Preface to the First Edition

This book is an account of physical chemistry designed for students in the sciences and in engineering. It should also prove useful to chemists in industry who desire a review of the subject.

The treatment is somewhat more precise than is customary in elementary books, and most of the important relationships have been given at least a heuristic derivation from fundamental principles. A prerequisite knowledge of calculus, college physics, and two years of college chemistry is assumed.

The difficulty in elementary physical chemistry lies not in the mathematics itself, but in the application of simple mathematics to complex physical situations. This statement is apt to be small comfort to the beginner, who finds in physical chemistry his first experience with such applied mathematics. The familiar *x*'s and *y*'s of the calculus course are replaced by a bewildering array of electrons, energy levels, and probability functions. By the time these ingredients are mixed well with a few integration signs, it is not difficult to become convinced that one is dealing with an extremely abstruse subject. Yet the alternative is to avoid the integration signs and to present a series of final equations with little indication of their origins, and such a procedure is likely to make physical chemistry not only abstruse but also permanently mysterious. The derivations are important because the essence of the subject is not in the answers we have today, but in the procedure that must be followed to obtain these and tomorrow's answers. The student should try not only to remember facts but also to learn methods.

There is more material included in this book than can profitably be discussed in the usual two-semester course. There has been a growing tendency to extend the course in basic physical chemistry to three semesters. In our own course we do not attempt to cover the material on atomic and nuclear physics in formal lectures. These subjects are included in the text because many students in chemistry, and most in chemical engineering, do not acquire sufficient familiarity with them in their physics courses. Since the treatment in these sections is fairly descriptive, they may conveniently be used for independent reading.

In writing a book on as broad a subject as this, the author incurs an indebtedness to so many previous workers in the field that proper acknowledgement becomes impossible. Great assistance was obtained from many excellent standard reference works and monographs.

To my colleagues Hugh M. Hulburt, Keith J. Laidler, and Francis O. Rice, I am indebted for many helpful suggestions and comments. The skillful work of Lorraine Lawrence, R.S.C.J., in reading both galley and page proofs, was an invaluable assistance. I wish to thank the staff of Prentice-Hall, Inc. for their understanding cooperation in bringing the book to press. Last, but by no means least, are the thanks due to my wife, Patricia Moore, who undertook many difficult tasks in the preparation of the manuscript.

PREFACE TO THE SECOND EDITION

In preparing the second edition of this book, numerous corrections of details and improvements in presentation have been made in every chapter, but the general plan of the book has not been altered. My fellow physical chemists have contributed generously of their time and experience, suggesting many desirable changes. Special thanks in this regard are due to R. M. Noyes, R. E. Powell, A. V. Tobolsky, A. A. Frost, and C. O'Briain. A new chapter on photochemistry has been added, and recent advances in nuclear, atomic, and molecular structure have been described.

W. J. MOORE

Bloomington, Indiana

Contents

CHAPTER 1

The Description of Physicochemical Systems

1. The description of our universe. Since man is a rational being, he has always tried to increase his understanding of the world in which he lives. This endeavor has taken many forms. The fundamental questions of the end and purpose of man's life have been illumined by philosophy and religion. The form and structure of life have found expression in art. The nature of the physical world as perceived through man's senses has been investigated by science.

The essential components of the scientific method are experiment and theory. Experiments are planned observations of the physical world. A theory seeks to correlate observables with ideals. These ideals have often taken the form of simplified models, based again on everyday experience. We have, for example, the little billiard balls of the kinetic theory of gases, the miniature hooks and springs of chemical bonds, and the microcosmic solar systems of atomic theory.

As man's investigation of the universe progressed to the almost infinitely large distances of interstellar space or to the almost infinitesimal magnitudes of atomic structures, it began to be realized that these other worlds could not be adequately described in terms of the bricks and mortar and plumbing of terrestrial architecture. Thus a straight line might be the shortest distance between two points on a blackboard, but not between Sirius and Aldebaran. We can ask whether John Doe is in Chicago, but we cannot ask whether electron *A* is at point *B*.

Intensive research into the ultimate nature of our universe is thus gradually changing the meaning we attach to such words as "explanation" or "understanding." Originally they signified a representation of the strange in terms of the commonplace; nowadays, scientific explanation tends more to be a description of the relatively familiar in terms of the unfamiliar, light in terms of photons, matter in terms of waves. Yet, in our search for understanding, we still consider it important to "get a physical picture" of the process behind the mathematical treatment of a theory. It is because physical science is at a transitional stage in its development that there is an inevitable question as to what sorts of concepts provide the clearest picture.

