E}^\circ$ in Eq. (59) or (60) a measurement of the potential $\mathcal{E}$ for any value of m leads immediately to the value of the product $\gamma_{H^+}\gamma_{Cl^-}$ for an HCl solution of that molality.

This procedure supplies no way of determining the individual quantities γ_{H^+} and γ_{Cl^-}. Indeed we have found no way and do not expect to find any

way to determine the activity coefficient of hydrogen ion or of any other individual ion. All attempts to do this lead to cells with liquid-junction potentials which introduce uncertainties as large as the term involving the activity coefficient in the equation for the potential. We therefore find it convenient to introduce a quantity $\gamma_{\pm}$, the *mean ionic activity coefficient*, which is defined in this case by the relation

$$\gamma_{\pm} = \sqrt{\gamma_{H^+}\gamma_{Cl^-}} \tag{61}$$

The definition is somewhat more complicated with unsymmetrical salts like Na_2SO_4 or $Fe(ClO_4)_3$. Since the observed potential of cell (*D*) is -0.3750 at 25°C when $m = 0.06268$, the mean ionic activity coefficient of HCl at this molality can be computed from Eq. (60) to be 0.819. It should be emphasized that the measurement of a cell containing this molality of HCl is not by itself sufficient for the calculation of the activity coefficient. It is necessary to measure the series of cells of varying molality to obtain the results plotted in Fig. 2 in order to calculate the value of $\mathcal{E}°$, and the activity coefficient can be calculated only when $\mathcal{E}°$ is known.

Distribution Equilibrium in Nonideal Systems. One of the simplest and most important applications of the idea of molal free energy is to the transfer of a single substance from one phase to another. Suppose the substance X has the molal free energy $\bar{F}_1$ in phase 1 and $\bar{F}_2$ in phase 2. If the quantity of substance dx is transferred from phase 1 to phase 2, the free-energy change will then be given by

$$df = \Delta\bar{F}\, dx = (\bar{F}_2 - \bar{F}_1)\, dx \tag{62}$$

The transfer from phase 1 to phase 2 can therefore be a spontaneous one only if $\bar{F}_1 > \bar{F}_2$, because only then will df be negative, which is the necessary condition for a spontaneous process. If $\bar{F}_2 > \bar{F}_1$, the spontaneous transfer of X from phase 2 to phase 1 will be possible because this process will then be accompanied by a decrease in free energy. If $\bar{F}_2 = \bar{F}_1$, the quantity $df/dx = 0$, and this is the necessary condition for equilibrium with respect to the transfer. The situation is therefore extremely simple; a chemical substance will transfer spontaneously from one phase to another only if it has a higher molal free energy F in the first phase than in the second, and no spontaneous transfer will occur in either direction if the $\bar{F}$ values are the same in the two phases. The molal free energy $\bar{F}$ has therefore the same relation to the transfer of substance that temperature has to the transfer of heat from one body to another and that electrical potential has to the transfer of electric charge. It is for this reason that $\bar{F}$ is frequently called chemical potential.

If the substance is an ideal solute in both phases, the condition for equilibrium becomes by virtue of Eq. (30)

$$\bar{F}_1^\circ + \mathbf{R}T \ln c_1 = \bar{F}_2^\circ + \mathbf{R}T \ln c_2 \tag{63}$$

where c_1 and c_2 are the concentrations of X in phase 1 and phase 2, respectively. From this

$$\frac{c_2}{c_1} = e^{-(\bar{F}_2^\circ - \bar{F}_1^\circ)/\mathbf{R}T} \tag{64}$$

This is the distribution law with the constant K of Eq. (75) of Chap. VII given by

$$K = e^{-(\bar{F}_2^\circ - \bar{F}_1^\circ)/\mathbf{R}T} \tag{65}$$

If one phase is gaseous and the other liquid, we may write

$$\frac{P_X}{c_X} = e^{-(\bar{F}_g^\circ - \bar{F}_s^\circ)/\mathbf{R}T} \tag{66}$$

which is Henry's law. $\bar{F}_g^\circ$ is the standard free energy of X in the gas phase and $\bar{F}_s^\circ$ the corresponding value for the solution.

If we use the exact relationship [Eq. (44)] instead of Eq. (30), we get

$$\frac{c_2}{c_1} = K \frac{\gamma_1}{\gamma_2} \tag{67}$$

for the distribution between two liquid phases, K being still given by Eq. (65). For the distribution between gas and liquid we get

$$\frac{P_X}{c_X} = K \frac{\gamma_s}{\gamma_g} \tag{68}$$

γ_s being activity coefficient in the solution and γ_g fugacity coefficient in the gas. Equations (67) and (68) are the exact statements of the distribution law and of Henry's law.

If $\bar{F}_1^\circ$ is much larger than $\bar{F}_2^\circ$, K will be a large number [*cf.* Eq. (65)]. Under such conditions the concentration c_1 at equilibrium may be so much smaller than c_2 that the ideal laws are a close approximation to the behavior in phase 1 and a poor approximation for phase 2, that is, γ_1 may be almost exactly unity and therefore constant over a considerable range of concentrations while γ_2 varies considerably. Under these conditions we may put Eq. (67) in the logarithmic form without including a term in γ_1, getting

$$\ln \frac{c_2}{c_1} = \ln K - \ln \gamma_2 \tag{69}$$

If then measurements of c_1 and c_2 are made over a range of concentrations, it is possible to extrapolate to the limit of $c_2 \rightarrow 0$ a plot of $\ln (c_2/c_1)$ against c_2. In the limit $\ln \gamma_2 = 0$; hence the limiting value of the ordinate of this plot is $\ln K$. With K known any experimental value of the ratio c_2/c_1 leads immediately to the value of γ_2 for a solution of concentration c_2 in phase 2. If phase 1 is gaseous, the usual form of the equation employed is

$$\ln \frac{P_X}{c_X} = \ln K + \ln \gamma_X \tag{70}$$

instead of that of Eq. (69).

PROBLEMS

1. From Table 2 of Chap. X calculate approximate values of the total reversible work and of the free-energy change for the following reactions at 25°C:

$$Pb(s) + SO_4^{--}(1\ M) + 2H^+(1\ M) \rightleftarrows PbSO_4(s) + H_2(1\ atm)$$
$$Mn^{++}(1\ M) + 2H_2O(l) \rightleftarrows MnO_2(s) + H_2(1\ atm) + 2H^+$$

2. Prove from the second law that the potential of the cell Pt: H_2, HCl; HCl, Hg_2Cl_2: Hg must equal the sum of the potentials of the cells Pt: H_2, HCl; HCl, Cl_2: Pt and Pt: Cl_2, HCl; HCl, Hg_2Cl_2; Hg provided the concentration of HCl and the partial pressures of the reacting gases are the same in the different cells.

3. A certain cell in which the reaction is accompanied by no significant volume change shows a reversible potential of 1 volt when measured by a potentiometer. When the cell is used to drive a certain motor, the potential difference across the terminals of the cell is 0.9 volt. If the efficiency of the motor is 90 per cent, how much work is done by the system consisting of cell and motor for each coulomb that traverses the circuit? What is the change in free energy of the cell per coulomb?

4. When the same cell is charged from a generator, the potential across the terminals is 1.1 volts. How much work is done on the cell per coulomb? What is the change in free energy of the cell per coulomb?

5. What is the reversible work of the conversion of 1 mole of liquid water at 100°C and 1 atm to water vapor at the same temperature and pressure? What is the free-energy change of the process?

6. Consider the cell containing a lead and a mercury electrode immersed in a saturated aqueous solution of lead chloride which is in contact with excess of solid lead chloride. The solution in the neighborhood of the mercury electrode also contains an excess of solid mercurous chloride. Show that the potential as measured by a potentiometer is not altered by allowing a considerable amount of current to flow in the direction of discharge of the cell between two measurements with the potentiometer. Show also that the potential is not altered by forcing a current through the cell in the direction of charge between two measurements with the potentiometer. Would the same conclusions be possible if the electrolyte of the cell consisted of an unsaturated rather than a saturated solution of lead chloride?

7. Show that the numerical magnitude of the potential of a cell can never be increased by discharge but may be decreased.

8. What is the difference between the values of $\bar{F}$ for an ideal solute in 1 M and 0.1 M solution, both being at the same temperature and pressure?

9. What is the difference in $\bar{F}$ between ice and liquid water, both at 0°C and 1 atm? Which will have the larger $\bar{F}$ value at −10°C?

10. Will the $\bar{F}$ value of rhombic sulfur be higher or lower than that of monoclinic sulfur, both being at 25°C and 1 atm?

11. At 25°C the potential of the cell Pt: H_2(1 atm), HBr(m); HBr(m), AgBr: Ag is 0.47561 for m = 0.0003968 and 0.36173 for m = 0.003719. What is the ratio of the mean ionic activity coefficients of HBr in these two solutions?

12. If the limiting value as $m \to 0$ of the quantity $\varepsilon + (2RT/F) \ln m$ is 0.07111 for the cells of Prob. 11, what is the mean ionic activity of HBr in each of the solutions involved?

13. A cell contains an electrolyte of thallous sulfate, Tl_2SO_4. One electrode consists of a solution of Tl in Hg containing 4.93 per cent Tl; the other is a similar amalgam containing 10.02 per cent Tl. The potential at 30°C is 0.02997 volt, the more dilute amalgam being positive. What is the difference between the $\bar{F}$ values of Tl in these two amalgams? What is the ratio of the activity coefficients?

14. Picric acid is very nearly an ideal solute in dilute solution in benzene but is far from ideal in water solution. The following values have been found for the distribution equilibrium of picric acid between water and benzene at 18°C:

Conc. in water, moles/liter	0 00701	0.0199
Conc. in benzene, moles/liter	0.0101	0 0700

What is the difference in the $\bar{F}$ values of picric acid in the two water solutions? What is the ratio of the activity coefficients?

15. Obtain an expression analogous to Eq. (59) for the cell

$$\text{Pb: } PbCl_2(m);\ PbCl_2(m),\ AgCl(s)\text{: Ag}$$

and also for the cell

$$\text{Pt: } H_2(1\text{ atm}),\ Ba(OH)_2(m);\ Ba(OH)_2(m);\ \text{Ba amalgam}$$

16. At 25°C the partial pressure of HCl in equilibrium with a 4 m solution of HCl in water is 2.395×10^{-5} atm; the corresponding value for 6 m HCl is 1.842×10^{-4}. What is the difference in the $\bar{F}$ values of HCl in these two solutions? What is the ratio of the activity coefficients?

17. At 25°C the vapor pressure of water over a 6.83 m solution of sulfuric acid in water is 12.95 mm; over a 2.467 m solution it is 20.86 mm. What is the difference in the $\bar{F}$ values of water in these two solutions? What would the difference be if the solutions were ideal?

CHAPTER XII

THE INTERPRETATION OF PHASE DIAGRAMS

Degrees of Freedom. We saw in Chap. IV that the state of any system may be completely determined by fixing the values of a limited number of properties and that we may therefore be certain that two states are identical in all their properties without measuring the infinite number of properties which any state possesses. We saw also that there is an important classification of properties, intensive properties, of which pressure, temperature, density, and chemical composition are examples, whose magnitudes are essentially independent of the total mass of the system. Within any single phase the magnitude of an intensive property is either constant or varies continuously from one point to another in space. We now wish to examine the number of intensive properties which must be fixed in any system in order that the values of all the intensive properties of the system shall be determined. This number is called the number of *degrees of freedom* of the system.

Number of Components. We define as the number of components of any system or series of systems under consideration the minimum number of chemical substances whose amounts must be specified in order to fix for any given temperature and pressure the composition of each phase present in any of the systems under consideration. Note that this is a definition of the phrase "number of components," and not one of the word "component." In principle we can prepare any sulfuric acid–water mixture from SO_3 and H_2O just as well as from H_2SO_4 and H_2O, and we can specify the composition of a particular mixture just as completely by saying that it is a mixture of 41.2 parts of SO_3 with 58.8 parts of H_2O as we can by saying that it is a mixture of 50 parts of H_2SO_4 with 50 parts of H_2O. We may therefore say that the system contains the components H_2SO_4 and H_2O or that it contains the components SO_3 and H_2O. The choice of the substances we name as components is arbitrary, but the fact that we can specify the composition of a particular solution by specifying the amounts of two materials and two only is definite and inescapable.

The number of components is frequently less than the number of molecular species known to be present. Thus a sulfuric acid–water mixture contains OH_3^+, HSO_4^-, SO_4^{--}, and probably other kinds of molecules. But these are in mobile equilibrium with the acid and the water, and their

concentrations are therefore fixed and determined at any given temperature and pressure, although the actual values may be unknown, when the proportions of acid and water are specified. In spite of the fact that more than two chemical individuals are present, the number of components is only two.

An Important Limitation. The definition of number of components and all the applications we shall make of the definition have meaning only for systems which are either in what is called complete equilibrium or in what is called metastable equilibrium. Consider a mixture of hydrogen, oxygen, and water vapor at a temperature so high that the reversible reaction

$$2H_2O \rightleftharpoons 2H_2 + O_2 \tag{I}$$

proceeds rapidly in the one direction or the other until the state of equilibrium is reached. In this state of equilibrium there will be a definite relation between the partial pressures of the three substances given by the equation

$$\frac{P_{H_2}^2 P_{O_2}}{P_{H_2O}^2} = K \frac{\gamma_{H_2O}^2}{\gamma_{H_2}^2 \gamma_{O_2}} \tag{1}$$

Consequently there is at any given temperature and pressure only one value that P_{H_2O} can have with any given pair of values of P_{H_2} and P_{O_2}. This will be true, except for the small time interval required to reach equilibrium, both for mixtures which initially contained more than the equilibrium proportion of water and for those which contained less. Consequently the complete and detailed composition of any such system may be specified at any particular temperature and pressure by specifying the amounts of hydrogen and oxygen, and the system is one of two components only. A system like this in which all the chemical substances present are in mobile equilibrium with each other is said to be in *complete equilibrium.*

At room temperature, however, the rate of reaction (I) in the absence of a catalyst is too slow to be detected even over long periods of time. Consequently two samples containing the same partial pressures of hydrogen and oxygen may possess different partial pressures of water vapor, and we must specify the amount of water as well as the amounts of hydrogen and oxygen if we wish to describe the composition and to fix the properties of the system. The system is therefore one of three components. Such a system as this is said to be in *metastable equilibrium* with respect to reaction (I).

There is, of course, an intermediate region of temperature in which the rate of chemical change is significant but in which periods of months or years are required to reach a close approximation to the state of equilib-

rium. It does not make any sense to try to state the number of components in systems of this sort. We therefore use the term number of components and the related ideas only for systems in which all chemical reactions are extremely fast or for systems in which some or all of the possible reactions are extremely slow.

Systems of One Phase. We may now state as a generalization from experience that: In any system containing a single phase in which the effects of surface area and of gravitational, electrical, and magnetic fields may be neglected, the number of degrees of freedom Φ is one more than the number of components C, that is,

$$\Phi = C + 1 \qquad \text{(one phase)} \tag{2}$$

Consider an ethanol-water mixture at 20°C and 1 atm containing 25.00 per cent by weight ethanol. We know from experience that these three figures, temperature T, pressure P, and weight fraction of ethanol x, suffice to determine the values of all of the intensive properties of the system. Any other ethanol-water mixture of this composition at this temperature and pressure will have intensive properties identical with those of the first one. Specifically all such systems will have a density ρ of 0.96165 g/cc and a refractive index n_D for the sodium D line of 1.345047. We may give this principle mathematical formulation in the equations

$$\rho = f_1(T,P,x) \tag{3}$$
$$n_D = f_2(T,P,x) \tag{4}$$

We may not know the form of the functions f_1 and f_2, but we do know that to any set of values of T, P, and x there corresponds a single value of ρ and a single value of n_D.

It is implicit in the very notion of a mathematical function that such equations as

$$x = f_3(T,P,\rho) \tag{5}$$
$$x = f_4(T,P,n_D) \tag{6}$$

and

$$x = f_5(T,\rho,n_D) \tag{7}$$

are necessary corollaries of Eqs. (3) and (4). That is, if fixing temperature, pressure, and composition fixes the density, then fixing temperature, pressure, and density determines the composition. Indeed the commonest method of analyzing a mixture known to consist of ethanol and water only, *i.e.*, of determining the value of x in an unknown mixture, is to measure the value of ρ or of n_D and to obtain the value of x from tabulations which show the relation between x and ρ or n_D at a given tempera-

ture and pressure. Such tabulations are in fact ways of representing the functional relationships indicated by Eqs. (5) and (6).

In systems containing the three components water, ethanol, and methanol we obviously need to specify the proportions of the three components in order to fix the composition at a particular temperature and pressure. This requires two concentration variables, for instance the weight fraction x_1 of ethanol and the weight fraction x_2 of methanol. The value of any intensive property is then fixed if pressure, temperature, and x_1 and x_2 are fixed. The system has four degrees of freedom, and we may write

$$\rho = f_6(T,P,x_1,x_2) \tag{8}$$

and

$$n_D = f_7(T,P,x_1,x_2) \tag{9}$$

It must also be true that such relations as

$$x_1 = f_8(T,P,\rho,n_D) \tag{10}$$

and

$$x_2 = f_9(T,P,\rho,n_D) \tag{11}$$

also exist. This means that the composition of any mixture of these substances is completely determined if the values of temperature, pressure, density, and refractive index are fixed. Indeed a common method of analyzing a mixture of water, ethanol, and methanol is to determine the refractive index and the density and to obtain the composition variables x_1 and x_2 from tabulations which are equivalent to the functions f_8 and f_9 for fixed values of T and P.

Restrictions on the Rule. The rule of Eq. (2) is valid only for systems for which the quantity C has a real meaning, *i.e.*, for systems in complete or metastable equilibrium. We have to be very careful about using the rule for solids and for very viscous liquids even when no slow chemical reactions are involved. Thus we find that hammering a piece of soft annealed copper changes its properties measurably; it is, for instance, much harder. While we have confidence that the effects of the hammering would disappear if we could wait long enough, we often find no measurable change in what by human standards are long periods of time. Such effects as these are fortunately not very important with solids other than metals and are not significant in many properties even of metals.

The limitation to systems in which the effects of surface area and of gravitational, electrical, and magnetic fields may be neglected must be made because the properties of a substance are changed by fields of this sort or by changes in the degree of subdivision which alter the surface possessed by a fixed quantity of material (page 57).

Finally we must recognize that some of the functions about which we have been talking are multiple-valued. Thus it does not uniquely determine the properties of liquid water to specify a density of 0.99991 g/cc and a pressure of 1 atm because a sample of water with these properties may have a temperature of either 1° or 7°C. And a sulfuric acid–water mixture of specific gravity 1.834 at 20°C and 1 atm may contain either 95 or 99 per cent acid. Fortunately such phenomena are rather rare.

Molal Free Energy as a Determining Property. Since the molal free energy $\bar{F}_e$ of ethanol in an ethanol-water mixture is an intensive property (page 240) we may write for such a mixture

$$\bar{F}_e = f_{10}(T,P,x) \tag{12}$$

This equation records the fact that in this one-phase system the value of $\bar{F}_e$ is determined if the values of temperature, pressure, and proportion of ethanol are fixed, *i.e.*, that all solutions of a given composition have the same value of $\bar{F}_e$ at a given temperature and pressure. It does not mean necessarily that we know the value of $\bar{F}_e$ at any temperature, pressure, and composition or the way in which the quantity changes with changes in temperature, pressure, and composition, but it does mean that we know that a fixed relationship exists.

By the considerations of the previous paragraphs we may also write for an ethanol-water system

$$x = f_{11}(T,P,\bar{F}_e) \tag{13}$$

and since $\bar{F}_w$, the molal free energy of the water in the mixture, is an intensive property we have, further,

$$F_w = f_{12}(T,P,\bar{F}_e) \tag{14}$$

This may also be put in the form

$$f_{13}(T,P,\bar{F}_e,\bar{F}_w) = 0 \tag{15}$$

By the same argument we have for the three-component system of water, ethanol, and methanol

$$f_{14}(T,P,\bar{F}_e,\bar{F}_w,\bar{F}_m) = 0 \tag{16}$$

in which $\bar{F}_m$ is the molal free energy of the methanol.

The significance of this equation is that in the three-component system a relationship exists between temperature, pressure, and the three $\bar{F}$ variables. If the values of any four of these variables are fixed, the value of the fifth is automatically fixed also and so, by the considerations of page 256, are all the other intensive properties of the system.

Effect of a Second Phase. Suppose that this liquid system is in equilibrium with a gas phase containing the same components, water, ethanol, and methanol, as the liquid phase, and these components only. If the system is in equilibrium, the temperature must have the same value in the two phases; otherwise heat would flow from one to the other. The pressure must also be the same, for there is no way in which a difference can be maintained between the pressure applied to one phase and that applied to the other if they are in immediate contact. By the argument of page 250 the $\bar{F}$ value of water in the liquid phase must be the same as it is in the gas, otherwise water would evaporate from the solution or condense from the gas. Similarly $\bar{F}_e$ must have the same value in the liquid as in the gas, and so must $\bar{F}_m$. But the functional relationship between the values of T, P, and the $\bar{F}$'s is not necessarily or probably the same in the gas as it is in the solution, and we must write for the gas phase a new relationship,

$$f_{15}(T,P,\bar{F}_e,\bar{F}_w,\bar{F}_m) = 0 \tag{17}$$

which is not the same as Eq. (16).

With two equations connecting the five variables we no longer need to fix the values of four variables to determine the value of the fifth; indeed we cannot expect that there will be any value of the fifth variable which will satisfy the two equations if the values of the other four variables have already been fixed. Consider the relationship

$$x + y + z - 1 = 0 \tag{18}$$

If we fix the value of x at $\frac{1}{2}$, we do not determine the values of y and z; we merely determine that they are two numbers whose sum is $\frac{1}{2}$. We need to fix the values of the two variables x and y in order to determine the value of z, and we have therefore two degrees of freedom. But if we also know that

$$x + 2y + 4z - 2 = 0 \tag{19}$$

we determine the values of both y and z if we fix the value of x. Thus if x is $\frac{1}{2}$, y is $\frac{1}{4}$ and can have no other value, and the only possible value of z is $\frac{1}{4}$. By adding Eq. (19) to Eq. (18) we have therefore reduced the number of degrees of freedom from two to one. If we had a third relation, say

$$x + 3y - 4z - \tfrac{1}{4} = 0 \tag{20}$$

we should have zero degrees of freedom, for we could not arbitrarily fix the value of any variable. Thus if we tried to fix the value of x at $\frac{1}{4}$, it would be impossible to find values of y and z which satisfy all three equations.

The Phase Rule. In general, then, each new relationship between a set of variables reduces by one the number of degrees of freedom. Consequently each new phase in a material system reduces by one the number of degrees of freedom of the system. Since a system containing C components in one phase has $C + 1$ degrees of freedom [Eq. (2)], the general relationship for a system containing P phases is

$$\Phi = C - P + 2 \tag{21}$$

This is the phase rule of Willard Gibbs.

Methods of Representing Functional Relationships. The conditions for the coexistence of two or more phases are data of great practical importance. Consequently much effort has gone into the experimental determination of such conditions and much ingenuity into the development of schemes for the recording of the resulting information in the most useful way. In all this the phase rule is a guiding principle of much value. Consider the conditions for the coexistence of liquid and gaseous water. By the phase rule this system of one component in two phases possesses one degree of freedom. Fixing the value of one intensive property therefore determines the values of all of the intensive properties of the system, and it is possible to plot or to tabulate the values of one property which correspond to a range of values of any other. The "steam tables" which will be found in any chemistry or engineering handbook tabulate for each even value of centigrade temperature from 0° to 220°C the values of pressure, of the heat and entropy of vaporization of unit weight of the liquid, of the entropy of unit weight of the liquid, and of three other properties of engineering interest. If it is convenient, any one of these properties may be plotted as a function of any other, and if desirable empirical or semiempirical equations may be fitted to the relationship. It is important to recognize that the tabulation, the graph, and the equation are just different ways of representing the functional relationship between the two variables. None of them has any virtue compared with the others except that of convenience and precision in a particular problem.

Consider specifically the relation between the temperature and the pressure at which gaseous and liquid water are in equilibrium, called the *vapor pressure of water*. We have an exact differential equation relating these variables, namely,

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta \bar{V}} \tag{22}$$

[Eq. (39) of Chap. XV] and an approximate relationship valid to the precision of the perfect-gas laws,

$$\frac{d \ln P}{dT} = \frac{\Delta H}{\mathbf{R}T^2} \tag{23}$$

[Eq. (66) of Chap. VIII]. If the pressure is low and the range in temperature small, we can integrate the latter on the assumption that ΔH is constant, obtaining

$$\ln P = -\frac{\Delta H}{\mathbf{R}T} + \text{constant} \tag{24}$$

But the approximation of Eq. (23) and much more that of Eq. (24) are clearly invalid if we are to cover the whole range from a pressure of 0.0063 to one of 22.9 atm and from a temperature of 0° to one of 220°C. The most we can hope to do is to insert empirically determined relationships between ΔH and ΔV on the one hand and temperature and pressure on the other, and we often end up with an equation so complicated that we turn to tabulations or graphs in relief.

One-component System Water. The graph has the virtue of yielding immediately a general understanding of the nature of the relationships involved, and we shall confine our further discussion to the graphical representation of the functional relationships involved in a number of typical cases. We must first, however, meet a practical difficulty of frequent occurrence. If, for instance, we wish to plot the vapor pressure of water against the temperature and to include the highest values, which run to over 20 atm, our scale of pressure becomes such that the lower pressures are not visually distinguishable from zero. A simple way to circumvent this is to plot the logarithm of pressure or, what amounts to the same thing, to plot on logarithmic or semilogarithmic paper. Thus curve *A* of Fig. 1 plots the logarithm of the vapor pressure of liquid water against the reciprocal of the absolute temperature. This function of temperature is employed because of the approximate linearity predicted by Eq. (24).

The phase rule also tells us that the equilibrium system consisting of ordinary ice and water vapor must also have one degree of freedom. Consequently there is a functional relationship between pressure and temperature which such systems must obey and which may be plotted on the same diagram. This is done as curve *B* in Fig. 1. The pressure at which ice and vapor coexist in equilibrium is called the *vapor pressure of ice*. It must also be possible to represent any other two-phase system by a line on this diagram, and curve *C* is the pressure-temperature relationship for a system consisting of ordinary ice and liquid water.

The phase rule also tells us that a three-phase system possesses zero degrees of freedom, which means that ice, liquid water, and water vapor can coexist in equilibrium only at a single pressure and temperature. The

corresponding point on the diagram must lie on curve A since liquid water and water vapor are in equilibrium, it must lie on curve B since ice and water vapor are in equilibrium, and it must lie on curve C since ice and liquid water are in equilibrium. The three curves must therefore intersect in a single point, which is called a *triple point.*

There are at least four allotropic modifications of solid water in addition to ordinary ice, which is called ice I. Each of these represents a distinct phase, differing from the others in the same kind of way that monoclinic sulfur differs from rhombic sulfur. Consequently for each pair of such phases that may coexist in stable or metastable equilibrium there is a relationship between pressure and temperature which must be satisfied

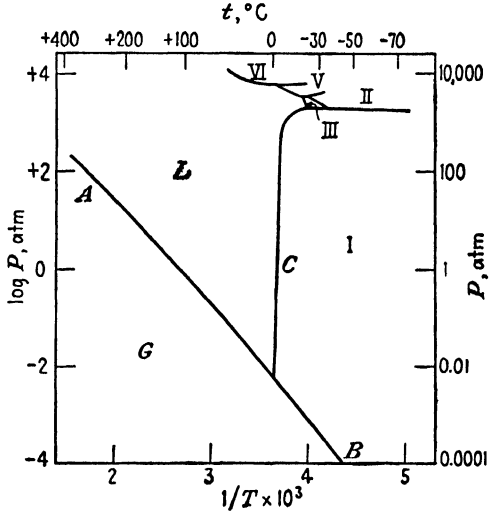


FIG. 1. Complete phase diagram for the one-component system water.

if the two phases are to coexist. These relationships may be added to curves A, B, and C of Fig. 1 as shown in that figure.

The areas in a plot of this sort may usefully be labeled. There is, for instance, only one temperature, 100°C, at which liquid and gaseous water can coexist in equilibrium if the pressure is 1 atm. If at this pressure the temperature is higher than 100°C, all the water is gaseous; if the temperature is lower than 100°, it is all liquid. Generalizing this reasoning, we see that if the point which represents the temperature and pressure of water lies to the left of lines A and B, that is, at higher temperature than the points on the line, the water will all be gaseous. We therefore label this area G for gas. In the same way we conclude that the system must be wholly liquid if the representative point lies in the area marked L, that the system will consist solely of ice I if the representative point lies in the

area marked I, and that the system will consist of any one of the other forms of ice if the representative point lies in the area marked with the numeral which characterizes that kind of ice.

Metastable Equilibria. Water which is free from ice crystals can usually be cooled many degrees below the triple point without the appearance of ice, especially if it is dust-free and if the walls of the container are not scratched or rubbed. It is therefore possible to investigate the conditions for the coexistence of liquid and gaseous water at temperatures considerably below the triple point. That such systems are metastable and

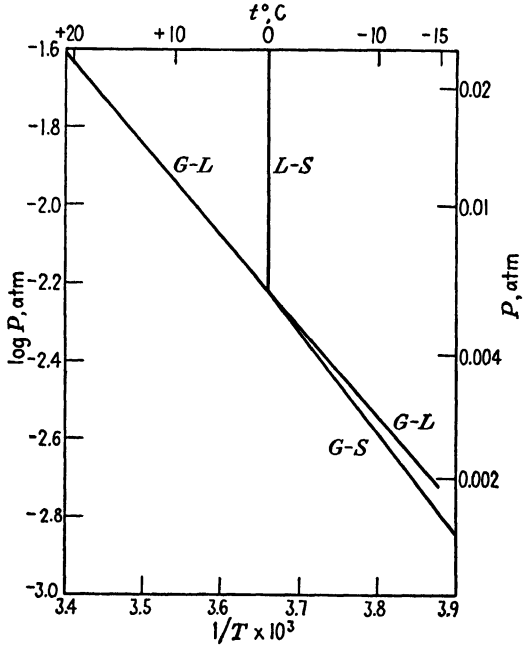


FIG. 2. Phase diagram for water in the neighborhood of 0°C.

not in complete equilibrium is shown by the fact that the introduction of a minute ice crystal will lead to a rapid crystallization of part of the liquid and a return of the temperature and pressure to the values characteristic of the triple point. Data for this metastable equilibrium between liquid and gaseous water form that part of the line marked *G-L* in Fig. 2 which lies to the right of the triple point, *i.e.*, at lower temperatures. This figure replots on a larger scale the part of Fig. 1 which lies within a few degrees of the triple point. It will be noted that there is no discontinuity in the slope of the plot of the vapor pressure of water at the triple point. In so far as the equilibrium between liquid and gas is concerned, the existence of ice is an adventitious circumstance which interrupts the smooth

functional relationship between temperature and pressure characteristic of the liquid-gas system only when the ice actually forms.

Two-component Systems. A system containing two components possesses three degrees of freedom if only one phase is present and two degrees of freedom if two phases are present. If we fix the value of one variable, the number of degrees of freedom of the two-phase system is reduced to one and we may therefore plot in a two-dimensional diagram the corresponding values of any two variables of interest. We have already used this kind of plot in Figs. 2 and 3 of Chap. III. Specifically we have plotted in Fig. 2 of Chap. III three different functional relationships. These all apply to a two-phase system consisting of a liquid mixture of benzene and toluene in equilibrium with a gaseous mixture of the same two substances. The variable which is fixed so that the number of degrees of freedom is reduced to one is the temperature, which is held constant at 20°C. In all the three plots the abscissas are the mole fractions of toluene in the liquid phase; in one the ordinates are the partial pressures of toluene in the gas, in another they are the partial pressures of benzene, and in the third the total pressures of the gaseous mixture.

Boiling-point–Composition Diagrams. Instead of fixing the temperature we may fix the pressure. It then becomes useful to plot two functional relationships. One of these, the curve marked l in Fig. 3, is a plot of the temperature at which the liquid and gas phases coexist in equilibrium against the composition of the liquid phase. The other, the curve marked g, is a plot of the same temperature against the composition of the gas phase. The ordinate in diagrams of this sort is what is called the *boiling point* of the liquid, since this is by definition the temperature at which liquid and gas are in equilibrium under the prevailing pressure. The diagrams are therefore called boiling-point–composition diagrams or merely boiling-point diagrams. The procedure of plotting two different quantities as abscissas against a single quantity as ordinate is less common than that illustrated in Fig. 2 of Chap. III, in which different quantities are plotted as ordinates against a common abscissa. The advantages of superimposing the l and g plots in a single diagram are considerable, namely:

First, we may obtain the composition of the vapor in equilibrium with a liquid of any given composition merely by drawing a horizontal line from the point representing this composition on the curve which plots compositions of the liquid to the curve which plots the composition of the gas. Such a line is LG in Fig. 3. The abscissa of point L is the composition of the liquid which can coexist in equilibrium with the gas at the temperature given by the ordinate of the point; the abscissa of point G is the com-

position of the gas which can coexist in equilibrium with liquid at the same temperature. Gas whose composition is given by the abscissa of point G will therefore be in equilibrium with liquid whose composition is given by the abscissa of point L. Obviously one can also read from the plot the composition of the liquid which will be in equilibrium with gas of any given composition. Such information as this is clearly of great usefulness in all problems connected with fractional distillation.

Second, one may label the areas of the diagram. In so doing one gives a third meaning to the abscissa of a point in the diagram, namely, that of

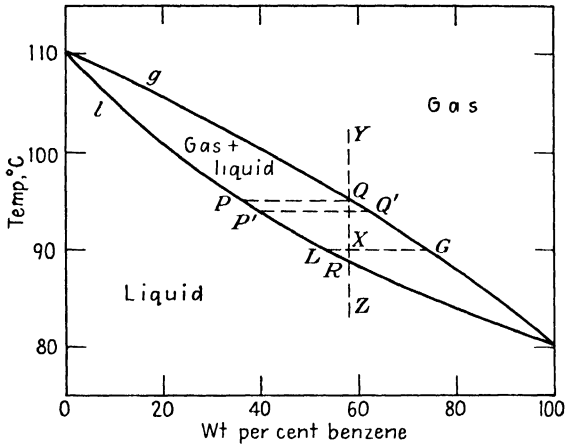


FIG. 3. Boiling point diagram for benzene-toluene mixtures at 1 atm. The abscissas for the lower curve (l) are the weight per cents of benzene in the liquid whose boiling point is given by the ordinate. The abscissas for the upper curve (g) are the weight per cents of benzene in the vapor which is in equilibrium with liquid at the temperature given by the ordinate. (*Based on data computed by Robinson and Gilliland, "The Elements of Fractional Distillation," 3d ed., McGraw-Hill Book Company, Inc., New York,* 1939.)

the *gross composition* of the system, computed without regard to the proportions of the two phases present. Consider a system at a temperature so high that all of the material is gaseous. The point, say Y in Fig. 3, whose coordinates are gross composition and temperature lies in the upper part of the diagram. If the temperature is lowered, the gross composition must remain unchanged and the representative point will follow the line YZ. Not until the temperature drops to the point Q on the g curve will it be possible to have the liquid phase coexist with the gas. The first drop of liquid which condenses will, by the argument of the last paragraph, have the composition represented by point P. It will therefore contain a smaller proportion of benzene than the vapor, and the condensation will consequently increase the proportion of benzene in the gas phase. With

this change in composition the gas phase can be in equilibrium with the liquid only at a lower temperature, and the point representing the *composition of the gas phase* must move along the g curve to, say, Q'. At this point the *composition of the liquid* in equilibrium with the gas is represented by P'. If this process continues until the composition of the gas is represented by point G, the composition of the liquid will be represented by point L and the gross composition will be represented by point X. When the gross-composition point reaches R, we have the situation in which a liquid of composition R is in equilibrium with a gas phase richer in benzene yet has a composition identical with the gross composition. This is possible only if the quantity of gas present is negligible. At lower temperatures, *e.g.*, at point Z, the system is completely liquid. It follows from a generalization of this argument that whenever the point representing gross composition and temperature lies in the area between the l and g curves the system consists partly of liquid, partly of gas. When the point lies in the area above the g curve, the system is wholly gaseous; when it lies below the l curve, the system is wholly liquid. We have labeled these areas appropriately in Fig. 3.

Third, the relative amounts of liquid and gas in a two-phase system may be determined from the geometry of the diagram. Suppose we have a mixture of benzene and toluene which is partly liquid and partly gaseous, whose gross composition corresponds to a weight fraction f_x of benzene. Let the temperature and gross composition be represented by the point X in Fig. 3. Then the weight fraction f_l of benzene in the liquid phase is represented by point L, and the weight fraction f_g of benzene in the gas phase is represented by point G. Let x be the fraction of the total weight of the mixture which is gaseous. Then the fraction of the total weight which is gaseous benzene is the product xf_g, and the fraction which is benzene in the liquid phase is $(1 - x)f_l$. The sum of these quantities must be the fraction f_x of the total mixture which is benzene, *i.e.*,

$$f_x = xf_g + (1 - x)f_l \tag{25}$$

From this

$$x = \frac{f_x - f_l}{f_g - f_l} \tag{26}$$

The result corresponds to a simple geometry in the diagram. For the quantity $f_x - f_l$ is represented in the diagram by the length LX, and the quantity $f_g - f_l$ by the length LG. Consequently

$$x = \frac{LX}{LG} \tag{27}$$

It is easily shown that the fraction, $1 - x$, of the mixture which is liquid is given by

$$1 - x = \frac{XG}{LG} \tag{28}$$

It can be shown by similar methods that the fraction y of the total moles present in the gas phase in a two-phase mixture is given by

$$y = \frac{N_x - N_l}{N_g - N_l} \tag{29}$$

where N_x is the mole fraction of component A in the mixture, N_l the mole fraction of A in the liquid, and N_g its mole fraction in the gas. The value of y can be read from a diagram in which the abscissas are mole fractions by the same geometry as that used to read the weight fraction present as vapor when the abscissas are weight fractions.

Character of Boiling-point Curves. A boiling-point diagram for benzene-toluene mixtures in which the abscissas are mole fractions instead of weight fractions differs only insignificantly from Fig. 3 because the molecular weights of the components are so nearly the same. In particular the l curve is concave upward. This illustrates the fact that the boiling-point curve for an ideal solution is not linear although the vapor-pressure curve, as illustrated in Fig. 2 of Chap. III, is linear. A positive deviation from ideality (page 43) makes the vapor pressures of the mixtures greater than those of ideal solutions and therefore makes the boiling points lower than those of ideal solutions. Consequently the l plots in the boiling-point diagrams for solutions which show positive deviation from ideality show even more of a sag than those for an ideal solution like benzene-toluene. With negative deviations the l curves lie higher than those of ideal solutions, and the curve is frequently concave downward instead of upward.

With large deviations from ideality these curvatures may lead to the appearance of a maximum or a minimum in the curve. It may be shown from thermodynamic reasoning that at a maximum or minimum, but here only, the g and l curves will coincide. This coincidence is indicated in the plots of Fig. 4, which illustrates a system with a maximum, and Fig. 5, which illustrates one with a minimum. Because of this property of the systems the vapor obtained from a liquid having the composition corresponding to a maximum or a minimum is identical in composition with the liquid. Consequently the composition of the liquid does not change when the liquid is distilled, and the boiling point remains constant. For this reason such solutions are called *constant-boiling mixtures.* They are also called *azeotropes.*

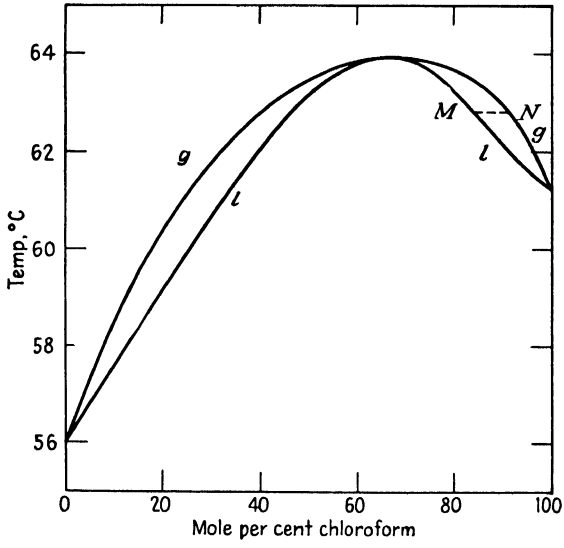


FIG. 4. Boiling-point diagram for acetone-chloroform mixtures at 1 atm. [*From data of Tyrer, J. Chem. Soc.*, **101**, 81, 1104 (1912).]

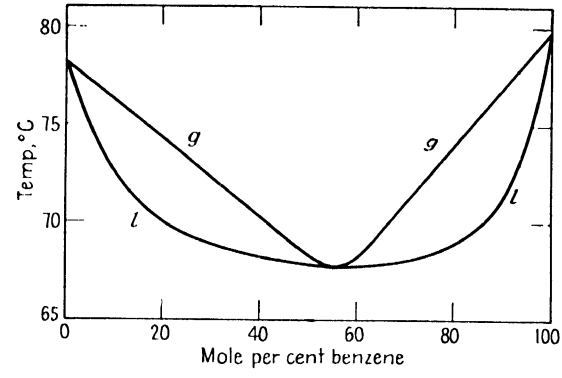


FIG. 5. Boiling-point diagram for ethanol-benzene mixtures at 750 mm. [*From data of Tyrer, J. Chem. Soc.*, **101**, 81, 1104 (1912).]

Fractionation. Except in the case of liquids which can form a constant-boiling mixture a vapor phase is always richer in the more volatile component, the one of lower boiling point, than is the liquid. Consequently distillation, which consists in the removal and condensation of the vapor as it forms, leads in general to a fractionation by which the distillate is richer in the more volatile component, constant-boiling mixtures being an exception.

By itself a single fractionation of this kind is not an effective way of separating two substances unless there is a large difference in the boiling points of the components. Otherwise the composition of the vapor and hence of the distillate does not differ largely from that of the residual liquid. If any considerable portion of material is distilled, the situation rapidly gets worse. If a liquid of the composition represented by the point L in Fig. 3 is distilled, the first minute portion of distillate would have the composition represented by the point G. The removal as distillate of this material, which is richer in benzene than is the liquid, leaves the residual liquid poorer in benzene than it was originally, and the representative point for the composition of the liquid must therefore move along the l curve toward the left. Meanwhile the composition of the vapor must move in the same direction along the g curve. If the distillation is stopped when the composition of the liquid is that represented by point P, the last drop of distillate will have the composition represented by point Q. The composition of the whole distillate will therefore be some sort of an average richer in benzene than Q but poorer than point G. Fortunately it has been possible to develop devices known as *fractionating columns* in which the process of fractionation is repeated automatically many times in a system in which a refluxing liquid flows counter current to a rising stream of vapor. Remarkably effective separations may be obtained in good columns.

Fractionation When Constant-boiling Mixtures Are Involved. The more complicated situation that exists when the components form a constant-boiling mixture may always be analyzed by treating the diagram as if it contained two independent parts, one composed of the region to the right of the constant-boiling mixture, the other of the region to the left. Thus in the system of Fig. 4 the vapor of composition N obtained from a liquid of composition M is richer in the *less* volatile component chloroform than is the liquid. In terms of that part of the diagram lying to the right of the constant-boiling mixture, however, chloroform is more volatile than is the constant-boiling mixture. Refractionation of a mixture represented by point M of Fig. 4 can lead to a volatile fraction which approximates pure chloroform and a residue whose composition approaches that of the constant-boiling mixture. No fractionation by distillation at the pressure at which the diagram is valid can possibly lead to a product richer in acetone than the constant-boiling mixture.

In the interpretation of such systems as these it is helpful to remember that the g curve in a boiling-point diagram never lies below the l curve.

Partially Miscible Liquids. A positive deviation from ideality which leads to the kind of boiling-point curve shown in Fig. 5 results from forces between the unlike molecules, which are weak compared with those

between like molecules (page 38). The situation in which the liquids are only partially miscible is only an extreme case of this tendency of like molecules to cling together. For such systems the sagged boiling-point diagram of Fig. 5 goes over to one of the type of Fig. 6. There are now two kinds of liquid phase, one, which we represent by the letter W, rich in water, the other, represented by A, rich in isobutyl alcohol. Line AM is the plot of the relation between the temperature and the composition of the W phase when it is in equilibrium with vapor. Curve BP is the

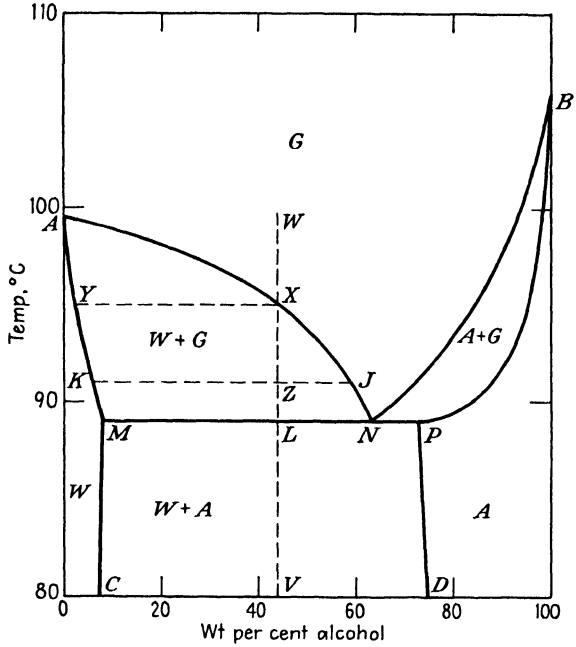


FIG. 6. Boiling-point diagram for water–isobutyl alcohol mixtures at 750 mm. [*From data of Michels, Arch. néerland. sci.*, **5**, 127 (1921).]

corresponding plot for temperature and composition of phase A in equilibrium with vapor. MC is the plot of the relation between temperature and composition of the W phase when it is in equilibrium with the A phase, and the triple point M is the composition of phase W when it is in equilibrium both with vapor and with phase A. The triple point P is the composition of the A phase when it is in equilibrium with vapor and with phase W. AN shows the relation between temperature and the composition of vapor which is in equilibrium with phase W. BN is a similar plot for the composition of vapor in equilibrium with phase A, and the triple point N represents composition and temperature of the gas

phase, which is in equilibrium with two liquid phases simultaneously, one of these having the composition of point M, the other that of point P.

We may then label the areas in such a way that the area in which the point representing the *gross composition* of a mixture and its temperature lies will determine the nature and proportions of the phases present. Obviously the high-temperature area corresponds to wholly gaseous materials. If a gaseous mixture whose representative point is W is cooled until the point reaches X, liquid of composition represented by Y will appear. Further cooling to Z will increase the amount of liquid, and at this point the system will consist of a liquid phase of composition K and a vapor phase of composition J. By the argument of page 266 the ratio of the amount of vapor to the amount of liquid will be the ratio of the lengths KZ/ZJ.