2. Physical chemistry. There are therefore probably two equally logical approaches to the study of a branch of scientific knowledge such as physical chemistry. We may adopt a synthetic approach and, beginning with the structure and behavior of matter in its finest known states of subdivision, gradually progress from electrons to atoms to molecules to states of aggregation and chemical reactions. Alternatively, we may adopt an analytical treatment and, starting with matter or chemicals as we find them in the laboratory, gradually work our way back to finer states of subdivision as we require them to explain our experimental results. This latter method follows more closely the historical development, although a strict adherence to history is impossible in a broad subject whose different branches have progressed at very different rates.

Two main problems have occupied most of the efforts of physical chemists: the question of the position of chemical equilibrium, which is the principal problem of chemical thermodynamics; and the question of the rate of chemical reactions, which is the field of chemical kinetics. Since these problems are ultimately concerned with the interaction of molecules, their final solution should be implicit in the mechanics of molecules and molecular aggregates. Therefore molecular structure is an important part of physical chemistry. The discipline that allows us to bring our knowledge of molecular structure to bear on the problems of equilibrium and kinetics is found in the study of statistical mechanics.

We shall begin our introduction to physical chemistry with thermodynamics, which is based on concepts common to the everyday world of sticks and stones. Instead of trying to achieve a completely logical presentation, we shall follow quite closely the historical development of the subject, since more knowledge can be gained by watching the construction of something than by inspecting the polished final product.

3. **Mechanics: force.** The first thing that may be said of thermodynamics is that the word itself is evidently derived from "dynamics," which is a branch of mechanics dealing with matter in motion.

Mechanics is still founded on the work of Sir Isaac Newton (1642–1727), and usually begins with a statement of the well-known equation

$$f = ma$$

with

$$a = \frac{dv}{dt} = \frac{d^2r}{dt^2} \tag{1.1}$$

The equation states the proportionality between a vector quantity f, called the *force* applied to a particle of matter, and the acceleration a of the particle, a vector in the same direction, with a proportionality factor m, called the *mass*. A vector is a quantity that has a definite direction as well as a definite magnitude. Equation (1.1) may also be written

$$f = \frac{d(mv)}{dt} \tag{1.2}$$

where the product of mass and velocity is called the *momentum*.

With the mass in grams, time in seconds, and displacement r in centimeters (CGS system), the unit force is the *dyne*. With mass in kilograms, time in seconds, and displacement in meters (MKS system), the unit force is the *newton.*

Mass might also be introduced by Newton's "Law of Universal Gravitation,"

$$f = \frac{\mu m_1 m_2}{r_{12}^2}$$

which states that there is an attractive force between two masses proportional to their product and inversely proportional to the square of their separation. If this *gravitational mass* is to be the same as the *inertial mass* of eq. (1.1), the proportionality constant $\mu = 6.66 \times 10^{-8}$ cm³ sec⁻² g⁻¹.

The weight of a body, W, is the force with which it is attracted towards the earth, and naturally may vary slightly at various points on the earth's surface, owing to the slight variation of r_{12} with latitude and elevation, and of the effective mass of the earth with subterranean density. Thus

$$W = mg$$

At New York City, $g = 980.267$ cm per sec²; at Spitzbergen, $g = 982.899$; at Panama, $g = 978.243$.

In practice, the mass of a body is measured by comparing its weight by means of a balance with that of known standards ($m_1/m_2 = W_1/W_2$).