It follows, therefore, that when the representative point for the gross composition lies anywhere in the area marked $W + G$ the system consists of vapor and liquid phase W. If the cooling of the system which started at W is continued until the gross-composition point reaches L, the system must consist of a liquid phase of composition M and a vapor phase of composition N. The next drop of liquid produced by the further removal of heat must have the same composition as the vapor from which it was formed. Otherwise the composition of the vapor would be changed, and a change in the composition of a vapor of composition N can only lead to a rise in temperature along line NA or NB. Since the removal of heat cannot lead to a rise in temperature, the point is proved. A liquid whose composition and temperature are represented by N must be a two-phase mixture of the phases W and A in the proportions of the lengths NP to MN. It follows that removal of heat from the system whose gross composition point is L leads to the appearance of phase A. With two liquid phases and the gas phase present the constant-pressure two-component system now has zero degrees of freedom, and the temperature and the compositions of each of the phases must remain unchanged so long as the three phases remain. The continued removal of heat must therefore lead to the continued conversion of gas of composition N to a mixture of the two liquid phases of compositions M and P, respectively. When the vapor phase has just disappeared, the liquid system will consist of these two liquids in the proportion of the lengths ML and LP. Further removal of heat carries the representative point into the area below the line in which the system must consist of the two liquid phases only, as is indicated by the label in the diagram.

The line MNP, unlike the other lines in the diagram, is not the locus of points representing the composition of a single phase when it is in equilibrium with another phase. It is the locus of points representing the *gross*

composition and temperature of the two-phase liquid systems which are in equilibrium with gas of composition N. Such loci of points representing the gross composition of two-phase mixtures are called *tie lines.*

Mutual Solubility of Liquids. The abscissa of point C measures the proportion of alcohol present in the water-rich phase when it is in equilibrium with the alcohol-rich phase at 80°C. A water-rich phase which is in equilibrium with an alcohol-rich phase is properly called a *saturated* solution of alcohol in water, and the abscissa of C represents therefore the solubility of alcohol in water at 80°. Similarly the horizontal distance of point D from the right edge of the diagram measures the solubility of water in alcohol at 80°.

Although there are exceptions in a few special cases, it is the usual thing for the mutual solubility of two liquids to increase with rising temperature. The inward slope of lines CM and DP in Fig. 6 is therefore the normal effect. If the fixed pressure at which a diagram of this sort is determined is raised, the boiling points increase rapidly and the whole network represented by the lines which join points A, M, N, P, and B rises to a higher level in the diagram. The solubility curves are, however, little affected by pressure, and the length of the line MP will therefore decrease with rising temperature in the usual case. At a high enough pressure (above 4.33 atm in the case of water and isobutyl alcohol) the two liquids will become completely miscible at a temperature below the boiling point of any mixture, and a diagram of the sort represented by Fig. 7 results. How high a pressure will be necessary to produce the transition from a diagram of the type of Fig. 6 to one of the type of Fig. 7 depends on the magnitude of the attractive forces between the molecules of the components of the mixture compared with the forces between like molecules, and on the normal boiling points of the liquids.

If on the other hand one imagines a series of systems in which the positive deviations from ideality increase, one sees that the limiting case of complete immiscibility must lead to a diagram of the kind represented by Fig. 8. Here the two sections marked W and A in Fig. 6 have narrowed until they have been reduced to the lines AMS and BPT.

Distillation of Immiscible Liquids. If one heats the two-phase system whose representative point is V in Fig. 6 and which consists of the two liquid phases W and A, vapor begins to form when the temperature reaches the level of MNP at point L. So long as the three phases, two liquid and one gaseous, are present, the temperature remains at this level and the composition of each of the phases also is constant, that of the vapor at the composition of point N, that of liquid W at point M, and that of liquid A at point P. Since the vapor contains more isobutyl alcohol than the liquid, continued heating to produce more vapor must

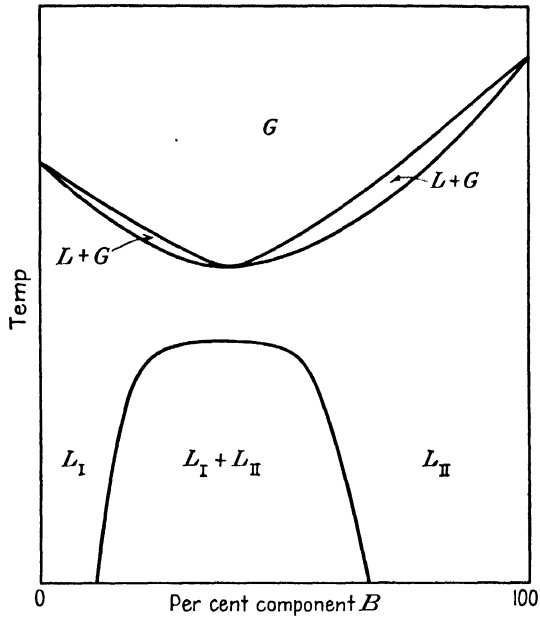


FIG. 7. Schematic boiling-point diagram for a system involving two partially miscible liquids, A and B, which become completely miscible below the boiling point. L_I is a liquid phase relatively rich in component A, L_{II} a liquid phase relatively rich in component B.

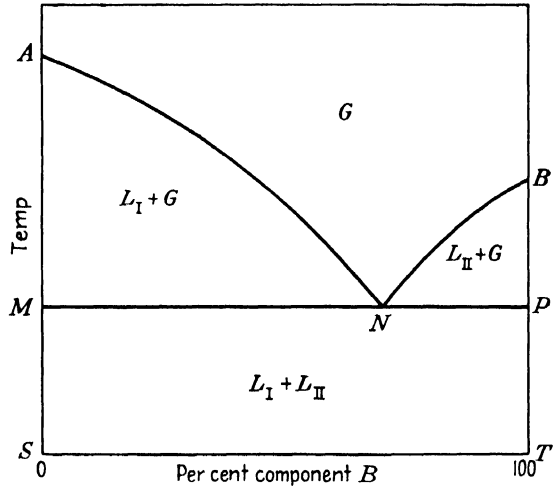


FIG. 8. Schematic boiling-point diagram for two completely immiscible liquids.

decrease the proportion of the alcohol-rich layer A in the system. When this finally disappears, the system regains a degree of freedom and behaves like any other two-component system consisting of a single liquid phase and a gas phase. The temperature rises gradually while the point representing the composition of the liquid phase moves from M toward A, and the composition of each increment of distillate is given by the abscissa of the point on NA corresponding to the instantaneous temperature.

Steam Distillation. The frequently convenient method of steam distillation may be understood by means of Fig. 6. If one passes a current of steam into isobutyl alcohol, some of the alcohol will vaporize and will be carried by the steam current on to the condenser. The heat which must be supplied for the evaporation of the alcohol can come only from the condensation of some of the water vapor, and more water vapor will condense to supply heat lost through conduction and radiation to the surroundings. The net effect is a gradual decrease in the amount of alcohol and an increase in the amount of water. This eventually results in the appearance of the water-rich phase as well as the alcohol-rich one, and the temperature then remains constant at 89° while vapor containing 63 per cent or somewhat less isobutyl alcohol is carried into the condenser, where it condenses to a separable mixture of phases W and A. When the proportion of alcohol in the liquid drops to 8 per cent, the A layer disappears and the temperature gradually rises to the boiling point of water, the proportion of alcohol in the vapor following along curve NA. Steam distillation is convenient because it escapes the danger of overheating the material to be distilled, which is always present with direct heating, and because the current of steam carries over that quantity of the other component which would otherwise remain in the distilling flask as vapor or as condensate on the walls.

Freezing-point Diagrams. A two-phase system maintained at a fixed pressure high enough so that vapor is absent may contain both solid and liquid phases. Because of the fixed pressure the number of degrees of freedom characteristic of a two-component system is reduced by one, and the system has two degrees of freedom if one phase is present, one degree of freedom if two phases are present, and no degrees of freedom if three phases are present. More than three phases cannot generally coexist in equilibrium. The single degree of freedom of the two-phase system makes it amenable to plotting in two dimensions. The commonest plot is one in which the coordinates are the composition of one phase and the temperature at which it is in equilibrium with another phase.

The simplest case is that in which the two components are completely miscible in the liquid state and completely immiscible in the solid state. Figure 9 is a diagram of this sort for the system consisting of benzene and

naphthalene. Curve AE is the locus of points whose coordinates are the composition of the liquid phase which is in equilibrium with solid benzene and the temperature at which that equilibrium exists. Curve BE bears the same relation to liquids which are in equilibrium with solid naphthalene. The *cutectic point* E, which lies on both curves, must represent temperature and composition of the liquid which is in equilibrium with both solid phases. It is an invariant point, *i.c.*, has no degrees of freedom, because three phases are present.

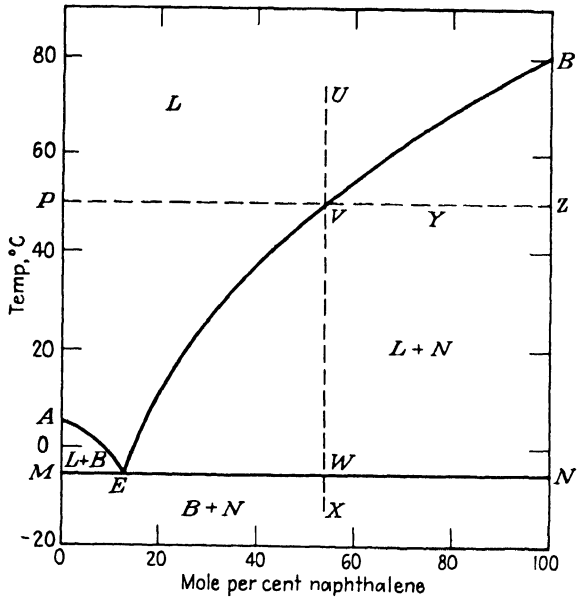


FIG. 9. Freezing-point diagram for mixtures of benzene and naphthalene. (*From data in International Critical Tables, Vol.* IV, *p.* 177.)

The geometry of this diagram is obviously identical with that of Fig. 8, and we may therefore use for these freezing-point or melting-point diagrams the same kind of reasoning that was used for boiling-point diagrams. Thus the region marked L is the locus of points representing temperature and *gross composition* of systems consisting of liquid only, the area marked $B + N$ is the locus of points representing temperature and gross composition of systems consisting of solid benzene and solid naphthalene, area $L + B$ is the locus for mixtures of liquids of various composition with solid benzene, and area $L + N$ that for mixtures of liquids with solid naphthalene. Points representing the constant temperature and varying gross composition of three-phase mixtures of liquid of composition E with the two solid phases lie on the tie line MEN. The argu-

ment of page 266 shows that a mixture of gross composition and temperature represented by the point Y must consist of solid naphthalene and liquid of composition V in the ratio of the lengths VY/YZ. This ratio will be a ratio of weights if the abscissas of the diagram are expressed in weight fractions; it will be a ratio of moles if the abscissas are mole fractions.

Curve BE is called the *freezing-point curve for naphthalene* because the temperature of point V, for instance, is the temperature at which solid naphthalene first appears in equilibrium with the liquid when a solution of composition U is cooled. The same curve is called a *melting-point curve for naphthalene* because point V represents the temperature at which the last trace of solid naphthalene disappears in the melt when the mixture of solid benzene and naphthalene whose representative point is X is heated. The names imply the definition of freezing point as the temperature of first appearance of solid on cooling and of melting point as the temperature of complete disappearance of solid on heating.

If mixture U is cooled below point V, the crystallization of pure naphthalene reduces the proportion of naphthalene in the liquid and the representative point for the *composition of the solution* moves along VE until at E benzene also crystallizes. Further removal of heat leads to the conversion of the liquid of composition E to a mixture of the two crystalline phases, which is called the *eutectic mixture* and which contains the two substances in the proportion of point E. The temperature and composition of the melt remain unchanged until the liquid has disappeared. Consequently the total process of freezing extends over the temperature range from V to W. Similarly heating of the mixture of two crystalline phases whose representative point is X leads to an initial appearance of liquid when the gross-composition point reaches W, and the process of melting extends over the temperature range from W to V.

Curve BE may also be called the *solubility curve of naphthalene* in benzene, for the distance PV measures the mole fraction of naphthalene in a solution which is in equilibrium with solid naphthalene. This is by definition the solubility of naphthalene expressed in terms of the mole fraction as a measure of composition.

Freezing-point Diagrams in the Presence of the Vapor Phase. In the last section we specified that no gas phase should be present and that the pressure should be fixed. Suppose instead that we specify that a gas phase consisting of benzene and naphthalene shall always be present. Then if P_c represents the number of solid or liquid phases (condensed phases) present, the total number of phases will be $P_c + 1$ and the number of degrees of freedom for the two-component system becomes $3 - P_c$. A system containing two condensed phases will therefore have one degree of

freedom, just as it did in the case considered in the last section, and a system containing three condensed phases will have no degrees of freedom. The freezing-point diagram would in principle differ somewhat from Fig. 9 because the pressure has different values for different temperatures and compositions. The effect of moderate changes of pressure on condensed phases is, however, so small that the two diagrams are practically indistinguishable unless very large pressures are involved.

Suppose we now add a gas such as nitrogen, which is not very soluble in benzene and naphthalene. This adds a component and increases the number of degrees of freedom to $4 - P_c$. But if we then specify a constant pressure, we reduce the number to $3 - P_c$, the same as in the

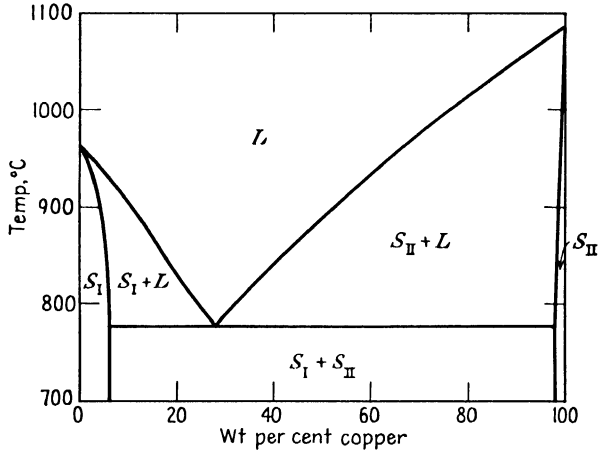


FIG. 10. Freezing-point diagram for mixtures of silver and copper. (*Based on data from International Critical Tables, Vol.* II, *p.* 421.) S_I is a solid solution rich in silver, S_{II} a solid solution rich in copper.

previous case. In principle the freezing-point diagram of this system will not be identical with Fig. 9; in practice the difference will be small if the solubility of nitrogen in the condensed phases is small.

Finally we might add oxygen, which is a new component and increases the number of degrees of freedom by one. If, however, we specify a fixed ratio of oxygen to nitrogen, as in air, we sacrifice the added degree of freedom and return to the value $3 - P_c$.

Solid Solutions. Figure 8 for a liquid-vapor system represents the limiting case of decreasing miscibility of the two liquid components. The geometrically similar figure 9 also represents a limiting case, namely, that of complete immiscibility of the two solid components. But solid solutions, *i.e.*, solid phases whose composition and properties may vary continuously, are of common occurrence. The diagrams of systems involving solid solutions such as Fig. 10 for partial miscibility in the solid state and

Fig. 11 for complete miscibility are therefore geometrically similar to Fig. 6 and Fig. 3, respectively, and the interpretation of the freezing-point diagrams follows straightforwardly along the lines of the interpretation of the boiling-point diagrams. In a practical sense there is a difference between the two cases which arises from the slowness of diffusion in

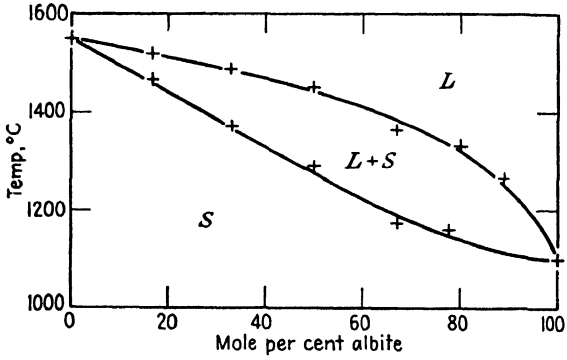


FIG. 11. Freezing-point diagram for mixtures of albite, $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$, with anorthite, $CaO \cdot Al_2O_3 \cdot 2SiO_2$. [*From data of Bowen, Z. anorg. Chem.*, **82**, 283 (1913).] The points are experimental.

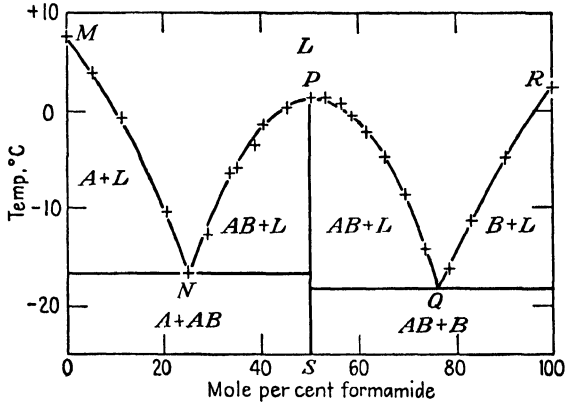


FIG. 12. Freezing-point diagram for mixtures of formic acid and formamide. [*From data of English and Turner, J. Chem. Soc.*, **107**, 774 (1915).] The symbol *A* is used for solid formic acid, *B* for solid formamide, and *AB* for the solid compound. The points are experimental.

solids. This makes it difficult to establish equilibrium in systems involving solid solutions.

Compound Formation. Freezing-point diagrams offer one feature not observed with boiling-point diagrams, namely, the formation of solid compounds between the components. Figure 12 illustrates the phenome-

non by a simple case, that of formamide and formic acid. The curve *NPQ* is the locus of points whose coordinates are the temperature and the composition of liquids which are in equilibrium with a crystalline compound composed of 1 mole of formic acid and 1 mole of formamide. The maximum of this curve appears at the composition of the solid compound, and it may be shown by thermodynamic reasoning that this is a necessary phenomenon. Line *MN* is the locus of points whose coordinates are the temperature and the composition of solutions which are in equilibrium with solid formic acid, and curve *QR* is the corresponding locus for solutions in equilibrium with solid formamide. Points *N* and

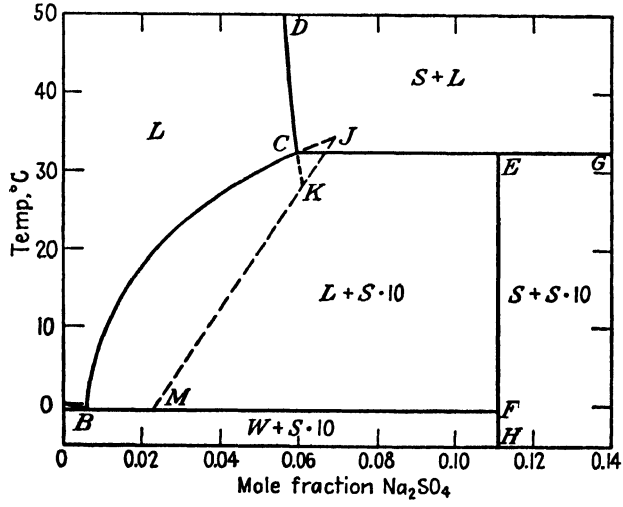


FIG. 13. Freezing-point–solubility diagram for Na_2SO_4 and water. *S* represents solid Na_2SO_4, S·10 solid $Na_2SO_4 \cdot 10H_2O$, *W* solid water, *L* liquid. (*From data in International Critical Tables, Vol.* IV, *pp.* 236, 258.)

Q are eutectics, and the horizontal lines through these eutectic points are tie lines. This diagram amounts to the juxtaposition of two simple freezing-point diagrams, one for systems composed of formic acid and the compound, the other of the compound and formamide. Each of these portions of the total diagram has all the features of the kind of diagram we met in Fig. 9 and permits the same kind of predictions that that diagram does.

Transition Points. In the diagram of Fig. 13 for the water–sodium sulfate system a compound $Na_2SO_4 \cdot 10H_2O$, as well as the anhydrous salt and ice, appear as stable solid phases. *OB* is the locus of points whose coordinates are temperature and composition of solutions in equilibrium with ice, *BC* is the corresponding plot for solutions in equilibrium with the hydrate, and *CD* is part of the plot for solutions in equilibrium with the

anhydrous salt. The triple point C represents the unique temperature and composition of the solution in equilibrium with both hydrate and anhydrous salt. If one adds water or sodium sulfate to this three-phase mixture, the temperature and the composition of the solution must remain constant since there are no degrees of freedom (pressure being assumed constant and the gas phase absent). The point representing the gross composition of the mixture will of course move back and forth along the horizontal CEG, and this line is therefore the locus of points representing the gross composition of mixtures of liquid with hydrate and anhydrous salt. The vertical line HFE, whose abscissa is the mole fraction of Na_2SO_4 in the crystalline hydrate, is the locus of points representing this hydrate in the crystalline condition. A mixture whose gross composition is represented by a point in the area marked $S + L$ can be obtained by adding solid Na_2SO_4 to a solution whose representative point lies on CD and which is therefore already in equilibrium with that salt. Any system for which the point representing gross composition and temperature lies in this area must therefore consist of liquid and anhydrous salt only. If the solid hydrate is heated, its temperature can then rise above point E only if it is converted to a mixture of liquid and anhydrous salt. The conversion is of course gradual, the proportion of hydrate decreasing as heat is added, but so long as the three phases are present, the temperature and the composition of the liquid portion remain unchanged. The temperature at which a change of this sort occurs is called a *transition point.* Transition points are as useful reference points for the calibration of thermometers as are the freezing points of pure substances, and they are frequently employed for this purpose. Point C in the diagram is frequently called a *peritectic point*, and the compound $Na_2SO_4 \cdot 10H_2O$ is said to melt incongruently or to show a concealed maximum.

Na_2SO_4 and $Na_2SO_4 \cdot 10H_2O$ both supersaturate readily, and it is therefore possible to observe equilibria involving the metastable $Na_2SO_4 \cdot 7H_2O$. The dotted line MK in Fig. 13 is the locus of points whose coordinates are temperature and composition of solutions in equilibrium with $Na_2SO_4 \cdot 7H_2O$. Point K is a metastable peritectic point representing the composition and temperature of the solution which is in equilibrium simultaneously with the heptahydrate and the anhydrous salt, and J is a metastable peritectic point representing the composition and temperature of the solution which is in equilibrium with heptahydrate and decahydrate.

Three-component Systems. With three components we can get useful diagrams in two dimensions only by fixing the values of two variables. Temperature and pressure are usually chosen for this purpose. With these fixed, a two-phase system has one degree of freedom and a three-

phase system none. The most useful form of diagram is the triangular one, which depends upon the geometrical theorem that the sum of the perpendiculars from a point within an equilateral triangle upon the three sides of the triangle is equal to the altitude of the triangle. Consequently, if we call the altitude of the triangle in Fig. 14 unity and represent the weight fraction of component A in a mixture of the components A, B, and C by the distance a_n and the weight fraction of B by the distance b_n, the distance c_n will have the value $1 - a_n - b_n$ and will represent the fraction of C in the mixture. On this basis the vertex marked A represents pure

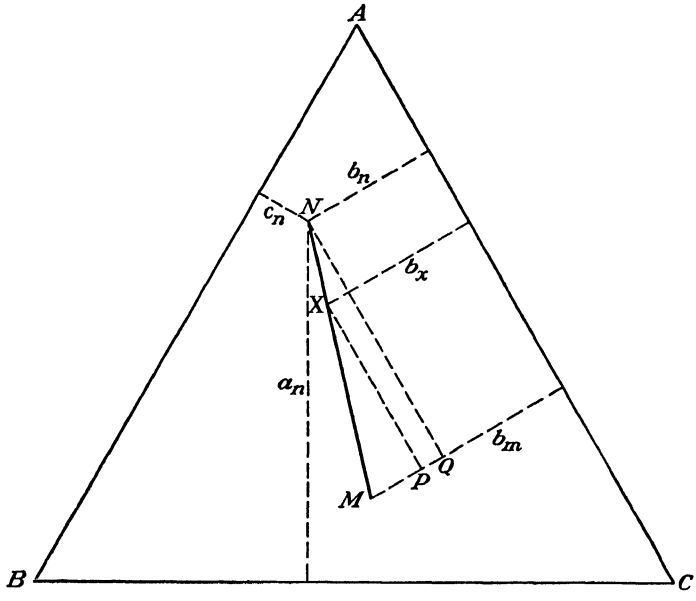


FIG. 14.

A, and a point anywhere on the opposite base represents a system containing no A. Point N or any point on a horizontal line through N represents a system containing 65 per cent A because the perpendicular a_n has a length which is 65 per cent of the altitude of the triangle.

A diagram of this sort may of course be set up in terms of mole fractions just as well as in terms of weight fractions. Other quite different schemes of plotting are sometimes used. Thus the ratio of the weight of A to the weight of C can be plotted as ordinate and the ratio of the weight of B to the weight of C as abscissa in a rectangular cartesian scheme, or, if C is the solvent, the molalities of A and B may be used as coordinates in the cartesian diagram. The triangular diagram, whether in terms of weight fractions or of mole fractions, has the advantage of yielding certain simple

relations between the geometry of the diagram and the proportions of the various phases present in the material system.

Figure 15 is a diagram of this sort on the weight-fraction scale for systems composed of water, Li_2SO_4, and $(NH_4)_2SO_4$ at 30°C and 1 atm. Four solid phases have been observed in such systems, namely, Li_2SO_4, $Li_2SO_4 \cdot H_2O$, NH_4LiSO_4, and $(NH_4)_2SO_4$. Line AB is a plot of the composition of solutions which are in equilibrium with $Li_2SO_4 \cdot H_2O$ and shows how the solubility of this substance in water is affected by the presence of

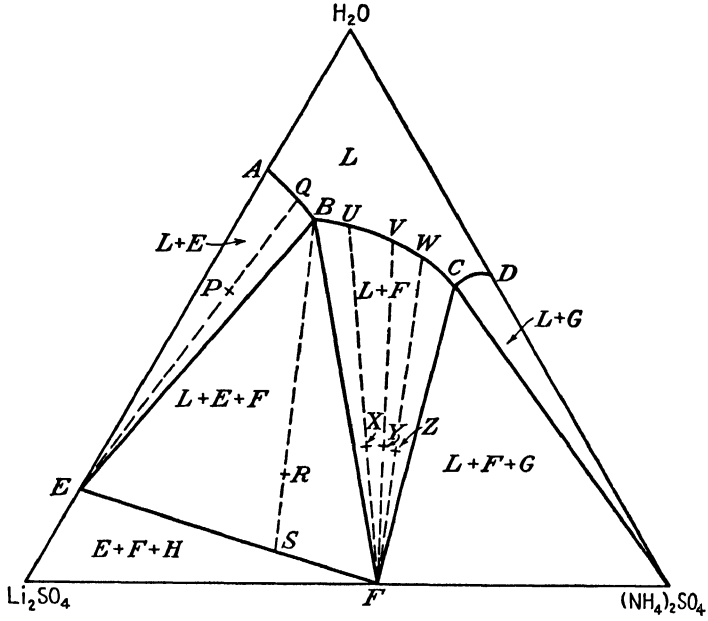


FIG. 15. The system H_2O, Li_2SO_4, $(NH_4)_2SO_4$ at 30°C and 1 atm. E represents solid $Li_2SO_4 \cdot H_2O$, F solid NH_4LiSO_4, G solid $(NH_4)_2SO_4$, and L solution. [*From data of Schreinemakers, Z. physik. Chem.*, **59**, 641 (1907).]

ammonium sulfate in the solution. Thus the weight fraction of lithium sulfate in the saturated solution represented by point Q is 23.5 per cent, this being the solubility in a solution containing 7 per cent ammonium sulfate. The solubility of lithium sulfate in water, represented by point A, is 25 per cent. This line represents, as a line in this kind of diagram always does, a system of one degree of freedom. Thus if one specifies that the solution shall be saturated with lithium sulfate hydrate, it is necessary only to specify one variable, the proportion of ammonium sulfate, to determine the composition of the solution.

Line BC is a plot of the composition of solutions in equilibrium with the double salt NH_4LiSO_4. The intersection of lines AB and BC, point B,

must represent the composition of the unique solution which is in equilibrium simultaneously with lithium sulfate hydrate and double salt. Similarly line CD represents the composition of solutions in equilibrium with solid ammonium sulfate, and point C represents the composition of the solution which is in equilibrium with both ammonium sulfate and double salt. The system of lines and points $ABCD$ includes everything in this diagram that has to do with the composition of the solution; the remainder of the diagram is to be interpreted in terms of *gross compositions.*

The Proportioning Rule. For this interpretation we need a principle, called the *proportioning rule,* which we illustrate in terms of Fig. 14 as follows: If a material X is made by mixing x parts of a material whose composition is represented by point N in the diagram with $1 - x$ parts of a material whose composition is represented by point M, then the point which represents the composition of X lies on a straight line through M and N and the value of x will be given by the ratio of the lengths

$$x = \frac{MX}{\overline{MN}} \tag{30}$$

The rule holds both in the case that the composition is plotted in terms of weight fractions and in the case that it is plotted in mole fractions. In the latter case x is a number of moles rather than a number of grams.

To prove this result for the weight-fraction case, consider the geometry of any three points M, X, and N lying on a straight line in the triangular diagram as shown in Fig. 14. Drop perpendiculars b_m, b_x, and b_n on the side AC of the diagram. The lengths of these lines represent the fractions of component B in the three materials whose compositions are represented by the points M, X, and N. Draw NQ and XP perpendicular to b_m. Let x equal the ratio of the lengths MX/MN. Then by similar triangles

$$x = \frac{MX}{MN} = \frac{MP}{MQ} = \frac{b_m - b_x}{b_m - b_n} \tag{31}$$

This may be rearranged to

$$b_x = xb_n + (1 - x)b_m \tag{32}$$

This is exactly the relationship required if the point X is to represent the composition of a mixture of x parts of material containing the fraction b_n of B with $1 - x$ parts of material containing the fraction b_m. The same argument may be carried through with the A and with the C component, and the rule is thereby proved.

Tie Lines and Areas in the Three-component Diagram. It follows from the result of the last section that the tie line BE of Fig. 15 is the locus

of the points which represent the gross composition of all mixtures that may be obtained from materials of the composition represented by points B and E. Since point E represents the composition of solid $Li_2SO_4 \cdot H_2O$ and B represents the composition of the solution which is in equilibrium simultaneously with this solid and with the double salt, the representative points for all mixtures of this solution with lithium sulfate hydrate lie on BE. It follows also that any point P lying in the area ABE must represent the gross composition of a mixture of solid lithium sulfate hydrate with a liquid phase whose composition lies on the intersection Q of a straight line drawn through E and P with the line AB. A point on the line BF must represent the gross composition of liquid of composition B with solid ammonium lithium sulfate, whose composition is represented by F. A point lying in the area BEF can therefore only represent something intermediate between the systems represented by a point on BE and by one on BF, that is, it must represent the gross composition of a mixture of the three phases, solution of composition B, $Li_2SO_4 \cdot H_2O$, and NH_4LiSO_4. In this way all the areas in the diagram may be labeled as we have done in Fig. 15.

For systems containing two phases the application of the proportioning rule is straightforward. Thus point P represents a mixture of solid lithium sulfate hydrate with solution of composition Q in which the weight fraction of the solid is given by QP/QE and in which the ratio of the weights of solid and liquid is given by QP/PE. For three-phase systems such as that represented by point R the rule leads to the conclusion that the fraction of the mixture which is solid is given by the ratio BR/BS and that the fraction of the solid which is $Li_2SO_4 \cdot H_2O$ is given by FS/FE.

Some Problems of Experimental Method. The experimental problem involved in drawing a phase diagram requires the determination of the conditions for *coexistence* at *equilibrium* of two or more phases of *known composition*. The italicized words are the critical ones in this statement.

It is easy to know whether or not two phases coexist when one studies the boiling point or the freezing point of a dilute aqueous solution at moderate pressures. The materials are transparent, the operations can easily be carried out in transparent vessels, and visual observation suffices to distinguish the presence of vapor bubbles or of crystals in the liquid or of liquid droplets in the vapor. The problem becomes more difficult if one is measuring a boiling point at 100 atm or so, where glass vessels or even quartz windows become impossible, or if one is studying the freezing point of an opaque material like a metallic alloy. For such cases we must depend upon devices, one of which we have already described (page 2). In that case a discontinuity in a plot of volume against pressure at constant temperature betrayed the appearance of the liquid phase in a gas or

of the gas phase in a liquid. The method may equally well be used where only condensed phases are involved, as in the study of the freezing point of water and of the equilibria between the various ices at high pressures.

Thermal Analysis. Another device which is useful in the study of condensed systems involves placing a sample of the material in a container so arranged that heat is removed at a constant or nearly constant rate. The temperature of the material is then plotted against time. So long as no new phase appears, a continuous and nearly linear plot is obtained; a new phase results in a discontinuity. If the new phase or mixture of phases is of the same composition as the original one, there will be a horizontal segment as in Fig. 16*a*, which usually is preceded by a dip due to supercooling of the liquid before the new phase appears. This kind of plot is characteristic of the freezing of a pure substance or of a

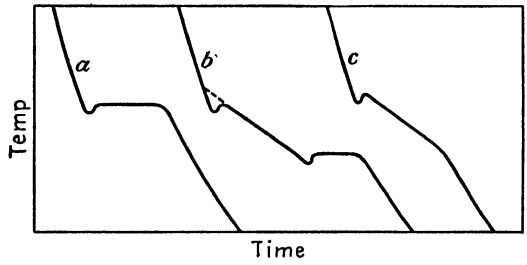


FIG. 16. Typical cooling curves.

liquid whose composition is that of a eutectic or of the maximum or minimum in a system showing solid-solution phenomena. From this point of view a liquid of the composition of the formic acid–formamide compound of Fig. 12 is just as much a pure substance as is either formic acid or formamide. A liquid of the composition and temperature represented by point *U* in Fig. 9 shows a cooling curve like that of Fig. 16*b*. At the temperature of point *V* of Fig. 9 a first discontinuity appears because more heat must be abstracted from the system to freeze out the naphthalene than is needed merely to cool the liquid. But the removal of the naphthalene alters the composition of the liquid in a way which lowers the freezing point as the crystallization proceeds. The plot therefore slopes downward, although not as steeply as it did before crystallization started. When the temperature reaches point *W*, the liquid will have attained the eutectic composition, benzene as well as naphthalene freezes out, and the freezing point stays constant until the liquid has disappeared. Hence the second discontinuity is followed by a flat segment. If there is a continuous series of solid solutions without a maximum or minimum, as in Fig. 11, the cooling curve will be of the type shown in Fig. 16*c*. At

the first discontinuity, freezing starts; at the second, it is complete. The composition of the liquid changes as the freezing proceeds and the temperature drops; hence the segment between the two discontinuities slopes downward. With systems like that of Fig. 10 and in cases where a continuous series of solid solutions shows a maximum or minimum freezing point, cooling curves of the type of Fig. 16b are obtained.

The problem of establishing equilibrium is usually that of maintaining intimate contact between the phases, although there are many cases in which the transfer of material from one phase to another is inherently slow. But even the matter of intimate contact often proves troublesome, and without this kind of contact one encounters very serious superheating, supercooling, and supersaturation situations. Thus the measurement of the boiling point of a solution with any useful precision was an extremely difficult problem until the Cottrell apparatus solved the problem of relieving supersaturation.

Determination of the Composition of Phases. The obvious method of determining the composition of the phases which coexist under particular conditions in a system of more than one component is to separate the phases mechanically. This is often impossible because a clean separation is impossible. We can, of course, filter crystals from a liquid, but they will be wet with the mother liquor, and analysis of the wet crystals will not represent the composition of the crystalline phase. Sometimes the mother liquor can be washed off with a volatile solvent, which can then be removed by evaporation. This is not always possible, and, even when it is, one runs great danger of changing the composition of the solid. With two-component systems the method of thermal analysis is of great assistance, particularly if it is supplemented by X-ray diffraction methods. Thus the extrapolation represented by the dotted line in Fig. 16*b* leads to a useful estimate of the temperature at which a liquid phase of the composition of the initial material is in equilibrium with solid. The flat portion of the plot shows that either a eutectic mixture or a solid solution of minimum freezing point exists, and yields the temperature at which this is in equilibrium with the liquid. By X-ray diffraction measurements on the final crystalline material it is possible to distinguish between the eutectic and the solid solution, and from a sufficient number of cooling curves and diffraction measurements starting with various liquid mixtures the complete phase diagram can be worked out.

With three-component systems the composition of a compound may be determined, provided solid-solution phenomena are absent, by the following method: In the case represented by Fig. 15 suppose a mixture of liquid and crystalline phase be filtered and that analysis of the filtrate shows that its composition is represented by point U. This must lie on the

curve $ABCD$, which represents the composition of all liquids which are in equilibrium with a solid phase. Suppose further that analysis shows that the composition of the mush of crystals wet with mother liquor is that represented by point X. By the argument of page 283 X must lie on a straight line joining the composition of the crystalline phase with point U. That is, the crystalline phase, which is in equilibrium with solution of composition U, must lie on the extension beyond X of the line UX. Let this process be repeated at least twice, giving points V and Y and points W and Z. Then the composition of the solid phase in equilibrium with solution V must lie on the extension of VY, and the composition of the solid phase in equilibrium with solution W must lie on the extension of WZ. If, but only if, the solid phase in equilibrium with all three solutions is of constant composition, these three lines must go through a single point, whose coordinates establish the composition of that phase.

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PROBLEMS

1. How many components are present in each of the following systems, all at 25°C:

a. $Na_2SO_4(s)$, $Na_2SO_4 \cdot 10H_2O(s)$, $H_2O(g)$

b. $NaHCO_3(s)$, $Na_2CO_3(s)$, gas consisting of H_2O and CO_2

c. $K_2HPO_4(s)$, $K_4P_2O_7 \cdot 3H_2O(s)$, $H_2O(g)$

d. An aqueous solution prepared by dissolving in water portions of NaCl, $NaNO_3$, KCl, and KNO_3.

2. The boiling points and the mole per cents of acid in the liquid and in the vapor for acetic acid–water mixtures at 1 atm are

Temp., °C	100	100.5	101.2	102.1	103.2	104.3	105.8	109.0	111.9	118.1
Per cent acid in liquid	0	10.0	20.0	30.0	40.0	50.0	60.0	75.0	85.0	100
Per cent acid in vapor	0	6.3	12.2	18.5	26.0	34.0	43.0	60.0	73.8	100

Estimate the boiling point of a liquid mixture of 2 moles of water with 1 mole of acetic acid and the composition of the vapor in equilibrium with this mixture. If the mixture is distilled until the temperature rises by 0.5°, what will be the approximate composition of the distillate and of the residue?

3. Water boils at 100°C at 1 atm, and decane, $C_{10}H_{22}$, boils at 174°. The two liquids are essentially immiscible. An intimate mixture of the two liquids boils at 96.8°C, at which temperature the vapor pressure of water is 677.1 mm. What is the composition of the distillate obtained from such a mixture in mole per cent and in weight per cent?

4. Assuming that benzene and naphthalene form ideal solutions and that the heats of fusion are independent of the temperature and composition of the liquid, calculate the eutectic temperature and composition for the benzene-naphthalene system from the following data: The melting point of benzene is 5.5°C, and its heat of fusion is 2351 cal/mole. The melting point of naphthalene is 80.2°, and its heat of fusion 4564 cal/mole.

5. Figure 17 represents the freezing points of sulfuric acid–water mixtures. What phases will be present and in what proportion in a system whose gross composition is

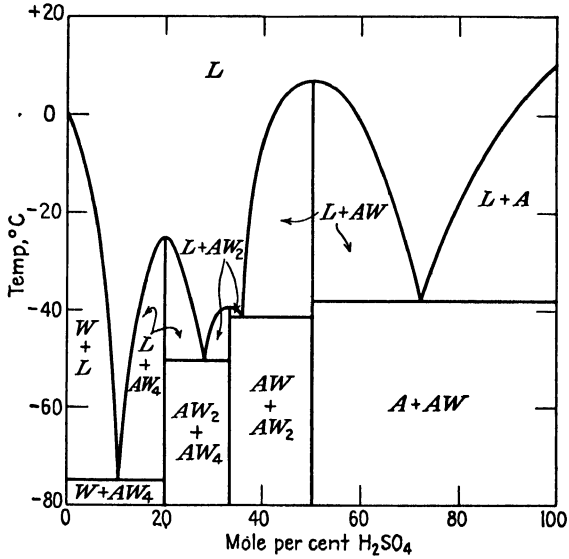


FIG. 17. Freezing-point diagram for water and sulfuric acid. L represents liquid, W water, A H_2SO_4, AW the 1:1 compound of sulfuric acid and water, AW_2 the compound of two molecules of water with one molecule of acid, etc. (*From data reported in International Critical Tables, Vol.* IV, *pp.* 217, 255.)

40 mole per cent acid at −50°C; of a system whose gross composition is 20 mole per cent acid at −50°; of one whose gross composition is 15 mole per cent acid at −60°? Describe the phenomena which may be observed when a 50 mole per cent mixture is heated from −70° to +20°; when a 40 mole per cent mixture is heated through the same temperature range.

6. Describe in detail all the changes that occur when H_2SO_4 is added in small increments to a sample of ice, the temperature at all times being maintained at −30°C.

7. The transition temperature for $Na_2SO_4 \cdot 10H_2O$—Na_2SO_4 is 32.48°C at 1 atm, and the solution in equilibrium with the two solid phases has a mole fraction of sodium sulfate of 0.0594. How much anhydrous sodium sulfate will be present if 1 mole of decahydrate is heated until 0.5 mole of this hydrate remains; how much if the heating

is continued until the last crystal of hydrate just disappears? If the heating of the decahydrate is continued until the temperature reaches 50°, how much solid anhydrous salt will be present? The coordinates of point *D* in Fig. 13 are 0.0558 and 50°.

8. Gold melts at 1066°C, lead at 327°. The compounds Au_2Pb and $AuPb_2$ have been observed. There are peritectic points at 436° and 45 per cent lead and at 254° and 72 per cent lead. There is a eutectic at 220° and 85 per cent lead. Sketch the essential elements of a freezing-point diagram for this system.

9. Label each of the areas in Fig. 18, which is a freezing-point diagram for silver-tin alloys, and explain the significance of each of the points of intersection.

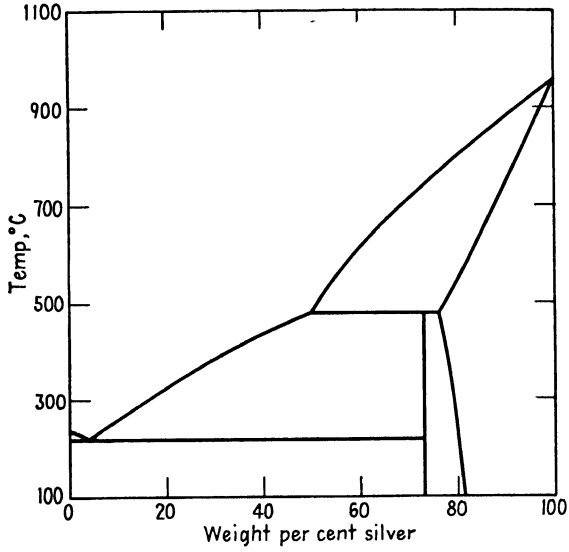


FIG. 18. Freezing-point diagram for tin-silver alloys. (*From International Critical Tables, Vol.* II, *p.* 416.)

10. How many degrees of freedom does a system consisting of $CuSO_4 \cdot 5H_2O(s)$, $CuSO_4 \cdot 3H_2O(s)$, and $H_2O(g)$ possess? If water vapor is gradually pumped out of a closed vessel containing the material at a fixed temperature, what happens to the pressure of the system?

11. Aqueous solutions in equilibrium at 25°C and 1 atm with the solid phases named have the following compositions:

Solid	Per cent KCl	Per cent $MgCl_2$
KCl	26.74	0
KCl	13.56	12.11
KCl	7.90	19.83
KCl and $KCl \cdot MgCl_2 \cdot 6H_2O$	3.19	26.66
$KCl \cdot MgCl_2 \cdot 6H_2O$ and $MgCl_2 \cdot 6H_2O$	0.52	35.47
$MgCl_2 \cdot 6H_2O$	0	35.5

If solid carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$, is completely dissolved in water and the solution evaporated at 25°, what will be the first solid to separate? If the evaporation is continued until a second solid phase appears, what will be its composition? What fraction of the KCl present in the carnallite could be separated as crystalline KCl uncontaminated with another solid phase? If the solution is evaporated until the water content is 50 per cent by weight, what fraction of the total KCl will be present as crystalline KCl?

12. Given a saturated solution of KCl in water at 25°, what fraction of the KCl present could be removed from the solution by adding solid $MgCl_2$? How much $MgCl_2$ would be required to reduce the KCl concentration in solution to the lowest possible value? What fraction of the KCl in a saturated solution could be removed from the solution by the addition of $MgCl_2 \cdot 6H_2O$?

13. Sketch the type of cooling curve to be expected from a liquid silver-copper alloy containing 3 per cent copper (Fig. 10). Repeat for a 40 per cent and for a 70 per cent alloy. Would the halt at the eutectic temperature be longer or shorter in the 70 per cent case than in the 40 per cent case?

14. A series of aqueous solutions in equilibrium with and containing an excess of solid were prepared and filtered. The filtrates and the moist solids thus obtained were found to have the following compositions in mole per cent at 30°C:

Filtrate		Moist solid	
V_2O_5	SO_3	V_2O_5	SO_3
1.060	11.11	2.68	12.55
0.578	13.75	2.01	14.63
1.690	20.73	3.49	20.08

What is the composition of the solid phase?

CHAPTER XIII

ELECTRICAL CONDUCTION IN SOLUTIONS

Concentration Polarization at Electrodes. Consider a pair of identical electrodes immersed in an aqueous electrolyte solution to which a potential is applied from outside. At the electrode to which the negative side of the potential is applied, negative current will be forced from the electrode into the solution, and the electrode will act as a cathode. By the nature of the conduction processes in the metallic and in the electrolytic conductors this can happen only by virtue of a chemical process, a reduction (page 204). What reduction will occur at a given metallic surface in a given solution is a complicated resultant of equilibrium and kinetic factors depending both on the metal and on the composition of the solution, but if nothing else is easier, the process

$$2OH_3^+ + 2e \rightleftharpoons H_2 + 2H_2O \qquad (I)$$

is always possible in an aqueous solution. Whether this process, which produces the reductant hydrogen and consumes the oxidant hydronium ion, or some other process occurs, there will inevitably be the production of some reductant and the consumption of some oxidant. Now an increase in the concentration of reductant and a decrease in the concentration of oxidant both tend to make the solution more positive relative to the electrode, *i.e.*, to make the electrode more negative relative to the solution, and this changed potential is in the direction which opposes the potential imposed from outside. The process at the other electrode must be an oxidation and can always be

$$4H_2O \rightleftharpoons O_2 + 4OH_3^+ + 4e \qquad (II)$$

in an aqueous solution if no other process is easier. Whatever the oxidation may be, it also causes changes in concentration which give rise to a potential opposing the one imposed from outside.

The amount of chemical change at the electrode increases with the quantity of electricity which has flowed; hence the magnitude of the counter emf produced by the change in concentration increases with time, and the net emf available for driving current through the system decreases and the current decreases along with it. The chemical changes occur in a layer of solution of molecular thickness immediately adjacent to the

electrode. But as soon as this layer differs in composition from the remainder of the solution, diffusion starts to even up the difference and is usually assisted by convection currents arising from differences in temperature and density. These lessen the counter emf, but they also give rise to a liquid whose composition varies from point to point in ways that are extremely difficult to predict or control. All these complications make it impossible to measure the resistance of an electrolytic solution by the naïve process of applying a known potential difference to two electrodes, even identical ones, immersed in the solution, of measuring the current, and of taking the ratio of potential difference to current to be the resistance.

Measurement of Electrolytic Resistance by Alternating Current. It has been found that an alternating potential of moderate frequency, *i.e.*, of the order of 1000 cycles, applied to electrodes of large area so that the current density across the solution-electrode boundary is small gives rise to a simpler situation. The explanation appears to be that each half cycle exactly reverses the chemical changes produced by the previous half cycle so that no net change occurs. The solution-electrode emfs set up by the flow of current do affect the magnitude of the current, but they are just as likely to help, which they do just after the applied potential changes sign, as to hinder. The net effect is that the current alternates with the same frequency as the potential but is always a jump ahead of the potential. Such a lead of current over potential is recognized in alternating-current circuits as a capacity (MWM 459, Sears II, 368) not as a resistance, and alternating current theory permits us to set up a bridge in which capacity in the electrolytic cell is balanced by an adjustable capacity in another arm of the bridge while the resistance of the cell is independently balanced by known resistances in the other arms. From the latter resistances the resistance of the cell can be computed.

That the resistance so measured is a property of the solution, unaffected by the phenomena at the electrodes, is evidenced by the fact that the resistance is independent of time and by a very exact proportionality of resistance to the length of the column of solution. If the electrode phenomena played a part, we should expect the resistance R to be given by $R = a + bd$, where d is the length and a and b are coefficients. The observed relationship is $R = bd$, which implies that the resistance is not affected by the phenomena at the electrodes.

Resistivity and Conductivity. The resistance of electrolytic conductors resembles that of metallic conductors not only in the proportionality to the length of the conductor but in a similarly exact inverse proportionality to the area of cross section. Since furthermore the resistances of two samples of the same conducting material of the same length and the same

cross section are identical, it is possible to define a *specific resistance*, or *resistivity* (MWM 368, Sears II, 93), which is a characteristic property of a kind of material independent of its dimensions. This is the resistance of a portion of the material of unit length and unit cross section; consequently resistivity ρ is given by

$$\rho = \frac{RA}{d} \tag{1}$$

where A is the area of cross section and d the length. The reciprocal of the specific resistance, called the *specific conductance*, or *conductivity*, of the material and symbolized by κ, is likewise a specific property of a kind of material,

$$\kappa = \frac{1}{\rho} = \frac{d}{RA} \tag{2}$$

Since by Ohm's law $R = \mathcal{E}/I$, where $\mathcal{E}$ is potential difference and I is current, Eq. (2) can be written

$$\kappa = \frac{Id}{A\mathcal{E}} \tag{3}$$

The specific conductance is therefore equal to the current in amperes through a column of material 1 cm long and of the uniform cross section 1 cm^2 across which a potential difference of 1 volt is applied.

Determination of Specific Conductance. It is not easy to set up a column of liquid of known and exactly uniform cross section and to bound it by parallel electrodes of known distance apart. In the experimentally more accessible situation in which two electrodes are immersed in a vessel of solution the current spreads out in a complicated fashion throughout the liquid, some even proceeding from the back of one electrode to the back of the other. This makes the quantities d and A of Eq. (2) not merely unmeasurable but meaningless. This difficulty may be avoided as a result of the following rule: Given a series of solutions A, B, C, etc., and two cells 1 and 2. Then if R_{A1} is the resistance of solution A in cell 1, R_{A2} the resistance of solution A in cell 2, R_{B1} the resistance of solution B in cell 1, etc.,

$$\frac{R_{A1}}{R_{A2}} = \frac{R_{B1}}{R_{B2}} = \frac{R_{C1}}{R_{C2}} = \cdots = \text{constant} \tag{4}$$

This relationship is theoretically reasonable and has been found to be valid to a precision of 0.01 per cent for a wide range of composition and concentration of solution and of size and shape of cell. It will therefore be valid if cell 2 contains a body of solution 1 cm long and 1 cm^2 in cross

section and is bounded by plane-parallel electrodes. In this case R_{A2} may be replaced by ρ_A, the specific resistance of solution A, and we can write

$$\frac{R_{A1}}{\rho_A} = k \tag{5}$$

with k a constant whose value depends only on the size and shape of cell 1. By the definition of specific conductance this can be transformed to

$$\varkappa = \frac{k}{R} \tag{6}$$

The quantity k is called the *cell constant.* Its value for any cell may be determined once and for all by measuring the resistance of the cell when it is filled with a solution whose specific conductance is accurately known. Such accurate values are available for a series of potassium chloride solutions of various concentrations from measurements in cells to which Eq. (2) may be applied with precision. With the cell constant known the specific conductance $\varkappa$ of any solution is obtained through Eq. (6) from a measurement of the resistance R of the cell filled with that solution.

Equivalent Conductance. For solutions of electrolytes the specific conductance decreases as the concentration decreases. This would be expected since the portion of material involved contains a smaller quantity of the conducting solute. The decrease in specific conductance is not, however, proportional to the decrease in concentration. Thus the specific conductance of a 0.1 M solution of hydrochloric acid is 9.498 times, not 10 times, that of a 0.01 M solution, and the corresponding ratio for acetic acid solutions is 3.203. This means that in both cases the efficiency of the solute as a current carrier is greater in the more dilute solution. To take account of these effects, it is convenient to define a quantity called the *equivalent conductance,* Λ, by the equation

$$\Lambda = \frac{1000\varkappa}{c} \tag{7}$$

in which c is the concentration in gram-equivalents per liter. Since $1/c$ is the volume in liters which contains 1 equiv, the factor $1000/c$ is the volume in milliliters which contains 1 equiv. Using Eq. (3), we may also write

$$\Lambda = \frac{1000d}{cA\mathcal{E}} I \tag{8}$$

It follows from this that Λ is the current in amperes that would flow through a portion of the solution $1000/c$ cm^2 in cross section and 1 cm long under a potential difference of 1 volt (this neglects the small difference

between the cubic centimeter and the milliliter). The volume of this portion of solution is $1000/c$ cc; hence it contains 1 equiv of solute. Consequently we may visualize Λ as a measure of the current-carrying efficiency of the solute, namely, as the coulombs carried in 1 sec by 1 equiv through a distance of 1 cm, under a potential difference of 1 volt. If this picture is to be correct, we must first subtract from the measured specific conductance of the solution the conductance possessed by the solvent alone, so that the difference which is substituted as κ in Eq. (7) really refers to the solute. The correction may be substantial in dilute solutions, especially because we must include in the conductance of the

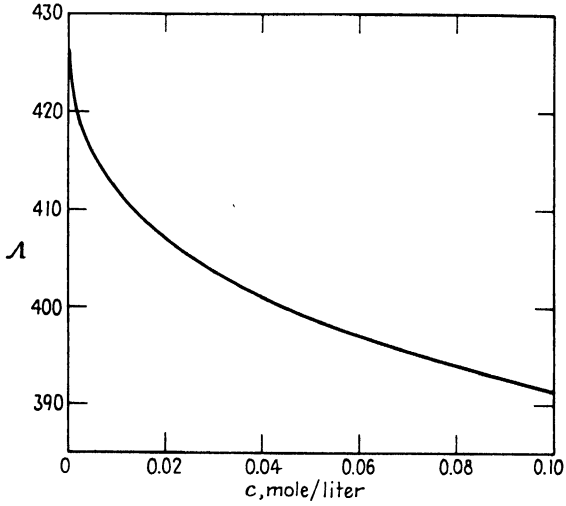


FIG. 1. Equivalent conductance and concentration of aqueous HCl at 25°C. [*From data of Shedlovsky, J. Am. Chem. Soc.*, **54**, 1411 (1932).]

solvent the conductance due to impurities like CO_2 and NH_3, which are difficult to remove.

Conductance and Concentration: Strong Electrolytes. If the equivalent conductance of a strong electrolyte, *i.e.*, one like aqueous NaCl or HCl whose ionization we have reason to believe is essentially complete, is plotted against concentration, a curved line results. This is illustrated in Fig. 1. The plot has the particularly unpleasant property that the curvature increases as the concentration becomes smaller. This makes the problem of estimating the quantity

$$\Lambda_0 = \lim_{c \to 0} \Lambda \tag{9}$$

difficult. We have theoretical reasons to be especially interested in this quantity, because it represents the current-carrying efficiency of the

solute for the limiting case that the ions are infinitely far apart, under which condition any mutual interference in the conduction process must disappear. Fortunately theory, preceded by empirical observation, has developed the rule that a plot of Λ against the square root of the concentration has less curvature than a plot against the first power of the concentration and that the curvature decreases as the concentration decreases. This is illustrated in Fig. 2. We see therefore that a power series in $c^{1/2}$, that is,

$$\Lambda = \Lambda_0 - Ac^{1/2} + Bc - Cc^{3/2} \cdots \tag{10}$$

is an excellent function for the representation of the conductance-concentration relationship, while a power series in c is not. The extrapolation

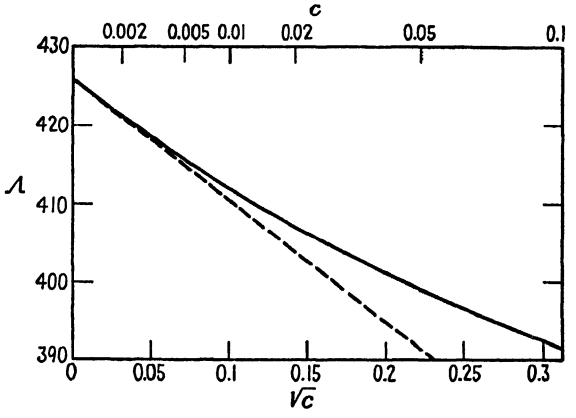


FIG. 2. Plot of equivalent conductance of aqueous HCl at 25°C against the square root of the concentration.

to obtain the value of Λ_0 may therefore be carried out in terms of the $c^{1/2}$ plot with considerable confidence, a confidence which is justified by the properties possessed by the resulting values.

Failure of the Ideal Law of Equilibrium for the Ionization of Strong Electrolytes. The current-carrying efficiency, measured by Λ, of an electrolyte is determined by two factors: (1) the number of ions produced by the ionization of 1 equiv of the substance; (2) the rate at which the ions move under unit electrical field. In the first approximation of the ionic theory as stated by Arrhenius all changes in equivalent conductance with changing concentration were attributed to the first of these effects. By the ideal law of chemical equilibrium the fraction of the neutral molecules of an electrolyte which has reacted to form ions must decrease with increasing concentration of the electrolyte. If, for instance, the electrolyte MX is initially in equilibrium with its ions according to the relation

$$\frac{[M^+][X^-]}{[MX]} = K \tag{11}$$

at a particular concentration and if the solution could then be concentrated to one-half of the original volume without any change in the degree of ionization, each factor in both numerator and denominator of the left-hand member of the equation would be doubled and this would make the left-hand member twice as great as K. Equilibrium can be maintained, therefore, only if some of the ions react to form MX. The resulting decrease in the fraction ionized would decrease the equivalent conductance.

The Arrhenius assumptions would therefore appear to be in qualitative agreement with the facts, and they turn out also to be in good although not perfect quantitative agreement for weak electrolytes. They are, however, in emphatic disagreement with the facts for strong electrolytes, as the following development shows: Let c represent what we shall call the *titer concentration* of a substance MX, and let α be the fraction converted to the ions M^+ and X^-. By the titer concentration of MX we mean the concentration which we should calculate, neglecting the existence of the ionization, either from an analysis or from the proportions in which the solution was prepared. The actual concentration of MX is less than the titer concentration by virtue of the ionization. A precise definition, although one unpleasantly reminiscent of income-tax phraseology, is that the titer concentration of MX is the sum obtained by adding to the actual concentration of MX either the concentration of M^+ or that of X^-, whichever is smaller.

The Arrhenius assumption amounts to supposing that Eq. (11) is valid and exact and that

$$\alpha = \frac{\Lambda}{\Lambda_0} \tag{12}$$

Noting that

$$[M^+] = [X^-] = c\alpha \tag{13}$$

$$[MX] = c(1 - \alpha) \tag{14}$$

we get by substitution in Eq. (11) and cancellation of a factor c between numerator and denominator

$$\frac{c\alpha^2}{1 - \alpha} = K \tag{15}$$

This equation, which is frequently called the *Ostwald dilution formula*, may be solved explicitly for α to give

$$\alpha = \frac{-K + \sqrt{K^2 + 4Kc}}{2c} = \frac{K}{2c}\left(-1 + \sqrt{1 + \frac{4c}{K}}\right) \tag{16}$$

If c is small compared with K, the radical may be expanded as a power series in $4c/K$ (Appendix A),

$$\sqrt{1 + \frac{4c}{K}} = 1 + \frac{2c}{K} - 2\left(\frac{c}{K}\right)^2 + 4\left(\frac{c}{K}\right)^3 \cdots \tag{17}$$

Combining this with Eqs. (16) and (12), we get

$$\Lambda = \Lambda_0\left[1 - \frac{c}{K} + 2\left(\frac{c}{K}\right)^2 \cdots\right] \tag{18}$$

These assumptions lead therefore to the conclusion that a power series in c should be a good representation of the variation of equivalent conductance with concentration when K is large, which must be the case with strong electrolytes, and that a plot of Λ against c should tend to straighten out at low concentrations. These conclusions are directly in conflict with the facts for strong electrolytes, and it is therefore necessary to find some other basis than the Arrhenius assumption to account for the phenomena observed.

The Debye-Hückel Approach. We shall not attempt a discussion of the somewhat involved mathematics employed in the treatment by Debye and Hückel of the alternative to the Arrhenius assumption, namely, that the changes in conductance with concentration result in whole or in part from changes in the mobility of the ions, but the underlying assumptions and the conclusions are both easily intelligible.

The theory recognizes that the electrical energy of interaction between ions must be significant at larger distances than the interaction energy between electrically neutral molecules. Deviations from the dilute-solution laws must therefore become important at much lower concentrations where ions are concerned than with neutral molecules. In particular there must be deviations from the random distribution which would exist if there were no forces between the ions in such a direction as to make the average distance between ions of opposite charge smaller than the average distance between ions of like charge. The magnitude of this effect should increase with the concentration of the electrolyte, should be larger with doubly or triply charged ions than with singly charged ions, and should be greater in solvents of low dielectric constant than in those of high dielectric constant. This means that positive ions tend to cluster around a negative ion in the same way that the molecules of the earth's atmosphere cluster around the earth, to which they are attracted by the gravitational field. Basically the Boltzmann equation applies to the clustering in both cases, but the detailed effect is considerably simpler in the case of the atmosphere because we may neglect the force between

molecule and molecule compared with the force between earth and molecule.

When a negative ion starts to move under the influence of an electrical field imposed from outside, this positively charged "ion atmosphere" acts in two ways to retard the motion. First, the negative ion is displaced from its equilibrium position in such a way that there are more positive ions behind it than before, and these hold back on its motion. Second, the positive atmosphere is moving in the other direction, so that the negative ion is moving against the current. Since these effects become greater the greater the concentration, the net effect is that any ion moves more slowly the greater the total ion concentration of the solution. The development of these ideas leads to the conclusion that the equivalent conductance should be given by the power series in $c^{1/2}$ of Eq. (10).

The theory leads further to definite quantitative predictions about the magnitude of the coefficient A in Eq. (10) and about its dependence on the charge and mobility of the ions, the dielectric constant of the medium and the temperature. The dotted line plotted in Fig. 2 represents the equation $\Lambda = \Lambda_0 - Ac^{1/2}$, with the value of the coefficient A predicted in this way from the theory. It is clear that the actual behavior closely approaches that predicted by this equation in dilute solutions. The prediction that the slope A should be steeper with electrolytes containing multiply charged ions or in solutions of lower dielectric constant is also in qualitative and moderately good quantitative agreement with the available data. Finally the theory predicts certain deviations from Ohm's law at very high current densities and changes in conductance at very high frequencies which have been found experimentally. A related theory based on the same assumptions predicts quantitatively in very dilute solutions the deviations from the ideal law of equilibrium which are observed in reactions involving ions (page 316); consequently the sum total of verification is impressive. It is a point of considerable importance that the quantitative conclusions of the theory derive from the assumption that the ionization of strong electrolytes is essentially complete and that the validity of the conclusions justifies this assumption.

One corollary has considerable practical importance, namely, that the ratio Λ/Λ_0 has nearly the same value for all strong electrolytes of a given charge type in a given medium. Thus the value of this ratio in 0.01 M aqueous solution at 25° for common uni-univalent electrolytes lies in the range from 0.933 for LiCl to 0.967 for HCl. That the ratio varies at all arises partly from the fact that the coefficient A in Eq. (10) depends upon the value of Λ_0, being less the greater the value of that quantity, and partly from the fact that the coefficients B and C depend specifically on the particular electrolyte involved.

Additivity of Λ_0 Values. To a very high precision the Λ_0 values of strong electrolytes are additive properties of the ions. This is to be expected, for the Λ_0 value 149.86 for KCl at 25°C is clearly the sum of the current-carrying efficiencies of 1 mole of K^+ ion and 1 mole of Cl^- ion, and the value 126.45 is similarly the sum of the values for Na^+ and for Cl^-. The difference, 23.41, is therefore the difference in current-carrying efficiency of 1 mole of K^+ ion and 1 mole of Na^+ ion. Since these values are limiting values for infinitely dilute solution in which any mutual interference between positive and negative ions disappears, the difference must be independent of the nature of the anion. Actually the Λ_0 values for KI and NaI are 150.38 and 126.94, and the difference is 23.44. If we are to separate the Λ_0 value for an electrolyte into the individual values for its ions, we must have some kind of information other than the conductance measurements, for these lead only to sums of the conductances of oppositely charged ions and differences of the conductances of like charged ions. Such information is supplied by the transference number of the electrolyte.

Transference Experiments. While more accurate techniques exist for the determination of what are called *transference numbers*, the direct transference experiment is so instructive with respect to what actually occurs when a solution is electrolyzed that we shall consider it in detail. Suppose we have two silver electrodes immersed in a solution of silver nitrate in an apparatus of the sort pictured in Fig. 3 and that a potential is applied so that positive current traverses the cell from right to left. Then for each faraday 1 mole of silver is converted to silver ion at the right-hand electrode, and 1 mole of silver ion is converted to silver at the left-hand electrode. Within the solution both the silver ions and the nitrate ions move, the former toward the left, the latter toward the right, and the task of carrying the current is shared between them. One mole of silver ion cannot therefore move from right to left within the solution even though this much is produced at the right-hand electrode and disappears at the left-hand one, because this motion of the silver ions would account for the whole flow of electricity and would leave nothing for the nitrate ion. The solution in the neighborhood of

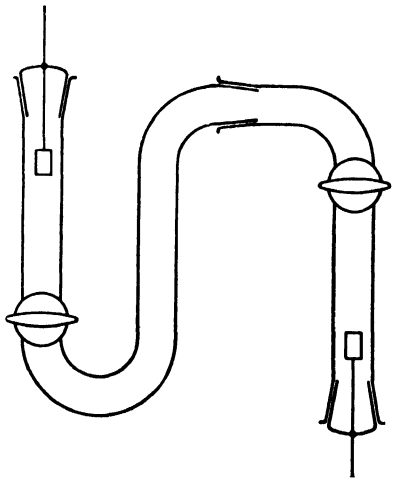


FIG. 3. A transference apparatus.

the anode gets therefore from the electrode process more silver ions than it loses by the migration of the silver ions through the solution. The anode portion of the solution also accumulates nitrate ions because these migrate toward the anode and take no part in the anode reaction. Since the solution must remain electrically neutral, the accumulation of nitrate ions must be just equivalent to the net gain in silver ions and the over-all effect is an increase in the concentration of silver nitrate near the anode. By the same token there is a decrease in concentration near the cathode. The total quantity of silver nitrate in the solutions must remain unchanged, because there is no way in which nitrate ions are lost or gained, and because the quantity of silver ion gained at the anode is equal to the quantity lost at the cathode.

If we represent the fraction of the current through the solution carried by the silver ion by the symbol t_c and the fraction carried by the nitrate ion by t_a, then

$$t_c + t_a = 1 \tag{19}$$

The quantity t_c is called the transference number of the cation, t_a is the transference number of the anion. When the total quantity of electricity which has traversed the cell is q coulombs or $q/\mathbf{F}$ faradays, then $q/\mathbf{F}$ equiv of silver ion have entered the solution from the anode, but only $t_c q/\mathbf{F}$ have migrated away from the anode through the solution. Hence the net change Δ_a in quantity of silver ion in the solution around the anode is given by

$$\Delta_a = \frac{q}{\mathbf{F}} - \frac{t_c q}{\mathbf{F}} \tag{20}$$

By Eq. (19) this becomes

$$\Delta_a = \frac{t_a q}{\mathbf{F}} \tag{21}$$

Meanwhile t_a equivalents of nitrate ion have migrated to the neighborhood of the anode and remain unaffected by the anode process so that the solution around the anode gains $t_a q/\mathbf{F}$ equiv of nitrate ion as well as of silver ion. It is easily shown by similar reasoning that the solution in the neighborhood of the cathode loses the same quantity of silver ions and nitrate ions.

Consequently the value of t_a can be calculated from an experiment involving a known quantity of electricity q if either the net gain of silver nitrate in the neighborhood of the anode or the net loss in the neighborhood of the cathode is measured. By Eq. (19) the value of t_c is then also known. The measurement of the net gain or loss involves some experimental difficulties because the changes in concentration which occur in a

layer of molecular thickness at the surface of the electrode spread out into the solution by diffusion and convection (page 292). It is therefore necessary to collect all of the solution near the electrode within which there has been a change in concentration, to mix it well, to measure its weight or volume, to determine its concentration by analysis, to compute from this the total quantity of silver nitrate in the collected portion, and to compare this result with the quantity of solute which the same volume or weight of the initial solution contained. The difference is the desired value of Δ_a or Δ_c.

In practice it is possible to determine whether or not a large enough volume of solution has been taken by the following method: The solution after the electrolysis is divided into three sections by stopcocks or the equivalent, and each section is analyzed. If the middle section possesses the same concentration that it did before the electrolysis, the presumption is strong that it has not been contaminated by diffusion or mixing from the end sections and therefore that each of these contains all of the excess or deficiency of solute produced in the neighborhood of the electrode.

It should not be supposed that Eq. (21) is valid for all electrolytes and all electrode systems. If HCl is electrolyzed between Ag-AgCl electrodes, the solution gains HCl in the cathode region and loses it in the anode region and the value of Δ_c is given by $t_c q/\mathbf{F}$.

Ionic Conductance. The product of the transference number of an ion by the equivalent conductance of the electrolyte is called the *ionic conductance*, λ; hence

$$\lambda_c = t_c\Lambda \qquad \lambda_a = t_a\Lambda \tag{22}$$

In view of Eq. (19)

$$\lambda_c + \lambda_a = \Lambda \tag{23}$$

Since both Λ and the transference numbers vary with concentration, the latter less sharply than the former, the ionic conductances also depend on concentration. Like Λ they approach limiting values at zero concentration according to a square-root law. Unless we specify otherwise in a particular case, we shall understand the symbol λ to represent this limiting value.

Since Λ is the quantity of electricity carried across a distance of 1 cm in 1 sec by 1 equiv of the electrolyte under a potential difference of 1 volt, λ_c is the quantity of electricity transported by 1 equiv of the cation under the same conditions. From the considerations of page 300 it follows that for very dilute solutions and to a moderate approximation for more concentrated ones, the ionic conductance of nitrate ion must be the same in a sodium nitrate solution as it is in a silver nitrate solution. If then we have learned the transference number of nitrate ion in silver nitrate from

a transference experiment on that salt, Eq. (22) yields the conductance of nitrate ion and subtraction of this quantity from the equivalent conductance of sodium nitrate yields the conductance of sodium ion. In this way one could proceed from a single transference measurement to derive the conductances of various ions from the equivalent conductances of electrolytes containing the ions. Actually many transference measurements on different electrolytes have been made without the appearance of significant discrepancies. We may therefore set up, as in Table 1, a tabulation of ionic-conductance values, from which the value of any electrolyte composed of ions appearing in the table follows by simple addition.

TABLE 1. IONIC CONDUCTANCES AT 25°C IN AQUEOUS SOLUTION*

K^+	73.52	Cl^-	76.34
Na^+	50.11	Br^-	78.4
OH_3^+	349.82	I^-	76.8
Ag^+	61.92	NO_3^-	71.44
Li^+	38.69	OH^-	198
NH_4^+	73.4	$CH_3CO_2^-$	40.9
Ca^{++}	59.50	ClO_4^-	68.0
Ba^{++}	63.64	SO_4^{--}	79.8
La^{3+}	69.6	$Fe(CN)_6^{3-}$	101.0
$Co(NH_3)_6^{3+}$	102.3	$Fe(CN)_6^{4-}$	110.5

* From the tabulation by MacInnes, "The Principles of Electrochemistry," p. 342, Reinhold Publishing Corporation, New York, 1939. These are limiting values for $c \to 0$.

Relation of Specific Conductance to Ion Conductances. In a column of solution of an electrolyte of unit length and cross section under a potential difference of 1 volt the current equals the specific conductance, and by Eq. (7) this equals $\Lambda c/1000$. Consequently the current carried under these conditions by the cation is $\lambda_c c/1000$. If one has a mixed electrolyte containing the ions x, y, z, etc., the total current is the sum of the quantities of electricity carried in unit time by the individual ions. But total current under these conditions is specific conductance. Hence we have for such a system

$$\kappa = \tfrac{1}{1000}(\lambda_x c_x + \lambda_y c_y + \lambda_z c_z + \cdots) \tag{24}$$

The current carried by each ion is therefore proportional to the product of its concentration by its conductance. This result is important for the understanding of the processes which occur in mixed electrolytes, and its corollary that an ion present in negligible concentration carries a negligible fraction of the current is illuminating for a number of electrolytic phenomena. Consider a neutral or alkaline solution of a sodium salt of, say, 0.1 M concentration. The process which occurs at the cathode is reaction (I) instead of the more difficult reduction of sodium ion to sodium.

This process consumes OH_3^+ ion and can continue to do so in spite of the minute concentration of this ion (10^{-7} or less) because the supply is continuously and rapidly replenished by the ionization of water. Yet only a minute fraction of the current in the solution is carried by OH_3^+ because conduction in solution depends on the actual and not on the potential concentration of the ion.

Ion Conductance and Ion Mobility. The quantity of electricity transported by 1 equiv of an ion through a given distance is the same for all ions; consequently the differences in the values of the conductances of various ions depend upon differences in the velocities with which the ions move under the influence of the same electrical field.

Consider a column of electrolyte solution of uniform cross section A to which is applied an electric field of uniform strength $\mathcal{E}/d$. Let v_x be the average velocity in centimeters per second of the ions of kind x, whose concentration is c_x equiv/liter. Then the number of ions which cross a plane perpendicular to the length of the column in unit time will be just the number contained in that portion of the column extending upstream v_x cm from the plane. For, as Fig. 4 shows, an ion initially at M will travel v_x cm and reach N, and an ion initially at P will reach Q. Both of these will cross the plane AB, and so will any other ion whose initial position is between plane AB and plane CD, which is v_x cm from it. The volume of this column is v_xA cc, and the number of ions contained in it is $\mathbf{N}c_xv_xA/1000$ if ion x is singly charged, one half as many if it is doubly charged, etc. In any case these ions carry the charge $\mathbf{eN}c_xv_xA/1000$, which is equal to $\mathbf{F}c_xv_xA/1000$ coulombs, through AB in unit time, and this is therefore the current carried by the x ions. On the other hand we know from Eq. (8) in the light of the relation between Λ and λ that this current is given by $\lambda_xc_xA\mathcal{E}/1000d$. Equating these two values, we have

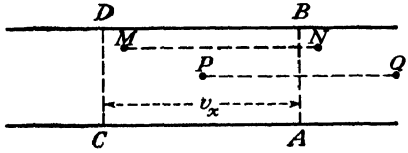


FIG. 4.

$$\frac{\mathbf{F}Ac_xv_x}{1000} = \frac{\lambda_xc_xA\mathcal{E}}{1000d} \tag{25}$$

from which

$$v_x = \frac{\lambda_x}{\mathbf{F}}\frac{\mathcal{E}}{d} \tag{26}$$

This result shows that the velocity of an ion is directly proportional to the electrical field strength $\mathcal{E}/d$. If we represent the velocity of ion x when the field strength is unity by u_x, we have

$$u_x = \frac{\lambda_x}{\mathbf{F}} \tag{27}$$

The quantity u_x is called the *mobility* of the ion x. Values for aqueous solutions at room temperature run from 3×10^{-4} to 3×10^{-3} cm^2/volt-sec.

Stokes' Law Relationships. It can be shown from hydrodynamic theory that the steady-state velocity v of a spherical body of radius r immersed in a continuous medium of viscosity η under the influence of the force f is given by Stokes' law (MWM 220, Sears I, 339),

$$v = \frac{f}{6\pi\eta r} \tag{28}$$

This works excellently for large bodies, but it is known to fail significantly when the radius of the body approaches molecular dimensions. This was indeed a major concern in Millikan's oil-drop measurement of the electronic charge, in which a corrected Stokes' law was employed to derive the radius of the drop from its rate of fall in the gravitational field.

If Stokes' law were exactly valid for ions, we should have

$$\lambda = \frac{10^7\mathbf{F}^2}{\mathbf{N}} \cdot \frac{1}{6\pi\eta r} \tag{29}$$

That the law is valid to the extent that velocity is proportional to force, *i.e.*, to field strength, we have already seen to be true to high precision. Any test of the predicted inverse proportionality between conductance on the one hand and viscosity and ionic radius on the other is severely complicated by the fact that ions are solvated. We do not know the radius of the solvated ions, and we do not know how the radius is changed by changing solvation when we compare solutions in solvents of differing viscosity. For large, symmetrical, and therefore not heavily solvated ions like tetramethylammonium, tetraethylammonium, etc., the conductance is fairly closely proportional to the inverse of the viscosity of the medium and to the expected radius of the unsolvated ion.

If on this basis we assume that Stokes' law has at least qualitative validity for all ions, we must attribute the low conductance of lithium ion, which in the unsolvated state is the smallest alkali ion, to an extremely heavy solvation and may generally derive some knowledge of the extent of solvation from the conductance. The high mobility of hydronium and hydroxyl ions in water and of similar ions in some other media has, however, been shown to depend upon a bucket-brigade transfer of protons from one water molecule to another and not to a high mass-transfer rate of OH_3^+ or OH^- ions.

Conductance and Diffusion. On the molecular scale the conductance phenomena depend upon the same kind of jumping of a solute particle from one equilibrium position to another which is responsible for the diffusion of a solute. In the case of diffusion there is a net transfer in one direction because the concentration gradient makes the rate of transfer in one direction greater than in the opposite direction. In the conductance case the electric field has the same kind of effect. There should therefore be a relation between the diffusibility of an electrolyte and the conductance of its ions.

Some complications arise because the cation and the anion have in general different mobilities. Consequently the ion with the greater mobility tends to get ahead when an electrolyte is diffusing down a concentration gradient. The resulting separation of charges sets up an electric field which slows down the motion of the faster ion and accelerates the slower one. A steady state is soon reached in which the electrolyte diffuses as a whole except that the faster ion is on the average a little ahead of the slower one. The potential difference due to the charge separation is of course the junction potential of page 210. It can be shown that the diffusion constant D of an electrolyte in solution free of any other electrolyte is related to the ion conductances λ_+ and λ_- by the equation

$$\frac{1}{D} = \frac{\mathbf{N}}{\mathbf{R}T}\left(\frac{1}{\lambda_+} + \frac{1}{\lambda_-}\right) \tag{30}$$

with **R** in ergs/mole-deg. If, however, a second electrolyte is present at constant concentration throughout the solution, each ion of the diffusing electrolyte approaches a diffusion rate that is determined solely by its own mobility.

Determination of Ion Concentrations through Conductance Measurements. A considerable variety of problems requiring the determination of an unknown ion concentration may be attacked by conductance measurements. These include the determination of the degree of ionization of a weak electrolyte, and of the extent of other reactions involving ions, the determination of the solubility of difficulty soluble strong electrolytes, and the determination of the rate of reaction in processes which involve either the production of ions from neutral substances or, like the neutralization of nitromethane

$$CH_3NO_2 + OH^- \rightleftarrows CH_2NO_2^- + H_2O \tag{III}$$

the substitution of a low-conductance ion for one of high conductance. The principle employed in every case is the use of Eq. (24). In order to use this, further information, the nature of which depends on the particu-

lar situation involved, must be supplied. The simplest cases are of course those in which only two kinds of ion are present, since an electrolyte solution contains at least two kinds of ion.

Degree of Ionization of a Weak Electrolyte. When a weak electrolyte is dissolved in a solvent which is very weakly ionized, the concentration of its cation c_+ is very closely (page 329) the same as the concentration of its anion c_- and no other ions will be present in significant concentration. If we write c for the titer concentration of the electrolyte and α for its degree of ionization, we have therefore

$$c_+ = c_- = c\alpha \tag{31}$$

Substituting this result in Eq. (24), we get

$$\kappa = \frac{c\alpha}{1000}(\lambda_+ + \lambda_-) \tag{32}$$

λ_+ and λ_- being the conductances of the cation and anion, respectively. In a 0.1 *M* solution of acetic acid the concentration of the ions is of the order of 0.001, and we shall not therefore make a large error if we take for the value of the sum $\lambda_+ + \lambda_-$ in this equation the sum of the conductances of hydronium and acetate ions from Table 1, although these are in fact the limiting values for zero ion concentration. This sum 390.7 together with the observed specific conductance of the solution 5.200×10^{-4} leads through substitution in Eq. (32) to the value 0.01331 for the degree of ionization of acetic acid in 0.1 *M* solution. If we need to be more precise, we can estimate the decrease in conductance due to the Debye-Hückel effect (page 298) either from theory or more precisely by observing the effect of concentration on the equivalent conductances of hydrochloric acid, sodium acetate, and sodium chloride. The latter procedure leads to a value of 385.3 for the sum $\lambda_+ + \lambda_-$ and to 0.01350 for the degree of ionization of the 0.1 *M* acid.

If one wished to use this method for determining the degree of ionization of a weak acid the conductance of whose anion is unknown, the simplest procedure would be to measure the conductance of a salt of the acid with a cation of known conductance, such as sodium or potassium. Subtraction of the known conductance of the cation from the measured equivalent conductance of the salt would then yield the conductance of the anion.

Strictly speaking the specific conductance of a weak acid is given by

$$\kappa = \tfrac{1}{1000}\left(c_{H^+}\lambda_{H^+} + c_{A^-}\lambda_{A^-} + \sum_i c_i\lambda_i\right) \tag{33}$$

instead of Eq. (32). The term $c_{H^+}\lambda_{H^+}$ represents the contribution to the conductance of OH_3^+, the term $c_{A^-}\lambda_{A^-}$ the contribution of the anion of the acid, and the quantity $\sum_i c_i\lambda_i$ the contribution of all the other ions which derive from the solvent itself or from impurities. In this degree of refinement of the treatment one must also recognize that c_{H^+} is not exactly equal to c_{A^-} (page 329). The former quantity is increased and the latter decreased by the tendency of water and of acidic impurities like CO_2 to ionize, whereas basic impurities like NH_3 decrease c_{H^+} and increase c_{A^-}. The ionization of water and of traces of CO_2 is so largely repressed by a moderate concentration of an acid of the strength of acetic acid that both the difference between c_{H^+} and c_{A^-} and the contributions of OH^-, HCO_3^-, and the like, to the conductance can usually be neglected, in which case Eq. (33) reduces to Eq. (32). The problem is more serious if basic impurities like NH_3 are present.

Determination of the Solubility of a Difficultly Soluble Salt. The specific conductance of a saturated solution of the salt MX is given by

$$\kappa = \tfrac{1}{1000}\left(c_{M^+}\lambda_{M^+} + c_{X^-}\lambda_{X^-} + \sum_i c_i\lambda_i\right) \tag{34}$$

Since the c's in this equation are equivalent, not molar, concentrations, this relation is valid if the ions are multiply charged and even if the salt is of an unsymmetrical type like MX_2. The quantity $\sum_i c_i\lambda_i$ represents the contribution to the conductance of the ions which arise from the ionization of the solvent and of impurities in the solvent. If the ions of the salt are not themselves acids or bases of significant strength, this quantity may be set equal to κ_0, the conductance of the solvent used in preparing the saturated solution. The solubility s in equivalents per liter of the salt is equal to c_{M^+} and also to c_{X^-}, and Eq. (34) reduces to

$$\kappa - \kappa_0 = \frac{s}{1000}(\lambda_{M^+} + \lambda_{X^-}) \tag{35}$$

If λ_{M^+} and λ_{X^-} are known or can be determined from measurements on soluble compounds, the solubility can be calculated from a measurement of the specific conductance of the saturated solution.

Determination of Degree of Hydrolysis. Aqueous solutions of aniline hydrochloride are acid because of the reaction

$$C_6H_5NH_3^+ + H_2O \rightleftharpoons C_6H_5NH_2 + OH_3^+ \tag{IV}$$

a reaction which is frequently called the *hydrolysis* of the salt. Let c represent the titer concentration of the salt and α the fraction which has

reacted by (IV). Assuming that effects due to the ionization of the solvent and of impurities can be neglected, Eq. (24) takes the form

$$\kappa_1 = \tfrac{1}{1000}(c_{AH^+}\lambda_{AH^+} + c_{H^+}\lambda_{H^+} + c_{Cl^-}\lambda_{Cl^-}) \tag{36}$$

where AH^+ refers to $C_6H_5NH_3^+$ and H^+ to OH_3^+. We have

$$c_{AH^+} = c(1 - \alpha) \tag{37}$$

$$c_{H^+} = c\alpha \tag{38}$$

$$c_{Cl^-} = c \tag{39}$$

Consequently Eq. (36) can be written as

$$\kappa_1 = \frac{c}{1000}\{(1 - \alpha)\lambda_{AH^+} + \alpha\lambda_{H^+} + \lambda_{Cl^-}\} \tag{40}$$

Everything in this equation is known except λ_{AH^+} and α. A series of solutions is now made up, each containing c moles/liter of aniline hydrochloride and in addition successively increasing concentrations of aniline. The aniline tends to suppress reaction (IV), and as the concentration of aniline increases, the specific conductance approaches a limiting value in which this reaction is negligible. In the presence of such an excess of aniline the conductance is therefore given by

$$\kappa_2 = \frac{c}{1000}(\lambda_{AH^+} + \lambda_{Cl^-}) \tag{41}$$

The value of λ_{AH^+} can be derived from this, and by substitution in Eq. (40) the value of α follows. The method fails, because the equations are indeterminate, if $\lambda_{AH^+} = \lambda_{H^+}$, and is more precise the greater the difference between λ_{AH^+} and λ_{H^+}.

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For further study:

MACINNES: "The Principles of Electrochemistry," Chap. III, the measurement of conductance, Chap. IV, transference, Chaps. VII, XVIII, the interionic attraction theory, Reinhold Publishing Corporation, New York, 1939.

PROBLEMS

1. In a certain conductance cell 0.1 *M* KCl solution at 25°C, whose specific conductance is known to be 0.012852 reciprocal ohm, showed a resistance of 1922.8 ohms. The resistance of the same cell filled with NaCl of 0.0031862 *M* concentration was 63,631 ohms. The specific conductance of the water used in preparing the sodium chloride solution was 0.60×10^{-6} reciprocal ohm. Calculate the specific conductance and the equivalent conductance of the sodium chloride solution.

2. The following equivalent conductances at the concentrations indicated have been observed for aqueous silver nitrate at 25°C:

10^4c, moles/liter	0.27575	0.72453	1.0710	3.5387	4.6704	7.5380	10.026	12.297	14.530	29.054
Λ	132.91	132.64	132 48	131.58	131.46	130.82	130.45	130.10	129.86	128.44

Estimate the value of Λ_0.

3. Show that when $c \gg K$, the fraction ionized of a weak electrolyte approaches the value $\sqrt{K/c}$.

4. In a transference cell with Ag-AgCl electrodes a 0.1 m solution of KCl was electrolyzed at 25°C for 23 hr at an approximately constant current. The deposit of silver formed in a silver coulometer in series with the transference cell weighed 0.6136 g. The anode portion of the solution after the electrolysis weighed 117.51 g and was found to have a KCl content of 0.56662 per cent by weight, whereas the KCl content of the middle portion was unchanged at 0.74200 per cent. What are the transference numbers of cation and anion in KCl at this temperature and concentration? If a cathode portion weighing 120.17 g were examined, what would be the expected per cent of KCl?

5. If a 0.1 m solution of HCl is electrolyzed between Ag-AgCl electrodes until 6000 coulombs have passed through the cell, what will be the concentration of HCl after thorough mixing in a 100-g portion of solution which includes the whole region near the cathode in which a concentration change has occurred? If the same experiment is repeated with Pt-H_2 electrodes, what will be the concentration of HCl in the cathode portion of 100 g?

6. A solution is prepared so that its concentration of HCl is 0.1 M and its concentration of KCl is 0.1 M. What fraction of the current carried by such a solution is transported by each of the ions present?

7. What ionic conductance would you expect from Stokes' law for a singly charged ion of radius 5 A in water at 25°C?

8. Account for the fact that the equivalent conductances of doubly charged and triply charged ions differ so little from those of singly charged ions even though the force acting on the multiply charged ion in a given electric field must be two or three times greater than that acting on a singly charged ion.

9. At 25°C in methanol Λ_0 for HCl is 204.2, for NaCl 104.2, for sodium picrate, $NaC_6H_2O_7N_3$, 101.3. The specific conductance of 0.1 M picric acid in this solvent at this temperature is 9.323×10^{-4} reciprocal ohm. What estimate of the degree of ionization of picric acid under these conditions can you make from these data? Would you expect the error to be greater or less than the error in the value 0.01331 computed on page 307 for 0.1 M aqueous acetic acid?

10. At 25°C the value of Λ_0 for sodium butyrate is 82.70. The equivalent conductance of 0.1 M butyric acid is 4.641. What degree of ionization of butyric acid at this concentration is computed if interionic effects are neglected?

11. In water at 25°C the coefficient A in Eq. (10) is given by theory as

$$A = 0.226\Lambda_0 + 50.3.$$

Using this relation and neglecting the higher terms in Eq. (10), obtain a better value for the degree of ionization of butyric acid in 0.1 molar solution than that obtained in Prob. 10.

12. For water at 25°C the equilibrium relation $[OH_3^+][OH^-] = 1 \times 10^{-14}$ is valid at low ion concentrations. Predict the specific conductance of pure water.

13. The specific conductance of a saturated silver iodate solution at 18°C has been found to be 1.30×10^{-5} when the specific conductance of the water used in preparing

the solution was 1.1×10^{-6}. From measurements on other silver salts and other iodates the sum $\lambda_+ + \lambda_-$ is known to have the value 87.3 for silver iodate at this temperature. What is the solubility of silver iodate in water at this temperature?

14. At 25°C the specific conductance of a $\frac{1}{128}$ *M* solution of aniline hydrochloride in water is 8.88×10^{-4} reciprocal ohm. When aniline at $\frac{1}{64}$ *M* concentration is present in addition to the $\frac{1}{128}$ *M* hydrochloride, the specific conductance is 7.67×10^{-4}; with $\frac{1}{32}$ *M* aniline, it is 7.66×10^{-4}. What fraction of the aniline hydrochloride is hydrolyzed in $\frac{1}{128}$ *M* solution in the absence of added aniline?

15. When Cl_2 was dissolved in water to a titer concentration of 0.03836 *M* the specific conductance was found to be 3.848 at 0°C. If the value of Λ_0 for HCl at this temperature is 250, what fraction of the chlorine has reacted according to $Cl_2 + 2H_2O \rightleftharpoons OH_3^+ + Cl^- + HOCl$? The ionization of HOCl is negligible under the conditions.

16. If you planned to measure the specific rate of the second-order reaction $CH_3NO_2 + OH^- \rightarrow CH_2NO_2^- + H_2O$ at 5°C by means of conductance measurements, what measurements would you make and what equation or equations would you use to compute the specific rate? Assume that you must measure every quantity for which you cannot find a reliable figure in the literature.

17. At 18°C the specific conductance of a saturated solution of CaF_2 in water was found to be 3.86×10^{-5} when the water used in preparing the solution had a specific conductance of 1.5×10^{-6}. At this temperature the value of Λ_0 for $CaCl_2$ is 116.7, for NaCl 108.9, for NaF 90.2. What is the solubility of CaF_2 in water in moles per liter?

CHAPTER XIV

SPECIAL PROPERTIES OF CHEMICAL REACTIONS IN IONIC SOLUTIONS

Special Characteristics of Electrolyte Solutions. As we have seen, electrically charged solutes deviate widely from ideality even in very dilute solutions. This fact would itself justify the separate chapter on ionic solutions, but there are additional peculiarities. One is the usefulness of techniques based on the presence of charged bodies, *i.e.*, on conductance, as a method of investigation. The other, to which we shall devote considerable attention in this chapter, is the necessity in many important types of problems of reckoning with the presence of two or more simultaneous equilibria in a single solution.

Methods of Determination of Activity Coefficients: Galvanic-cell Methods. In principle we can derive values of activity coefficients from studies of the equilibrium in a chemical reaction or of the potential of galvanic cells. This is for the same reason that we must consider activity coefficients in any problem involving an equilibrium or the potential of a cell. We have already seen (Chap. XI) how the mean ionic activity coefficient of HCl may be obtained from measurements of the potentials of a certain type of galvanic cell. It is not so easy to get the mean activity coefficient of sodium and chloride ions or of hydrogen and acetate ions from measurements of potential, but it can be done with excellent precision, and a considerable body of data from sources of this sort is available.