4. Work and energy. The differential element of work dw done by a force f that moves a particle a distance dr in the direction of the force is defined as the product of force and displacement,

$$dw = f\,dr \tag{1.3}$$

For a finite displacement from r_0 to r_1, and a force that depends only on the position r,

$$w = \int_{r_0}^{r_1} f(r)\,dr \tag{1.4}$$

The integral over distance can be transformed to an integral over time:

$$w = \int_{t_0}^{t_1} f(r)\,\frac{dr}{dt}\,dt$$

Introducing Newton's Law of Force, eq. (1.1), we obtain

$$w = \int_{t_0}^{t_1} m\,\frac{d^2r}{dt^2}\,\frac{dr}{dt}\,dt$$

Since $(d/dt)(dr/dt)^2 = 2(dr/dt)d^2r/dt^2$, the integral becomes

$$w = \int_{t_0}^{t_1} d\left[\tfrac{1}{2}\,m\left(\frac{dr}{dt}\right)^2\right] = \tfrac{1}{2}\,m\int_{t_0}^{t_1} d(v^2)$$

$$w = \tfrac{1}{2}mv_1^2 - \tfrac{1}{2}mv_0^2 \tag{1.5}$$

The *kinetic energy* is defined by

$$E_K = \tfrac{1}{2}mv^2$$

It is evident from eq. (1.5), therefore, that the work expended equals the difference in kinetic energy between the initial and the final states,

$$w = \int_{r_0}^{r_1} f(r)\,dr = E_{K1} - E_{K0} \tag{1.6}$$

An example of a force that depends only on position r is the force of gravity acting on a body falling in a vacuum; as the body falls from a higher to a lower level it gains kinetic energy according to eq. (1.6). Since the force is a function only of r, the integral in eq. (1.6) defines another function of r, which we may write

$$\int f(r)\,dr = -U(r)$$

Or

$$f(r) = -dU/dr \tag{1.7}$$

This new function $U(r)$ is called the *potential energy*. It may be noted that, whereas the kinetic energy E_K is zero for a body at rest, there is no naturally defined zero of potential energy; only differences in potential energy can be measured. Sometimes, however, a zero of potential energy is chosen *by convention*; an example is the choice $U(r) = 0$ for the gravitational potential energy when two bodies are infinitely far apart.

Equation (1.6) can now be written

$$\int_{r_0}^{r_1} f(r)\,dr = U(r_0) - U(r_1) = E_{K1} - E_{K0}$$

$$U(r_0) + E_{K0} = U(r_1) + E_{K1} \tag{1.8}$$

The sum of the potential and the kinetic energies, $U + E_K$, is the total mechanical energy of the body, and this sum evidently remains constant during the motion. Equation (1.8) has the typical form of an *equation of conservation*. It is a statement of the mechanical principle of the *conservation of energy*. For example, the gain in kinetic energy of a body falling in a vacuum is exactly balanced by an equal loss in potential energy. A force that can be represented by eq. (1.7) is called a *conservative force*.

If a force depends on velocity as well as position, the situation is more complex. This would be the case if a body is falling, not in a vacuum, but in a viscous fluid like air or water. The higher the velocity, the greater is the frictional or viscous resistance opposed to the gravitational force. We can no longer write $f(r) = -dU/dr$, and we can no longer obtain an equation such as (1.8). The mechanical energy is no longer conserved.

From the dawn of history it has been known that the frictional dissipation of energy is attended by the evolution of something called *heat*. We shall see later how the quantitative study of such processes finally led to the inclusion of heat as a form of energy, and hence to a new and broader principle of the conservation of energy.

The unit of work and of energy in the CGS system is the *erg*, which is the work done by a force of one dyne acting through a distance of one centimeter. Since the erg is a very small unit for large-scale processes, it is often convenient to use a larger unit, the *joule*, which is the unit of work in the MKS system. Thus,

$$1 \text{ joule} = 1 \text{ newton meter} = 10^7 \text{ ergs}$$

The joule is related to the absolute practical electrical units since

$$1 \text{ joule} = 1 \text{ volt coulomb}$$

The unit of power is the watt.

$$1 \text{ watt} = 1 \text{ joule per sec} = 1 \text{ volt coulomb per sec} = 1 \text{ volt ampere}$$

5. Equilibrium. The ordinary subjects for chemical experimentation are not individual particles of any sort but more complex *systems*, which may contain solids, liquids, and gases. A *system* is a part of the world isolated from the rest of the world by definite boundaries. The experiments that we perform on a system are said to measure its *properties*, these being the attributes that enable us to describe it with all requisite completeness. This complete description is said to define the *state* of the system.

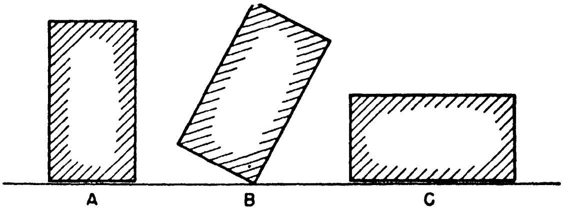


Fig. 1.1a. Illustration of equilibrium.