Activity Coefficients from Conductance Measurements. By way of Eq. (32) of Chap. XIII the degree of ionization α of a weak acid HA may be derived from measurement of the conductance of its solution. Equation (15) of Chap. XIII shows that we may then compute the value of the quantity $[H^+][A^-]/[HA]$, which would be constant if the ideal law of equilibrium were exact, from the relation

$$\frac{[H^+][A^-]}{[HA]} = \frac{c\alpha^2}{1 - \alpha} \tag{1}$$

where c is the titer concentration of the acid. By the considerations of (Chap. XI) the quantity is not constant to high precision but is given by

$$\frac{[H^+][A^-]}{[HA]} = K^\circ \frac{\gamma_{HA}}{\gamma_{H^+}\gamma_{A^-}} \tag{2}$$

where γ's are activity coefficients and $K°$ is rigidly constant at constant temperature and pressure. If we define the quantity K by

$$K = \frac{c\alpha^2}{1 - \alpha} \tag{3}$$

then by Eqs. (1) and (2)

$$\log K = \log K° - \log \frac{\gamma_{H^+}\gamma_{A^-}}{\gamma_{HA}} \tag{4}$$

Since an activity coefficient approaches 1 and its logarithm approaches 0 as the concentration of the solution approaches 0, we have from Eq. (4)

$$\lim_{c \to 0} (\log K) = \log K° \tag{5}$$

It should be possible from a series of measurements at different concentrations to estimate the value of this limit, and, once $K°$ is known, the experimental value of K at any concentration leads through Eq. (4) to a value of the ratio $\gamma_{H^+}\gamma_{A^-}/\gamma_{HA}$. Since HA is an uncharged molecule for which the deviations from ideality are relatively small, γ_{HA} may to a good approximation be taken to be unity, especially in the more dilute solutions. To the precision to which this is justified, $\gamma_{H^+}\gamma_{A^-}$ and its square root, the mean ionic coefficient, are therefore known.

In Fig. 1 values of log K for aqueous acetic acid at 25°C are plotted against $\sqrt{c_i}$, with c_i given by

$$c_i = [H^+] = [A^-] = c\alpha \tag{6}$$

The data derive from very careful measurements of the conductance of acetic acid, due regard being taken of the variation of Λ with ionic concentration (page 307). The data in the more dilute solutions approximate closely to a straight line, which makes the extrapolation required to obtain the value of log $K°$ relatively easy. The value of log $K°$ obtained from the data of Fig. 1 is -4.7565, from which $K° = 1.752 \times 10^{-5}$. The mean activity coefficient when the titer concentration is 9.842×10^{-3} M and $c_i = 4.156 \times 10^{-4}$ comes out to be 0.978.

Activity Coefficients from Solubility Measurements. The condition for equilibrium in the solution of the salt MX, which dissolves to form the ions M^+ and X^-, is

$$[M^+][X^-] = \frac{K°}{\gamma_{M^+}\gamma_{X^-}} \tag{7}$$

If we define a quantity K, which we shall call the solubility product, by

$$K = [M^+][X^-] \tag{8}$$

we have

$$\tfrac{1}{2} \log K = \tfrac{1}{2} \log K^\circ - \log \gamma_\pm \tag{9}$$

where $\gamma_\pm$ is the mean activity coefficient of the ions M^+ and X^-. In a saturated solution of MX in water or in a solution of the electrolyte NY

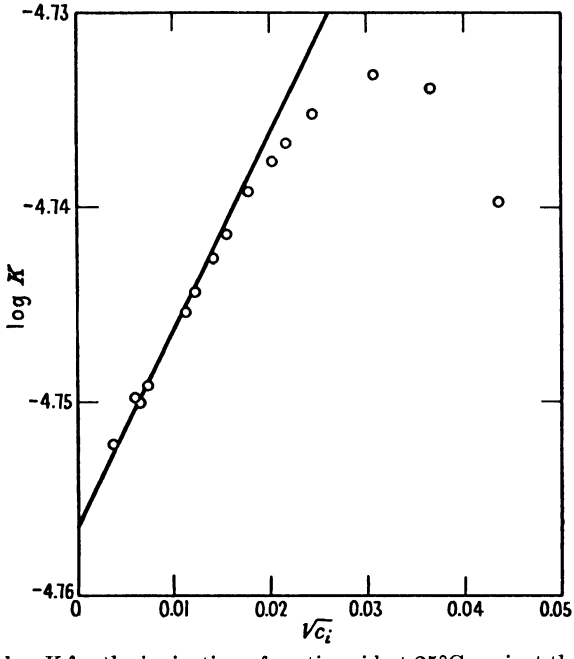


FIG. 1. Plot of log K for the ionization of acetic acid at 25°C against the square root of the ion concentration c_i. [*From data of MacInnes and Shedlovsky, J. Am. Chem. Soc.*, **54**, 1429 (1932).]

we have for the solubility s, if complications due to hydrolysis (page 346) can be neglected,

$$s = [M^+] = [X^-] = K^{1/2} \tag{10}$$

and K can therefore be determined from a measurement of solubility.

If the solubility is determined in a solution containing c moles/liter of the salt MY, we have

$$[X^-] = s \tag{11}$$

$$[M^+] = s + c \tag{12}$$

and consequently K is given by

$$K = s(s + c) \tag{13}$$

and the value of K can again be derived from a solubility measurement.

In Fig. 2 there is plotted as ordinate the quantity $\frac{1}{2}$ log K obtained from measurements of the solubility of the salt $[Co(NH_3)_4C_2O_4][Co(NH_3)_2(NO_2)_2C_2O_4]$ in the presence of other electrolytes. This salt is a strong electrolyte consisting of the cation $Co(NH_3)_4C_2O_4^+$ and the anion $Co(NH_3)_2(NO_2)_2C_2O_4^-$. Such cobaltammine salts are admirably suited to investigations of this kind because they are difficultly soluble yet accessible to accurate analytical determination and because they show no complicating reactions such as hydrolysis. The ordinate is the square

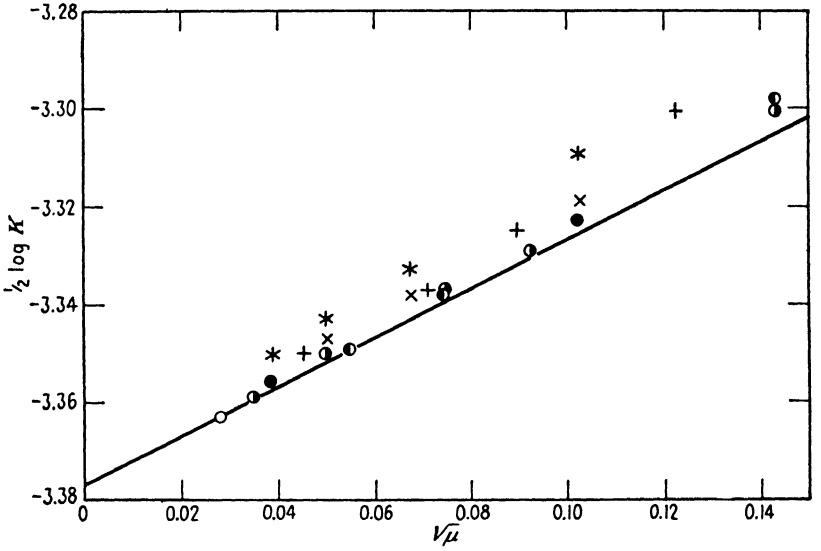


FIG. 2. Effect of added salts on the solubility of a salt containing a singly charged cation and a singly charged anion. Plot of $\frac{1}{2}$ log K, where K is the solubility product, against the square root of the ionic strength μ. Added salt: ◑ NaCl, ◐ KNO_3, + $BaCl_2$, × $MgSO_4$, * $K_3Co(CN)_6$. [*From data of Brønsted and LaMer, J. Am. Chem. Soc.*, **46**, 555 (1924).]

root of a measure of concentration μ called the *ionic strength*. In so far as solutions containing only singly charged ions are concerned, the ionic strength is identical with the total concentration of electrolyte in moles/liter. The points representing these solutions, the circles in Fig. 2, lie reasonably well along a straight line, whose intercept on the axis of ordinates is −3.377. Since the quantity log $\gamma_\pm$ in Eq. (9) must approach 0 as the ion concentration approaches 0, this intercept is the value of $\frac{1}{2}$ log $K°$. With this known, the experimental value of K for any solution can be substituted in Eq. (9) to obtain the mean ionic activity coefficient for the saturating salt.

Activity Coefficients from Freezing-point Data. Some of our most precise data on ionic activity coefficients in aqueous solutions containing a single electrolyte derive from measurements of the freezing-point depression produced by the salt over a range of concentrations. We shall not discuss the details of these computations.

Nature of the Dependence of Activity Coefficients on Ion Concentration. All these methods show that the activity coefficients of ions decrease with increasing ion concentration. The effect is of the sort to be expected from the discussion of the Debye-Hückel theory in Chap. XIII. If there is a clustering of positive ions in the neighborhood of a negative ion and of negative ions in the neighborhood of a positive ion, attractive energies must predominate over repulsive ones and the energy of an ion in a solution containing other ions must be lower than it would be in the absence of other ions. The more ions there are, the bigger the effect will be; consequently the work required to remove the ion from the solution must be greater and the molar free energy of the ion more negative the larger the concentration of ions in the solution. By Eq. (43) of Chap. XI the activity coefficient of an ion must then be decreased by an increase in the total concentrations of ions present in the solution. The effect should be larger the larger the charge on the ions and the lower the dielectric constant of the medium.

Debye-Hückel Limiting Law. The detailed working out of this kind of theoretical consideration leads to the conclusion that in very dilute solution the activity coefficient of an ion should approach as a limiting law the behavior given by the relation

$$\log \gamma = -az^2 \sqrt{\mu} \tag{14}$$

which is called the Debye-Hückel limiting law. Here z is the charge on the ion whose activity coefficient is γ (1 for Na, -2 for SO_4^{--}, etc.), and μ, the ionic strength, is defined by the relation

$$\mu = \sum_i c_i z_i^2 \tag{15}$$

c_i is the concentration of the ion of kind i, and z_i is the charge on an ion of this kind. The summation is taken over all the kinds of ions present in the solution. If a solution contains only a 1:1 electrolyte like NaCl, the ionic strength is identical with the molar concentration; if it contains only a 2:1 electrolyte like $BaCl_2$, the ionic strength is three times the molar concentration, etc. In a mixture of electrolytes the ionic strength may be obtained as the sum of contributions computed in this way for each electrolyte present.

The coefficient a is given by the theory as

$$a = 0.4343 \frac{\mathbf{e}^3(2\pi\mathbf{N})^{1/2}}{(10D\mathbf{k}T)^{3/2}} \tag{16}$$

and has the value 0.5091 in aqueous solution at 25°C. The quantity shows the expected dependence on the dielectric constant D, that is, the activity coefficient decreases with increasing concentration more rapidly in a medium of low dielectric constant. Because of the factor z^2 in Eqs. (14) and (15) the activity coefficient also decreases more rapidly the greater the charges on the ions involved.

The theory predicts that Eq. (14) should be a limiting law in the sense that the perfect-gas law may be called a limiting law. One should not expect the actual behavior of an electrolyte to agree exactly with the predictions of this law any more than one expects the actual behavior of a gas to agree with the equation $PV = \mathbf{R}T$, but one may expect that the behavior of a real electrolyte will approach more closely to that predicted by Eq. (14) the more nearly the ionic strength of the solution approaches zero, just as one expects the behavior of a real gas to approach more closely to that predicted by the perfect-gas law the more nearly the pressure approaches zero.

To the precision of the limiting law the theory predicts that all ions of the same charge shall have the same activity coefficient in a solution of given ionic strength; further that two ions A and B of the same numerical charge present at the same concentration shall have identical effects on the activity coefficient of a third ion. To the same precision the theory predicts quantitatively the effect of different numerical charges. On the other hand the theory predicts that the deviations from the limiting law exhibited by real electrolytes shall depend in a specific fashion upon the particular ions present in the solution. It expects the activity coefficient of an ion to depend upon its size, its symmetry, its polarizability,* and the degree and strength of its solvation, and also upon the corresponding properties of the other ions present in the solution, especially those of opposite sign to its own.

If one needs to predict the activity coefficient of an ion with greater precision than that permitted by the limiting law, one needs, therefore, information which can be obtained only from empirical observation. The situation is closely analogous to that involved in predicting the properties of gases. If the precision supplied by the perfect-gas law is sufficient for a particular problem, one may predict many properties of a gas or mixture

* The polarizability of an atom, molecule, or ion is a measure of the ease with which its structure is distorted by an external electric field.

of gases from no data other than the molecular weights and the value of **R**. But the deviations of real gases from the perfect-gas law cannot be predicted from theory and have different magnitudes for different gases.

As a limiting law Eq. (14) has been verified by a large amount of experimental investigation on dilute solutions of not too highly charged ions in media of high dielectric constant, and there is no serious doubt of the essential validity of the theoretical considerations involved in the development of the equation. The kind of verification obtained is illustrated by Figs. 1 and 2, in both of which the straight lines drawn have the slopes predicted from the limiting law.

By the definition of mean ionic activity coefficient for singly charged ions [Eq. (60) of Chap. XI] we have

$$\log \gamma_{\pm} = \tfrac{1}{2}(\log \gamma_{+} + \log \gamma_{-}) \tag{17}$$

Substituting the value of $\log \gamma$ from Eq. (14) leads to

$$\log \gamma_{\pm} = -a\sqrt{\mu} \tag{18}$$

Using this in Eq. (9), we get for the dependence of the solubility product on ionic strength

$$\tfrac{1}{2} \log K = \tfrac{1}{2} \log K^{\circ} + a\sqrt{\mu} \tag{19}$$

The line drawn in Fig. 2 has the slope given by the value of a from Eq. (16). The agreement with experiment is good where singly charged ions alone are involved. Even when multiply charged ions are present, the discrepancies are far from being as large as they would be if the total ion concentration in moles/liter or in equivalents per liter were plotted as abscissa instead of the ionic strength.

In similar fashion Eq. (4) may be converted to a limiting law for the ionization constant of an acid HA,

$$\log K = \log K^{\circ} + 2a\sqrt{\mu} \tag{20}$$

The line plotted in Fig. 1 has the slope $2a$, and the agreement is excellent in the more dilute solutions.

Mean Ionic Activity Coefficient. We adopt as a general definition of the mean ionic activity coefficient of an electrolyte, valid for multiply charged as well as for singly charged ions, the relation

$$\gamma_{\pm} = (\gamma_{+}^{\nu_{+}}\gamma_{-}^{\nu_{-}})^{1/(\nu_{+}+\nu_{-})} \tag{21}$$

where ν_{+} is the number of cations of charge z_{+} contained in one formula weight of the electrolyte and ν_{-} the number of anions of charge z_{-}. Since

the electrolyte must be electrically neutral, these quantities are also related by the equation

$$\nu_+ z_+ + \nu_- z_- = 0 \tag{22}$$

Putting Eq. (21) in the logarithmic form and substituting from the limiting law, we have

$$\log \gamma_\pm = -a\sqrt{\mu}\left(\frac{\nu_+ z_+^2 + \nu_- z_-^2}{\nu_+ + \nu_-}\right) \tag{23}$$

If we multiply Eq. (22) separately by z_+ and by z_- and add the resulting equations, we have

$$\nu_+ z_+^2 + \nu_- z_-^2 = -z_+ z_1(\nu_+ + \nu_-) \tag{24}$$

From this and Eq. (23) we get for the limiting law for the mean activity coefficient

$$\log \gamma_\pm = +z_+ z_- a\sqrt{\mu} \tag{25}$$

Since z_+ and z_- necessarily have opposite signs, their product is negative and the prediction of the limiting law is that $\gamma_\pm$ shall always decrease with increasing ionic strength.

Solubility of Salts Containing Multiply Charged Ions. Consider the solubility of a salt AB_3 in water or in a solution of another electrolyte *which does not contain the ions* A^{3+} *or* B^-. The process of solution is

$$AB_3(s) \rightleftarrows A^{3+} + 3B^- \tag{I}$$

and the expression of the equilibrium law is therefore

$$[A^{3+}][B^-]^3 = \frac{K^\circ}{\gamma_A \gamma_B^3} \tag{26}$$

If we represent by s the solubility of AB_3 in formula weights per liter, the concentration of A^{3+} in moles per liter must be equal to s but the concentration of B^- must be $3s$, since each formula weight of salt yields on solution 3 moles of B^-. Substituting these values in Eq. (26), we have

$$s(3s)^3 = \frac{K^\circ}{\gamma_A \gamma_B^3} \tag{27}$$

By Eq. (21) we have for the mean activity coefficient in this case

$$\gamma_\pm = (\gamma_A \gamma_B^3)^{1/4} \tag{28}$$

and combining this with Eq. (27) we have

$$s = \frac{(K^\circ/3^3)^{1/4}}{\gamma_\pm} \tag{29}$$

The solubility of AB_3 in a solution of an electrolyte which contains A^{3+} or B^- shows a "common ion effect" and obeys a different law from Eq. (29) (page 344).

A generalization of the argument leading to Eq. (29) shows that, in the absence of a common ion, the solubility of an electrolyte of any valence type is given by a constant divided by the mean ionic activity coefficient.

With $z_+ = +3$ and $z_- = -1$, Eq. (25) takes the form $\log \gamma_\pm = -3a\sqrt{\mu}$. The limiting law for the solubility of the salt is therefore

$$\log s = \frac{1}{4}\log \frac{K^\circ}{27} + 3a\sqrt{\mu} \tag{30}$$

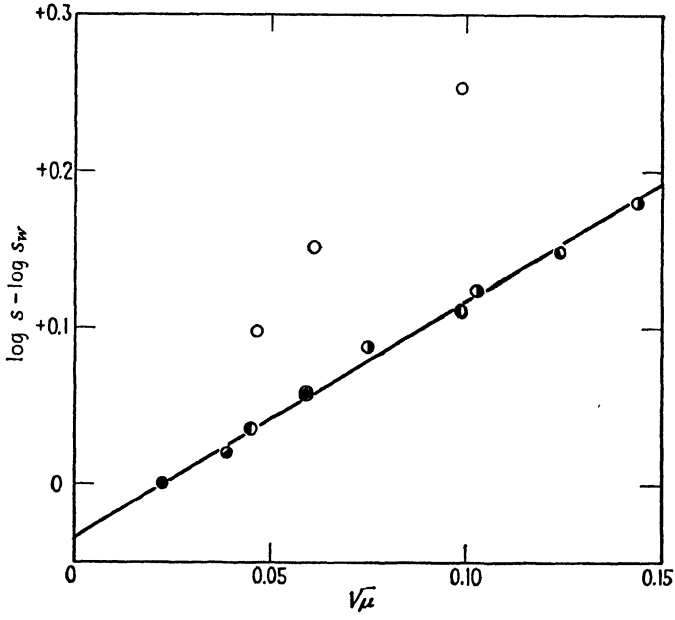


FIG. 3. Effect of added salts on the solubility of a salt consisting of a triply charged cation and a singly charged anion. Plot of $\log s - \log s_w$, where s is solubility and s_w solubility in water, against the square root of the ionic strength. Added salt: ● none, ◑ KNO_3, ◐ $BaCl_2$, ○ K_2SO_4. [*Data from LaMer and Mason, J. Am. Chem. Soc.*, **49**, 410 (1927).]

Figure 3 shows the results of measurements on the solubility of a salt of this type whose cation is $Co(NH_3)_6^{3+}$ and whose anion is $CO(NH_3)_2(NO_2)_2C_2O_4^-$. The ordinates are the values of the quantity $\log s$ diminished by the constant quantity $\log s_w$, where s_w is the solubility in water, the abscissas are the values of ionic strength, and the line drawn has the slope $3a$. Note that the scale of ordinates differs from that of Fig. 2. When the added salt is KNO_3 or $BaCl_2$, the limiting law is in good agree-

ment with the experimental results; when the added salt is K_2SO_4, the disagreement is violent. We have to deal in the last case with the effect of a doubly charged negative ion on a triply charged positive one. The electrical force between these ions is six times that between two singly charged ions, and it appears to pull them together so closely that effects are important at very low concentrations which become significant with singly charged ions only at much larger concentrations. This kind of serious failure of the limiting law is likely to appear whenever multiply charged ions of opposite sign are present. It also appears in solvents of low dielectric constant.

Activity Coefficients at Ionic Strengths Up to 0.1. The data we have been discussing involve ionic strengths of not over 0.02. They are important because they demonstrate the essential correctness of the Debye-Hückel assumptions, but they have little bearing on practical problems in analytical chemistry, in technical electrochemistry, and in biological chemistry. As we shall see shortly, the assumption that the limiting law is valid is sometimes more seriously in error than the assumption that all activity coefficients are unity, and the assumption that they are all unity may lead to gross errors. If activity coefficients were unity, the solubility of $La(IO_3)_3$ would be the same in 0.1 N K_2SO_4 as it is in water; actually the solubility is 3½ times greater in the salt solution. If activity coefficients were unity, the solubility of $La(IO_3)_3$ would be materially less in 0.1 N $La_2(SO_4)_3$ than in water; actually the solubility is 1.55 times greater in the salt solution.*

At ionic strengths of not over 0.1 some useful regularities have been observed. Figure 4 plots against the square root of the ionic strength the quantity $(\log \gamma_\pm)/(-z_+z_-)$ for some typical electrolytes in this concentration region. These data are for solutions containing a single electrolyte only; thus the plot for HCl represents the mean activity coefficients of the ions of HCl in a solution containing no electrolyte but HCl. The deviations of the observed data from the limiting law and the variation of the values for various electrolytes at a given ionic strength are of about the same magnitude when the effect of one electrolyte upon the activity coefficient of another is measured. Thus the mean coefficient for the ions of the difficultly soluble $TlIO_3$ at an ionic strength of 0.1025 is 0.703 when the added electrolyte is KNO_3, 0.667 when it is KCl, and

* Physical chemists sometimes seem to have a predilection for investigating odd and unusual compounds. This is an appearance which is rarely deserved. The solubility of lanthanum iodate was investigated because its solubility is in an interesting range, because it is not significantly hydrolyzed as so many salts of triply charged cations are, and because the analytical determination of iodate ion is a very favorable one both for precision and for ease.

0.752 when it is $MgSO_4$, whereas the limiting-law value at this ionic strength is 0.688.

All of the existing data on solutions containing a single electrolyte can be represented with good precision by a sheaf of nonintersecting curves in the plot of Fig. 4 which lie between the curve for HCl and the curve marked *LL*, which represents the limiting law. The single curve marked

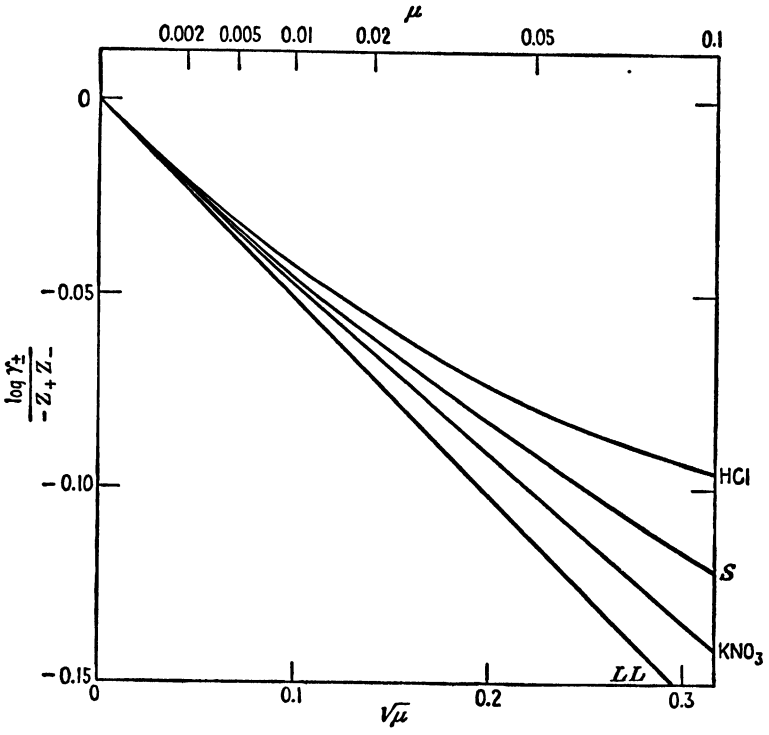


FIG. 4. Plot of $(\log \gamma_\pm)/(-z_+z_-)$ against the square root of the ionic strength at ionic strengths up to 0.1. *LL* is the Debye limiting law. The other curves are plots of Eq. (31) [*according to Guggenheim, Phil. Mag.*, **19**, 628 (1935)].

S agrees within the precision of plotting with the data for $NaNO_3$, $CsNO_3$, K_2SO_4, $MgSO_4$, and $La_2(SO_4)_3$. The data for sodium and potassium iodates nearly coincide with the limiting law. These curves in the range up to $\mu = 0.1$ can be fitted with excellent precision by the equation

$$\frac{\log \gamma_\pm}{-z_+z_-} = \frac{-a\sqrt{\mu}}{1+\sqrt{\mu}} + b\mu \tag{31}$$

Since a is given by Eq. (16), this equation involves only one coefficient,

b, which must be fitted to each particular case. Table 1 illustrates the quality of the agreement obtained in the case of HCl solutions.

TABLE 1. VALUES OF THE MEAN IONIC ACTIVITY COEFFICIENT OF HCl AT 20°C*

Molality	0.005	0.010	0.020	0.050	0.100
$\gamma_\pm$(expt'l)	0.929	0.906	0.880	0.834	0.801
$\gamma_\pm$(computed)	0.929	0.906	0.877	0.833	0.801

* From the tabulation given by Guggenheim, *Phil. Mag.*, **19**, 626 (1935). The experimental values derive from the galvanic-cell measurements of Harned and Ehlers, the computed values from the equation $\log \gamma_\pm = -\frac{0.05\sqrt{\mu}}{1+\mu} + 0.240\,\mu$ suggested by Guggenheim.

The constant b shows some regularities, which are helpful in estimating its value in unknown cases. These amount to a rule that the activity coefficient of the ion M^+ in a solution containing the salts MX, $M'X'$, $M''X''$, etc., is determined by the kind and concentration of the negative ions X^-, X'^-, X''^-, etc., and that the activity coefficient of the ion X^- is determined by the positive ions M^+, M'^+, M''^+, etc. The rule derives from the reasonable expectation that the deviations from the limiting law depend upon the mutual influence of ions that are especially near each other, which are likely to be ions of opposite sign. One may also estimate values of b from the rule that electrolytes whose ions have similar size, symmetry, and polarizability should have nearly identical activity coefficients in closely similar situations.

In default of the information required to make any estimate of b the equation

$$\frac{\log \gamma_\pm}{-z_+z_-} = \frac{a\sqrt{\mu}}{1+\sqrt{\mu}} \tag{32}$$

is a reasonable sort of an average function for the dependence of $\gamma_\pm$ on μ. This function is plotted as the curve marked S in Fig. 4. As we have already mentioned, a number of electrolytes agree closely with this curve and it lies in the middle of the range occupied by all the electrolytes for which data are available.

Ionic Activity Coefficients in Concentrated Solutions. Figure 5 shows the way in which the mean ionic activity coefficients of some typical electrolytes vary with concentration in relatively concentrated solutions. The data are for solutions containing a single electrolyte only. There is little that one can do in the way of predicting the values of activity coefficients in such systems as these.

Ionic Activity Coefficients at High but Constant Ionic Strength. The assumption that ionic activity coefficients are constant is not nearly so poor an approximation in problems involving a high ionic strength as the assumption that they are unity. Inspection of the data of Fig. 5 shows that the plots of activity coefficient against ionic strength are considerably flatter in the region around $\mu = 0.5$ than they are in more dilute solutions. This means that the change in activity coefficient which arises from a

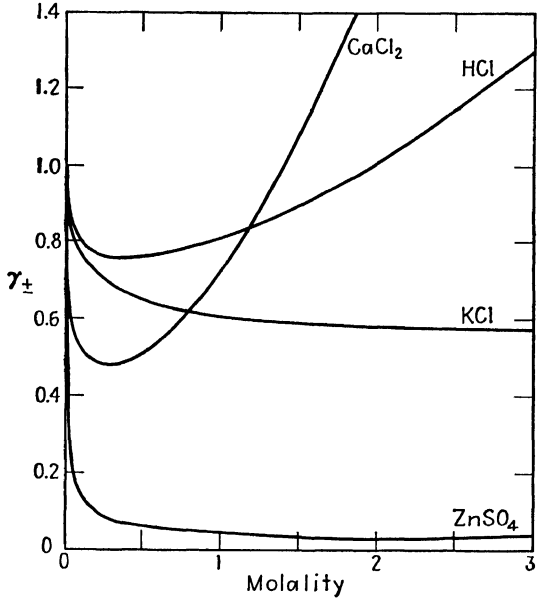


FIG. 5. Plots of mean ionic activity coefficient $\gamma_\pm$ against molality at high concentrations.

given change in ionic strength is smaller in this region. Thus the equilibrium

$$Fe^{3+} + I^- \rightleftharpoons Fe^{++} + \tfrac{1}{2}I_2 \qquad (II)$$

must be very sensitive to changes in ionic strength because of the multiple charges on the iron atoms. But when this equilibrium is examined in solutions all of which contain 1.65 *M* KCl and 0.1 *M* HCl but in which the concentrations of the reacting substances are small, the data illustrated in Table 2 are obtained. The quantity

$$K = \frac{[Fe^{++}][I_2]^{\frac{1}{2}}}{[Fe^{3+}][I^-]} \qquad (33)$$

is satisfactorily constant in spite of wide variations in the individual concentrations.

TABLE 2. EQUILIBRIUM CONSTANT AT 25°C OF THE REACTION $Fe^{3+} + I^- \rightleftharpoons Fe^{++} + \frac{1}{2}I_2$ IN SOLUTIONS ALL OF WHICH ARE 1.65 *M* IN KCl AND 0.1 *M* IN HCl*

$[Fe^{++}]$	$[Fe^{+++}]$	$[I_2]$	$[I^-]$	K
0.001257	0.001223	0.0053	0.00114	20.7
0.003536	0.002644	0.00129	0.00224	21.4
0.007535	0.00483	0.00238	0.00358	21.3
0.01574	0.00900	0.00415	0.00549	20.5
0.003856	0.001104	0.00104	0.00526	21.4
0.000804	0.000436	0.00032	0.00161	20.5
0.01045	0.00192	0.00185	0.01117	21.0
0.005752	0.00043	0.00076	0.01713	21.6

* From data of Brønsted and Pedersen, *Z. physik. Chem.*, **103**, 307 (1923).

While this scheme of maintaining a high and nearly constant ionic strength is often useful (*cf.* pages 212 and 352), it is important to remember that the constant, such as the K of Eq. (33), may have a value which differs considerably from that of $K°$, which is the limiting value which K approaches as the ionic strength approaches zero. It is $K°$ values that one finds in tabulations of equilibrium constants or of standard free energies.

Study of Ionic Equilibria. If by virtue of or in spite of the discussion of the last few pages we assume that ionic activity coefficients may be estimated or measured in particular cases with sufficient precision to yield useful values of the equilibrium constants K, we may approach the consideration of problems connected with chemical equilibria in ionic solutions. We shall take our examples mostly from the field of proton transfer reactions.

Nomenclature. Nomenclature in this field is not standardized, and differences in nomenclature have sometimes been confused with differences in basic theory. We shall use the following system:

We define an *acid* as any molecular species which can transfer a proton (a proton or a deuteron, to be exact and general) to a suitable acceptor, and we define a *base* as any proton acceptor. These definitions include electrically charged as well as uncharged species; thus acids include NH_4^+ and $H_2PO_4^-$ as well as HCl, and bases include Cl^- and OH^- as well as NH_3. Such pairs as HCl-Cl^- and NH_4^+-NH_3 are called *conjugate acid-base pairs*. We define the *acidity constant* of any molecular species as the equilibrium constant of its reaction with a standard base. For aqueous solutions the solvent water is naturally taken as the standard base; consequently we measure the acidity constant of the acid acetic acid by the equilibrium constant

$$K_a = \frac{[C_2H_3O_2^-][OH_3^+]}{[HC_2H_3O_2]} \tag{34}$$

of the reaction

$$HC_2H_3O_2 + H_2O \rightleftharpoons C_2H_3O_2^- + OH_3^+ \qquad \text{(III)}$$

and the acidity constant of the acid ammonium ion by the equilibrium constant

$$K_a = \frac{[OH_3^+][NH_3]}{[NH_4^+]} \qquad (35)$$

of the reaction

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + OH_3^+ \qquad \text{(IV)}$$

The acidity constant is just as much a property of the base formed in such reactions as (III) and (IV) as it is of the acid reacting; consequently we can characterize the strength of a base by the acidity constant of the conjugate acid, the relation being, of course, an inverse one. We shall call the ion OH_3^+ *hydronium ion.* It is often called oxonium ion.

No more definitions than these are really needed for the consideration of acid-base equilibria, but some other terms are so common that their meaning must be learned. Before stating these other definitions, we note that we shall usually use H^+ as an abbreviation for OH_3^+, A^- for such formulas as Cl^-, acetate ion, and the like, HA for HCl, acetic acid, etc., B for such substances as NH_3, $C_6H_5NH_2$, and the like, and BH^+ for such ions as NH_4^+, $C_6H_5NH_3^+$, etc.

Supplementary Definitions. The *basicity constant* of NH_3, acetate ion, etc. may be defined by

$$K_b = \frac{[BH^+]}{[B][H^+]} \qquad \text{or} \qquad K_b = \frac{[HA]}{[H^+][A^-]} \qquad (36)$$

These basicity constants are the reciprocals of the acidity constants of the conjugate acids NH_4^+ and acetic acid.

The processes

$$HC_2H_3O_2 + H_2O \rightleftharpoons C_2H_3O_2^- + OH_3^+ \qquad \text{(V)}$$
$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{--} + OH_3^+ \qquad \text{(VI)}$$
$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad \text{(VII)}$$

are all called *ionizations*, and their equilibrium constants are called *ionization constants.* For neutral or negatively charged acids, such as acetic acid or $H_2PO_4^-$, the ionization constant is identical with the acidity constant. For neutral bases like ammonia and also for positively charged bases, the ionization constant

$$K_i = \frac{[BH^+][OH^-]}{[B]} \qquad (37)$$

is related to the acidity constant K_a of the conjugate acid BH^+ by the relation

$$K_i = \frac{K_w}{K_a} \tag{38}$$

in which

$$K_w = [OH_3^+][OH^-] \tag{39}$$

is the equilibrium constant of the ionization of the solvent

$$2H_2O \rightleftharpoons OH_3^+ + OH^- \tag{VIII}$$

Equation 38 may be derived by dividing Eq. (39) by the equation

$$K_a = \frac{[B][OH_3^+]}{[BH^+]} \tag{40}$$

and comparing the result with Eq. (37).

The acidity constant of ammonium ion as defined by Eq. (35) is also called the *hydrolysis constant* of an ammonium salt of a strong acid, such as ammonium chloride, and the name hydrolysis constant is also applied to the equilibrium constant

$$K_h = \frac{[HA][OH^-]}{[A^-]} \tag{41}$$

of such reactions as

$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^- \tag{IX}$$

It is easily shown that the hydrolysis constant K_h of acetate ion is related to the acidity constant K_a of acetic acid by the equation

$$K_h = \frac{K_w}{K_a} \tag{42}$$

Ionization Constant of the Solvent. The ionization constant of a solvent may in principle be determined by measuring the conductance of the pure liquid (*cf.* Prob. 12 of Chap. XIII). In most cases, including that of water, the conductance is so small and so largely affected by impurities that the results are not very reliable. An approximate value for water may be obtained by electrometric measurement of the pH of a moderately concentrated solution of sodium hydroxide. This determines the value of $[OH_3^+]$, the value of $[OH^-]$ is equal to the stoichiometric concentration of sodium hydroxide, and the product of these is the value of the ionization constant K_w. Precise values of K_w°, the limit for zero ionic strength, have been obtained from galvanic cells which involve no significant liquid junction. For water at 25°C this quantity has

the value 1.008×10^{-14}. In pure water the concentration of OH_3^+ necessarily equals that of OH^-; consequently at 25°C in pure water $[OH_3^+] = [OH^-] = \sqrt{K_w} = 1.004 \times 10^{-7}$.

A salt like NaCl, whose ions have negligible basicity, must increase the concentrations of both OH_3^+ and OH^- since in the equation

$$[OH_3^+][OH^-] = \frac{K_w^\circ}{\gamma_{H^+}\gamma_{OH^-}} \tag{43}$$

the γ's decrease with increasing ionic strength. If we may estimate the activity coefficient from Eq. (32) at 0.755 for an ionic strength of 0.1, we get for a 0.1 molar sodium chloride solution at 25°

$$[OH_3^+] = [OH^-] = \sqrt{1.008 \times 10^{-14}/(0.755)^2} = 1.33 \times 10^{-7}.$$

Problem of Simultaneous Equilibria. When we add an acid or base to water, we must in principle consider at least two proton transfer equilibria, one or more concerned with the transfer of protons between solute and solvent, and one concerned with the transfer between molecules of the solvent [reaction (VIII)]. Provided the system is stoichiometrically defined, it is not difficult to write down a set of simultaneous algebraic equations for any such system which are determinate and which permit the calculation of the concentrations of all of the constituents of the solution from known values of the equilibrium constants or the calculation of the equilibrium constants from measured values of concentration. However, a set of four or more nonlinear simultaneous equations is not an easy thing to solve or to make any sense of by inspection, and the computations can easily involve laborious sequences of successive approximations. It is therefore important to recognize that many practically important problems can be reduced to simpler and more comprehensible forms by intelligent approximations.

Ionization of a Weak Acid. In considering the determination of the degree of ionization of an aqueous electrolyte of the nature of acetic acid we pointed out (Chap. XIII) that we could neglect the effect of the ionization of the water. We now give a detailed justification of this procedure and show the limits within which an approximation of this sort is sound. In the ionization of the weak acid HA in aqueous solution there are two equilibrium conditions which must be satisfied, namely,

$$\frac{[H^+][A^-]}{[HA]} = K_a \tag{44}$$

$$[H^+][OH^-] = K_w \tag{45}$$

These two equations involve four variables since the quantity $[H^+]$ must have the same value in both of them. Another equation is supplied in

this case, as in all others involving ionic solutions, by the requirement that the solution must be electrically neutral. This means that the sum of the concentrations of all of the positive ions must equal the sum of the concentrations of all of the negative ions, *i.e.*, in this case that

$$[H^+] = [A^-] + [OH^-] \tag{46}$$

The necessary fourth equation required to make the system determinate must be supplied by some condition of the particular problem. Thus it might be specified that the titer concentration of the acid shall be c. Since the c moles/liter of A radical which were put into the solution must be present either as HA or as A^-, we have then

$$[HA] + [A^-] = c \tag{47}$$

This system of equations is not too intractable; for instance, it is possible to reduce it to the equation

$$K_a = \frac{[H^+]^2 - K_w}{c - [H^+] + \{K_w/[H^+]\}} \tag{48}$$

which involves only one variable, is only of the third degree in that variable, and can be solved numerically by standard methods.

In most cases it is easier to attempt an approximate solution, to test the validity of the approximation, and if necessary to base a second approximation on the first one. Suppose that the conductance of a 0.1 M solution of pure acetic acid in pure water has been measured with the result reported on page 307 and that by using the approximate equation (32) of Chap. XIII we have calculated the degree of ionization to be 0.0135, from which by Eq. (31) of Chap. XIII we get $[H^+] = 0.00135$. If this is correct, Eq. (45) shows that $[OH^-] = 7 \times 10^{-12}$; but even if it were wrong by an order of magnitude or two, the hydroxyl-ion concentration must be minute compared with the concentrations of hydronium ion and of acetate ion. The contribution of the hydroxyl ion to the total conductance of the solution must therefore be negligible. Furthermore Eq. (46) shows that the relation $[H^+] = [A^-]$ required for the use of Eq. (32) of Chap. XIII is in error by a matter of no more than parts per billion. Only if the acid were much weaker than acetic or the solution much more dilute than 0.1 M would we need to take into account the ionization of the water.

In the problem of calculating the hydronium-ion concentration of a c molar solution of an acid of known ionization constant K_a we may reasonably start with the approximation $[H^+] = [A^-]$, which is equivalent to assuming that the ionization of the water can be neglected. Sub-

stituting this relation together with Eq. (47) in Eq. (44), we get

$$\frac{[H^+]^2}{c - [H^+]} = K_a \tag{49}$$

a quadratic which may be solved for $[H^+]$ with little trouble. The value thus obtained is clearly a lower limit to the actual hydronium-ion concentration because the ionization of the water cannot possibly decrease $[H^+]$ below the value it would possess if the ionization of the water were negligible; the only way the ionization of the water can change the concentration is to increase it. Suppose the hydronium-ion concentration calculated in this way comes out to be 10^{-6}. Equation (45) leads to $[OH^-] = 10^{-8}$. Because the value of $[H^+]$ was a lower limit, this value of $[OH^-]$ is an upper limit. By Eq. (46) we then see that $[H^+]$ can differ from $[A^-]$ by no more than $10^{-8}/10^{-6}$, that is, by no more than 1 per cent. All four of the relations Eq. (44) to (47) are therefore satisfied to a precision of 1 per cent by the values $[H^+] = 10^{-6}$, $[OH^-] = 10^{-8}$, $[A^-] = 10^{-6}$, $[HA] = c - 10^{-6}$. If this precision is sufficient, the initial approximation was justified. If it is not, one may insert the relation $[H^+] = [A^-] + 10^{-8}$ into Eq. (44) and solve this with Eq. (47) to get a better value of $[H^+]$ than the first one. This process can be continued to obtain any precision desired. If the first approximation should lead to $[H^+] = 10^{-5}$, the upper limit of $[OH^-]$ would be 10^{-9} and the first approximation would be valid to 1 part in 10,000.

Choice of the Value of K. Since such quantities as the acidity constant of acetic acid depend upon the nature and quantity of the ions present in the solution, it is necessary to employ the proper value of K in any problem in which it is used in the computation. This means that, if we wish to be exact in computing the degree of ionization of acetic acid, we must use the value of K which corresponds to the ion concentration of the solution, and this ion concentration is exactly the quantity we wish to calculate. The matter is not very important with acetic acid, since the ionic strength of a 0.1 M solution is only 0.0013 and $\gamma_\pm$ is about 0.98, but it can be a serious matter with stronger acids. The most satisfactory approach is one of successive approximations. One estimates the ionic strength of the solution, perhaps by computing the ion concentration from the tabulated value of K° and an activity coefficient value of 1, uses this to select a better value of K, computes the ion concentration from this value of K, and repeats until no change in the values results from the repetition.

Ionization of a Base in Water. The equations which apply to a c molar solution of a neutral base like NH_3 dissolved in water are

$$\frac{[B][H^+]}{[BH^+]} = K_a \tag{50}$$

$$[H^+][OH^-] = K_w \tag{51}$$

$$[H^+] + [BH^+] = [OH^-] \tag{52}$$

$$c = [BH^+] + [B] \tag{53}$$

An effective approach to a solution of these equations is to combine Eqs. (50) and (51) to

$$\frac{[BH^+][OH^-]}{[B]} = \frac{K_w}{K_a} \tag{54}$$

to solve this on the assumption that $[BH^+] = [OH^-]$, and to use the resulting hydroxyl-ion concentration in Eq. (51) to get a value of $[H^+]$. If this hydronium-ion concentration is enough smaller than the hydroxyl-ion concentration, the first approximation is adequate; if not, a second approximation can be carried out along the lines suggested in the discussion of the ionization of an acid.

Equilibrium with Two Acids Present. The same kind of considerations permit a considerable simplification of many problems involving two or more acids or bases in addition to the solvent. Suppose a solution contains 0.01 M acetic acid ($K_a = 1.8 \times 10^{-5}$) and also 0.01 M boric acid ($K_a = 5.8 \times 10^{-10}$). The ionization of the weak acids water and boric acid can add to the hydronium-ion concentration which would result from the ionization of the more acidic substance acetic acid if this were present alone but cannot reduce the concentration below this value. If therefore we solve Eq. (44) with $K_a = 1.8 \times 10^{-5}$, the value of 4.3×10^{-4} which we obtain for the hydronium-ion concentration is a minimum value. As we saw in the last section, this is amply large enough to justify neglecting the effects of the ionization of water. We note further from the expression for equilibrium in the ionization of boric acid,

$$\frac{[H^+][H_2BO_3^-]}{[H_3BO_3]} = 5.8 \times 10^{-10} \tag{55}$$

that if $[H^+] \geq 4.3 \times 10^{-4}$, then

$$\frac{[H_2BO_3^-]}{[H_3BO_3]} \leq \frac{5.8 \times 10^{-10}}{4.3 \times 10^{-4}}$$

Since $[H_3BO_3]$ cannot be greater than 0.01, it follows that the concentration of borate ion is not greater than 1.35×10^{-8}. This must equal the total number of moles per liter of boric acid which have ionized and is therefore an upper limit to the number of moles per liter of hydronium ion contributed by the ionization of the boric acid. This quantity is negligible compared with the concentration which would be supplied by the

acetic acid in the absence of the boric acid, and the value 4.3×10^{-4} for the hydronium-ion concentration of the solution containing the two acids is therefore in error by no more than 1 part in 10,000 as a result of the assumption that the effect of the ionization of the boric acid on the hydronium-ion concentration may be neglected. Putting this value of $[H^+]$ in Eq. (55) together with the allowable approximation $[H_3BO_3] = 0.01$, one gets $[H_2BO_3^-] = 1.35 \times 10^{-8}$. The concentration of acetate ion is 4.3×10^{-4}, and that of hydroxyl ion is 2.4×10^{-11}. With acids of more nearly the same strength than acetic and boric acids the result obtained in this way would serve as a useful first approximation from which to proceed to a more precise solution of the equations.

Ionization of a Polybasic Acid. Similar considerations apply to a solution of a polybasic acid in water. Thus carbon dioxide reacts in two steps,

$$CO_2 + H_2O \rightleftharpoons OH_3^+ + HCO_3^- \qquad (X)$$

$$HCO_3^- + H_2O \rightleftharpoons OH_3^+ + CO_3^{--} \qquad (XI)$$

for which the equilibrium equations are

$$\frac{[H^+][HCO_3^-]}{[CO_2]} = K_1 = 4.52 \times 10^{-7} \qquad (56)$$

$$\frac{[H^+][CO_3^{--}]}{[HCO_3^-]} = K_2 = 5.59 \times 10^{-11} \qquad (57)$$

We are here using the symbol $[CO_2]$ for what is actually the sum $[CO_2] + [H_2CO_3]$ (page 118). Consider a CO_2 solution with the titer concentration of 0.001 M. The hydronium-ion concentration cannot be smaller than the value which would result from reaction (X), and by Eq. (56) this sets a minimum value of 2.1×10^{-5} for $[H^+]$. This is large enough so that the ionization of water may be neglected. If reaction (X) alone were involved, the concentration of bicarbonate ion would also be 2.1×10^{-5}. The actual value must be somewhat less than this both because the extent to which reaction (X) proceeds is decreased by the hydronium ions which arise from reaction (XI) and because reaction (XI) converts to carbonate ion some of the bicarbonate ion produced by (X). The ratio $[H^+]/[HCO_3^-]$ cannot therefore be less than 1 but may be very little greater than 1. Putting this value of the ratio into Eq. (57), we find $[CO_3^{--}] = 5.6 \times 10^{-11}$. In terms of the requirement of electrical neutrality,

$$[H^+] = [HCO_3^-] + 2[CO_3^{--}] + [OH^-] \qquad (58)$$

this means that our initial assumption that $[H^+] = [HCO_3^-] = 2.1 \times 10^{-5}$ was in error by no more than a few parts per million. A similar precision

applies to the value 5.6×10^{-11} for the carbonate-ion concentration, to the value of 4.8×10^{-10} for the hydroxyl-ion concentration obtained from Eq. (45), and to the value of 0.98×10^{-3} for the value of $[CO_2]$ obtained from the relation

$$0.001 = [CO_2] + [HCO_3^-] + [CO_3^{--}] \tag{59}$$

Hydrolysis of Salts. The detailed composition of the solution obtained by dissolving such a substance as aniline hydrochloride in water is determined by the equations

$$\frac{[H^+][B]}{[BH^+]} = K_a \tag{60}$$

$$[H^+][OH^-] = K_w \tag{61}$$

$$[BH^+] + [H^+] = [OH^-] + [Cl^-] \tag{62}$$

$$[BH^+] + [B] = c \tag{63}$$

Because the reaction

$$Cl^- + OH_3^+ \rightleftharpoons HCl + H_2O \tag{XII}$$

takes place to an entirely negligible extent in dilute aqueous solution, we may write $[Cl^-] = c$, and replace Eq. (62) by

$$[BH^+] + [H^+] = [OH^-] + c \tag{64}$$

A reasonable first approximation is to suppose that $[H^+] = [B]$, which leads through Eqs. (60) and (63) to

$$\frac{[H^+]^2}{c - [H^+]} = K_a \tag{65}$$

This quadratic may be solved, and the procedures for testing the precision of the result and, if necessary, for carrying out a second approximation are closely analogous to those previously discussed for the case of the electrically neutral acid.

The problem of calculating the hydronium- and hydroxyl-ion concentrations of a solution of sodium borate or potassium acetate bears the same relation to that of calculating these quantities in an ammonia solution that the aniline hydrochloride problem does to the problem of acetic acid. Borate and acetate ions are moderately strong bases, while sodium and potassium ions have negligible acidity.

In the c molar aqueous solution of a salt like aniline acetate the equilibrium relations

$$\frac{[B][H^+]}{[BH^+]} = K_1 \tag{66}$$

$$\frac{[H^+][A^-]}{[HA]} = K_2 \tag{67}$$

and

$$[H^+][OH^-] = K_w \tag{68}$$

must be satisfied. We have further

$$[BH^+] + [H^+] = [A^-] + [OH^-] \tag{69}$$
$$[BH^+] + [B] = c \tag{70}$$
$$[HA] + [A^-] = c \tag{71}$$

The key to an intelligent approximation in this case, as in many others, is an examination of the requirement for electrical neutrality. In the present case this is embodied in Eq. (69). The equation necessarily contains the concentrations of hydronium and of hydroxyl ion. In nearly every case of practical interest either $[H^+]$ or $[OH^-]$ is small compared with other terms in the equation, the only significant exception being the region near the end point in the titration of a strong acid with a strong base. In many cases both of these quantities are small compared with the other terms. If we try the hypothesis in this case that both can be neglected, Eq. (69) reduces to

$$[BH^+] = [A^-] \tag{72}$$

From this with Eqs. (70) and (71) we have

$$[B] = [HA] = c - [BH^+] \tag{73}$$

Combining these with the relation obtained by dividing Eq. (66) by (67), we get

$$\frac{\{c - [BH^+]\}^2}{[BH^+]^2} = \frac{K_1}{K_2} \tag{74}$$

which reduces to

$$[BH^+] = \frac{c}{1 + (K_1/K_2)^{1/2}} \tag{75}$$

The concentration of A^- is the same as that of BH^+ and by Eq. (73)

$$[B] = [HA] = \frac{(K_1/K_2)^{1/2}c}{1 + (K_1/K_2)^{1/2}} \tag{76}$$

With these values the concentration of hydronium ion can be obtained either from Eq. (66) or Eq. (67) as

$$[H^+] = (K_1K_2)^{1/2} \tag{77}$$

If this value is negligible compared with $[BH^+]$ and $[A^-]$ in Eq. (69), the problem has been solved; if not, one may use this first approximation to

a value of $[H^+]$ in Eq. (69), obtaining

$$[BH^+] + (K_1K_2)^{1/2} = [A^-] \tag{78}$$

This may be combined with Eqs. (70) and (71) and the ratio of Eq. (66) to Eq. (67) to obtain a quadratic in $[BH^+]$ whose solution will provide a better approximation to the concentrations of the various constituents of the solution than Eq. (72) does.

Buffer Solutions. The name *buffer solution* is applied to a solution which contains considerable concentrations of an acid and its conjugate base, with the proviso that neither the acid nor the base shall be strong electrolytes. Such a solution can be prepared by dissolving acetic acid and sodium acetate in water or by partial neutralization with sodium hydroxide of an acetic acid solution. A buffer can also be prepared from a mixture of ammonia and ammonium chloride or by partial neutralization of ammonia with hydrochloric acid. A solution containing NaH_2PO_4 and Na_2HPO_4 would also be a buffer because it contains the acid $H_2PO_4^-$ and its conjugate base HPO_4^{--}. Considering first the case of the electrically neutral acid HA, we have Eqs. (44) and (45) for the equilibrium conditions. If we write c_a for the titer concentration of HA and c_b for that of NaA, then, because sodium salts are strong electrolytes, we have $[Na^+] = c_b$ and the requirement of electrical neutrality can be written

$$[H^+] + c_b = [A^-] + [OH^-] \tag{79}$$

The fourth relation needed is supplied by a material balance on the A radical,

$$c_a + c_b = [HA] + [A^-] \tag{80}$$

If, as a first approximation, we neglect both $[H^+]$ and $[OH^-]$ in the requirement of electrical neutrality, Eq. (79) reduces to

$$c_b = [A^-] \tag{81}$$

From this, with Eq. (80),

$$c_a = [HA] \tag{82}$$

and from Eq. (44)

$$[H^+] = K_a \frac{c_a}{c_b} \tag{83}$$

To the precision of this relation a buffer solution containing equal concentrations of acetic acid and sodium acetate is moderately acid, pH = 4.75, an equimolar carbon dioxide–sodium bicarbonate buffer is nearly neutral, pH = 6.35, and an equimolar boric acid–sodium borate buffer is alkaline, pH = 9.24. As we shall see, the buffer property requires that neither c_a nor c_b be very small; hence the range of practical

buffers prepared from acetic acid and sodium acetate will extend not more than 1½ or 2 units on either side of 4.75, and the range of the other buffers will be similarly limited.

In considering the adequacy and precision of Eq. (83), we note first that if the $[H^+]$ predicted by this equation lies in the region of 10^{-6} to 10^{-8} the hydronium-ion concentration can certainly be neglected compared with c_b in Eq. (79). Since the hydroxyl-ion concentrations of these solutions will range from 10^{-8} to 10^{-6}, the neglect of the quantity $[OH^-]$ is also justified. Equation (83) is therefore valid to high precision if the pH lies between 6 and 8 and is not in serious trouble if it lies between 5 and 9.

If HA is a relatively strong acid, and especially if c_b is small, it may be necessary to retain the quantity $[H^+]$ in Eq. (79), obtaining

$$[H^+] + c_b = [A^-] \tag{84}$$

Combining this with Eq. (80) and (44), we get

$$\frac{[H^+]\{c_b + [H^+]\}}{c_a - [H^+]} = K_a \tag{85}$$

This is often written in the form

$$[H^+] = K_a \frac{c_a - [H^+]}{c_b + [H^+]} \tag{86}$$

which suggests a convenient method of solution by successive approximations.

If HA is a relatively weak acid, it may be necessary to retain the quantity $[OH^-]$ in Eq. (79) if adequate precision is to be obtained. This leads to

$$c_b = [A^-] + [OH^-] \tag{87}$$

It is convenient in this case to eliminate $[H^+]$ between Eqs. (44) and (45), obtaining

$$\frac{[HA][OH^-]}{[A^-]} = \frac{K_w}{K_a} \tag{88}$$

From Eqs. (80), (87), and (88) we then get

$$[OH^-] = \frac{K_w}{K_a} \frac{c_b - [OH^-]}{c_a + [OH^-]} \tag{89}$$

In a buffer composed of c_a moles/liter of ammonium chloride and c_b moles/liter of ammonia we have Eqs. (50) and (51) for the equilibrium relations. Since we may take $[Cl^-] = c_a$, the requirement of electrical neutrality is

$$[H^+] + [BH^+] = [OH^-] + c_a \tag{90}$$

and the material-balance relation is

$$c_a + c_b = [B] + [BH^+] \tag{91}$$

It is easily shown that these four equations reduce to the form of Eq. (83) for solutions in the neutral region, to Eq. (86) for solutions in which $[H^+]$ cannot be neglected compared with c_a, and to Eq. (89) for solutions in which $[OH^-]$ cannot be neglected in comparison with c_a.

Equations 83, 86, and 89 are also found to apply each in its appropriate range for buffers composed of c_a moles/liter of NaH_2PO_4 and c_b moles/liter of Na_2HPO_4, K_a being then the acidity constant of the acid $H_2PO_4^-$.

Buffer solutions have the characteristic property of being insensitive to the addition of acid or base. We may write Eq. (83) in the form

$$pH = pK_a - \log c_a + \log c_b \tag{92}$$

with pK_a defined by

$$pK_a = -\log K_a \tag{93}$$

By differentiation of Eq. (92) we have

$$\left(\frac{\partial\, pH}{\partial c_a}\right)_{c_b} = -\frac{1}{c_a} \tag{94}$$

The quantity on the left is the rate at which the pH of the solution changes on addition of HA. For an acetate buffer with $c_a = c_b = 0.01$, whose pH is 4.75, the value of the quantity $(\partial\, pH/\partial c_a)_{c_b}$ is -100. A solution of the same pH could be prepared from HCl; in fact it would consist of a 1.8×10^{-5} molar solution of the acid. If c_a is the concentration of the HCl, then $[H^+] = c_a$, $\log [H^+] = \log c_a$, and $d\, pH/dc_a = -1/c_a$, whose value is -5.5×10^4. The pH of the "unbuffered" HCl solution is 5500 times more sensitive to the addition of acid than is that of the buffer of the same pH. It is easily shown that the pH is similarly insensitive to the addition of base.

The term "buffer capacity" is often used in discussions of this subject. It is defined as the quantity

$$\left(\frac{\partial c_a}{\partial\, pH}\right)_{c_a+c_b}$$

which shows that it is the reciprocal of the slope of a titration curve. It can be shown that

$$\left(\frac{\partial c_a}{\partial\, pH}\right)_{c_a+c_b} = \frac{c_a c_b}{c_a + c_b} \tag{95}$$

Titration Curves. If we mix a solution containing an acid with another solution containing a base not conjugate to that acid, we get a chemical

reaction which results in a pH intermediate between the values of the original solutions. A plot of pH against the quantity of one solution added to a given amount of the other is called a *titration curve*. We shall consider the titration of an acid HA by a strong base such as sodium hydroxide and shall simplify the problem by neglecting the volume changes. If then a equals the moles per liter of HA in the initial solution and x the moles per liter of base added, we have, since $[Na^+] = x$,

$$[H^+] + x = [A^-] + [OH^-] \tag{96}$$

as the condition for electrical neutrality and

$$a = [HA] + [A^-] \tag{97}$$

from material-balance considerations. The equilibrium equations are Eqs. (44) and (45). Comparing these equations with those involved in the buffer-solution problem we see that the two sets are identical if $x = c_b$ and $a = c_a + c_b$. Obviously then $c_a = a - x$. Substituting these values in Eq. (83), we get

$$[H^+] = K_a \frac{a - x}{x} \tag{98}$$

which should be valid to good precision for solutions whose pH is near 7. For the relatively acid solutions in which x is small we get from Eq. (85)

$$\frac{[H^+]\{x + [H^+]\}}{a - x - [H^+]} = K_a \tag{99}$$

For alkaline solutions Eq. (89) reduces to

$$[OH^-] = \frac{K_w}{K_a} \frac{x - [OH^-]}{a - x + [OH^-]} \tag{100}$$

which looks a bit confusing. It is helpful to write it as

$$[OH^-] = x - a + \frac{K_w}{K_a} \frac{x - [OH^-]}{[OH^-]} \tag{101}$$

The quantity K_w/K_a is necessarily a small quantity, otherwise we should not recognize the substance HA as an acid in aqueous solution, and the ratio $\{x - [OH^-]\}/[OH^-]$ approaches zero at large values of $[OH^-]$. Consequently $[OH^-]$ approaches $x - a$ in strongly alkaline solutions, which is what we should expect on qualitative grounds.

Figure 6 presents a titration curve calculated from these equations, each being used in its proper range, for the titration of 0.01 M acetic acid with sodium hydroxide. The curve is relatively steep at the beginning and very steep near the end point; it is relatively flat in the buffer region where $x \approx \frac{1}{2}a$.

Curves of this sort may be constructed for a great variety of systems, the labor involved increasing rapidly with the number of equilibria to be considered. Thus it is considerably more laborious to calculate the titration curve for the addition of ammonia to acetic acid than it is for the addition of sodium hydroxide to the same acid. Even here, however, much of the curve may be calculated rapidly from simplifying approximations. Thus the ammonia–ammonium-ion equilibrium for which

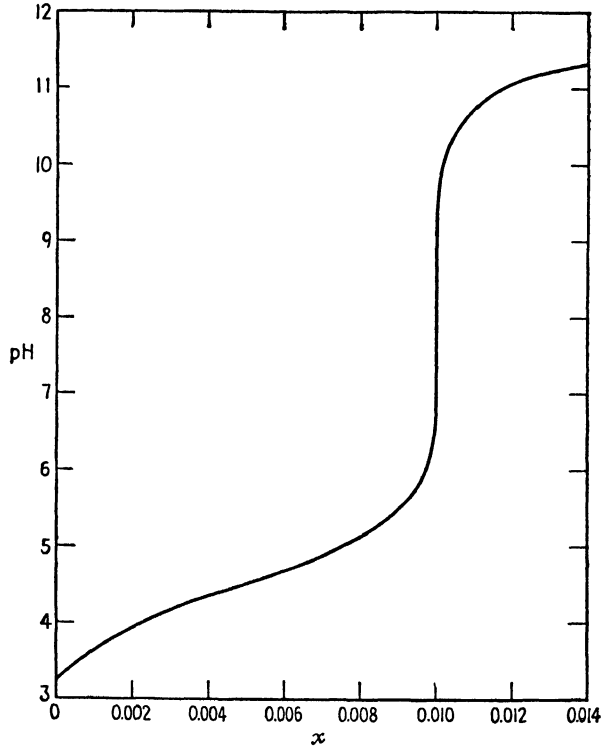


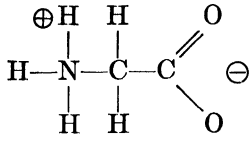
FIG. 6. Titration curve for 0.01 M acetic acid titrated with NaOH assuming constant volume and a constant ionic strength of 0.1.

$K_a = 6 \times 10^{-10}$ may be neglected in the region of acetic acid–ammonium acetate buffers where $[H^+] \approx 10^{-5}$. Similarly in the titration of CO_2 with sodium hydroxide the second ionization of carbonic acid, $K_a = 6 \times 10^{-11}$, may be neglected in the region of carbon dioxide–bicarbonate buffers where $[H^+] \approx 10^{-7}$, and the effect of the first ionization may be neglected in the region of bicarbonate-carbonate buffers where $[H^+] \approx 6 \times 10^{-11}$.

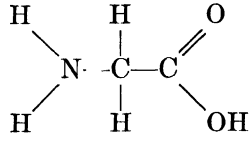
It is just as proper to speak of the behavior of an aniline hydrochloride solution when sodium hydroxide is added as the titration of the acid anilinium ion with a base as it is to use the same term for the behavior of

acetic acid when sodium hydroxide is added. The pertinent equations are identical. Similarly the addition of hydrochloric acid to sodium carbonate or to sodium bicarbonate solution is the titration of the base, carbonate ion or bicarbonate ion, with the acid.

Aminoacids and the Like. A wide variety of evidence points to the conclusion that glycine in aqueous solution is largely in the form of what is called a *dipolar ion*, or *zwitterion*, whose structure may be represented by



rather than in the form



This has no effect upon the form of the equations which describe the effects of adding acid or base to a glycine solution, although it may have a powerful effect on the magnitude of the equilibrium constants. If we write $[HA]$ for the sum $[H_2NCH_2COOH] + [^+H_3NCH_2COO^-]$, $[H_2A^+]$ for $[^+H_3NCH_2COOH]$, and $[A^-]$ for $[H_2NCH_2COO^-]$, we have, for reasons similar to those involved in the discussion of the ionization of carbon dioxide,

$$\frac{[H^+][HA]}{[H_2A^+]} = K_1 \tag{102}$$

$$\frac{[H^+][A^-]}{[HA]} = K_2 \tag{103}$$

The K's of these equations are the acidity constants listed for glycine H^+ and for glycine in Table 3.

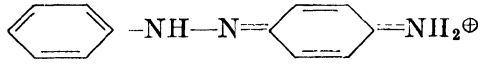
A quantity which plays an important part in most discussions of aminoacids and of the polymerized aminoacids called proteins is the isoelectric point. This is defined as the pH at which the concentration of the cation H_2A^+ is equal to that of the anion A^-. If we multiply Equation (102) by (103) and make this substitution, we get

$$[H^+]^2 = K_1K_2 \tag{104}$$

from which we see that the isoelectric pH is given by

$$pH = \tfrac{1}{2}(pK_1 + pK_2) \tag{105}$$

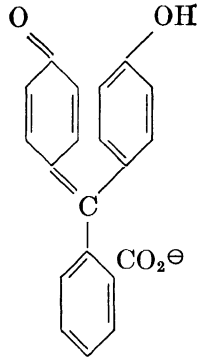
Indicators. The properties which we recognize as those of an indicator depend upon the presence of a conjugate acid and base pair in which the acid, the base, or both are intensely colored. If both are colored, the two colors must be distinctly different. The acid form of the indicator may be positively charged, as it is with aminoazobenzene,



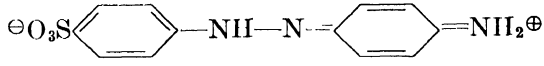
electrical neutral in *p*-nitrophenol,



or negatively charged in phenolphthalein,



In methyl orange it is a dipolar ion,



With all of these substances the loss of a proton produces a considerable shift of the internal electronic structure of the molecule in a way which changes materially the region of the spectrum in which the substance absorbs. The charge on the indicator acid has a significant effect on the way in which the indicator equilibrium is affected by changes in ionic strength; in other respects the differences in charge have trivial effects. In each case there will be an equilibrium determined by the equation

$$\frac{[H^+][I]}{[HI]} = K \tag{106}$$

in which I represents the basic form of the indicator, regardless of its charge, and HI the acid form. Because of the color the ratio $[HI]/[I]$ may be measured experimentally by the methods of colorimetry or spectrophotometry if the sum $[HI] + [I]$ is known and provided that neither

$[HI]$ nor $[I]$ is vanishingly small. Instead of determining the sum directly it is usually easier to determine the intensity of the absorption obtained when a sample of solution for which the sum has the same value is almost wholly converted to the acid form by an excess of acid or to the base form by an excess of alkali. With the ratio $[HI]/[I]$ thus determined, the hydronium-ion concentration follows immediately from Eq. (106). The requirement that neither $[HI]$ nor $[I]$ be too small to permit precise measurement of the ratio implies that a given indicator can be used only in a limited pH region in the neighborhood of the pK value of the indicator. Because indicators absorb strongly, the amount which must be added to a solution in order to make the measurement possible can be very small, namely, of the order of 10^{-5} mole/liter for most practical indicators. Consequently the addition of the indicator can have only a negligible effect on the pH of the solution provided the system has any reasonable buffer capacity. Within this restriction the pH measured by the indicator is essentially that possessed by the solution before the indicator was added.

Experimental Determination of Acidity Constants. An experimental value of the acidity constant for any acid-base pair may be derived from measurements of the pH of properly chosen solutions, the measurements being either electrometric or by use of an indicator. If only one equilibrium is involved, as with acetic acid or ammonium ion, only one measurement is required, this being preferably made on a buffer solution because this is less sensitive to the effects of impurities. The computation of K_a merely involves substitution of the measured hydronium-ion concentration along with the titer concentration of the acid and its conjugate base in the appropriate equation, which may be Eq. (83), (86), or (89). When more than one equilibrium is involved, as with carbon dioxide or phosphoric acid, or with dipolar ions like glycine, a series of measurements of the pH of partially neutralized solutions of the acid at varying degrees of neutralization can supply an ample number of simultaneous equations from which the unknown K_a values can be computed. The computation can be laborious in unfavorable cases but may often be simplified when the K_a values concerned differ considerably from each other. Thus, as we have noted, the pH value of a carbon dioxide–sodium bicarbonate mixture is very simply related to the first acidity constant of the acid, and the pH value of a sodium bicarbonate–sodium carbonate mixture is simply related to the second acidity constant.

Because of the essentially approximate nature of the electrometric pH measurement such measurements cannot give highly precise values of K_a. Indicator measurements, if properly corrected for the effect of the ionic strength of the solution upon the indicator equilibrium can give appreci-

ably more reliable values, but they are rarely used in such a way as to exploit this possibility. Extremely accurate values of the acidity constants of simple monobasic acids like acetic acid and simple monoacid bases like ammonia may be obtained from conductance measurements, suitably corrected for the variation of conductance with ionic strength. Other methods employ specialized galvanic cells without appreciable liquid-junction potentials and are capable of high precision. Here, as is so often the case, the easy methods give poor precision and reliability, the precise and reliable ones are laborious.

The values of K_a and of the related constants which one finds in the literature are therefore of widely varying precision, and tabulations usually fail to bring out the reliability of any particular value. A few values of relatively high precision are listed in Table 3.

TABLE 3. ACIDITY CONSTANTS AT 25°C*

Formic acid	1.772×10^{-4}
Acetic acid	1.754×10^{-5}
Propionic acid	1.336×10^{-5}
Chloracetic acid	1.378×10^{-3}
Glycolic acid	1.475×10^{-4}
Glycine H^+	4.47×10^{-3}
Glycine	1.67×10^{-10}
H_3PO_4	7.537×10^{-3}
$H_2PO_4^-$	6.226×10^{-8}
HSO_4^-	1.20×10^{-2}
H_3BO_3	5.80×10^{-10}
$CO_2 + H_2CO_3$	4.52×10^{-7}
HCO_3^-	5.59×10^{-11}
Benzoic acid	6.09×10^{-5}
Phenol	1×10^{-10}
NH_4^+	6.18×10^{-10}
$CH_3NH_3^+$	2.45×10^{-11}
$C_6H_5NH_3^+$	2.55×10^{-5}

* Data on the first eleven items from Harned and Owen, *Chem. Rev.*, **25**, 46 (1939); on the last three items from Everett and Wynne-Jones, *Trans. Faraday Soc.*, **35**, 1384 (1939); on the two ionizations of carbon dioxide from MacInnes and Belcher, *J. Am. Chem. Soc.*, **55**, 2630 (1933), **57**, 1683 (1935); on benzoic acid from Rule and LaMer, *ibid.*, **60**, 1974 (1938); on phenol from Boyd, *J. Chem. Soc.*, **107**, 1538 (1915).

Effect of Temperature on Reactions Involving Ions. Any reaction which produces ions in solution, whether the process is homogeneous like reactions (V) and (VII) or consists in the solution of a salt, goes much more easily in certain kinds of solvents. These are liquids whose molecules possess the structures favorable to hydrogen bonding or other structures which involve intense electrical fields. A similar effect is observed with reactions like (VI) in which two ions are derived from one, the charge on one of the products being greater in magnitude than the

charge on the initial ion. The implication is strong that the binding of solvent molecules to the ions, called the *solvation* of the ions, plays an important part in reducing to a value which permits significant reaction the energy increase associated with the formation of the ions. This binding represents a restraint on the freedom of motion of the solvent molecules, and restraints of this sort tend to decrease the value of the partition-function ratio of a reaction. It is not therefore surprising that ionization processes offer a pronounced case of the type of behavior illustrated in Fig. 8 of Chap. VIII. For typical reactions of this sort like the ionization of carboxylic acids in aqueous solution ΔH is near zero at room temperature but is decreasing rapidly with increasing temperature. The value

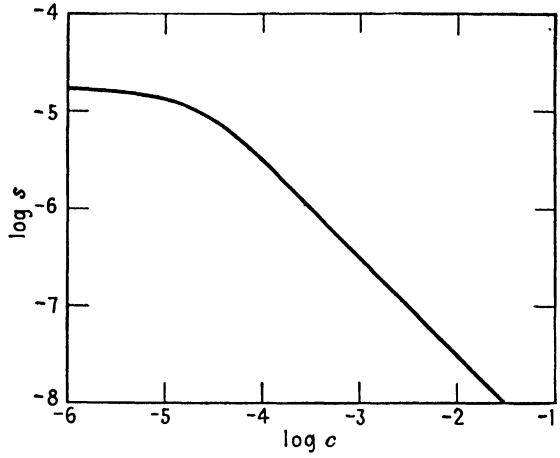


FIG. 7. The effect of sodium chloride on the solubility of silver chloride at a fixed ionic strength of 0.1. s is the solubility of silver chloride; c is the concentration of sodium chloride.

of ΔC_p is in the neighborhood of -40 cal/mole-deg and ΔS in the neighborhood of -20 cal/mole-deg. K goes through a maximum at the temperature at which $\Delta H = 0$.

Common Ion Effects in the Solubility of Salts. We have already considered the effect of a salt MY in solution upon the solubility in that solution of the difficultly soluble salt MX and have derived Eq. (13). In Fig. 7 we have plotted the effects computed from this equation for the influence of added sodium chloride on the solubility of silver chloride, the ionic strength being maintained constant at 0.1 by suitable amounts of some electrolyte which does not contain silver ion or chloride ion. The ordinate is the logarithm of the solubility of the silver chloride, the abscissa the logarithm of the concentration of sodium chloride. The plot, which starts with a horizontal tangent, curves downward and attains

a limiting slope of -1. In the region of linearity the solubility is inversely proportional to the first power of the concentration of sodium chloride. The plot for the effect of silver nitrate on the solubility of silver chloride would be identical with Fig. 7.

If a salt of the valence type of silver chromate, Ag_2CrO_4, is dissolved in a solution containing c molar silver nitrate we may write for the solubility s

$$s = [CrO_4^{--}] \tag{107}$$

The silver-ion concentration will be

$$[Ag^+] = c + 2s \tag{108}$$

The condition for equilibrium is

$$[Ag^+]^2[CrO_4^{--}] = K \tag{109}$$

Combining these three relations we have

$$(c + 2s)^2 s = K \tag{110}$$

When c is much larger than s, this approaches the relation $s = K/c^2$. Curve A in Fig. 8 shows the effect of silver nitrate on the solubility of silver chromate at a constant ionic strength of 0.1. As expected, the logarithmic plot approaches a slope of -2 at high values of c.

For a saturated solution of silver chromate in a solution containing c molar potassium chromate we have

$$[Ag^+] = 2s \tag{111}$$
$$[CrO_4^{--}] = c + s \tag{112}$$

and by substitution in Eq. (109)

$$(2s)^2(c + s) = K \tag{113}$$

Values of log s computed from this equation are plotted against log c as curve B in Fig. 8. When $c \gg s$, the equation approaches $s = \frac{1}{2}\sqrt{K/c}$ and the slope of the logarithmic plot approaches $-\frac{1}{2}$.

Some Other Solubility Effects. If a difficultly soluble salt is brought in contact with a solution which contains a substance which reacts with one of the ions of the salt, the solubility may be considerably increased over the value which it shows in water. The magnitude of the effect is frequently useful as a means of determining the equilibrium constant of the reaction involved. Thus the variation of the solubility of silver chloride with added ammonia may be used to determine the equilibrium constant of the reaction

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3 \tag{XIII}$$

This constant is called the *instability constant* of the silver-ammonia complex ion and has the value 6.0×10^{-8} at room temperature.

The solvent itself reacts with the ions of many electrolytes, and this complicates the solubility phenomena considerably. In a saturated

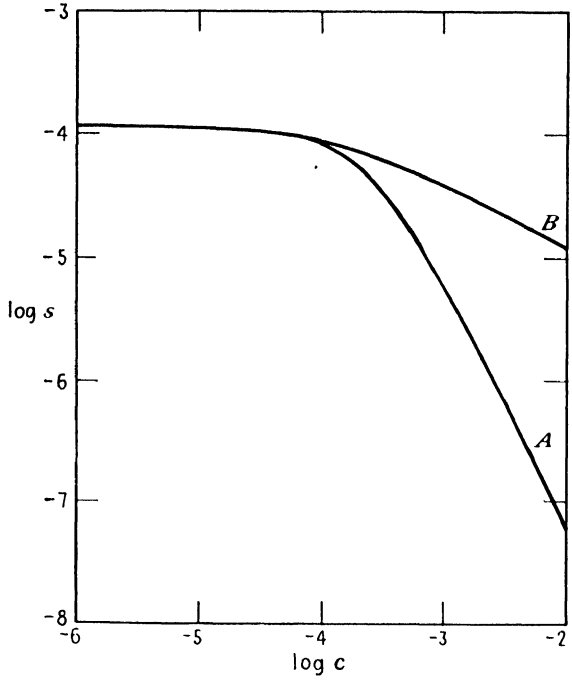


FIG. 8. Effect of silver nitrate (curve A) and of potassium chromate (curve B) on the solubility of silver chromate at a constant ionic strength of 0.1. s is the solubility of silver chromate; c is the molar concentration of silver nitrate or of potassium chromate.

aqueous solution of calcium carbonate at 25°C we have the following equilibria:

$$[Ca^{++}][CO_3^{--}] = K_s(4.82 \times 10^{-9}) \tag{114}$$

$$\frac{[H^+][CO_3^{--}]}{[HCO_3^-]} = K_1(5.59 \times 10^{-11}) \tag{115}$$

$$[H^+][OH^-] = K_w(1.01 \times 10^{-14}) \tag{116}$$

The requirement for electrical neutrality takes the form

$$2[Ca^{++}] + [H^+] = 2[CO_3^{--}] + [HCO_3^-] + [OH^-] \tag{117}$$

The necessary fifth equation

$$[Ca^{++}] = [CO_3^{--}] + [HCO_3^-] \tag{118}$$

is essentially a result of the requirement that the solid calcium carbonate remain electrically neutral. This makes it necessary that one carbonate ion enter the solution for every calcium ion. Once in the solution the carbonate ion may remain as such or be converted to a bicarbonate ion. We have assumed that the concentration of CO_2 is negligible and that $Ca(OH)_2$ is a strong electrolyte. If there were no reaction of the ions of the salt with the solvent, the concentrations of calcium ion and of carbonate ion would be equal to $\sqrt{K_s}$, that is, 7×10^{-5}, and the concentrations of hydronium and hydroxyl ions would be 1×10^{-7}. The reaction

$$CO_3^{--} + OH_3^+ \rightleftharpoons HCO_3^- + H_2O \qquad \text{(XIV)}$$

may reduce the hydronium-ion concentration below the value of 1×10^{-7}, and if it does, the concentration of hydroxyl will become larger than this value. Consequently we may safely neglect the quantity $[H^+]$ in Eq. (117) but cannot with certainty omit $[OH^-]$. We therefore try the approximation

$$2[Ca^{++}] = 2[CO_3^{--}] + [HCO_3^-] + [OH^-] \qquad (119)$$

A rather obvious next step is to eliminate $[H^+]$ between Eqs. (115) and (116), getting

$$\frac{[HCO^-][OH^-]}{[CO_3^{--}]} = \frac{K_w}{K_i} \qquad (120)$$

Combining this with Eq. (119), we have

$$2[Ca^{++}] = 2[CO_3^{--}] + [HCO_3^-] + \frac{K_w}{K_i}\frac{[CO_3^{--}]}{[HCO_3^-]} \qquad (121)$$

Eliminating $[Ca^{++}]$ between this and Eq. (118), we get

$$[HCO_3^-]^2 = \frac{K_w}{K_i}[CO_3^{--}] \qquad (122)$$

and by elimination of $[Ca^{++}]$ between Eqs. (114) and (118) we get

$$[CO_3^{--}]^2 + [CO_3^{--}][HCO_3^-] = K_s \qquad (123)$$

Finally by elimination of $[HCO_3^-]$ between Eqs. (122) and (123) we have

$$[CO_3^{--}]^2 + \left(\frac{K_w}{K_i}\right)^{1/2}[CO_3^{--}]^{3/2} = K_s \qquad (124)$$

This may be solved by successive approximations or graphically. Using the numerical values of the constants given in Eqs. (114) to (116), we get $[CO_3^{--}] = 3.92 \times 10^{-5}$. From Eq. (114) $[Ca^{++}] = 1.23 \times 10^{-4}$; from Eq. (118) $[HCO_3^-] = 8.4 \times 10^{-5}$; from Eq. (119) or (120) $[OH^-] = 8.4 \times 10^{-5}$; from Eq. (116) $[H^+] = 1.198 \times 10^{-10}$. These values satisfy Eqs. (114)

to (118) with considerable precision, thus justifying the approximation of Eq. (119). From the first ionization constant of CO_2, 4.52×10^{-7}, we calculate $[CO_2] = 2.2 \times 10^{-8}$. This justifies our neglect of the effects of the reaction

$$HCO_3^- + OH_3^+ \rightleftharpoons CO_2 + 2H_2O \qquad \text{(XV)}$$

The solubility of the calcium carbonate is equal to the calcium-ion concentration of the saturated solution, that is, 1.23×10^{-4}; without the reaction with the solvent it would have been equal to $\sqrt{K_s}$, that is, 0.69×10^{-4}.

Membrane Equilibria. Consider the situation in which a membrane separates two solutions, one of which contains an ion which is incapable of passing through the membrane. Such a situation is presented when a cellophane membrane separates a solution of the sodium salt of polymerized acrylic acid from another solution. The polymeric anion

$$\left[\begin{array}{l}\text{—CH—CH}_2\text{—} \\ \quad | \\ \quad \text{CO}_2^{\ominus}\end{array}\right]_n$$

cannot get through the membrane; the sodium ion can. A similar situation exists in a solution of a protein at any pH but the isoelectric point. The protein is a substance of high molecular weight which acts toward acids and bases much as an aminoacid does. If HCl is added to a protein at its isoelectric point, protons are added to the protein molecule, producing a cation of high molecular weight to which many membranes are impermeable. If NaOH is added to the isoelectric protein, protons are removed, forming an anion of high molecular weight.

Let M^+ represent the cation which can pass the membrane in such a system and X^{n-} the anion which cannot get through the membrane. We wish to determine the distribution at equilibrium between the two solutions of another electrolyte MY both of whose ions can traverse the membrane. Let c_1 and y_1 represent the concentrations of M^+ and Y^- in the solution which contains the polymeric anion X^{n-} and c_2 and y_2 the corresponding concentrations in the solution free of X^{n-}. We suppose that the volumes of the two solutions are maintained constant and that the solutions are dilute and that there is therefore no important transfer of solvent from one side of the membrane to the other. At first sight one might suppose that the condition for equilibrium would be that $\bar{F}_{M1} = \bar{F}_{M2}$ and $\bar{F}_{Y1} = \bar{F}_{Y2}$, that is, that the molal free energy of each constituent must have the same value on both sides of the membrane. This would be true if each ion could traverse the membrane independently of the other. But the transfer of more than extremely small quantities of M^+ from solution

1 to solution 2 would charge solution 2 positively, and this would increase the work required to transfer more M^+ and decrease the work required to transfer Y^-. Consequently to a very close approximation M^+ can transfer from 1 to 2 only if Y^- does so also, and we need consider only the simultaneous transfer of both ions. The free energy change df which accompanies the transfer of dx moles from solution 1 to solution 2 is therefore

$$df = (\bar{F}_{M2} + \bar{F}_{Y2} - \bar{F}_{M1} - \bar{F}_{Y1})\, dx \tag{125}$$

and the condition for equilibrium, that $df/dx = 0$, requires that

$$\bar{F}_{M2} + \bar{F}_{Y2} = \bar{F}_{M1} + \bar{F}_{Y1} \tag{126}$$

To the precision of the dilute-solution laws this becomes

$$\bar{F}^\circ_M + \mathbf{R}T \ln c_2 + \bar{F}^\circ_Y + \mathbf{R}T \ln y_2 = \bar{F}^\circ_M + \mathbf{R}T \ln c_1 + \bar{F}^\circ_Y + \mathbf{R}T \ln y_1 \tag{127}$$

which is equivalent to

$$c_2 y_2 = c_1 y_1 \tag{128}$$

Since both solutions must be to a very close approximation electrically neutral, we have

$$c_1 = y_1 + nx \tag{129}$$

where x is the molar concentration of the ion X^{n-} in solution 1. Further

$$c_2 = y_2 \tag{130}$$

The two further equations required to make Eqs. (128), (129), and (130) determinate can be supplied from material-balance considerations on MY and M_nX. Certain qualitative conclusions of importance can be drawn without becoming involved in the detail of particular cases. Equation (129) tells us that $c_1 > y_1$ since c_1 equals y_1 plus a positive quantity. Equations 128 and 130 tell us that $c_2 = y_2 = \sqrt{c_1 y_1}$. These two conditions can hold only if

$$c_1 > c_2 = y_2 > y_1 \tag{131}$$

The concentration of cation is larger in the solution containing the nondiffusible anion than in the other solution, but the concentration of diffusible anion is smaller in the first than in the second solution. These effects have been verified to the precision which the use of the ideal laws in Eq. (127) permits.

In the almost inevitable case that the membrane is permeable to the solvent the volumes of the two solutions can be maintained constant only if a sufficient pressure is applied to prevent the flow of solvent (osmosis) from solution 2 to solution 1. Equation (128) is equivalent to the state-

ment that $cy = k$, a constant, from which the sum $c + y$ equals $(k/y + y$. This sum will have a minimum value when $-(k/y)^2 + 1 = 0$, which can be true only if $c = y$. Since $c_2 = y_2$ and $c_1 \neq y_1$, this proves that $c_2 + y_2 < c_1 + y_1$. Consequently the total concentration of solute particles in solution 2, $c_2 + y_2$, is less than the corresponding concentration in solution 1, $c_1 + y_1 + x$. By a completely general rule the molal free energy of the solvent must then be lower in solution 1 than in solution 2 unless a sufficiently larger pressure (page 364) is applied to solution 1 to make the two molal free energies identical.

Strictly speaking neither of the two solutions will be electrically neutral, but solution 2 will have a slight excess of positive charge, and solution 1 a slight excess of negative charge. Only because this is so is it possible to have a higher concentration of M^+ in solution 1 than in solution 2, the natural tendency of a solute to diffuse from higher to lower concentration being balanced by the electrical potential difference which arises from the net charges on the solutions. If then we write a Boltzmann relation for the M^+ ions in the two solutions,

$$\frac{c_2}{c_1} = e^{-(\epsilon_2 - \epsilon_1)/\mathbf{k}T} \tag{132}$$

where ϵ_2 and ϵ_1 are the energies of an M^+ ion in solution 1 and solution 2, respectively, we can set

$$\epsilon_2 - \epsilon_1 = \mathcal{E}\mathbf{e} \tag{133}$$

where $\mathcal{E}$ is the potential of solution 2 relative to that of solution 1. This is equivalent to

$$\mathcal{E} = \frac{\mathbf{R}T}{\mathbf{F}} \ln \frac{c_1}{c_2} \tag{134}$$

By the same reasoning,

$$\mathcal{E} = \frac{\mathbf{R}T}{\mathbf{F}} \ln \frac{y_2}{y_1} \tag{135}$$

Measurements in cells of the type

Hg: Hg_2Cl_2(s), KCl(satd); MY, M_nX; membrane; MY; KCl(satd), Hg_2Cl_2: Hg

verify these equations to the precision permitted by the assumption that the junction potentials can be neglected.

Salt Effects on the Rates of Ionic Reactions. According to the transition-state theory of reaction rates the specific rate k of a chemical reaction is determined by the equation [Eq. (109) of Chap. IX]

$$k = \frac{\mathbf{k}T}{\mathbf{h}} K^{\ddagger} \tag{136}$$

in which $K^{\ddagger}$ is a quasi-equilibrium constant for the formation of the transition state. We may suppose that $K^{\ddagger}$ like any equilibrium constant should satisfy the relation

$$K^{\ddagger} = K_0^{\ddagger} \frac{\gamma_A \gamma_B \cdots}{\gamma_{\ddagger}} \tag{137}$$

in which γ_A, γ_B, etc., are the activity coefficients of the reactants, $\gamma_{\ddagger}$ is the activity coefficient of the transition state, and $K_0^{\ddagger}$ is the limiting value approached by $K^{\ddagger}$ as the ionic strength approaches zero. This leads to

$$k = k^{\circ} \frac{\gamma_A \gamma_B \cdots}{\gamma_{\ddagger}} \tag{138}$$

with k° the limiting value of the specific rate for zero ionic strength.

The equation cannot be verified directly because the activity coefficient of the transition state is not accessible to measurement, but at least a qualitative prediction may be made for reactions involving ions. In a second-order reaction between ion A of charge z_a and ion B of charge z_b the charge on the transition state is $z_a + z_b$. If the Debye limiting law were applicable, we should have

$$\log \frac{\gamma_A \gamma_B}{\gamma_{\ddagger}} = -a \sqrt{\mu} \{z_a^2 + z_b^2 - (z_a + z_b)^2\} = a z_a z_b \sqrt{\mu} \tag{139}$$

from which

$$\log k = \log k^{\circ} + a z_a z_b \sqrt{\mu} \tag{140}$$

If the reacting ions have charges of the same sign, as they do in the reaction

$$BrCH_2COO^- + S_2O_3^{--} \rightarrow {}^-S_2O_3CH_2COO^- + Br^- \tag{XVI}$$

the product $z_a z_b$ is positive and the specific rate should increase with increasing ionic strength μ. If the reacting ions are of opposite charge, as in the reaction

$$Co(NH_3)_5Br^{++} + OH^- \rightleftharpoons Co(NH_3)_5OH^{++} + Br^- \tag{XVII}$$

the product $z_a z_b$ is negative and the rate should decrease with increasing ionic strength. The qualitative prediction is in fact fulfilled in every one of the cases which have been examined: all reactions between ions of like charge sign have specific rates which increase with increasing ion concentration; all reactions between ions of unlike charge sign have specific rates which decrease with increasing ion concentration. The result is one of the strongest reasons for accepting the transition-state theory of reaction rate.

Most of the reactions between ions which have been studied carefully involve ions of large charge, and we should not expect nor do we usually find quantitative agreement with the Debye limiting law even in solutions of very low ionic strength.

The salt effects can be of considerable magnitude, large enough indeed to complicate considerably the problem of determining reaction order in reactions involving ions. Thus LaMer and Fessenden, *J. Am. Chem. Soc.*, **54,** 2351 (1932), found that the rate of the second-order reaction (XVI) is increased by a factor of 35 instead of by a factor of 25 when the concentrations of each of the reacting ions in the form of their barium salts is increased from 0.001 to 0.005 mole/liter. The large magnitude of the effect arises (page 321) primarily from the interaction of the doubly positive barium ion with the triply negative transition state. An even larger effect is produced by the triply positive lanthanum ion, whose addition in 0.00343 *M* concentration to the same reactants at 0.001 *M* concentration in the form of the sodium salts increases the rate by a factor of 8.6.

It is therefore sound practice to investigate the reaction order when ions are involved by maintaining in all the solutions used a concentration of an electrolyte not involved in the reaction which is large compared with the concentrations of the reacting ions. Under such conditions changes in concentration of the reacting ions will have little effect (page 324) on the activity coefficients of reactants and of transition state, and the determination of the effect of such changes on the rate of reaction will reveal directly the order of the reaction.

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PROBLEMS

1. From the following data obtained by conductance measurements on chloracetic acid at 25°C compute the mean ionic activity coefficient for an ion concentration of 3.164×10^{-3} *M*:

Titer conc. of acid $\times 10^3$	4.048	5.222	6.230	8.407	9.464
Ion conc. $\times 10^3$	1.844	2.176	2.438	2.944	3.164
$K \times 10^3$	1.543	1.554	1.567	1 587	1.589

2. What is the ionic strength of each of the following solutions: (*a*) 0.01 *M* KCl; (*b*) 0.01 *M* K_2SO_4; (*c*) 0.01 *N* K_2SO_4; (*d*) 0.01 *M* $MgSO_4$; (*e*) 0.01 *M* $La_2(SO_4)_3$; (*f*) a solution which contains 0.01 *M* KCl and 0.01 *M* K_2SO_4?

3. The solubility of the cobaltammine salt of Fig. 2 in 0.005 *N* $MgSO_4$ is 5.446×10^{-4} mole/liter at 25°C, and the solubility in water is 4.900×10^{-4} mole/liter. What is the mean ionic activity coefficient of the ions of the cobaltammine salt in the $MgSO_4$ solution? What value would be estimated from Eq. (32)?

4. If the solubility-product constant $K°$ for silver chloride is 1.7×10^{-10} compute the solubility of silver chloride in: (*a*) water; (*b*) 0.01 *M* KNO_3; (*c*) 0.01 *M* KCl.

5. If the limiting value $K°$ of the solubility-product constant of $AgBrO_3$ at 25°C is 5.20×10^{-5}, calculate the solubility of silver bromate in: (*a*) water; (*b*) 0.01 *M* KNO_3; (*c*) 0.01 *M* $KBrO_3$.

6. If the solubility-product constant $K°$ for silver chromate is 1.1×10^{-12} compute the solubility of Ag_2CrO_4 in: (*a*) water; (*b*) 0.01 *M* K_2CrO_4; (*c*) 0.01 *M* $AgNO_3$; (*d*) 0.01 *N* K_2CrO_4.

7. The solubility-product constant of CaC_2O_4 is 2.27×10^{-9}; that of CaF_2 is 3.9×10^{-11}. Which of these salts is the less soluble in water? In the form of which of these salts can calcium ion be most completely precipitated from aqueous solution by a 0.1 *N* excess of the anion?

8. A slightly soluble salt of the empirical formula $NaSbO_3 \cdot 3H_2O$ was once thought to be the sodium salt of a divalent anion $H_2Sb_2O_7^{--}$. Indicate how this idea could be verified or refuted by studying the solubility of the salt in solutions containing known concentrations of other electrolytes.

9. The solubility-product constants of $BaSO_4$ and $BaCO_3$ are 9.9×10^{-11} and 4.93×10^{-9}, respectively. If excess of solid barium sulfate is treated with 50 cc of 0.1 *M* sodium carbonate solution, how much barium carbonate will be formed?

10. If the solubility-product constant of $PbCO_3$ is 1.5×10^{-13}, what should be the solubility of the salt in water, assuming that $Pb(OH)_2$ is a strong electrolyte?

11. Obtain an equation analogous to Eq. (20) for the effect of ionic strength on the equilibrium constant K for: (*a*) the reaction $H_2PO_4^- + H_2O \rightleftharpoons OH_3^+ + HPO_4^{--}$; (*b*) the reaction $NH_4^+ + H_2O \rightleftharpoons OH_3^+ + NH_3$.

12. Equation (32) agrees closely with the actual behavior of the salts $NaNO_3$, K_2SO_4, $MgSO_4$, and $La_2(SO_4)_3$. Calculate for each of them the mean ionic activity coefficient at an ionic strength of 0.1.

In Probs. 13 to 26 calculate the hydronium-ion concentration and the hydroxyl-ion concentration at 25°C of the aqueous solution cited.

13. 0.01 M formic acid.

14. 0.1 M methylamine.

15. 0.1 M sodium phenolate.

16. 0.1 M aniline hydrochloride.

17. A solution containing 0.1 M formic acid and 0.01 M sodium formate.

18. A solution containing 0.01 M formic acid and 0.001 M sodium formate.

19. A solution containing 0.01 M sodium bicarbonate and 0.01 M sodium carbonate.

20. 0.01 M sodium bicarbonate.

21. An acetic acid solution of 0.01 M concentration half neutralized with ammonia.

22. A 0.01 M solution of acetic acid to which an exactly equivalent amount of ammonia has been added.

23. A 0.01 M solution of acetic acid to which an exactly equivalent amount of aniline has been added.

24. 0.01 M $NaNH_4HPO_4$.

25. 0.01 M glycine hydrochloride.

26. 0.01 M glycine.

27. Using Eq. (32) to estimate activity coefficients, compute the sodium acetate concentration required to yield a hydronium-ion concentration of 2×10^{-5} in a solution whose titer concentration of acetic acid is 0.1 M. What will be the value if the titer concentration of acetic acid is 0.01 M?

28. If 100 cc of a solution of the sodium salt of polyacrylic acid whose concentration is 0.01 N is separated by a membrane impermeable to the polyacrylate ion but permeable to sodium and to chloride ions from 100 cc of a 0.1 M sodium chloride solution, and if the volumes of the two solutions are maintained unchanged, what will be the concentration of sodium ions and of chloride ions on each side of the membrane after equilibrium has been established?

29. How many cubic centimeters of a 0.1 M solution of sodium hydroxide must be added to 100 cc of a solution containing 0.1 M formic and 0.1 M acetic acids to make the hydronium-ion concentration 2×10^{-5}?

30. By measuring the rate of a reaction whose rate is known to be proportional to the hydroxyl-ion concentration, it was found that $[OH^-] = 8.8 \times 10^{-4}$ M in an aqueous solution of potassium cyanide of titer concentration 0.05094 mole/liter. Compute the acidity constant of HCN.

31. Prove that the solubility of calcium carbonate in water containing carbon dioxide should to a useful approximation be proportional to the cube root of the partial pressure of gaseous CO_2 in equilibrium with the solution.

CHAPTER XV

THE EFFECTS OF PRESSURE AND OF TEMPERATURE ON FREE ENERGY

Effect of Pressure. Consider a system which can change by a *finite* amount from a state A at pressure P and temperature T in which its free energy is f_a and its volume v_a to a state B at the same pressure and temperature in which its free energy and volume are f_b and v_b. Consider also a state A' which is produced from A by an increase in the pressure from P to $P + dP$, and a state B' which is produced from B by the same increase in pressure. States A' and B' are both at the same temperature as states A and B. The infinitesimal pressure change will be accompanied by infinitesimal changes in free energy and volume. Consequently the free energy in state A' will be $f_a + df_a$, and the free energy in state B' will be $f_b + df_b$. The quantities df_a and df_b are not necessarily identical. Similarly the volumes in states A' and B' will be $v_a + dv_a$ and $v_b + dv_b$.

If the system changes reversibly from state A to state B, the total work will be $-(f_b - f_a) + P(v_b - v_a)$ by the considerations of page 234. If it then changes to state B', the work will be the product of the infinitesimal volume change dv_b and the average pressure $P + \frac{1}{2}\,dP$ which prevails during the change. The total reversible work of the sequence $A \rightarrow B \rightarrow B'$ is therefore

$$f_a - f_b + P(v_b - v_a) + (P + \tfrac{1}{2}\,dP)\,dv_b$$

On the same basis we find that the reversible work of the sequence $A \rightarrow A' \rightarrow B'$ is

$$(P+\tfrac{1}{2}\,dP)\,dv_a + (f_a + df_a) - (f_b + df_b) + (P + dP)(v_b + dv_b - v_a - dv_a)$$

Since these two sequences proceed from the same initial state to the same final state, the two quantities of reversible work must be the same. On equating the two values and simplifying we get

$$df_a - df_b + dP(v_b - v_a) + \tfrac{1}{2}\,dP(dv_b - dv_a) = 0 \qquad (1)$$

The last term may be dropped since it is the product of two infinitesimals, and we get

$$\left[\frac{\partial(f_b - f_a)}{\partial P}\right]_T = v_b - v_a \qquad (2)$$

We write this as a partial derivative as a reminder that the development of the equation involved changes in which the temperature was fixed.

This development could equally well be carried through for the states A and C, both at pressure P and temperature T, leading to

$$\left[\frac{\partial(f_c - f_a)}{\partial P}\right]_T = v_c - v_a \tag{3}$$

and analogous formulas could be derived involving states D, E, etc., in place of B. The only way in which it is possible for all these equations to hold is to have $\partial f_a/\partial P = v_a$. We may therefore write as an equation of general validity

$$\left(\frac{\partial f}{\partial P}\right)_T = v \tag{4}$$

f being the free energy of any state and v its volume.

We obtain an important relationship by differentiating Eq. (4) with respect to the number of moles n_i of some component of the system. By a general theorem of the calculus (Appendix A) we have for the left-hand member

$$\left[\frac{\partial}{\partial n_i}\left(\frac{\partial f}{\partial P}\right)_{T,n_i}\right]_{T,P} = \left[\frac{\partial}{\partial P}\left(\frac{\partial f}{\partial n_i}\right)_{T,P}\right]_{T,n_i} = \left(\frac{\partial \bar{F}_i}{\partial P}\right)_{T,n_i} \tag{5}$$

with $\bar{F}_i$ the molal free energy of component i. We define a quantity $\bar{V}_i$, called the *molal volume of component i in the system* (or the *partial molal volume of component i*), by the relation

$$\bar{V}_i = \left(\frac{\partial v}{\partial n_i}\right)_{T,P} \tag{6}$$

$\bar{V}_i$ is the rate at which the volume of the system increases as the quantity of component i is increased at constant temperature and pressure, the numbers of moles of all other components also being fixed. The result of the differentiation is then

$$\left(\frac{\partial \bar{F}_i}{\partial P}\right)_T = \bar{V}_i \tag{7}$$

Free Energy of a Perfect Gas. In a system consisting of a single perfect gas we have $v = n\mathbf{R}T/P$. Substituting this value in Eq. (4), separating variables, and integrating, we obtain

$$f = n\mathbf{R}T \ln P + \phi_1(T) \tag{8}$$

Since $\bar{F} = \partial f/\partial n = f/n$ for a one-component system (page 240), we have also

$$\bar{F} = \mathbf{R}T \ln P + \frac{\phi_1(T)}{n} \tag{9}$$

In these equations the temperature T is that defined by the perfect-gas thermometer, because only this definition of temperature makes the perfect-gas law valid.

We remind ourselves, because we shall soon need the information, that in the limiting case of the ideal gas enthalpy h is independent of pressure. We may therefore write

$$\left(\frac{\partial h}{\partial P}\right)_T = 0 \tag{10}$$

$$h = \phi_2(T) \tag{11}$$

Effect of Temperature. We have so far defined temperature only in terms of the perfect gas, *i.e.*, in terms of the limiting behavior approached by real gases as the pressure approaches zero. This is a limited definition because there are regions of low temperature in which it is impossible to measure the temperature in this way. In the logical structure of thermodynamics we therefore define temperature in a way which makes it possible to use magnetic, electrical, and other phenomena involving work for the measurement of temperature and which nevertheless coincides with the perfect-gas scale. This definition may be put in a variety of ways. The one we shall use is

$$\left(\frac{\partial f}{\partial \theta}\right)_P = \frac{f - h}{\theta} \tag{12}$$

We use the symbol θ for the temperature thus defined in order to distinguish it from the temperature T defined by the perfect-gas thermometer until we have proved the identity of the two quantities. The definition may seem abstract; consider a system in a state A at temperature θ in which its free energy and enthalpy are f_A and h_A, and also in a state A' at the same pressure but at a temperature $\theta - \Delta\theta$ at which the free energy is $f_A - \Delta f_A$. Then by Eq. (12) the quantity $\Delta f_A/(f_A - h_A)$ will be a good approximation to the relative difference in temperature $\Delta\theta/\theta$ if $\Delta\theta$ is small and will become an exact measure of the difference when it becomes infinitesimal.

Our next step is to prove the important theorem that the value of the temperature coefficient $(\partial f/\partial\theta)_P$ depends only on the numerical value of the quantity $(f - h)/\theta$ and is independent of the particular system which happens to have free energy f, enthalpy h, and temperature θ. For this purpose we consider in addition to the states A and A', which differ infinitesimally in θ and f, a state B at the same pressure and temperature as state A and differing in free energy from A by a finite amount. That

is, we suppose $f_B - f_A$ to be very large compared with df_A. We further consider a state B' related to B in the same way that A' is related to A. Now let the system be initially in state A and in contact with a very large body X at temperature θ, and let the system be carried through a cycle in which it (1) changes reversibly from state A to state B, absorbing heat from X; (2) is brought in contact with a very large body Y at temperature $\theta - d\theta$ and attains state B'; (3) changes reversibly from state B' to state A', giving up heat to Y; (4) is brought in contact with X and returns to temperature θ. In step 1, the system does the reversible work $-(f_B - f_A) + P(v_B - v_A)$; in step 2, it does the reversible work $-P\,dv_B$, where dv_B is the volume of state B minus that of state B'; in step 3, the reversible work $-(f_A - df_A - f_B + df_B) + P(v_A - dv_A - v_B + dv_B)$; and in step 4, $P\,dv_A$. The net reversible work of the cycle is therefore $-d(f_B - f_A)$. Since the cycled system has returned to its initial state, the only change undergone by any system is the loss of heat from body X and the transfer of this heat, diminished by the work done, to body Y. What we have been discussing is therefore a device by which work may be obtained from the transfer of heat from a body at temperature θ to one at temperature $\theta - d\theta$. Any other system which may operate in a cycle in which the same amount of heat is absorbed from X must do the same amount of reversible work; otherwise we could set up a perpetual motion by using the one which does more work to drive the other as a refrigerating machine which absorbs heat from Y and transfers it to X.

If the energies of states A and B are e_A and e_B, the heat absorbed from X in step 1 is $e_B - e_A - (f_B - f_A) + P(v_B - v_A)$, that is, $h_B - h_A - (f_B - f_A)$. Consequently what we have proved is that for any system which can undergo a constant-pressure change at temperature θ for which the change in free energy is equal to $f_B - f_A$ and the change in enthalpy to $h_B - h_A$ the value of the quantity $[\partial(f_B - f_A)/\partial\theta]_P$ is completely determined if the values of the quantities $f_B - f_A$, $h_B - h_A$, and θ are fixed. By an argument analogous to that which led from Eq. (2) to Eq. (4) this can be true only if the value of the quantity $(\partial f/\partial\theta)_P$ for any system is completely determined when the quantities f, h, and θ are fixed.

To prove the identity of the θ and T definitions of temperature, differentiate Eq. (12) with respect to P at constant θ. The left-hand member

$$\frac{\partial}{\partial P}\left(\frac{\partial f}{\partial \theta}\right) = \frac{\partial}{\partial \theta}\left(\frac{\partial f}{\partial P}\right) = \left(\frac{\partial v}{\partial \theta}\right)_P \tag{13}$$

by Eq. (4). By Eq. (4) also $\partial f/\partial P = v$; consequently we have

$$\left(\frac{\partial v}{\partial \theta}\right)_P = \frac{v}{\theta} - \left(\frac{\partial h}{\partial P}\right)_\theta \tag{14}$$

A system of fixed θ is necessarily a system of fixed T, because we know that a system of fixed composition has at most two degrees of freedom. At any given pressure fixing T then fixes all the properties including θ. It is therefore true that $(\partial h/\partial P)_\theta = (\partial h/\partial P)_T$.

If the system under consideration is a perfect gas, we have by Eq. (10) $(\partial h/\partial P)_\theta = 0$, and Eq. (14) becomes

$$\left(\frac{\partial v}{\partial \theta}\right)_P = \frac{v}{\theta} \tag{15}$$

Separating variables and integrating, we get

$$\ln v = \ln \theta + \phi_3(P)$$

This is equivalent to

$$\theta = k_1 v \tag{16}$$

with k_1 a constant at constant pressure. The perfect-gas definition of T is

$$T = k_2 v \tag{17}$$

The numerical value of k_2 derives from the arbitrary setting of the interval of temperature between the normal freezing point and the normal boiling point of water equal to 100°. If we adopt the same convention for θ, then θ and T become identical.

Our discussion of the definition of temperature has carried with it the solution of the problem of the effect of temperature on free energy. Temperature T is so defined that the equation

$$\left(\frac{\partial f}{\partial T}\right)_P = \frac{f - h}{T} \tag{18}$$

shall be valid.

By operations analogous to those which converted Eq. (4) to Eq. (7) we get

$$\left(\frac{\partial \bar{F}_i}{\partial T}\right)_P = \frac{\bar{F}_i - \bar{H}_i}{T} \tag{19}$$

The quantity $\bar{H}_i = (\partial h/\partial n_i)_{T,P}$ is called the *molal enthalpy* (or *partial molal enthalpy*) *of component i*. It is the slope of a plot of enthalpy against number of moles of i in a system in which temperature, pressure, and the numbers of moles of all other components are constant.

If f_1 and h_1 are free energy and enthalpy of a system in state 1 and f_2 and h_2 the corresponding quantities for the same system in state 2 at the same temperature, then by writing Eq. (18) for the system in state 1 and in state 2 and taking the difference we get

$$\left\{\frac{\partial(f_2 - f_1)}{\partial T}\right\}_P = \frac{(f_2 - f_1) - (h_2 - h_1)}{T} \tag{20}$$

This may also be written

$$\left(\frac{\partial \Delta f}{\partial T}\right)_P = \frac{\Delta f - \Delta h}{T} \tag{21}$$

The equation

$$\left(\frac{\partial \Delta \bar{F}}{\partial T}\right)_P = \frac{\Delta \bar{F} - \Delta \bar{H}}{T} \tag{22}$$

follows similarly from Eq. (19).

Entropy. We may define the entropy s of a system by the equation

$$s = \frac{h - f}{T} \tag{23}$$

Then by Eq. (18) we have also

$$s = -\left(\frac{\partial f}{\partial T}\right)_P \tag{24}$$

which makes entropy the negative of the temperature coefficient of free energy at constant pressure. It is easy to see that the molal (or partial molal) entropy $\bar{S}_i$ of component i of a system is given by

$$\bar{S}_i = \frac{\bar{H}_i - \bar{F}_i}{T} = -\left(\frac{\partial \bar{F}_i}{\partial T}\right)_P \tag{25}$$

and that the entropy change in a process is given by

$$\Delta s = \frac{\Delta h - \Delta f}{T} = -\left(\frac{\partial \Delta f}{\partial T}\right)_P \tag{26}$$

and

$$\Delta \bar{S} = \frac{\Delta \bar{H} - \Delta \bar{F}}{T} = -\left(\frac{\partial \Delta \bar{F}}{\partial T}\right)_P \tag{27}$$

Temperature Coefficient of the Equilibrium Constant. In Chap. XI we obtained by thermodynamic reasoning a relation

$$\Delta \bar{F}^\circ = -\mathbf{R}T \ln K \tag{28}$$

which related the constant K of the ideal law of chemical equilibrium to the difference $\Delta \bar{F}^\circ$ between the molal free energies of reactants and products each in its standard state. This standard free-energy difference, like any difference in molal free energies, must satisfy Eq. (22). Differ-

entiating Eq. (28), we get

$$\left(\frac{\partial \Delta \bar{F}^\circ}{\partial T}\right)_P = -\mathbf{R} \ln K - \mathbf{R}T\left(\frac{\partial \ln K}{\partial T}\right)_P \tag{29}$$

Putting in the value of $\mathbf{R} \ln K$ from Eq. (28), this reduces to

$$\left(\frac{\partial \Delta \bar{F}^\circ}{\partial T}\right)_P = \frac{\Delta \bar{F}^\circ}{T} - \mathbf{R}T\left(\frac{\partial \ln K}{\partial T}\right)_P \tag{30}$$

and comparison with Eq. (22) shows that

$$\mathbf{R}T^2\left(\frac{\partial \ln K}{\partial T}\right)_P = \Delta \bar{H} \tag{31}$$

We have obtained this important equation previously on a different basis (Chap. VIII) and now see that it is a necessary consequence of exact thermodynamics for any system for which the perfect-gas or dilute-solution approximations are valid.

Temperature Coefficient of the Potential of a Galvanic Cell. The potential $\mathcal{E}$ of a galvanic cell is related to a difference in molal free energies by the relation (Chap. XI)

$$\Delta \bar{F}^\circ = -n\mathbf{F}\mathcal{E} \tag{32}$$

By differentiating with respect to T and then using Eqs. (22) and (32) we have

$$\left(\frac{\partial \Delta \bar{F}}{\partial T}\right)_P = -n\mathbf{F}\left(\frac{\partial \mathcal{E}}{\partial T}\right)_P = \frac{\Delta \bar{F} - \Delta \bar{H}}{T} = \frac{-n\mathbf{F}\mathcal{E} - \Delta \bar{H}}{T} \tag{33}$$

This may also be written

$$\Delta \bar{H} = -n\mathbf{F}\mathcal{E} + n\mathbf{F}T\left(\frac{\partial \mathcal{E}}{\partial T}\right)_P \tag{33}$$

The quantity $\Delta \bar{H}$ in this equation is the difference in molal enthalpy between the substances on the right side and those on the left side of the cell reaction. As we have emphasized, $\Delta \bar{H}$ equals the heat absorbed in a process only if no work is done other than that against a constant confining pressure (page 61). The $\Delta \bar{H}$ of Eq. (33) is not therefore the heat absorbed by an operating cell in which electrical work is being done, but it is the heat absorbed if the reactants are simply mixed and allowed to react in direct contact.

Consider the cell

$$\text{Pb(s): } PbCl_2\text{(s), HCl(1 } m\text{); HCl(1 } m\text{), } PbCl_2\text{(s), AgCl(s): Ag} \quad (A)$$

for which the cell reaction is

$$\tfrac{1}{2}\mathrm{Pb(s)} + \mathrm{AgCl(s)} \rightleftharpoons \tfrac{1}{2}\mathrm{PbCl_2(s)} + \mathrm{Ag(s)} \qquad \text{(I)}$$

Gerke, *J. Am. Chem. Soc.*, **44,** 1684 (1922), reports that at 25°C $\mathcal{E} = +0.4900$ and $(\partial\mathcal{E}/\partial T)_P = -1.86 \times 10^{-4}$. From these figures the term $-n\mathbf{F}\mathcal{E}$, which by Eq. (32) is equal to $\Delta\bar{F}$, is $-11{,}300$ cal, and the term $n\mathbf{F}T(\partial\mathcal{E}/\partial T)_P$ is $-1{,}276$ cal. By Eq. (33) the value of $\Delta\bar{H}$ is therefore $-12{,}576$ cal. This should be the heat absorbed per mole of silver formed when solid lead is allowed to react with a suspension of lead and silver chlorides in HCl. The directly observed calorimetric value is $-12{,}000$, which agrees within the precision of the calorimetric measurement. This must also be the heat effect observed when the circuit of cell *A* is closed through a resistance and the heat absorbed or given out by the combination of cell and resistance is determined.

Suppose the cell operates reversibly. Then the electrical work done is $+n\mathbf{F}\mathcal{E}$, and the total work w is $n\mathbf{F}\mathcal{E} + P\,\Delta V$. Equation (33) becomes

$$\Delta H = -w + P\,\Delta V + n\mathbf{F}T\left(\frac{\partial\mathcal{E}}{\partial T}\right)_P \qquad (34)$$

from which

$$\Delta E = -w + n\mathbf{F}T\left(\frac{\partial\mathcal{E}}{\partial T}\right)_P \qquad (35)$$

By the first law of thermodynamics the heat absorbed is therefore $n\mathbf{F}T(\partial\mathcal{E}/\partial T)_P$. This quantity is also simply related to the entropy as we see by differentiating Eq. (32) with respect to temperature and comparing with Eq. (27) to get

$$\Delta\bar{S} = n\mathbf{F}\left(\frac{\partial\mathcal{E}}{\partial T}\right)_P \qquad (36)$$

The last term in Eq. (33), which equals the heat absorbed when the cell operates reversibly, is therefore identical with the quantity $T\,\Delta\bar{S}$.

With respect to cell A we see therefore that per faraday the cell gives out 1276 cal as heat when it operates reversibly and gives out 12,576 cal when it is short-circuited so that it does no work. An actual operating cell, which produces per faraday electrical work lying somewhere between 0 and 11,300 cal, evolves an amount of heat lying between 1276 and 12,576 cal. The cell

$$\mathrm{Pb(s)\colon PbCl_2(s),\ HCl}(1\ m);\ \mathrm{HCl}(1\ m),\ \mathrm{Hg_2Cl_2(s)\colon Hg} \qquad (B)$$

is found to have $\mathcal{E} = +0.5356$ and $\partial\mathcal{E}/\partial T = +1.45 \times 10^{-4}$. From these figures we find per faraday $\Delta\bar{F} = -12{,}351$, $T\,\Delta\bar{S} = +996$, $\Delta\bar{H} = -11{,}355$.

This cell evolves heat amounting to 11,355 cal/faraday on short circuit but *absorbs* 996 cal when operating reversibly. In reversible operation the cell yields more electrical energy than is obtained as heat by the direct reaction of lead metal with a suspension of lead and mercurous chlorides in HCl.

The Clausius Equation. Consider a one-component system consisting of two phases 1 and 2, the system being at equilibrium at temperature T and pressure P. Under these conditions the molal free energies $\bar{F}_1$ and $\bar{F}_2$ of the substance in the two phases must be identical. Now change the system to an infinitesimally different temperature and pressure at which also equilibrium exists. We now have $\bar{F}_2 + d\bar{F}_2 = \bar{F}_1 + d\bar{F}_1$. It follows that $d\bar{F}_2 = d\bar{F}_1$ and therefore (page 393) that

$$\left(\frac{\partial \bar{F}_2}{\partial T}\right)_P dT + \left(\frac{\partial \bar{F}_2}{\partial P}\right)_T dP = \left(\frac{\partial \bar{F}_1}{\partial T}\right)_P dT + \left(\frac{\partial \bar{F}_1}{\partial P}\right)_T dP \tag{37}$$

Writing $\Delta\bar{F} = \bar{F}_2 - \bar{F}_1$, $\Delta\bar{H} = \bar{H}_2 - \bar{H}_1$, and $\Delta\bar{V} = \bar{V}_2 - \bar{V}_1$, this becomes

$$\frac{dP}{dT} = -\frac{\partial \Delta\bar{F}/\partial T}{\partial \Delta\bar{F}/\partial P} = -\frac{\Delta\bar{F} - \Delta\bar{H}}{T\,\Delta\bar{V}} \tag{38}$$

Since $\bar{F}_2 = \bar{F}_1$, $\Delta\bar{F} = 0$ and

$$\frac{dP}{dT} = \frac{\Delta\bar{H}}{T\,\Delta\bar{V}} \tag{39}$$

$\Delta\bar{H}$ is the molal heat of transfer of the substance from phase 1 to phase 2 and $\Delta\bar{V}$ the molal volume change accompanying the same transfer. This equation determines such matters as the effect of temperature on the vapor pressure of a pure liquid or solid and the effect of pressure on the melting point of a solid or upon the transition temperature of one solid phase into another. In the vapor-pressure case the volume of the liquid or solid can often be neglected compared with that of the gas, and $\Delta\bar{V}$ reduces to the molar volume of the gas. If this is assumed to follow the perfect-gas law, Eq. (39) reduces to

$$\frac{dP}{dT} = \frac{\Delta\bar{H}}{\mathbf{R}T^2/P} \tag{40}$$

or

$$\frac{d \ln P}{dT} = \frac{\Delta\bar{H}}{\mathbf{R}T^2} \tag{41}$$

which we have met before.

Equation (39) is also valid for systems containing more than one component if the compositions of the two phases are unchanged by the change in temperature and pressure. This is for instance the case when on

phase consists of a liquid solution of a nonvolatile solute in a volatile solvent and the other phase consists of the vapor of the solvent.

Determination of Molal Free Energies from Vapor Pressures. Suppose one has two solutions which contain a nonvolatile solute or solutes in a volatile solvent, each of them being in equilibrium with the vapor of the solvent. Let the molal free energy of the solvent in solution 1 be $\bar{F}_1$ and that in solution 2 be $\bar{F}_2$. Then by the considerations of page 250 the molal free energy of the vapor in equilibrium with solution 1 is likewise $\bar{F}_1$, and that of the vapor in equilibrium with solution 2 is $\bar{F}_2$. If the vapors behave as perfect gases, we have by Eq. (9)

$$\bar{F}_2 - \bar{F}_1 = \mathbf{R}T \ln P_2 - \mathbf{R}T \ln P_1 \tag{42}$$

If the perfect-gas laws do not give sufficient precision, some more precise relation between volume and pressure can be used to integrate Eq. (4). The values of $\bar{F}_1$ and $\bar{F}_2$ for the solvent in the solution obtained in this way are values which correspond not only to different concentrations of solution but to different pressures since each solution is at the pressure at which it is in equilibrium with the vapor. The matter is rarely of importance because the molal free energy of a solid or liquid is so insensitive to pressure. For liquid water $(\partial F/\partial P)_T = 0.44$ cal/atm.

Osmotic Pressure. Consider two solutions containing the substance A in infinitesimally different proportions, the two solutions being separated by a membrane permeable to A but not to the other constituents of the solutions. Let the pressure on the first solution be P and that on the second be $P + dP$, and let the pressure difference be just sufficient to establish equilibrium with respect to transfer of A from 1 to 2 and from 2 to 1. Let the molal free energy of A in solution 1 at pressure P be $\bar{F}$, and let the value which the molal free energy would have in solution 2 if it were at pressure P be $\bar{F} + d\bar{F}$. The actual molal free energy in solution 2 must differ from this by the amount $(\partial \bar{F}/\partial P)_T\, dP$ and must also be identical with $\bar{F}$ since the two solutions are in equilibrium. Consequently

$$\bar{F} + d\bar{F} + \left(\frac{\partial \bar{F}}{\partial P}\right)_T dP = \bar{F} \tag{43}$$

from which with Eq. (7)

$$d\bar{F} = -\bar{V}\, dP \tag{44}$$

with $\bar{V}$ the molal volume of component A in the solution.

If the two solutions differ by finite amounts, the difference in $\bar{F}$ between them can be computed as the sum of a sequence of infinitesimal increments, each one satisfying Eq. (44), from which we have for states x and y

$$\bar{F}_y - \bar{F}_x = -\int_{P_x}^{P_y} \bar{V}\, dP \tag{45}$$

If system x is pure liquid A at 1 atm pressure, the osmotic pressure Π of solution y is defined as the extra pressure which must be applied to solution y to establish equilibrium across the membrane. Consequently

$$\bar{F}_y - \bar{F}_x = -\int_1^{\Pi+1} \bar{V}\, dP \tag{46}$$

To a moderate precision in dilute solutions we may take $\bar{V}$ to be independent of composition and pressure and equal to the molal volume V of pure liquid A. To this approximation Eq. (46) reduces to

$$\bar{F}_y - \bar{F}_x = -V\Pi \tag{47}$$

To the same approximation we may expect Raoult's law to hold, *i.e.*, that

$$\ln P = \ln N_a + \ln P^\circ \tag{48}$$

where P is the vapor pressure of A from the solution, P° the vapor pressure of pure liquid A, and N_a the mole fraction of A in the solution. By Eq. (42) then

$$F_y - F_x = -\mathbf{R}T \ln N_a \tag{49}$$

From this with Eq. (47)

$$\Pi V = -\mathbf{R}T \ln N_a \tag{50}$$

To the same precision we may write $\ln N_a = -n_b/n_a$, where n_b and n_a are the numbers of moles of solute and solvent, respectively (*cf.* page 148). The product $n_a V = v$, the volume of the solvent contained in the solution, and in dilute solution n_b/v is nearly enough the same as c, the concentration of solute in moles per liter. Consequently to the precision of the dilute-solution laws

$$\Pi = c\mathbf{R}T \tag{51}$$

This may also be written as

$$\Pi = \frac{c_w}{M}\mathbf{R}T \tag{52}$$

where c_w is concentration in grams per liter and M is molecular weight.

Osmotic Pressure of Solutions of High Polymers. For polymeric substances of molecular weight in the range from 10^4 to 10^6 the measurement of osmotic pressure is a useful method of determining molecular weight. It is relatively easy to find a membrane which is permeable to a solvent of low molecular weight and impermeable to the polymer, whereas it is extremely difficult to find membranes which select perfectly between substances which do not differ largely in molecular weight. The pressures which the membrane must withstand are moderate but easily measurable when the weight concentration lies in a reasonable range. At the same weight concentrations, freezing-point depressions, boiling-

point elevations, and vapor-pressure depressions are so small as to give these techniques poor precision and reliability as methods of estimating molecular weights.

Because solutions of high polymers often deviate widely from ideality, even at low concentrations, the proportionality between osmotic pressure and concentration predicted by Eqs. (51) and (52) frequently fails seriously with such solutions. Thus, as Fig. 1 shows, the ratio of osmotic pressure to concentration for solutions of polyisobutylene in cyclohexane varies by a factor of over 3 between a concentration of 5 g/liter and one of 20 g/liter. The plot of Π/c_w against c_w is, however, nearly linear, and the

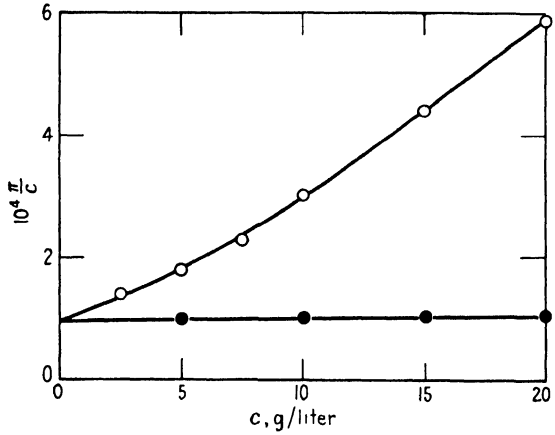


FIG. 1. Plot of the ratio of osmotic pressure Π in atmospheres to concentration c in grams per liter against c for a fractionated sample of polyisobutylene. ○ in cyclohexane, ● in benzene. [*From data of Flory, J. Am. Chem. Soc.*, **65**, 376 (1943).]

intercept $\lim_{c \to 0} \Pi/c_w$ is easily estimated. As the figure shows, the same intercept is obtained from solutions of the same solute in benzene, in which the plot has a very different slope. We may therefore employ this limit with considerable confidence in the equation

$$\lim_{c \to 0} \frac{\Pi}{c_w} = \frac{RT}{M} \tag{53}$$

for the purposes of estimating the molecular weight, which in this case was 255,000.

Actual polymers consist of a mixture of molecules of different molecular weights, and what is determined by Eq. (53) is obviously some kind of average molecular weight. For such a system we may replace Eq. (51) by

$$\sum_i n_i = \frac{\Pi v}{RT} \tag{54}$$

where the summation is the sum of the numbers of moles of all the kinds of solute present. For the total weight w we have

$$w = \sum_i n_i M_i \tag{55}$$

The average molecular weight $\bar{M}$ we get from Eq. (53) is

$$\bar{M} = \frac{w\mathbf{R}T}{\Pi v} \tag{56}$$

From this with Eqs. (54) and (55) we get

$$\bar{M} = \frac{\Sigma n_i M_i}{\Sigma n_i} \tag{57}$$

This kind of average molecular weight is known as the *number average molecular weight* of the polymer.

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PROBLEMS

1. At 25°C what is the difference between the molal free energy of a perfect gas at 1 atm and the value at 0.1 atm?

2. On the basis of the virial equation given on page 8 for oxygen at 0°C compute the difference between the molal free energy of oxygen at 10 atm and that at 1 atm.

3. At 25°C the pressure of water vapor in equilibrium with 10 per cent sulfuric acid is 22.4 mm; for 20 per cent acid it is 20.8 mm. What is the difference between the molal free energies of water in these two solutions?

4. At −15°C the vapor pressure of ice is 1.241 mm; that of liquid water at the same temperature is 1.436 mm. What is the difference between the molal free energies of ice and of water at this temperature, and which form of water has the higher molal free energy?

5. If a quantity a is defined by the equation $a = f - Pv$, show: (*a*) that for any isothermal process at constant pressure $-\Delta a$ equals the total reversible work; (*b*) that $-\Delta a$ equals the total reversible work of any isothermal process.

6. What is the difference between the molal entropies of a perfect gas at 1 atm and at 0.1 atm, both at 25°C?

7. Prove that $(\partial s/\partial T)_P = c_P/T$, and compute the difference between the molal entropy of a perfect monoatomic gas at 0° and at 100°C, both at 1 atm.

8. Prove that $s = (e - a)/T$, where s is entropy, e is energy, and a is defined in Prob. 5.

9. For the cell Hg: $Hg_2Br_2(s)$, HBr(c); HBr(c), AgBr(s): Ag, $\mathcal{E} = 0.06804$ volt and $(\partial\mathcal{E}/\partial T)_P = 3.12 \times 10^{-4}$ volt/deg. Calculate the values of the quantities $\Delta\bar{F}$, $\Delta\bar{S}$, and $\Delta\bar{H}$ in calories per faraday for the cell reaction. How much heat is absorbed per faraday when this cell operates reversibly? How much heat is absorbed per faraday when the cell is internally short-circuited?

10. Answer the same questions as in Prob. 9 for the cell Pt: H_2(1 atm), NaOH(c); NaOH(c), HgO(s): Hg for which $\mathcal{E} = 0.9257$ volt and $(\partial\mathcal{E}/\partial T)_P = -2.95 \times 10^{-4}$ volt-deg.

11. The heat of fusion of ice is 79.69 cal/g. The density of liquid water at 0°C is 0.9998 g/cc; that of ice at this temperature is 0.9168 g/cc. What is the value of the quantity dP/dT for a system consisting of ice and liquid water in equilibrium at 0°?

12. What is the entropy change when 1 mole of ice at 0°C melts?

13. At 100°C the quantity dP/dT for the vaporization of water is 27.1 mm/deg. The density of the liquid is 0.95838 g/ml, and the heat of vaporization is 538.7 cal/g. What volume will be occupied by 1 mole of water vapor at 100°C? By how many per cent does this differ from the molal volume calculated from the perfect-gas law?

14. Show that $(\partial s/\partial P)_T = -(\partial v/\partial T)_P = (1/T)[(\partial h/\partial P)_T - v]$.

15. If the enthalpy change for the transition from rhombic to monoclinic sulfur at the transition point under 1 atm, 95.5°C, is 95 cal/mole and the volume change is 0.442 cc/mole, what is the value of dP/dT for this transition?

16. For the transition of ice I to ice III at −30°C and 2087 atm, $\Delta V = -3.46$ cc/mole and $dP/dT = -3.1$ atm/deg. What is the molal enthalpy change for the transition?

17. At 25°C and 1 atm the molal entropy of diamond has been found to be 0.585 cal/deg by heat-capacity measurements extending to low temperatures; on the same basis the molal entropy of graphite at 25° and 1 atm is 1.365 cal/deg. For the combustion of 1 mole of diamond, $\Delta H = -94.484$ kcal; for graphite the corresponding value is −94.030 kcal. What is the molal free-energy change in the transition of diamond to graphite at 25° and 1 atm? Is diamond or graphite the more stable form of carbon under these conditions? The density of diamond at 25° and 1 atm is 3.513 g/cc; that of graphite is 2.260. Assuming that these densities are independent of pressure, estimate the pressure at which the relative stabilities at 25°C would be reversed. Do you think the assumption a sound one under the circumstances?

18. The osmotic pressures in cyclohexane of a certain polyisobutylene sample were found to have the following values at the concentrations listed:

c, g/liter	20.0	15.0	10.0	5.0
$10^3\Pi$, atm	15.9	9.8	5 22	2.01

What is the number average molecular weight of the polyisobutylene?

CHAPTER XVI

A BRIEF ACCOUNT OF SOME EFFECTS INVOLVING SURFACES

Surface Tension. Consider a particular molecule in the surface layer of a liquid which is in contact with its own vapor or with any dilute gas. Because of the intermolecular forces the nearest neighbors of the molecule exert a significant net force on it which is directed toward the interior of the liquid. This is not balanced by any important outward force because the molecules in the gas phase are relatively scarce and distant. In principle a molecule inside the body of the liquid will also be subjected to unbalanced forces unless it is equidistant from the opposite surfaces of the liquid; in practice the forces are almost exactly balanced unless the molecule is within a few molecular diameters of the surface because intermolecular forces die off so rapidly with increasing distance that only near neighbors of a particular molecule have any important effect on it.

As a result of this situation the transfer of a molecule from the surface to the interior of the liquid is accompanied by a decrease in potential energy. If the surface of the liquid remains constant, this transfer must be accompanied by the transfer of another molecule from interior to surface and the net change in potential energy is zero. But if the surface decreases because the shape of the body changes or because two separate portions of liquid coalesce, there is a net decrease in potential energy whose magnitude is proportional to the number of molecules transferred from surface to interior. This number is in turn proportional to the change in the surface. Consequently we have a potential energy change Δe given by

$$\Delta e = \gamma \, \Delta s \tag{1}$$

where Δs is the change in area of the surface. The proportionality constant γ is called the *surface tension* of the liquid. It has the dimensions of energy over surface, and since energy is force times length and surface is length squared, γ also has the dimensions of force over length (MWM 215–219, Sears I, 312–323).

The surface tension of a liquid is related quantitatively to a number of familiar phenomena, for example, the rise or fall of a liquid in a capillary tube, the pressure required to form a gas bubble within a liquid, the size of a hanging drop, etc., and may be measured in a variety of ways which

depend upon the magnitude of these effects (MWM 215–219, Sears I, 312–323).

What we have said about the decrease in potential energy which accompanies the transfer of a molecule from the surface to the interior of a liquid is of course true of the corresponding change in the case of a solid. Phenomena in which the surface of a solid is changed are, however, so slow that we have no direct method of measuring the surface tension of a solid.

The surface tension of most organic liquids at room temperature lies in the range from 18 to 30 dynes/cm; that of water is 72, that of mercury 480.

Temperature Coefficient of Surface Tension. Since liquid and gas become identical at the critical temperature, surface tension must disappear as the temperature rises toward the critical value. A number of equations have been suggested for the temperature dependence of surface tension, the most useful being that of MacLeod,

$$\frac{\gamma^{1/4}}{\rho_l - \rho_g} = C \tag{2}$$

C is a constant characteristic of the substance concerned, ρ_l is the density of the liquid, and ρ_g is the density of the gaseous substance, both densities being taken at a pressure equal to the vapor pressure. Since the densities of liquid and gas become identical at the critical temperature, the equation meets the requirement that γ shall vanish at the critical temperature.

The Parachor. The quantity MC, where M is molecular weight, is called the parachor, P; hence

$$P = \frac{M\gamma^{1/4}}{\rho_l - \rho_g} \tag{3}$$

At temperatures well below the critical ρ_g can be neglected compared with ρ_l, and M/ρ_l equals V, the molecular volume of the liquid. Under such conditions therefore

$$P = V\gamma^{1/4} \tag{4}$$

Consequently the parachors of a series of liquids may be taken to represent the molecular volumes at such temperatures in each case that the surface tension is unity. Since surface tension is in some degree a measure of intermolecular force, a comparison of parachors is in a sense a comparison of molecular volumes under such conditions that intermolecular forces are equal. In other words, this is a way of comparing the volumes of the molecules of the substances, uncomplicated by differences in the

magnitudes of the intermolecular forces which tend to decrease the volume of the liquid. In fact the parachor does depend in a very characteristic way on the composition and structure of the molecule, and the value of the parachor has often been a useful factor in determining or verifying the structure of a complicated molecule.

Interfacial Tension. Consider next the interface between two liquid phases. The very fact of the immiscibility implies (page 270) a smaller interaction energy between unlike molecules than between like molecules. A decrease in the area of the interface requires that molecules of each kind be transferred from the interface to the interior of the liquids, *i.e.*, from a situation in which the molecule is in contact with one or more unlike molecules to one in which it is completely surrounded by its own kind. This means a decrease in energy, and the situation is consequently very similar to that involved when the interface is that between a liquid and a gas; in both cases energy decreases with decrease in the area of the interface, and the change in energy is proportional to the change in surface. The proportionality constant in the case involving the interface between two liquids is called the *interfacial tension* of the two liquids.

The interfacial tension must be proportional to the quantity $e_{ai} - e_{av} + e_{bi} - e_{bv}$, where e_{av} is the energy of a molecule of kind a in the interior of liquid a, e_{ai} the energy of a molecule of a when it is situated at the interface between liquid a and liquid b, and the other terms are the corresponding quantities for molecules of kind b. At first sight the interfacial tension might be expected to parallel closely the magnitude of the positive deviation from ideality of the two liquids, and this is indeed the case when the molecules are highly symmetrical. A liquid like octyl alcohol, on the other hand, whose molecules consist of a hydrocarbon chain of considerable length which carries at one end a highly polar group, shows a relatively low interfacial tension against water. The interfacial tension between octyl alcohol and water at 20°C is only 8.5 dynes/cm, whereas that between octane and water is 50.8. The effect is specific to the interface; the surface tension of octyl alcohol is 27.5, while that of octane is 21.8. It appears probable that in such cases hydrogen bonding between the hydroxyl groups of different alcohol molecules pulls the hydroxyl group beneath the surface when the alcohol is in contact with the gas phase. In this case the surface is much like that of liquid octane, and the surface tensions are not very different. But when the alcohol is in contact with water, an even stronger hydrogen bonding between alcohol molecule and water molecule turns the alcohol molecules about so that the hydroxyl groups are in contact with the water. This lowers the energy of an alcohol molecule at the interface and decreases the interfacial tension.

Spreading. If a portion of pure hydrocarbon is placed on the surface of a container of water, it floats as a flattened sphere, as indicated in Fig. 1. A liquid like octyl alcohol on the other hand, whose hydroxyl group can hydrogen-bond with the water molecules, *spreads* on water in such a way that a small amount of the alcohol covers a large area. It is a familiar fact that such films of spreading liquids on water may easily be thin enough to give interference colors. If γ_b is the surface tension of the floating liquid (the octyl alcohol in this case) and γ_{ab} the interfacial tension, spreading can occur only if the surface energy per unit area of the spread system, which is $\gamma_b + \gamma_{ab}$, is less than γ_a, the surface energy per unit area of the uncovered surface of the supporting liquid. The difference $\gamma_a - (\gamma_b + \gamma_{ab})$ is called the *spreading coefficient;* only when it is positive will spreading occur. Spreading is obviously favored by a high surface tension of the supporting liquid and by low values of the surface tension of the spreading liquid and of the interfacial tension. Such cases as that of octyl alcohol on water are clearly favorable.

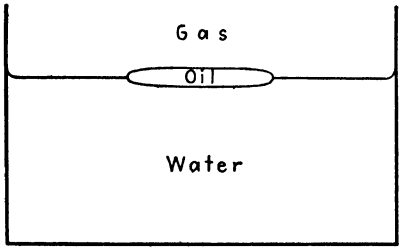


FIG. 1. A nonspreading oil on water.

If a film of spreading substance is confined between the barriers AB and CD on the surface of a trough of water as shown schematically in Fig. 2, it exerts a force on the barriers which although small can be measured with useful precision. Specifically one measures the force F per unit length of the barrier which must be applied to CD to prevent it from moving in either direction when the position of barrier AB is fixed and repeats the measurement at a series of positions of the latter. In this way one obtains a relation between F and the area A of the film. A typical case is that shown in Fig. 3 for a film of palmitic acid on water. At large areas the force is extremely small, but as the area decreases, there is a sudden rapid rise in force. A reasonable interpretation is that the acid molecules are relatively widely separated at large areas and exert little force on each other and that the rise occurs when the area available per molecule is so small that the molecules are in contact with each other. We should also expect from what we have learned about interfacial tensions that the acid molecules in the film would then be oriented with the carboxyl group attached to the water surface and the hydrocarbon chain extending

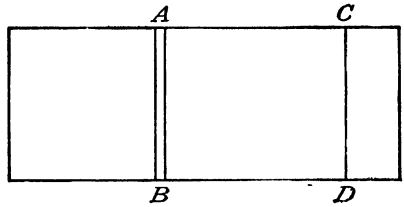


FIG. 2. Schematic diagram of a trough for measuring spreading force.

vertically. And in fact the area at which the rise begins is the same for stearic and for other long straight-chain saturated acids as it is for palmitic, and the value, 20.5×10^{-16} cm^2, agrees well with the cross-sectional area of a hydrocarbon chain computed from X-ray diffraction studies on the crystalline acids.

The detailed study of films of this sort has revealed a wide variety of interesting phenomena and has supplied extremely valuable information on many matters of molecular structure.

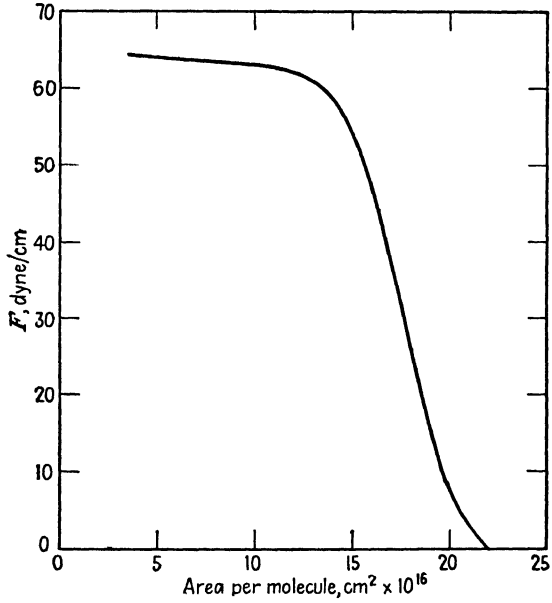


FIG. 3. Spreading of palmitic acid on water at 16°C [*from data of Langmuir, J. Am. Chem. Soc.*, **39**, 1873 (1917)].

Surface Tension and Interfacial Tension of Solutions. In a solution those molecules between which the intermolecular forces are relatively weak tend to concentrate in the surface layer, since this leads to lower surface energy. For the replacement in the surface layer of a molecule which exerts a strong force of attraction on its neighbors by one which exerts a weak force must have an effect in the same direction as the removal of a molecule from the surface. Consequently there is a tendency for the surface tension of the solution to approach that of the component of lower surface tension. For the same reason such a molecule as octyl alcohol dissolved in a hydrocarbon will concentrate at the interface between the hydrocarbon solution and water and will lower the interfacial tension. The effect may be very large even with small concentrations of the material of low surface or interfacial tension. Thus the addition of

0.002 mole/liter of sodium oleate to water lowers the surface tension from 72 to 25 dynes/cm and lowers the interfacial tension between water and benzene from 35 to 25 dynes/cm. Materials which exert this kind of effect on the surface tension of water and on the interfacial tension between water and immiscible liquids of low polarity are said to be *surface active.*

The Interface between Solid and Liquid. There is every reason to suppose that the same molecular interactions occur between the molecules of a liquid and those of a solid as occur at the interface between two liquids. Qualitatively many familiar phenomena are in agreement with this idea. Water spreads on clean glass, mercury does not. This kind of interfacial tension cannot, however, be investigated directly because of the immobility of the molecules of the solid.

On the other hand the changes in concentration at the interface between a solid and a liquid or a solid and a gas are readily accessible to investigation because the rigidity of the solid permits the establishment and maintenance of a form, such as a fine powder or a porous material, which possesses a large surface per unit weight. When the molecules of a gas or a solute adhere in this way to the surface of a solid, the adhering material is said to be adsorbed by the solid.

Adsorption. There is no sharp line of demarcation between a strong van der Waals force and a weak hydrogen bond or between a strong hydrogen bond and a weak valence link. We should therefore expect a rather continuous gradation between adsorption which arises from weak van der Waals forces on the one hand and adsorption which arises from strong and definite valence linkages on the other. Many adsorption processes do possess the properties which we should expect of the formation of valence linkages, namely, strong binding, relatively slow rates of adsorption and desorption, and high temperature coefficients of these rates.

Dependence of Adsorption on Concentration. Figure 4 presents a typical case of the adsorption of a gas by a solid, namely, that of nitrogen by mica. The ordinate x is the quantity of gas adsorbed by an amount of solid having a fixed surface, and the abscissa is the pressure P of the gas. Such data usually are in good agreement with the Langmuir equation

$$x = \frac{abP}{1 + aP} \tag{5}$$

in which a and b are constants at constant temperature. The equation may be rearranged to

$$\frac{P}{x} = \frac{1}{ab} + \frac{1}{b}P \tag{6}$$

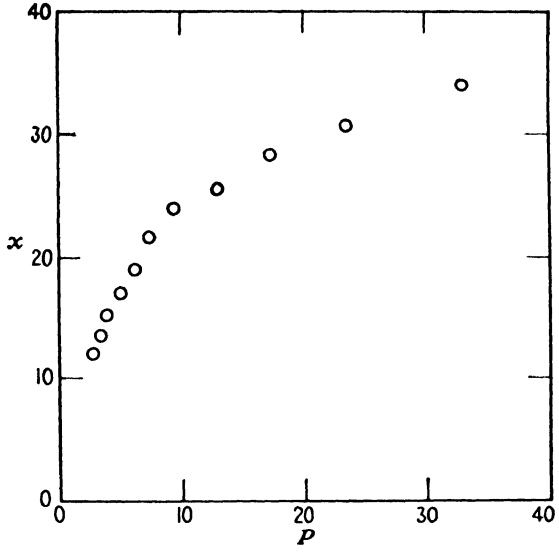


FIG. 4. Adsorption of nitrogen on mica at 90°K [*from data of Langmuir, J. Am. Chem. Soc.*, **40**, 1383 (1918)]. Plot of x, the quantity of nitrogen, in cubic millimeters measured at 20°C and 1 atm, adsorbed by a sample of mica having a surface of 5750 cm², against pressure P in centimeters of mercury.

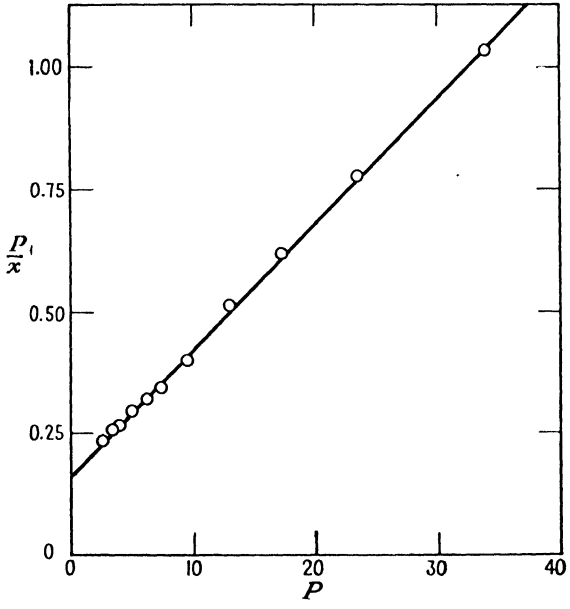


FIG. 5. Plot of the data of Fig. 4 according to the form P/x against P.

As Fig. 5 shows, a plot of P/x against P for the adsorption of nitrogen on mica is in fact linear to good precision.

In Fig. 6 the same data are plotted with log x as ordinate and log P as abscissa. Over a moderate range, but not over a wider one, the plot is linear. The equation

$$x = aP^m \tag{7}$$

with a and m constants, which the linearity suggests, is called the *Freundlich adsorption isotherm.*

For adsorption of a solute from solution either the Langmuir or the Freundlich equation may be used by substituting the concentration c of

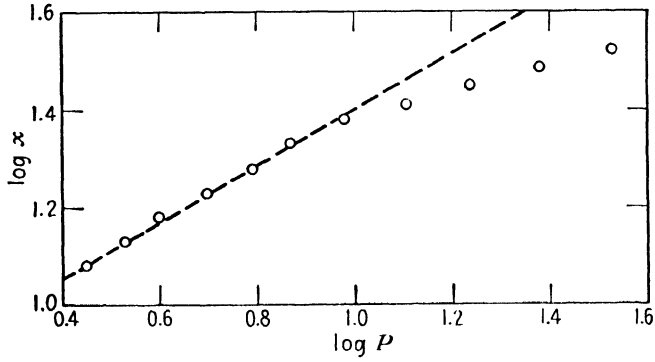


FIG. 6. Plot of the data of Fig. 4 according to log x against log P.

the solute for the P of Eq. (5) or (7). Either equation usually works moderately well over a useful range of concentration.

The Langmuir equation may be derived from gas kinetic theory. Let θ be the fraction of the suitable spots on the surface of the solid to which a molecule of the gas is attached. Then the rate r_c of further attachment of gas molecules should be proportional to the frequency of collision of gas molecules with the suitable spots which are not occupied. The total frequency of collision with the surface should be proportional to the pressure of the gas (page 19), and the frequency of collision with the unoccupied spots should therefore be proportional to the pressure multiplied by the fraction $1 - \theta$, that is,

$$r_c = k_c P(1 - \theta) \tag{8}$$

The rate at which adsorbed molecules leave the surface should be given by

$$r_e = k_e \theta \tag{9}$$

At equilibrium the two rates must be equal, which leads to

$$\theta = \frac{aP}{1 + aP} \tag{10}$$

with $a = k_c/k_e$. Since θ must be proportional to the quantity adsorbed per unit area of adsorbent, this equation is essentially identical with Eq. (5).

Chemical Reaction at a Surface; Diffusion Control. Any chemical reaction which involves on the one hand a solid, whether this be a reactant or a catalyst, and on the other hand a gas or liquid phase consists of a sequence of at least three processes. These are: (1) transport of reactant material in the fluid phase to the interface; (2) reaction at the interface; (3) transport of reaction product from the interface. As is the case with any system of successive processes (page 180) any one of these may be rate determining, or they may all be concerned in determining the rate.

Whenever the transport process is significant, stirring becomes of great importance. The case of a completely unstirred system can be handled mathematically, but the mathematics is rather complicated. More important from the chemist's point of view is the almost complete impossibility of preventing any stirring in a fluid material, because the reaction itself inevitably produces differences in temperature and density in different parts of the fluid which set up convection currents. The effect is not likely to be reproducible or susceptible to analysis.

The opposite case of thorough stirring is easily attainable, yields a reproducible situation suitable for measurement, conforms to simple mathematics, and is more likely to be related to practical chemical and engineering problems. Consider a large body of solution containing a reactant Y in contact with a solid, at whose surface Y reacts rapidly compared with its rate of diffusion up to the surface. If the solution is effectively stirred, the concentration of Y will at any given time be the same throughout most of the solution but will drop off in the near neighborhood of the interface in somewhat the way shown by the solid line in Fig. 7, in which the concentration c of reactant Y is plotted against x, the perpendicular distance from the surface of the solid.

It has been found to be an approximation of useful precision to suppose that the variation of concentration with distance is that represented by the dotted line of Fig. 7. This amounts to supposing that the stirring maintains the concentration constant up to a distance d from the interface and that the concentration varies linearly with x from $x = 0$ to $x = d$. The quantity d is often called the *thickness of the unstirred layer*. If we let c equal the concentration in the body of the solution and c_0 the concen-

tration at the interface, we can on this basis integrate Eq. (120) of Chap. IX for the diffusion process to obtain

$$\frac{dn}{dt} = DA\,\frac{c - c_0}{d} \tag{11}$$

A is the area of the interface at which reaction occurs.

The criteria which may be used to recognize a diffusion-controlled process are: sharp dependence on intensity of stirring, because this determines the value of d; a parallelism between rate and diffusion coefficient of reactant or product for a series of comparable reactions; a low energy of activation (page 199). By these criteria the rate-controlling step in most, but not in all, processes of solution of a solid in a liquid is diffusion of the dissolved material away from the interface. The dissolving of a

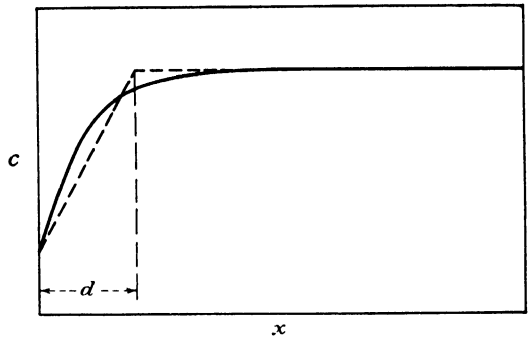


FIG. 7.

metal in an acid solution appears also to be diffusion-controlled, but controlled by diffusion of acid molecules up to the interface. The electrochemical reactions which occur at the surface of an electrode show every possible kind of situation, the control being in some cases entirely from diffusion, in others entirely from a chemical reaction, while in many cases both are important.

Heterogeneous Catalysis. The most thoroughly investigated case of the chemically controlled heterogeneous reaction is that in which the solid acts as catalyst for a reaction of gaseous substances. Consider first the case in which a single reacting substance is adsorbed on the catalyst surface according to Eq. (5) and reacts there at a rate proportional to the surface concentration, the moles per unit area of interface. For such a system we define rate of reaction as $-dn/dt$, where n is number of moles of reactant, not number of moles per liter. We therefore expect by Eq. (5) that

$$-\frac{dn}{dt} = \frac{kwP}{1 + aP} \tag{12}$$

P is the partial pressure of the reactant in the gas phase; w may be taken as the actual surface of the interface between solid and gas if this is known, or as the weight, which is proportional to surface for a catalyst of given degree of subdivision and structure; and k is proportional to the ab product of Eq. (5). We examine first two limiting cases.

If aP is small compared with unity, *i.e.*, if the adsorption is weak, Eq. (12) reduces to

$$-\frac{dn}{dt} = kwP \tag{13}$$

For a system of constant volume

$$\frac{dn}{dt} = \frac{v}{RT}\frac{dP}{dt} \tag{14}$$

Equating the two values of dn/dt, separating variables, and integrating, we have

$$\ln \frac{P_0}{P} = RT\frac{kw}{v}t \tag{15}$$

in which P_0 is the partial pressure of the reactant at time zero. This is of the form of the equation for a first-order homogeneous reaction. Figure 8 shows a plot of log P_0/P against time for the decomposition of

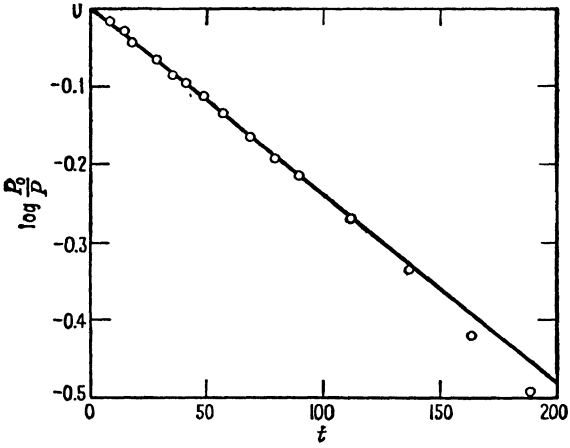


FIG. 8. Decomposition of phosphine on a glass surface at 446°C [*from data of Kooij, Z. physik. Chem.*, **12**, 155 (1893)]. P is partial pressure of phosphine at time t; P_0 is partial pressure of phosphine at time zero. Time in hours.

phosphine on a glass surface. Up to 50 per cent decomposition the plot is linear to good precision, but the rate seems to accelerate a bit toward the end of the reaction. Such deviations from simple laws are common in catalytic reactions of this kind.

If aP is large compared with unity, Eq. (12) reduces to

$$-\frac{dn}{dt} = \frac{kw}{a} \tag{16}$$

from which

$$\frac{dP}{dt} = -\mathbf{R}T\frac{kw}{av} \tag{17}$$

and

$$P = P^\circ - \mathbf{R}T\frac{kw}{av}t \tag{18}$$

Figure 9 plots the partial pressure P of ammonia in contact with a tungsten surface at 856°C against time. Over the range from 10 to 50 per cent

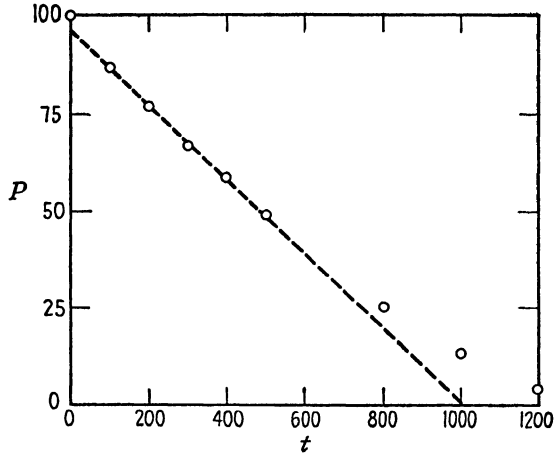


FIG. 9. Decomposition of ammonia on a tungsten surface at 856°C [*from data of Hinshelwood and Burk, J. Chem. Soc.*, **127**, 1105 (1925)]. P is partial pressure of ammonia in millimeters of mercury; t is time in seconds.

the plot is in good agreement with a straight line as indicated. Deviations appear both at the beginning and at the end of the reaction. The zero-order nature of the process is confirmed by the fact that the quantity of ammonia decomposed in 100 sec is equivalent to a drop in partial pressure of 14 mm in a certain volume when the initial pressure is 200 mm, to a drop of 13.5 mm when the initial pressure is 100 mm, and to a drop of 12 mm when the initial pressure is 50 mm.

In the general case we have from Eqs. (12) and (14)

$$\frac{dP}{dt} = \frac{\mathbf{R}Tkw}{v}\frac{P}{1+aP} \tag{19}$$

Separating variables and integrating, we get from this

$$\log \frac{P_0}{P} + a'P_0\left(1 - \frac{P}{P_0}\right) = k't \tag{20}$$

with $a' = 0.4343a$ and $k' = 0.4343\mathbf{R}Tkw/v$. Figure 10 plots data for the decomposition of stibine on an antimony surface. For the points marked

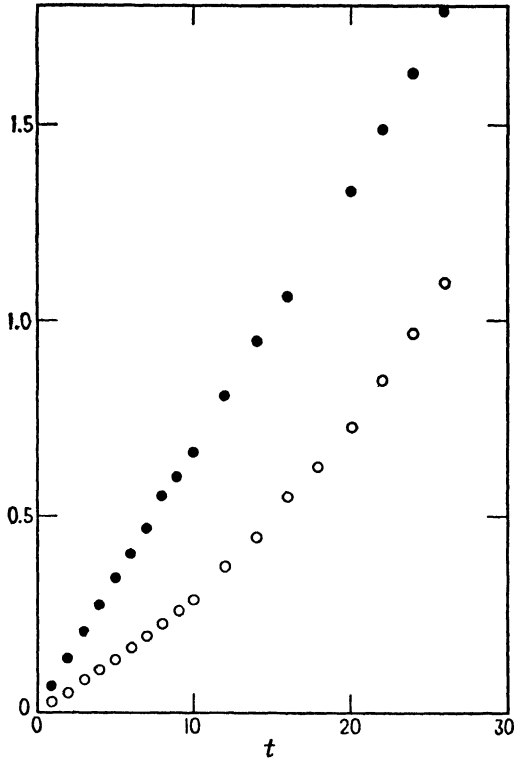


FIG. 10. Decomposition of stibine on an antimony surface [*from data of Stock and Bodenstein, Ber.*, **40**, 570 (1907)]. The abscissas are times. For the open circles the ordinate is log P_0/P, where P is partial pressure of stibine at time t and P_0 its partial pressure at time zero. For the closed circles the ordinate is log $(P_0/P) + 0.75\{1 - (P/P_0)\}$.

by the open circles the ordinates are log P_0/P, and the pronounced curvature shows that Eq. (15) does not apply. For the points marked by the closed circles the ordinates are $(\log P_0/P) + 0.75\{1 - P/P_0\}$. The linearity shows that it is possible to select a value of a' in Eq. (20) which makes k' constant. The data are therefore consistent with Eq. (20).

When two or more gases are present, they compete for the surface and in particular for the active spots, probably arising from irregularities in

the structure of the solid, at which reaction is most favored. A wide variety of effects can be predicted from theory and are found in practice. One phenomenon of considerable interest is a decrease in rate with increasing concentration of a particular substance. This substance would appear to compete so effectively and to lay claim to so large a proportion of the surface that the rate of reaction becomes proportional to the fraction of the surface not covered by this substance. In the simplest case, that in which the adsorption of the retardant is not affected by the other substances present, the fraction of the surface not covered by the retardant is given from Eq. (10) as $1/(1 + aP)$, where P is partial pressure of the retardant.

The retardant may be a substance not otherwise concerned in the reaction, in which case it is said to be a *catalyst poison*, especially if it is so strongly adsorbed that a small partial pressure produces a large retardation. It is not infrequently a product of the reaction, and in such cases the reaction rate drops off with time more rapidly than corresponds to the depletion of the reactant. It may even be one of the reactants when this is very strongly adsorbed and reaction depends upon molecules of another reactant reaching an unoccupied portion of the surface.

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PROBLEMS

1. Obtain an equation analogous to Eq. (20) for the reaction of a single substance adsorbed on a surface according to Eq. (7). Show that for such a system with $m < 1$ a plot of $\log P_0/P$ against time must be concave upward.

2. Suppose that gas 1 when present alone is adsorbed on a given adsorbent according to the equation $x_1 = a_1b_1P_1/(1 + a_1P_1)$ and that gas 2 when present alone is adsorbed according to $x_2 = a_2b_2P_2/(1 + a_2P_2)$. Show that the adsorption of gas 1 in the presence of gas 2 should follow the equation $x_1 = a_1b_1P_1/(1 + a_1P_1 + a_2P_2)$.

3. The parachor of a paraffin hydrocarbon is essentially independent of temperature, whereas the value for ethyl alcohol increases from 124.2 at −57°C to 131.0 at 200°C. Suggest an explanation for this difference.

4. If 1.0×10^{-4} g of stearic acid spread on water occupies an area of 470 cm^2 under conditions corresponding to the intersection of the curve of Fig. 3 with the axis of abscissas, calculate the area occupied by one stearic acid molecule and the length of the molecule. The density of stearic acid may be taken to be 0.84 g/cc.

5. From the following data on adsorption of acetic acid from aqueous solution by a sample of charcoal at 25°C calculate the constants of the Freundlich equation for the system:

c, mole/liter	0.018	0.031	0.062	0.126	0.268	0.471	0.882
x	0.47	0.62	0.80	1.11	1.55	2.04	2.48

6. At 0°C, 1 g of active carbon takes up the amounts of nitrogen x (in milliliters measured at 0°C and 1 atm) at the pressure P (in centimeters of mercury), as follows:

P	0.15	0.46	1.25	6.64	14.95	27.14	38 84	54.29	74.06
x	0.145	0.894	3.468	12.042	20.025	27.942	33 427	38.390	45.509

Obtain the constants of the Langmuir equation for this system.

7. If the reaction of a gaseous substance proceeds on the surface of a certain catalyst according to Eq. (13), what will be the effect on the quantity $-dP/dt$ of: (*a*) doubling the pressure of gas; (*b*) doubling the volume of the gas; (*c*) doubling the surface of the catalyst? Would any of these conclusions be altered if the reaction followed Eq. (16)?

8. The following data have been obtained for the decomposition of N_2O on a gold surface at 900°C, t being time in sec and x the quantity of N_2O reacted in cubic centimeters measured at 0°C and 1 atm:

t	900	1800	3180	3900	4800	6000	7200
x	33	64	100	114	130	146	156

Show that these data are consistent with Eq. (15).

APPENDIX A

SOME USEFUL MATHEMATICAL TECHNIQUES

I. THE SUMMATION SYMBOL

When one has to deal with the sum of a considerable number of terms, each of which can be distinguished by a numerical label, the summation symbol may be a useful abbreviation. We illustrate this by the pressure-volume product of a mixture of gases which we label as gas 1, gas 2, and gas 3. By Eq. (17) of Chap. I we have

$$Pv = (n_1 + n_2 + n_3)\mathbf{R}T \tag{1}$$

with the symbol n_1 meaning the number of moles of gas 1, n_2 the number of moles of gas 2, etc. This equation may also be written in the form

$$Pv = \left(\sum_{i=1}^{3} n_i\right)\mathbf{R}T \tag{2}$$

The symbol

$$\sum_{i=1}^{3}$$

means the sum of a series of terms, each of which is distinguished by a numerical *index* which may take any value from 1 to 3. The symbol i therefore stands for any of the integers in the range from 1 to 3 inclusive.

The number of moles n_1 of gas 1 is given by $n_1 = w_1/M_1$, where w is weight and M is molecular weight. Similarly for gas 2, $n_2 = w_2/M_2$, and more generally for gas i, or the "ith" gas,

$$n_i = \frac{w_i}{M_i} \tag{3}$$

Consequently we may write either

$$Pv = \left(\frac{w_1}{M_1} + \frac{w_2}{M_2} + \frac{w_3}{M_3}\right)\mathbf{R}T \tag{4}$$

or more compactly

$$Pv = \left(\sum_{i=1}^{3} \frac{w_i}{M_i}\right)\mathbf{R}T \tag{5}$$

The symbol w_i/M_i indicates unequivocally that the weight of each gas must be divided by *its own* molecular weight. To appreciate the value of this feature of the symbolism, write Eq. (4) as

$$Pv = \frac{w_1}{M_1}\mathbf{R}T + \frac{w_2}{M_2}\mathbf{R}T + \frac{w_3}{M_3}\mathbf{R}T \tag{6}$$

or in summation form

$$Pv = \sum_{i=0}^{3} \frac{w_i}{M_i}\mathbf{R}T \tag{7}$$

The *omission* of the subscript i from $\mathbf{R}$ and T indicates definitely that the weight of *each* gas is to be divided by the molecular weight of *that* gas and multiplied by a factor $\mathbf{R}T$ which has the *same* value for *all* the gases.

Comparing Eqs. (5) and (7), we see that

$$\sum_{i=1}^{3} \frac{w_i}{M_i}\mathbf{R}T = \mathbf{R}T \sum_{i=1}^{3} \frac{w_i}{M_i} \tag{8}$$

In general then we may take outside the summation sign any factor common to all the terms, and we can recognize a factor of this kind by the fact that the symbols involved do not carry the index i. Likewise we may insert into the expression following the summation sign any factor by which the whole sum is multiplied.

Suppose we wish to express in mathematical symbols and in the most general form the idea of which Eq. (1) is a limited example, namely, that the Pv product for a mixture of gases is equal to $\mathbf{R}T$ multiplied by the sum of the numbers of moles of all the gases present, no matter whether many gases are present or only one. We may then write

$$Pv = \mathbf{R}T \sum_i n_i \tag{9}$$

The summation symbol in this form means the sum of all the terms corresponding to the integers which may be represented by the index i in the problem under consideration. The important rules represented by Eqs. (5) and (8) are just as valid for this situation as for the more limited case. We have, for example,

$$Pv = \mathbf{R}T \sum_i n_i = \mathbf{R}T \sum_i \frac{w_i}{M_i} = \sum_i \frac{w_i}{M_i}\mathbf{R}T \tag{10}$$

The summation symbol may be used to represent the sum of a series of terms arranged in ascending order of the integral exponents of a variable,

the index being then the value of the exponent. We may, for instance, write the virial equation of Chap. I in the form

$$PV = a_0 + a_1P + a_2P^2 \tag{11}$$

In terms of the summation symbol this becomes

$$PV = \sum_{i=0}^{2} a_iP^i \tag{12}$$

In the particular case of oxygen at 0°C, $a_0 = 22.414$, $a_1 = -0.02226$, and $a_2 = 4.90 \times 10^{-5}$, but Eq. (12) is a way of making the general statement that a power series in P of three terms is a good fit to the actual properties of the gas.

We know that if we require high precision or if we wish to cover a wide range of pressures we must add terms of the nature of a_3P^3, a_4P^4, etc., to Eq. (11) and that in principle we have to deal with an infinite series even though the terms in higher powers of P may be neglected for many practical purposes. The infinite series may be written

$$PV = \sum_{i=0}^{\infty} a_iP^i \tag{13}$$

The infinite series into which various functions may be expanded by Taylor's theorem (ST 393–416) may sometimes be conveniently represented in terms of the summation symbol. Thus the expansion

$$(1 - x)^{-2} = 1 + 2x + 3x^2 + 4x^3 + \cdots \tag{14}$$

may be written as

$$(1 - x)^{-2} = \sum_{i=0}^{\infty} (i + 1)x^i \tag{15}$$

Sometimes the gain in compactness is compensated by a loss in clarity.

There is nothing in the process of going over from a limited number of terms to an infinite number of terms which restricts the validity of such relationships as Eq. (10). Thus if

$$y = \sum_{i=0}^{\infty} x_i \tag{16}$$

and if $x_1 = ak_1z_1$, $x_2 = ak_2z_2$, etc., then

$$y = a \sum_{i=0}^{\infty} k_iz_i \tag{17}$$

Although the symbols may seem complicated the derivation of Eq. (11) of Chap. VIII is a straightforward case of this kind of manipulation. We are able to insert the factor

$$e^{\epsilon_{a0}/kT}$$

into the summation over all values of i because none of the quantities in this factor are marked by the index i.

If

$$y = z_1 + z_2 + z_3 \tag{18}$$

then by a basic rule of the calculus

$$\frac{dy}{dx} = \frac{dz_1}{dx} + \frac{dz_2}{dx} + \frac{dz_3}{dx} \tag{19}$$

The question whether this kind of relationship remains valid if the number of terms in the series of Eq. (18) becomes infinite cannot be answered by simple mathematics. It has, however, been demonstrated for many series, including all power series, that

$$\frac{d}{dx}\sum_i z_i = \sum_i \frac{dz_i}{dx} \tag{20}$$

no matter whether the number of terms in the summation is finite or infinite. This rule is applied to an important problem on page 143.

It is also true for many series, including all power series, that

$$\int \sum_i a_i \, dx = \sum_i \int a_i \, dx \tag{21}$$

The result is almost obvious from the nature of an integral if the sum is finite.

The symbol $\sum_i a_i$ represents the sum of a series of quantities a_1, a_2, a_3, etc., which can be distinguished by an index i which takes successive integral values. The symbol $\sum_j b_j$ represents the sum of a series of quantities b_1, b_2, b_3, etc., which can similarly be distinguished by an index. To avoid confusion, we represent the index in this series by a different letter j. The product

$$\left(\sum_i a_i\right)\left(\sum_j b_j\right)$$

is therefore the sum of all possible products of one of the a quantities and one of the b quantities, *i.e.*, it is

$$(a_1b_1 + a_1b_2 + a_1b_3 + \cdots) + (a_2b_1 + a_2b_2 + a_2b_3 + \cdots) + (a_3b_1 + a_3b_2 + a_3b_3 + \cdots) + \cdots$$

Such a double summation is often represented by the symbol

$$\sum_i \sum_j a_i b_j$$

In terms of this we can express what we have said in this paragraph in the form

$$\left(\sum_i a_i\right)\left(\sum_j b_j\right) = \sum_i \sum_j a_i b_j \tag{22}$$

This relationship is used in an important argument on page 138.

II. PARTIAL DERIVATIVES

When we write as we did in Chap. I that the volume of a gas is inversely proportional to the pressure, we imply, even if we do not always express, a limitation, namely, that all pertinent variables except volume and pressure are being held constant. The expression $v = k/P$ or $Pv = k$ with a particular constant value of k is indeed usable only if the temperature and the total number of moles of gas are fixed. At some other temperature or with some other number of moles a similar expression would apply, but the constant k would have a different value. We could therefore write Boyle's law more accurately as

$$Pv = f(T,n) \tag{1}$$

This is to be read: The pressure-volume product is a function of temperature and number of moles. The implication is not merely that the value of the product changes when temperature or number of moles changes but also that the Pv product is constant if temperature and number of moles are kept constant, no matter what else changes.

Relationships involving only two variables are of course less complicated mathematically than relationships involving three or more variables. This is the reason the mathematics of two variable relationships is taught before the mathematics of three or more variables. Furthermore relationships involving two variables are easily represented graphically; those with more than two variables are not. Finally it is usually much easier to detect a relationship like Boyle's law from a set of measurements

of pressure and volume at a fixed temperature than it would be to recognize the applicability of the relationship

$$Pv = k(t + 273) \tag{2}$$

to a set of measurements of the values of P, v, and t when all of them vary.

For these reasons the physical scientist usually operates by first studying two-variable relationships, the other variables being either accidentally or deliberately maintained constant. Very typically the Boyle's law relationship between P and v was recognized before the general perfect-gas-law relationship involving P, v, n, and T. This procedure makes it easy to forget that the phenomena of nature always involve more than two variables and that the mathematics of two variables can be used for the description of natural phenomena only when all but two variables are kept constant. It is therefore important to have a set of symbols which avoids confusion. We have seen (page 75) that the energy change which accompanies the rise in temperature of a system by dT degrees has different values when the pressure is kept constant and when the volume is kept constant. In the first case the volume increases, in the second the pressure increases, so that the final volume is higher and the final pressure lower in the first case than in the second. The final states being different in the two cases, the energy changes involved in reaching these states need not be the same and are, in fact, quite different.

To keep track of such differences as these, we use the symbolism of the *partial derivative*. We write for the ratio of energy change to temperature change $(\partial E/\partial T)_P$ for the case that the pressure is constant and read this as "the partial derivative of energy with respect to temperature with pressure constant." Similarly the symbol for the case that volume is constant is $(\partial E/\partial T)_V$, which is read "the partial derivative of energy with respect to temperature with volume constant." If we wish to remind ourselves that some other variable is kept constant, we write its symbol also as a subscript. Thus if the system is a binary mixture of constant composition for which the mole fraction of one component is represented by N_1 and that of the other by N_2 we might write $(\partial E/\partial T)_{P,N_1}$ or $(\partial E/\partial T)_{P,N_2}$. We should not need to write $(\partial E/\partial T)_{P,N,N_2}$ because, in a binary solution in which N_1 is constant, N_2 is necessarily constant also.

When one is using the symbolism of partial derivatives, the symbol dE has the definite meaning of an infinitesimal change in energy without any restriction that pressure, volume, or any other variable is held constant. In pure mathematics one may have a functional relationship which involves two variables only. If, for instance, y is a function of x only, then dy/dx is completely unambiguous, because there are no other variables which may or may not be constant. In physical problems there are

always more than two variables, but the symbol dy/dx is often used in place of such symbols as $(\partial y/\partial x)_z$ when by the nature of the situation the quantity z is constant throughout the whole range of situations involved in the problem under consideration and a reiterated reminder of its constancy is not felt to be necessary.

On the experimental side one obtains the value of the partial derivative $(\partial E/\partial T)_P$ by setting up a system which can be maintained at constant pressure, by determining in this system the increments in energy which accompany various finite temperature rises, and by estimating the slope of the resulting plot of energy against temperature (page 74).

If on the other hand one possesses a known equation which relates the variables to each other and wishes to obtain the value of a partial derivative, one simply differentiates according to the rules for functions involving only two variables, treating the variables whose values are held constant in the same way that one would any other constant. Thus from the van der Waals equation

$$P = \frac{\mathbf{R}T}{V - b} - \frac{a}{V^2} \tag{3}$$

one obtains the derivative

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{\mathbf{R}T}{(V - b)^2} + \frac{a}{V^3} \tag{4}$$

by a straightforward differentiation with respect to V, the temperature T being treated just like the constant **R**. Similarly one can obtain the derivative

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\mathbf{R}}{V - b} \tag{5}$$

In addition to the fairly obvious things we have already pointed out we shall need in this book three theorems involving partial derivatives. The first has to do with the situation in which three or more variables change simultaneously. Consider a gaseous substance of fixed composition in a region of pressure and temperature in which condensation to a liquid or solid need not be considered. Then we know from experience (page 256) that the molal volume V is completely determined by the pressure P and the temperature T. If we choose some fixed temperature T', we can plot V against P and get a curve of the sort shown in Fig. 1. At some other temperature T'' we shall get a different curve as indicated. The slope at any point of any of the curves of this sort is the value at that point of the quantity $(\partial V/\partial P)_T$. Clearly the value of this derivative depends on both P and T; specifically the value at temperature T'' is different from the value at temperature T' even if the pressure is the same. We may

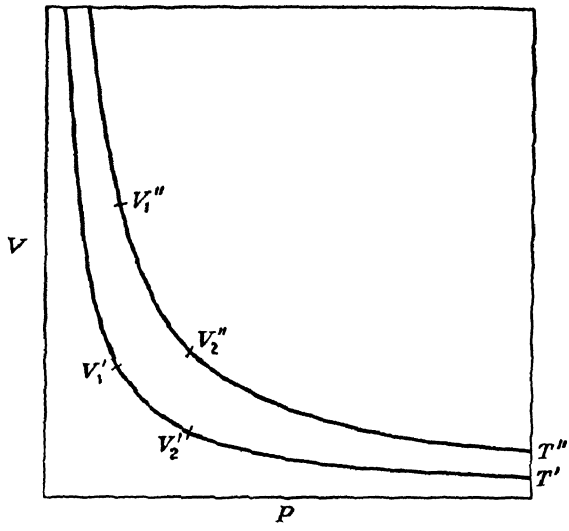


FIG. 1.

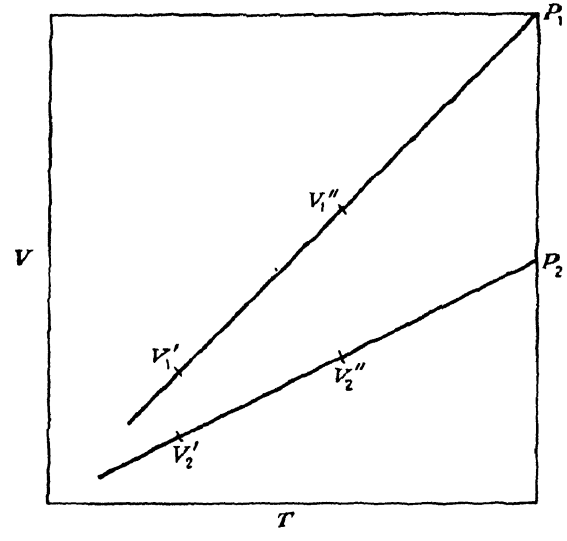


FIG. 2.

also plot V against T at some fixed pressure, getting what are nearly straight lines as indicated in Fig. 2. In Figs. 1 and 2 we have marked four points: V_1' is the volume at pressure P_1 and temperature T', V_1'' is the volume at pressure P_1 and temperature T'', V_2' is the volume at pressure P_2 and temperature T', etc. Consider now the difference $\Delta V = V_2'' - V_1' = (V_1'' - V_1') + (V_2'' - V_1'')$. The quantity $V_1'' - V_1'$

is not very different from $(\partial V/\partial T)_P(T'' - T')$, where $(\partial V/\partial T)_P$ is the slope of the upper curve in Fig. 2 at the point V_1''; in fact the two quantities would be identical if the gas were perfect and the plot truly linear. In any case the difference between them will decrease if the temperatures T'' and T' are brought closer together. In the same way the quantity $V_2'' - V_1''$ can be approximated by the quantity $(\partial v/\partial P)_T(P_2 - P_1)$, where $(\partial V/\partial P)_T$ is the slope of the upper plot of Fig. 1 at point V_1''. Because the plots of Fig. 1 are considerably curved, the approximation is not so good in this case as in the former one but it clearly is not bad if the difference between P_1 and P_2 is small. We have therefore the approximation

$$V_2'' - V_1' = \left(\frac{\partial V}{\partial T}\right)_P (T'' - T') + \left(\frac{\partial V}{\partial P}\right)_T (P_2 - P_1) \tag{6}$$

with the certainty that the approximation becomes better the smaller the intervals $T'' - T'$ and $P_2 - P_1$. If we go over to the limit, which we symbolize by writing dP for $P_2 - P_1$, dT for $T'' - T'$, and dV for $V_2'' - V_1'$, we have the exact equation

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \tag{7}$$

In the limit then the change in volume that results from simultaneous changes in both P and T is the sum of the changes that would result if each one of the independent variables changed alone while the other was constant.

This argument would fail if we were in the region of condensation. If the interval V_1' to V_2' included point A in Fig. 3, it would no longer be true or even unambiguous to state that lim $(V_2' - V_1') = (\partial V/\partial P)_T\, dP$. Equation (7) applies, therefore, only if the variables are continuous.

The argument can be extended to functions of more than two variables. Thus if the free energy f of a system at constant pressure and temperature is determined by the quantities n_A, n_B, and n_C of the three substances A, B, and C we may write

$$df = \left(\frac{\partial f}{\partial n_A}\right)_{T,P,n_B,n_C} dn_A + \left(\frac{\partial f}{\partial n_B}\right)_{T,P,n_A,n_C} dn_B + \left(\frac{\partial f}{\partial n_C}\right)_{T,P,n_A,n_B} dn_C \tag{8}$$

where df is the infinitesimal change in f that accompanies the changes dn_A, dn_B, and dn_C in the amounts of the three substances. The partial derivative $(\partial f/\partial n_A)_{T,P,n_B,n_C}$ is the rate at which f changes with changing n_A under conditions such that T, P, n_B, and n_C remain constant, *i.e.*, it is the slope of a plot of f against n_A for a system in which T, P, n_B, and n_C are

constant. Nothing we have said puts any limit on the kinds of variation in which n_A, n_B, and n_C may indulge. If, therefore, the substances A, B, and C may react according to $A + B \rightleftharpoons 2C$, and if we limit the changes

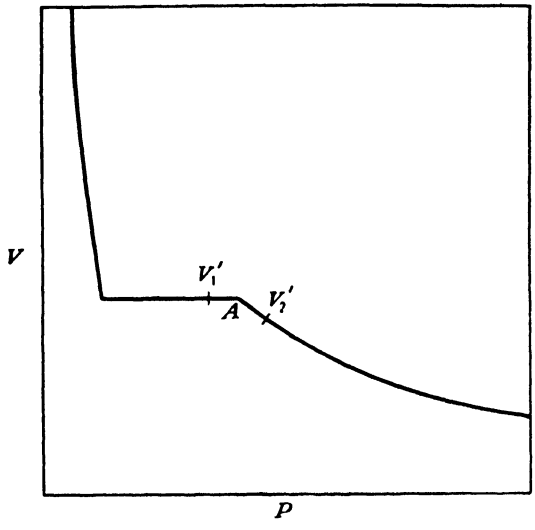


FIG. 3.

in n_A, n_B, and n_C to those which would result from this reaction, we may write in terms of the quantity of reaction dx (page 235)

$$dx = -dn_A = -dn_B = +\tfrac{1}{2}dn_C \tag{9}$$

Substituting in Eq. (8), we have

$$df = \left\{ -\left(\frac{\partial f}{\partial n_A}\right)_{T,P,n_B,n_C} - \left(\frac{\partial f}{\partial n_B}\right)_{T,P,n_A,n_C} + 2\left(\frac{\partial f}{\partial n_C}\right)_{T,P,n_A,n_B} \right\} dx \tag{10}$$

an equation which plays a very important role in chemical theory. It should be emphasized that even though we have specified that n_A can change only in such a way that n_B and n_C also change, the coefficient $(\partial f/\partial n_A)_{T,P,n_B,n_C}$ in Eq. (10) is the rate at which f changes with increasing n_A under such conditions that n_B and n_C do not change. This means that we can predict what happens in the complicated case in which the amounts of several substances change in an interlocking way in terms of the simpler situation in which the amount of a single substance changes.

The second theorem is concerned with second derivatives. If we take the derivative of both sides of Eq. (4) with respect to temperature, keeping volume constant, we get

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial V}\right)_T\right]_V = -\frac{\mathbf{R}}{(V-b)^2} \tag{11}$$

Similarly by differentiating Eq. (5) with respect to volume with temperature constant we get

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial P}{\partial T}\right)_V\right]_T = -\frac{\mathbf{R}}{(V-b)^2} \tag{12}$$

In this case then

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial V}\right)_T\right]_V = \left[\frac{\partial}{\partial V}\left(\frac{\partial P}{\partial T}\right)_V\right]_T \tag{13}$$

and we may write either of these second derivatives in the form

$$\frac{\partial^2 P}{\partial V \partial T} \quad \text{or} \quad \frac{\partial^2 P}{\partial T \partial V}$$

It can be shown that the relationship of which Eq. (13) is an example is generally valid provided the derivatives are continuous. Mathematicians usually dodge proving this principle in elementary courses in the calculus and merely show that the rule works in a number of examples, and we shall do no more.

We illustrate the third theorem by the following situation: Suppose we have the following information, but this only, about the properties of 1 mole of a gas: (1) if the volume and temperature are fixed, the pressure is completely determined, *i.e.*,

$$P = f(T,V) \tag{14}$$

(2) the partial derivative of pressure with respect to temperature is given by

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\mathbf{R}}{V-b} \tag{15}$$

with $\mathbf{R}$ and b constant. So long as we restrict ourselves to one fixed value of volume, we may treat this just as we do any relation between two variables and in particular we may separate variables (ST 230)

$$dP = \frac{\mathbf{R}}{V-b}\,dT \tag{16}$$

and integrate, obtaining

$$P = \frac{\mathbf{R}T}{V-b} + C \tag{17}$$

with C a constant. If we restrict ourselves to some other fixed volume, say V', we can carry out the corresponding integration, obtaining

$$P = \frac{\mathbf{R}T}{V'-b} + C' \tag{18}$$

Neither of the integration constants C and C' can be a function of temperature because differentiation of Eq. (17) leads to

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\mathbf{R}}{V - b} + \left(\frac{\partial C}{\partial T}\right)_V \tag{19}$$

This is identical with Eq. (15) only if $(\partial C/\partial T)_V = 0$, which is to say only if C is not a function of temperature. On the other hand there is nothing in the assumptions from which we started which enables us to say whether or not C or C' is a function of volume. Indeed we know that a van der Waals gas has properties consistent with Eqs. (14) and (15) and that the constant C takes the value a/V^2.

Consequently we may write as a more general and more explicit statement than Eq. (17) that, provided Eqs. (14) and (15) are valid,

$$P = \frac{\mathbf{R}T}{V - b} + f(V) \tag{20}$$

III. POWER-SERIES EXPANSIONS

In many areas of physical science, a number of which are discussed in this book, it is useful to convert a known function into an equivalent series in ascending integral powers of one of the variables. This is called *expanding* or *developing* the function in the form of a power series. Provided one accepts the rule that, if an infinite series of the form

$$y = a_0 + a_1x + a_2x^2 + a_3x^3 + a_4x^4 \cdots \tag{1}$$

converges, *i.e.*, has a finite sum, then its derivatives

$$\frac{dy}{dx} = a_1 + 2a_2x + 3a_3x^2 + 4a_4x^3 + \cdots \tag{2}$$

$$\frac{d^2y}{dx^2} = 2a_2 + 6a_3x + 12a_4x^2 + \cdots \tag{3}$$

etc., also converge, the technique is obvious (ST, 396). For if x approaches 0, then by Eq. (1) y approaches a_0; consequently

$$a_0 = \lim_{x \to 0} y \tag{4}$$

Similarly from Eq. (2), if x approaches 0, dy/dx approaches a_1; consequently

$$a_1 = \lim_{x \to 0} \frac{dy}{dx} \tag{5}$$

By similar reasoning

$$a_2 = \frac{1}{2} \lim_{x \to 0} \frac{d^2y}{dx^2} \tag{6}$$

$$a_n = \frac{1}{n!} \lim_{x \to 0} \frac{d^ny}{dx^n} \tag{7}$$

The series obtained by inserting these values of the a's in Eq. (1) is called a *Maclaurin's series*, and the procedure is called the expansion of the function y as a power series in the neighborhood of $x = 0$.

More generally, if we wish to obtain a power series of the form

$$y = a_0 + a_1(x - m) + a_2(x - m)^2 + a_3(x - m)^3 + \cdots \tag{8}$$

which is called a *Taylor's series* or an expansion of the function y in the neighborhood of $x = m$, we merely define a new variable $z = x - m$ and expand y as a Maclaurin's series in the variable z.

We illustrate the procedure by a fairly complicated example, that of obtaining a power series of the form

$$PV = A + BP + CP^2 + \cdots \tag{9}$$

which shall be equivalent to the van der Waals equation, which we put in the form

$$P = \frac{\mathbf{R}T}{V - b} - \frac{a}{V^2} \tag{10}$$

This requires that we obtain the quantities

$$A = \lim_{P \to 0} PV \tag{11}$$

$$B = \lim_{P \to 0} \frac{d(PV)}{dP} \tag{12}$$

etc. It is obvious from Eq. (10) that P can become zero only if V becomes infinite; hence we can write

$$A = \lim_{V \to \infty} PV \tag{13}$$

instead of Eq. (11), and similarly for Eq. (12), etc. By Eq. (10) we have

$$PV = \frac{\mathbf{R}TV}{V - b} - \frac{a}{V} \tag{14}$$

from which we see that as V increases without limit a/V approaches 0 and $V/(V - b)$ approaches 1; consequently

$$A = \mathbf{R}T \tag{15}$$

Equation (14) presents PV as an explicit function of V, and it cannot be converted into an explicit function of P. We could use the relation (ST 64)

$$\frac{d(PV)}{dP} = \frac{d(PV)}{dV}\frac{dV}{dP} \tag{16}$$

but the operations are easier if we use

$$\frac{d(PV)}{dP} = \frac{d(PV)}{dc}\frac{dc}{dP} \tag{17}$$

where $c = 1/V$ is concentration. In terms of c Eq. (10) becomes

$$P = \frac{\mathbf{R}Tc}{1 - bc} - ac^2 \tag{18}$$

from which

$$dP = \left\{\frac{\mathbf{R}T}{(1 - bc)^2} - 2ac\right\} dc \tag{19}$$

and

$$\frac{dc}{dP} = \frac{1}{\{\mathbf{R}T/(1 - bc)^2\} - 2ac} \tag{20}$$

Equation (14) becomes

$$PV = \frac{\mathbf{R}T}{1 - bc} - ac \tag{21}$$

from which

$$\frac{d(PV)}{dc} = \frac{\mathbf{R}Tb}{(1 - bc)^2} - a \tag{22}$$

Consequently we have

$$\frac{d(PV)}{dP} = \frac{\{\mathbf{R}Tb/(1 - bc)^2\} - a}{\{\mathbf{R}T(1 - bc)^2\} - 2ac} \tag{23}$$

Since we wish the limit of this quantity as $V \to \infty$ and since $c = 1/V$, we wish the limit for $c \to 0$. In this limit the quantity $1 - bc$ becomes 1 and $2ac$ becomes 0; consequently the right-hand member of Eq. (23) becomes $(\mathbf{R}Tb - a)/\mathbf{R}T$, and we have by Eq. (12)

$$B = b - \frac{a}{\mathbf{R}T} \tag{24}$$

To get the second derivative needed for the coefficient C, we use the relation

$$\frac{d^2(PV)}{dP^2} = \frac{d}{dP}\left\{\frac{d(PV)}{dP}\right\} = \frac{d}{dc}\left\{\frac{d(PV)}{dP}\right\}\frac{dc}{dP} \tag{25}$$

which leads to

$$\frac{d^2(PV)}{dP^2} = \frac{\left\{\frac{\mathbf{R}T}{(1-bc)^2} - 2ac\right\}\frac{2\mathbf{R}Tb^2}{(1-bc)^3} - \left\{\frac{\mathbf{R}Tb}{(1-bc)^2} - a\right\}\left\{\frac{2\mathbf{R}Tb}{(1-bc)^3} - 2a\right\}}{\left\{\frac{\mathbf{R}T}{(1-bc)^2} - 2ac\right\}^3} \tag{26}$$

From this

$$\lim_{c\to 0}\frac{d^2(PV)}{dP^2} = \frac{4\mathbf{R}Tab - 2a^2}{(\mathbf{R}T)^3} \tag{27}$$

Since the limit as $P \to 0$ is the same as the limit as $c \to 0$ and since further by Eq. (6)

$$C = \frac{1}{2}\lim_{P\to 0}\frac{d^2(PV)}{dP^2} \tag{28}$$

we have

$$C = \frac{2\mathbf{R}Tab - a^2}{(\mathbf{R}T)^3} \tag{29}$$

The following series occur frequently in physical chemical problems:

$$(1 \pm x)^{1/2} = 1 \pm \frac{1}{2}x - \frac{1\cdot 1}{2\cdot 4}x^2 \pm \frac{1\cdot 1\cdot 3}{2\cdot 4\cdot 6}x^3 \cdots \tag{30}$$

$$(1 \pm x)^{-1/2} = 1 \mp \frac{1}{2}x + \frac{1\cdot 3}{2\cdot 4}x^2 \mp \frac{1\cdot 3\cdot 5}{2\cdot 4\cdot 6}x^3 \cdots \tag{31}$$

$$(1 \pm x)^{-1} = 1 \mp x + x^2 \mp x^3 \cdots \tag{32}$$

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} \cdots \tag{33}$$

$$\ln(1 + x) = x - \tfrac{1}{2}x^2 + \tfrac{1}{3}x^3 - \tfrac{1}{4}x^4 \cdots \tag{34}$$

All these series converge provided $x^2 < 1$. They converge more rapidly, *i.e.*, a smaller number of terms are required to yield a given precision, the smaller the value of x.

IV. THE NUMERICAL SOLUTION OF EQUATIONS

Consider the problem of calculating from the known equilibrium constant the quantity of sulfur trioxide produced at equilibrium by the reaction of oxygen and sulfur dioxide. Specifically suppose a mixture of 1 mole of SO_2, 0.75 mole of O_2, and 7 moles of N_2 react at the constant pressure of 1 atm and at a temperature of 1000°K. At this temperature the equilibrium constant for the reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$ is 3.42 for

pressures in atmospheres. By Eq. (20) of Chap. VII the desired number of moles of SO_3 is the x of the equation

$$\frac{x^2\{1 + 0.75 + 7 - x/2)\}}{(1 - x)^2\{0.75 - x/2\}} = 3.42 \tag{1}$$

On rearranging and clearing of fractions this becomes

$$2.42x^3 + 5.53x^2 + 13.68x - 5.13 = 0 \tag{2}$$

which is a cubic.

Such an equation can be solved by computing the values of the quantity

$$f(x) = 2.42x^3 + 5.53x^2 + 13.68x - 5.13 \tag{3}$$

for each of a series of values of x, plotting $f(x)$ against x on suitable graph paper, and interpolating to find the intercept on the axis of abscissae, *i.e.*, the value of x which makes $f(x) = 0$. This is sometimes quite tedious, especially if any but a rough value is desired.

Newton's Method. We note first that a cubic equation may have three real roots but that the conditions of any unambiguous physical problem will make all but one root meaningless. In the present case the value of x cannot be greater than 1, since the quantity of SO_3 produced cannot be greater than the quantity of SO_2 available; it obviously cannot be less than 0. A rapid computation then shows that for $x = 0.3$, $f(x) = -0.5$, and for $x = 0.4$, $f(x) = +1.4$. We may therefore write

$$x = 0.3 + h \tag{4}$$

with the assurance that h will be considerably smaller than 0.3. The value of the first term in $f(x)$ may then be written in the form

$$2.42\{(0.3)^3 + 3(0.3)^2h + 3(0.3)h^2 + h^3\}$$

by using the binomial theorem. But if h is considerably smaller than 0.3, the quantity $3(0.3)h^2$ will be considerably smaller than the term $3(0.3)^2h$ and the term h^3 will be smaller yet. Consequently we may approximate the value of the braces by using only the first two terms, getting

$$2.42\{(0.3)^3 + 3(0.3)^2h\}$$

for the first term of $f(x)$. Similarly we may approximate the second term by $5.53\{(0.3)^2 + 2(0.3)h\}$. The original equation therefore becomes

$$2.42\{(0.3)^3 + 3(0.3)^2h\} + 5.53\{(0.3)^2 + 2(0.3)h\} + 13.68(0.3 + h) - 5.13 = 0 \tag{5}$$

This is linear in h and is easily solved to yield $h = 0.029$, from which $x = 0.329$. If we now set

$$x = 0.329 + h' \tag{6}$$

and repeat the process, we get $h' = -0.0030$, from which $x = 0.326$. This value of x satisfies the original equation to the precision to which the equilibrium constant is known; if it did not, the process could be repeated as many times as is necessary to obtain the desired precision.

This method is not limited to algebraic equations involving only integral powers of x or to algebraic equations generally; it can be used for equations containing e^x or $\ln x$ or any other function that can be expanded in a Taylor's series, of which the binomial theorem is a special case.

Other Methods of Approximation. Special methods of approximation often suggest themselves when some terms in an equation appear as small corrections to a much simpler equation. Consider the van der Waals equation in the form

$$V = \frac{RT}{P + (a/V^2)} + b \tag{7}$$

Provided the molal volume V is not very small, the term a/V^2 is small compared with the term P. Consequently a rough estimate of the value of V, obtained for instance from the perfect-gas equation, will yield a value of the quantity $P + a/V^2$ of respectable precision. If this is inserted in Eq. (7) and the value of the right-hand side calculated, the result should come fairly close to the actual value of V. For further precision this value of V can be used to calculate a new value of $P + (a/V^2)$, which can again be put into Eq. (7) to get a still better value of V.

V. CURVE FITTING AND PRECISION

We meet repeatedly in this book three questions which arise whenever experimental data are to be represented by a mathematical equation. These are: (1) Does the equation fit the data? (2) What are the best values of the constants of the equation? (3) What quantitative estimate can we furnish for the goodness of the fit of the equation? Consider for instance the data of Table 1 of Chap. I. The table contains a set of measurements of the corresponding values of pressure P and volume v for a particular sample of air at approximately constant temperature. It also contains the value of the product Pv for each set of values of P and v. If the equation

$$Pv = k \tag{1}$$

were exactly applicable to these data, the Pv values would be identical, whereas they actually vary over the range from 1400 to 1415, that is, by about 1 per cent. Yet we agreed in Chap. I, and any scientist would agree, that Eq. (1) is a "good" equation for these data because: (1) the 1 per cent variation in Pv is small compared with the fourfold range in the values of P and of v; (2) there is no tendency for the Pv values to be higher at one end, or the other end, or in the middle of the range of measurements.

If we were forced to give a completely unqualified answer to the question "Does Eq. (1) fit the data of this table?" we should have to say "No," but we should feel abused at being required to answer in this way and would know that a properly put question would allow a qualified answer, which we might try to phrase in such a form as "It fits reasonably well" or "as well as could be expected considering the techniques of measurement available." But this leads automatically to the problem of setting up some kind of quantitative definition of "goodness of fit."

This situation is inevitable in any problem of comparing an equation with experimental data. For a series of measurements of the volume of a sample of gas at a fixed pressure will show a scatter. The scatter may be large or small depending on the nature of the measuring instrument and on the extent to which pressure and temperature are controlled, but scatter there will be in honest and careful measurements no matter what the instrument and what the techniques of control. This is both an observed fact and a necessary conclusion from the kinetic molecular theory because the volume occupied by a gas under a fixed pressure is determined by the impacts of the molecules with the walls of the container and must in principle fluctuate.

The importance of the question "What are the best values of the constants of the equation" is illustrated by the data of Table 2 of Chap. I. These are in good agreement with the equation

$$Pv = a + bP \tag{2}$$

but not in exact agreement with it. Thus we can substitute the data of the first and last entries given for carbon dioxide into Eq. (2), obtaining

$$22.2643 = a + b$$
$$22.3897 = a + \frac{b}{6}$$

These simultaneous equations can be solved for a and b, yielding $a = 22.4148$ and $b = -0.1505$. But if we operated similarly on the first and fifth entries, we should get $a = 22.4152$ and $b = -0.1509$. Equation (2) is not therefore exactly applicable, because if it were, the values of a and b obtained in the second way should be identical with those

obtained in the first way. What then are the best values of a and b? The matter is important because our experimental definition of absolute temperature is that it is a quantity proportional to the value of a in Eq. (2). It is also important because our determinations of the atomic weights of the inert gases and some of our best determinations of other atomic weights depend upon the value of a in equations of the type of Eq. (2). If we do not do the best possible job in estimating the value of the constants in equations of this type, we decrease the precision with which we are able to measure the absolute temperature and to determine atomic weights.

Our third question arises because we inevitably wish to have some estimate of the reliability with which a temperature can be measured, and this depends upon the reliability with which a value of a can be obtained by fitting Eq. (2) to measurements of the pressure and volume of a gas.

In principle these questions can be answered only by making a very large number of experimental measurements and determining from them what is called a *frequency distribution.* In practice, however, physical scientists almost always answer the questions in ways which tacitly assume what is called a *normal distribution.* This is defined by the equation

$$y = \frac{h}{\sqrt{\pi}} e^{-h^2x^2} \tag{3}$$

Here x is the difference between a measured value of a particular qu[illegible] and the arithmetic mean of a large number of measurements of the [illegible] quantity, h is a constant, and y is such a quantity that $y\,dx$ is the fraction of the large number of measurements for which the difference lies between x and $x + dx$. A typical plot of y against x is shown in Fig. 4.

Probable Error. The mathematical theory of statistics shows that, if the measured values of a quantity such as the pressure-volume product k of Eq. (1) have a normal distribution, the best value of the quantity is the average or arithmetic mean of the observed values. The theory also permits the calculation of a quantity p called the *probable error* and given by

$$p = 0.6745 \sqrt{\frac{\sum_i (k_i - \bar{k})^2}{n - 1}} \tag{4}$$

where k_i is an individual observation of the value of the quantity, $\bar{k}$ is the mean of all the observed values, and n is the number of observations. The quantity $k_i - \bar{k}$ is what is called a *deviation;* it is the difference

between a single observed value of k and the average of all the values, and it may be either positive or negative. The square of the deviation is necessarily positive, and the quantity under the radical sign in Eq. (4) is the average of these squared deviations. According to the theory the probable error of a quantity has the important property that a new measurement of the quantity added to those from which the mean and the probable error were calculated is just as likely to differ from the mean by an amount less than p as it is to differ by an amount greater than p. The theory predicts further and more significantly that the chance that the new measurement will differ from the mean by an amount greater than

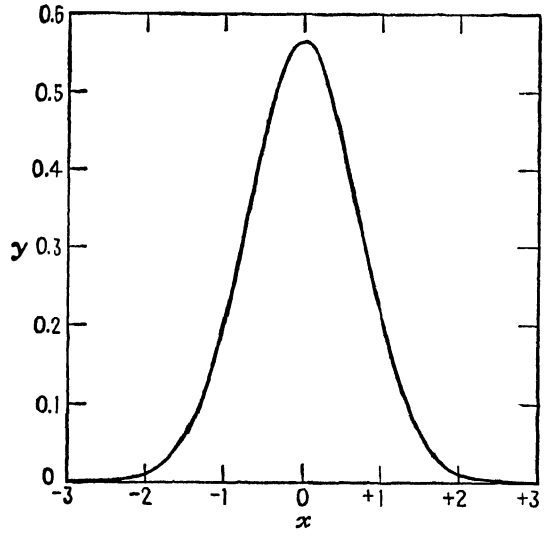


FIG. 4. The normal frequency distribution [Eq. (3)] for $h = 1$.

$3p$ is only 1 in about 20 and that the probability that it will differ from the mean by an amount greater than $5p$ is only 1 in a 1000.

The theory also predicts that the "probable error of the mean"

$$p_m = \frac{p}{\sqrt{n}} = \frac{0.6745}{\sqrt{n(n-1)}} \sqrt{\sum_i (k_i - \bar{k})^2} \tag{5}$$

is such a quantity that there is an even chance that the average of another set of n measurements will differ from the average from which p_m was computed by an amount less than p_m. The probability that the difference between the two averages shall be as much as 3 or 5 times p_m is expected to be small.

With respect to Eq. (1) or to any other one-constant equation we have then an answer to each of our three questions. The probable error of the

Pv product is a measure of the goodness of fit of the equation. The arithmetic mean of the observed Pv values is the best value of the constant k, and the probable error of the mean p_m is a measure of the reliability with which k is known.

These answers are, however, derived on the assumption of a normal distribution, and we know that many observed quantities do not show a normal distribution. Indeed it can be shown that if the observed values of P and of v in Table 1 of Chap. I each has a normal distribution the distribution of the values of the Pv product will not be normal. Nevertheless the accumulated experience of physical scientists has shown: (1) that the distribution of observed quantities is qualitatively similar to the normal distribution; (2) that the frequency of a large deviation from the mean drops off rapidly with the magnitude of the deviation; (3) that the mean is consequently a "good" value; (4) that the probability that an observed value shall differ from the mean by as much as $5p$ is extremely small; (5) that the probability that the averages of two sets of n measurements shall differ from each other by more than five times the value of p_m is likewise extremely small provided the number of measurements in a group is not too small. Furthermore the scatter in most measurements in physical science is small compared with the magnitude of the quantity measured, and the crucial judgments of the science depend upon differences which are many times greater than the observed scatter of the quantities compared. Consequently the physical scientist feels justified in limiting the number of measurements he makes of a given quantity to such a degree that it is impossible to estimate the actual frequency distribution. He also feels justified in using the conclusions derived for a normal distribution because these should represent at least a respectable approximation to the best value of a quantity and to a measure of the reliability with which the quantity is known. Biologists often need to use more exact statistical methods.

The probable error is one of a number of quantities which may be used as "precision indexes." Physical chemists often use the *standard deviation* σ given by

$$\sigma = \sqrt{\frac{\sum_i (k_i - \bar{k})^2}{n - 1}} \tag{6}$$

which is about 1½ times p. Provided the number of measurements is large and the distribution normal, the quantity h of Eq. (3) is related to p by the equation

$$p = \frac{0.477}{h} \tag{7}$$

and $1/h$ is therefore a measure of the scatter of the observations. The *average deviation* a is defined by

$$a = \frac{\sum_i |k_i - \bar{k}|}{n} \tag{8}$$

where $|k_i - \bar{k}|$ is the magnitude of the difference between the observed value k_i and the average value $\bar{k}$, that is, it is the difference taken positive regardless of its actual sign. For a large number of observations of a quantity with a normal distribution

$$a = 1.18p \tag{9}$$

Propagation of Errors. If one has reliable estimates of the scatter which affects a series of measurements of volume at constant pressure and of the scatter of a series of measurements of pressure at constant volume, another test for the goodness of fit of Eq. (1) may be applied. If we differentiate this equation for the situation that P is constant, we get

$$P\,dv = dk \tag{10}$$

It is a general principle of the calculus (ST 160) that the substitution of the small but finite quantities Δv and Δk for the differentials in an equation of this sort leads to an error which is small compared with the quantities Δv and Δk if the function involved is continuous. We may therefore write for the deviation Δk which results from a small deviation Δv with P constant

$$\Delta k = P\,\Delta v \tag{11}$$

If we divide this equation by Eq. (1), we get

$$\frac{\Delta k}{k} = \frac{\Delta v}{v} \tag{12}$$

This could also have been obtained by logarithmic differentiation of Eq. (1). By a similar argument we find for the situation that v is constant while P varies

$$\Delta k = v\,\Delta P \tag{13}$$

and

$$\frac{\Delta k}{k} = \frac{\Delta P}{P} \tag{14}$$

Suppose it is possible to determine that a series of measurements of volume at constant pressure shows a probable error Δv and that a series of measurements of pressure at constant volume shows a probable error

ΔP. Statistical theory shows that, provided the errors in the individual measurements are independent, the probable error in k is then given by the square root of the sum of the squares of the errors in k which would result from the separate errors in v and in P, that is,

$$\Delta k = \sqrt{(P\,\Delta v)^2 + (v\,\Delta P)^2} \tag{15}$$

and further that

$$\frac{\Delta k}{k} = \sqrt{\left(\frac{\Delta v}{v}\right)^2 + \left(\frac{\Delta P}{P}\right)^2} \tag{16}$$

The quantity $\Delta k/k$ is the relative probable error of k, the ratio of the probable error to the value of k.

A simple case, which may easily occur in practice, is offered by the situation in which both $\Delta v/v$ and $\Delta P/P$ are essentially constant, in which, therefore, the probability of a given per cent error in v is the same when v is small as it is when v is large. If these probable errors in v and in P can be estimated, it is possible to calculate a probable error in k by Eq. (16). It is also possible to calculate a probable error in k from the scatter of the values of the Pv product by Eq. (4). If the two values are nearly the same, we have further evidence that Eq. (1) is a good fit to the data; if not, we conclude either that Eq. (1) is not the best possible functional relationship between P and v or that other variables such as temperature have not been controlled with sufficient care.

If the probable errors in P and in v are not constant but can still be estimated, it is possible to calculate a series of values of $\Delta k/k$, one for small volumes, another for large volumes, and one or more for intermediate values of the volume. If the probable error calculated from the scatter of the Pv product is not much larger than the largest of these, Eq. (1) will be considered a good fit.

Weighted Means. Suppose we have evidence derived from an analysis of the kind considered in the last paragraph that values of the k of Eq. (1) derived from measurements at high pressures are more reliable than those at low pressures. The average of all the observed values of k would depend just as much on the less reliable low-pressure measurements as on the more reliable ones, whereas we obviously would wish to give more weight to the more reliable measurements. This can be done by taking the *weighted mean* defined by

$$\bar{k} = \frac{\sum_i w_i k_i}{\sum_i w_i} \tag{17}$$

Here k_i is an individual value of k and w_i is the weight, or measure of confidence, assigned to a value of k in this range of pressure. The weighted mean k is identical with the average one would obtain by repeating each individual measurement w times. Statistical theory leads to the conclusion that for a normal distribution the weight w of a quantity is related to its probable error p by the equation

$$w = \frac{m}{p^2} \tag{18}$$

where m is a constant for the series of measurements. If then one has obtained estimates of the probable error in k for various parts of the pressure range by the procedure of the last section, one can use the corresponding weights in Eq. (17). The value used for m makes no difference, since it cancels out between numerator and denominator of Eq. (17). The theory also predicts that the probable error of the weighted mean p_m is given by

$$p_m = 0.6745 \sqrt{\frac{\sum_i w_i(k_i - \bar{k})^2}{(n-1)\sum_i w_i}} \tag{19}$$

The Linear Equation in Two Variables. A relation between the experimental variables x and y of the form

$$y = a + bx \tag{20}$$

requires the selection of the best values of two constants a and b. Such a selection can often be made to a useful precision by graphical methods. One plots the values of y and x on graph paper on a suitably large scale and draws a line, using a transparent straightedge, in such a way that in any region of the plot the average distance from the line of the points lying on one side appears to equal the average distance from the line of the points on the other side. One then notes the values x_1, y_1 and x_2, y_2 of any two points lying in a convenient position on the line (these need not be experimental points) and obtains the value of b from

$$b = \frac{y_2 - y_1}{x_2 - x_1} \tag{21}$$

The value of a may be obtained from the intercept on the y axis, or, if this is inconvenient, the value may be computed, now that b has been chosen, from the coordinates of any point on the line, *e.g.*,

$$a = y_1 - bx_1 \tag{22}$$

Even if some method other than the graphical one is to be used for estimating the best values of a and b, it is desirable to make the plot as a first step. This shows easily whether or not a linear relation has any chance of success, it gives a quick idea of the scatter of the points from the line, and the graphically obtained values of the constants serve as a check against gross error in the other method of obtaining the values.

A serious disadvantage of the graphical method is the difficulty one has, even with the best of will, in avoiding a bias in the choice of the best line. One is likely either to pick a line which agrees more closely than the data justify with one's preconceived notion of where the line should lie or to overcompensate and err in the opposite direction.

The Method of Averages. A simple and often surprisingly satisfactory method of getting values of the constants of the linear equation is called the *method of averages*. We shall illustrate it by the data of Table 2 of Chap. I for carbon dioxide. If the equation

$$Pv = a + bP \tag{23}$$

were an exact fit to the data, the equation

$$22.2643 = a + b$$

would apply and so would the equations

$$\begin{aligned} 22.3148 &= a + \tfrac{2}{3}b \\ 22.3397 &= a + \tfrac{1}{2}b \\ 22.3654 &= a + \tfrac{1}{3}b \\ 22.3775 &= a + \tfrac{1}{4}b \\ 22.3897 &= a + \tfrac{1}{6}b \end{aligned}$$

Any two of these equations could be solved to obtain the values of a and b. But as we have seen, we should not get exactly the same a and b values from one pair of these equations as we should from another. We therefore select the half of these equations (as nearly as possible one-half if the number of equations is odd) for which P has the largest values and add them together to obtain

$$66.9188 = 3a + \tfrac{13}{6}b$$

Carrying out the same operation on the remaining three equations, we get

$$67.1326 = 3a + \tfrac{3}{4}b$$

These two equations may then be solved to obtain the values $a = 22.4154$ and $b = -0.1509$, for which we can at least say that they have been derived from all the experimental data and not from some arbitrarily selected pair. In particular it can be shown that these are the values of a

and b for which the sum of the deviations of the y values of the experimental points from those predicted by Eq. (23) is zero. It can also be shown that this method of selecting the values of a and b is the equivalent of the following procedure: One selects the three sets of P and v values corresponding to the larger values of P and averages the values of P to obtain a quantity $\bar{P}_1$. The average of the three v values is also computed to obtain $\bar{v}_1$. If the experimental points represented bodies of equal mass, a point having the coordinates $\bar{P}_1$, $\bar{v}_1$ would lie at the center of gravity of the three experimental points. By the same method one also computes the coordinates $\bar{P}_2$, $\bar{v}_2$ of a point which represents the center of gravity of the other three experimental points. Then the values of a and b obtained by the method of averages are the intercept and slope of a line drawn through $\bar{P}_1$, $\bar{v}_1$ and $\bar{P}_2$, $\bar{v}_2$.

The Method of Least Squares. If the equation

$$y = a + bx \tag{20}$$

is to be fitted to a series of measurements of the values of x and y, statistical theory shows that the best values of a and b are those which make the sum of the squares of the differences between the observed y values and those calculated from the equation a minimum provided: (1) the uncertainty in the measurement of x is negligible compared with that in the measurement of y; (2) the scatter of the y values in a series of measurements at the same value of x has a normal distribution. It can then be shown that the best values are given by

$$a = \frac{\Sigma x^2 \Sigma y - \Sigma x \Sigma xy}{n\Sigma x^2 - (\Sigma x)^2} \tag{24}$$

$$b = \frac{n\Sigma xy - \Sigma x \Sigma y}{n\Sigma x^2 - (\Sigma x)^2} \tag{25}$$

further that the probable error of a point p_y is given by

$$p_y = 0.6745 \sqrt{\frac{\Sigma(y - a - bx)^2}{n - 2}} \tag{26}$$

the probable error in the value of a by

$$p_a = p_y \sqrt{\frac{\Sigma x^2}{n\Sigma x^2 - (\Sigma x)^2}}$$

and the probable error in the value of b by

$$p_b = p_y \sqrt{\frac{n}{n\Sigma x^2 - (\Sigma x)^2}} \tag{27}$$

p_y is a quantity such that there is an even chance that the deviation of a

point from the line, expressed as $y - a - bx$, shall be less than p_y. p_b is a quantity such that there is an even chance that another series of n measurements of x and y would lead to a value of b which differed from the first set by an amount less than p_b. The quantity p_a bears a similar relation to the value of a.

A least-squares computation is somewhat tedious unless a calculating machine is available. And it is usually doubtful if the provisos which we mention in the first paragraph of this section are satisfied, and frequently certain that the first one is not. Nevertheless the least-squares method has become the standard and accepted method of obtaining the best values of the constants of a linear equation in all critical and important cases. The justification for this is essentially the same as for accepting the conclusions derived from the assumption of a normal distribution in the case of a single quantity (page 405).

Rectification of Equations. Many nonlinear equations involving two constants may be converted to the form of Eq. (20) by a suitable change in variables. This is called *rectification* of the plot. The problem of obtaining the coefficients then becomes the same as that involved with any linear equation. Some examples follow.

The equation

$$x = kP^m \tag{28}$$

may be changed to

$$\log x = \log k + m \log P \tag{29}$$

This is a linear relationship between the variables $\log P$ and $\log x$, whose slope is m and whose intercept on the axis of ordinates is $\log k$. The equation

$$c = c_0 e^{-kt} \tag{30}$$

is equivalent to

$$\log c = \log c_0 - 0.4343kt \tag{31}$$

This is a linear relationship between the variables t and $\log c$. The equation

$$PV = \mathbf{R}T + BP + CP^2 \tag{32}$$

is a two constant equation if $\mathbf{R}T$ is considered to be known exactly. It is equivalent to

$$\frac{PV - \mathbf{R}T}{P} = B + CP \tag{33}$$

which is a linear relationship between the variables P and $(PV - \mathbf{R}T)/P$. The equation

$$x = \frac{abP}{1 + aP} \tag{34}$$

can be rearranged either to

$$\frac{P}{x} = \frac{1}{ab} + \frac{1}{b}P \tag{35}$$

or to

$$\frac{1}{x} = \frac{1}{b} + \frac{1}{ab}\left(\frac{1}{P}\right) \tag{36}$$

Equation (35) is a linear relationship between the variables P and P/x; Eq. (36) is linear in the variables $1/P$ and $1/x$.

Other Two-constant Equations. Consider the van der Waals equation with the value of $\mathbf{R}T$ taken as known, and rearrange to the form

$$a = V^2\left(\frac{\mathbf{R}T}{V - b} - P\right) \tag{37}$$

If one makes a guess at a value of b, one can calculate a value of a for each pair of experimental P and v values. Unless the guess was very lucky, the set of a values obtained will show a trend, increasing or decreasing as P increases. Another guess at a value of b will lead to a new set of values of a which may show a greater or less trend than the first set. One can then usually make a third estimate of b on a more intelligent basis. By a continuation of this process one can determine the value of b for which the a values are most nearly constant. This calculation has been carried out for the data of Table 3 of Chap. I on the pressure-volume relationships of oxygen at 0°C, and the results are shown in Table 1. It is clear that the value $b = 0.025$ leads to a decrease in a with increasing pressure and that the value $b = 0.035$ leads to an increase. For $b = 0.029$ there is some evidence of a downward trend, and for $b = 0.031$ some evidence of an upward trend; further the average deviation is appreciably smaller with $b = 0.030$ than with either of the neighboring values. We conclude, therefore, that the best values of the van der Waals constants for these data are $a = 1.143$ and $b = 0.030$, but we have little certainty that either of the pairs of values 1.117 and 0.029 or 1.170 and 0.031 is not as good.

It should be noted that, while one can get nearly as good a fit with $b = 0.029$ as with $b = 0.030$, this is true only if the appropriate value of a is used with each value of b. The values $a = 1.117$ and $b = 0.030$ would fit poorly.

Three-constant Equations. When an equation involves three or more constants, the computation involved in selecting the constants so as to get the best fit to experimental data is inevitably tedious. We shall not attempt to discuss the methods here but refer to the discussion in Worthing and Geffner, "Treatment of Experimental Data," pp. 64–82, 250–260, John Wiley & Sons, Inc., New York, 1943.

TABLE 1

P	V	Value of a Calculated for b =				
		0.025	0.029	0.030	0.031	0.035
24.947	0.87816	1.021	1.117	1.141	1.165	1.262
24.993	0.87635	.....	1.120	1.144	1.168	
25.073	0.87335	.....	1.123	1.147	1.174	
49.721	0.43118	1.015	1.117	1.143	1.169	1.274
49.751	0.43090	.....	1.118	1.143	1.169	
73.744	0.28532	1.006	1.115	1.144	1.171	1.286
73.813	0.28509	.....	1.114	1.142	1.170	
98.486	0.21026	0.995	1.113	1.143	1.174	1.300
99.204	0.20864	.....	1.113	1.143	1.174	
Average.....	.....	.....	1.1166	1.1433	1.1704	
Average deviation.....	.....	.....	0.0025	0.0011	0.0025	

Empirical Differentiation. If y plots linearly against x, the derivative dy/dx is simply the coefficient b of the equation $y = a + bx$. We have already considered methods for obtaining the best value of this coefficient and of estimating its reliability. If the plot is not linear, one can plot the points, draw a best curve with a flexible splint, and estimate the slope of the tangent at any desired point. There are devices which can be of considerable help in obtaining the slope of the curve once this is drawn, but the problem of locating by eye the best curve to represent a set of experimental points is extremely difficult unless the points are very closely spaced and show less than the usual scatter.

Consequently it is almost always worth while to fit to the data some kind of an equation which can be differentiated analytically. Thus, if it can possibly be avoided, one does not estimate the rate of a chemical reaction by taking the slope of a curved plot like that of Fig. 2 of Chap. IX. Rather one tries such plots as that of $\log c$ against t and $1/c$ against t. If the plot of $\log c$ against t is linear, it is easy to get the slope and

$$\frac{d \log c}{dt} = \frac{0.4343}{c} \frac{dc}{dt} \tag{38}$$

The rate dc/dt follows immediately. If the plot of $1/c$ against t is linear, we have

$$\frac{d(1/c)}{dt} = -\frac{1}{c^2} \frac{dc}{dt} \tag{39}$$

Even if none of the plots suggested by theory is strictly linear, it may well happen that one of them has considerably less curvature than the plot of c against t. There is nothing about Eqs. (38) and (39) which restricts their

use to cases where the plot is linear. If then the plot of log c against t is nearly linear, it will be much easier to get a value of the slope than it would be from a plot of c against t and Eq. (38) will then give a value of the quantity dc/dt for any value of c. When all the plots suggested by theory have bad curvatures, it is sometimes possible to find empirical functions of the variables which give a more nearly linear plot, whose slope can be related to the desired derivative. An example of this kind of computation is given by Beste and Hammett, *J. Am. Chem. Soc.*, **62,** 2483 (1940).

Empirical Integration. It is frequently necessary to estimate the value of such a quantity as

$$\int_{x_1}^{x_2} y\,dx$$

The most desirable method involves fitting to the data an empirical equation of a form suitable for integration. Thus if $y = a + bx$, the value of the integral is given by

$$\int_{x_1}^{x_2} y\,dx = a(x_2 - x_1) + \tfrac{1}{2}b(x_2^2 - x_1^2) \tag{40}$$

If this technique is impossible or too inconvenient, a number of other methods are available.

A crude one involves plotting y as ordinate against x as abscissa on thin sheet metal or heavy paper of known weight per unit area, cutting out that section bounded by the curve and the axis of abscissas, and by the ordinates for $x = x_1$ and $x = x_2$, and weighing the section. The area of the section is of course equal to the desired integral and follows directly from its weight and the known weight per unit area. About the same kind of precision can be attained by counting squares and estimating fractions of squares on a plot on good graph paper. A somewhat better and certainly an easier job can be done with an instrument known as a *polar planimeter* (Worthing and Geffner, 98).

Various other methods require either that the original data consist of a set of values of y corresponding to a series of closely and *evenly* spaced values of x or that the curve be plotted and such a series of values of y and x be read from the curve. Call the values of the abscissas x_1, x_2, x_3, . . . , x_n and the corresponding values of the ordinate y_1, y_2, y_3, . . . , y_n. The "trapezoidal rule" corresponds to replacing the curve between each successive pair of points by a straight line. This leads to the result that

$$\int_{x_1}^{x_n} y\,dx = \Delta x\left(\frac{y_1 + y_n}{2} + \sum_{i=1}^{n-1} y_i\right) \tag{41}$$

Δx is the constant difference between successive values of x. "Simpson's one-third rule" usually, but not always, gives a closer approximation than the trapezoidal rule. It replaces the curve by a sequence of parabolas each one drawn through three successive points and leads to the result that

$$\int_{x_1}^{x_n} y\,dx = \frac{\Delta x}{3}\{(y_1 + y_n) + 2(y_3 + y_5 + \cdots + y_{n-2}) + 4(y_2 + y_4 + \cdots + y_{n-1})\} \quad (42)$$

It is necessary that n be an odd number.

REFERENCE

WORTHING and GEFFNER, "Treatment of Experimental Data," John Wiley & Sons, Inc., New York, 1943.

APPENDIX B

THE RELATION OF THE BOLTZMANN EQUATION TO CONSIDERATIONS OF PROBABILITY

The Case of a Single Perfect Gas. Consider the case of N molecules, all of the same kind, which compose a system whose energy E is fixed. We assume: (1) that the energy of interaction is negligible, *i.e.*, that we have essentially perfect-gas conditions; (2) that, except for the limitation imposed by the fixed number of molecules and the fixed total energy, the chance of a molecule being in one quantum state is the same as the chance of its being in another state; (3) that the multiplicity of most of the levels is large (this is true if the high multiplicity of the translational quantization is taken into account). It can then be shown from the theory of probability (Mayer and Mayer, "Statistical Mechanics," p. 438, John Wiley & Sons, Inc., New York, 1940) that the probability W_r that there will be N_r molecules in the group of g_r quantum states each of which has the energy ϵ_r is given by

$$W_r = \frac{(N_r + g_r - 1)!}{N_r!(g_r - 1)!} \tag{1}$$

Probabilities are multiplicative. The probability of having N_r molecules in the g_r states for each of which the energy is ϵ_r and also having N_q molecules in the g_q states of energy ϵ_q is the product of the individual probabilities, *i.e.*

$$W_{rq} = \frac{(N_r + g_r - 1)!}{N_r!(g_r - 1)!} \cdot \frac{(N_q + g_q - 1)!}{N_q!(g_q - 1)!} \tag{2}$$

The probability W of a "distribution" in which there are N_1 molecules in the states of energy ϵ_1, N_2 in the states of energy ϵ_2, etc., is therefore given by

$$W = \prod_i \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!} \tag{3}$$

The symbol $\prod_i$ stands for the product of a number of terms distinguished by an index i just as the symbol $\sum_i$ stands for a summation. From Eq. (3) we have

$$\ln W = \sum_i \{\ln (N_i + g_i - 1)! - \ln N_i! - \ln (g_i - 1)!\} \tag{4}$$

We now use the Stirling approximation

$$\ln n! \approx n \ln n - n \tag{5}$$

on each of the terms in Eq. (4). This is a good approximation when n is large. The quantities N_i and g_i will be large for most of the states, and it can be shown that the effect of those states for which these quantities are not large is negligible. Since we are committed to large values of N_i and g_i, we may properly neglect unity compared with g_i and with $N_i + g_i$. On this basis Eq. (4) becomes

$$\ln W = \sum_i \{(N_i + g_i) \ln (N_i + g_i) - N_i \ln N_i - g_i \ln g_i\} \tag{6}$$

We now wish to determine what is the most probable distribution, *i.e.*, that for which W and hence also $\ln W$ is a maximum. At the maximum a small variation $\delta \ln W$ produced by a small variation in any one of the N_i values must closely approximate zero. Consequently at the maximum

$$\delta \sum_i \{(N_i + g_i) \ln (N_i + g_i) - N_i \ln N_i - g_i \ln g_i\} = 0 \tag{7}$$

Carrying through the indicated differentiation, we have

$$\sum_i \{\ln (N_i + g_i) - \ln N_i\} \delta N_i = 0 \tag{8}$$

But since $N = \Sigma N_i$ and $E = \Sigma N_i \epsilon_i$ are constant, we know also that

$$\sum_i \delta N_i = 0 \tag{9}$$

$$\sum_i \epsilon_i \delta N_i = 0 \tag{10}$$

By Lagrange's method of undetermined multipliers the most general statement we can make about the variations is obtained by multiplying Eq. (8) by a quantity independent of the N_i's, which we represent by λ, by multiplying Eq. (10) by a similar quantity μ, and by subtracting the resulting equations from Eq. (8). This yields as the condition for the desired maximum probability

$$\sum_i \{\ln (N_i + g_i) - \ln N_i - \lambda - \mu \epsilon_i\} \delta N_i = 0 \tag{11}$$

This is to be true for all possible variations of the large number of quanti-

ties N_i. It must then be true if all the δN_i's are zero except δN_1, in which case Eq. (11) reduces to

$$\{\ln (N_1 + g_1) - \ln N_1 - \lambda - \mu\epsilon_1\}\ \delta N_1 = 0 \tag{12}$$

which can be valid only if the quantity in braces is zero. The same argument may be applied to any other level, and we therefore conclude that when W is a maximum the equation

$$\ln (N_i + g_i) - \ln N_i - \lambda - \mu\epsilon_i = 0 \tag{13}$$

must be satisfied for each of the energy levels. This can be rearranged to

$$N_i = \frac{g_i}{e^{(\lambda+\mu\epsilon_i)} - 1} \tag{14}$$

This result conforms to what are called *Bose-Einstein statistics*. If we had assumed that only one molecule could be present in any single quantum state, as is the case in quantum theory for the electrons in a metal, we should have obtained the result

$$N_i = \frac{g_i}{e^{(\lambda+\mu\epsilon_i)} + 1} \tag{15}$$

This conforms to what are called *Fermi-Dirac statistics*.

In the case of either variety of statistics the equation reduces to

$$N_i = g_i e^{-(\lambda+\mu\epsilon_i)} \tag{16}$$

provided

$$e^{(\lambda+\mu\epsilon_i)} \gg 1$$

This turns out to be the case in every situation of direct chemical interest. Equation (16) may conveniently be written as

$$N_i = \Lambda g_i e^{-\mu\epsilon_i} \tag{17}$$

with

$$\Lambda = e^{-\lambda}$$

It may be shown from quantum theory that the translational quantum states of a perfect gas, and hence all the quantum states of a perfect monoatomic gas at moderate temperatures, are such that the energy ϵ of a state is given by

$$\epsilon = \frac{\mathbf{h}^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2) \tag{18}$$

(Mayer and Mayer, 45). Here m is the mass of the molecule, a is the length of edge of the enclosure treated as a cube (any other enclosure may be treated as the sum of small cubes), and n_x, n_y, and n_z are quantum num-

bers which may have any integral value. If the n's are large, there are many combinations of individual sets of values of n_x, n_y, and n_z which lead to the same value of ϵ. The multiplicity of the levels is therefore large and may be shown (Mayer and Mayer, 53) to be given by

$$g_i = \frac{\sqrt{32}\,\pi m^{3/2} a^3}{\mathbf{h}^3}\,\epsilon_i^{1/2} \tag{19}$$

Consequently by Eq. (17) the number of molecules N_i which have the energy ϵ_i is given by

$$N_i = \Lambda \frac{\sqrt{32}\,\pi m^{3/2} a^3}{\mathbf{h}^3}\,\epsilon_i^{1/2} e^{-\mu\epsilon_i} \tag{20}$$

The energy of these N_i molecules is then

$$N_i\epsilon_i = \Lambda \frac{\sqrt{32}\,\pi m^{3/2} a^3}{\mathbf{h}^3}\,\epsilon_i^{3/2} e^{-\mu\epsilon_i} \tag{21}$$

and the energy E of all the molecules is given by

$$E = \sum_i N_i\epsilon_i = \Lambda \frac{\sqrt{32}\,\pi m^{3/2} a^3}{\mathbf{h}^3} \sum_i \epsilon_i^{3/2} e^{-\mu\epsilon_i} \tag{22}$$

Since the translational energy levels are closely spaced, the sum may be replaced by an integral, whose value is known, thus:

$$\sum_i \epsilon_i^{3/2} e^{-\mu\epsilon_i} \approx \int_0^\infty \epsilon^{3/2} e^{-\mu\epsilon}\, d\epsilon = \frac{1}{\mu^{5/2}} \frac{3\pi}{4} \tag{23}$$

Similarly the total number of molecules N is given by

$$N = \sum_i N_i = \Lambda \frac{\sqrt{32}\,\pi m^{3/2} a^3}{\mathbf{h}^3} \sum_i \epsilon_i^{1/2} e^{-\mu\epsilon_i} \tag{24}$$

This summation also may be replaced by an integral and evaluated as

$$\sum_i \epsilon_i^{1/2} e^{-\mu\epsilon_i} = \int_0^\infty \epsilon^{1/2} e^{-\mu\epsilon}\, d\epsilon = \frac{1}{\mu^{3/2}} \frac{\pi}{2} \tag{25}$$

From these results we get for the average energy of a molecule

$$\bar{\epsilon} = \frac{\sum_i N_i\epsilon_i}{\sum_i N_i} = \frac{3}{2}\frac{1}{\mu} \tag{26}$$

We know from kinetic theory that (page 24)

$$\bar{\epsilon} = \tfrac{3}{2}\mathbf{k}T \tag{27}$$

Consequently it must be true that

$$\frac{1}{\mu} = \mathbf{k}T \tag{28}$$

With this we convert Eq. (17) into the Boltzmann equation,

$$N_i = \Lambda g_i e^{-\epsilon_i/\mathbf{k}T} \tag{29}$$

Equilibrium in a Dissociation Reaction. Given a mixture of gases L, A, and B in which equilibrium prevails with respect to the reaction

$$L \rightleftharpoons A + B$$

The total probability of a distribution W is then given by

$$W = \prod_i \frac{(N_i^L + g_i^L - 1)!}{N_i^L!(g_i^L - 1)!} \times \prod_j \frac{(N_j^A + g_j^A - 1)!}{N_j^A!(g_j^A - 1)!} \times \prod_k \frac{(N_k^B + g_k^B - 1)!}{N_k^B!(g_k^B - 1)!} \tag{30}$$

in place of Eq. (3), and the equation for the variation [Eq. (8)] is replaced by

$$\sum_i \{\ln (N_i^L + g_i^L) - \ln N_i^L\}\ \delta N_i^L + \sum_j \{\ln (N_j^A + g_j^A) - \ln N_j^A\}\ \delta N_j^A + \sum_k \{\ln (N_k^B + g_k^B) - \ln N_k^B\}\ \delta N_k^B = 0 \tag{31}$$

In place of Eq. (9) we must now write the two equations

$$\sum_i \delta N_i^L + \sum_j \delta N_j^A = 0 \tag{32}$$

$$\sum_i \delta N_i^L + \sum_k \delta N_k^B = 0 \tag{33}$$

and in place of Eq. (10) we have

$$\sum_i \epsilon_i^L\ \delta N_i^L + \sum_j \epsilon_j^A\ \delta N_j^A + \sum_k \epsilon_k^B\ \delta N_k^B = 0 \tag{34}$$

We now multiply Eq. (32) by a factor λ_A, Eq. (33) by λ_B, and Eq. (34) by μ, subtract the resulting equations from Eq. (31), and carry through the same argument as in the case of a single gas. We get

$$N_i^L = e^{-\lambda_A} e^{-\lambda_B} g_i^L e^{-\epsilon_i^L/kT} \tag{35}$$

$$N_j^A = e^{-\lambda_A} g_j^A e^{-\epsilon_j^A/kT} \tag{36}$$

$$N_k^B = e^{-\lambda_B} g_k^B e^{-\epsilon_k^B/kT} \tag{37}$$

If now we form the ratio

$$\frac{\sum_j N_i^A \cdot \sum_k N_k^B}{\sum_i N_i^L}$$

we see that the factors $e^{-\lambda_A}$ and $e^{-\lambda_B}$ cancel out. This is the result used on page 94. We see also that by virtue of the proportionality between the g's and the volume a^3 indicated in Eq. (19), the N's involved in these summations are proportional to the volume (*cf.* page 135).

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Atomic Weights
1948

	Symbol	Atomic number	Atomic weight		Symbol	Atomic number	Atomic weight
Aluminum	Al	13	26.97	Molybdenum	Mo	42	95.95
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.2
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	30.98
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Carbon	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Protoactinium	Pa	91	231
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium	Cb	41	92.91	Rubidium	Rb	37	85.48
Copper	Cu	29	63.54	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150.43
Erbium	Er	68	167.2	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.06
Gadolinium	Gd	64	156.9	Silver	Ag	47	107.880
Gallium	Ga	31	69.72	Sodium	Na	11	22.997
Germanium	Ge	32	72.60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulfur	S	16	32.066
Hafnium	Hf	72	178.6	Tantalum	Ta	73	180.88
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium	Ho	67	164.94	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0080	Thallium	Tl	81	204.39
Indium	In	49	114.76	Thorium	Th	90	232.12
Iodine	I	53	126.92	Thulium	Tm	69	169.4
Iridium	Ir	77	193.1	Tin	Sn	50	118.70
Iron	Fe	26	55.85	Titanium	Ti	22	47.90
Krypton	Kr	36	83.7	Tungsten	W	74	183.92
Lanthanum	La	57	138.92	Uranium	U	92	238.07
Lead	Pb	82	207.21	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutecium	Lu	71	174.99	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	Hg	80	200.61	Zirconium	Zr	40	91.22