The idea of predictability enters here; having once measured the properties of a system, we expect to be able to predict the behavior of a second system with the same set of properties from our knowledge of the behavior of the original. This is, in general, possible only when the system has attained a state called *equilibrium*. A system is said to have attained a state of equilibrium when it shows no further tendency to change its properties with time.

A simple mechanical illustration will clarify the concept of equilibrium. Fig. 1.1a shows three different equilibrium positions of a box resting on a table. In both positions *A* and *C* the center of gravity of the box is lower than in any slightly displaced position, and if the box is tilted slightly it will tend to return spontaneously to its original equilibrium position. The gravitational potential energy of the box in positions *A* or *C* is at a minimum, and both positions represent *stable equilibrium* states. Yet it is apparent that position *C* is more stable than position *A*, and a certain large tilt of *A* will suffice to push it over into *C*. The position *A* is therefore said to be in ***metastable equilibrium***.

Position *B* is also an equilibrium position, but it is a state of ***unstable equilibrium***, as anyone who has tried to balance a chair on two legs will agree. The center of gravity of the box in *B* is higher than in any slightly displaced position, and the tiniest tilt will send the box into either position *A* or *C*. The potential energy at a position of unstable equilibrium is a maximum, and such a position could be realized only in the absence of any disturbing forces.

These relations may be presented in more mathematical form by plotting in Fig. 1.1b the potential energy of the system as a function of height r of the center of gravity. Positions of stable equilibrium are seen to be minima in the curve, and the position of unstable equilibrium is represented by a maximum. Positions of stable and unstable equilibrium thus alternate in any system. For an equilibrium position, the slope of the U vs. r curve, dU/dr, equals zero and one may write the equilibrium condition as

$$\text{at constant } r\ (= r_0), \qquad dU = 0$$

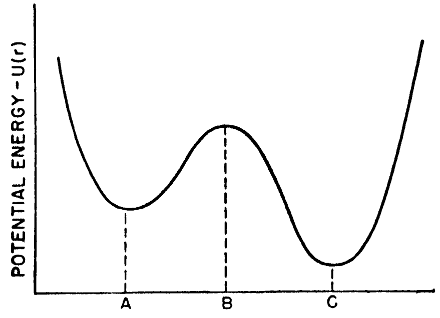


Fig. 1.1b. Potential energy diagram.

Although these considerations have been presented in terms of a simple mechanical model, the same kind of principles will be found to apply in the more complex physicochemical systems that we shall study. In addition to purely mechanical changes, such systems may undergo temperature changes, changes of state of aggregation, and chemical reactions. The problem of thermodynamics is to discover or invent new functions that will play the role in these more general systems that the potential energy plays in mechanics.

6. The thermal properties of matter. What variables are necessary in order to describe the *state* of a pure substance? For simplicity, let us assume that the substance is at rest in the absence of gravitational and electromagnetic forces. These forces are indeed always present, but their effect is most often negligible in systems of purely chemical interest. Furthermore let us assume that we are dealing with a fluid or an isotropic solid, and that shear forces are absent.

To make the problem more concrete, let us suppose our substance is a flask of water. Now to specify the state of this water we have to describe it in unequivocal terms so that, for example, we could write to a fellow scientist in Pasadena or Cambridge and say, "I have some water with the following properties. . . . You can repeat my experiments exactly if you bring a sample of water to these same conditions." First of all we might specify how much water we have by naming the mass m of our substance; alternatively we could measure the volume V, and the density ρ.

Another useful property, the *pressure*, is defined as the force normal to unit area of the boundary of a body (*e.g.*, dynes per square centimeter). In a state of equilibrium the pressure exerted by a body is equal to the pressure exerted upon the body by its surroundings. If this external pressure is denoted by P_{ex} and the pressure of the substance by P, at equilibrium $P = P_{ex}$.

We have now enumerated the following properties: mass, volume, density, and pressure (m, V, ρ, P). These properties are all mechanical in nature; they do not take us beyond the realm of ordinary dynamics. How many of these properties are really necessary for a complete description? We obviously must state how much water we are dealing with, so let us choose the mass m as our first property. Then if we choose the volume V, we do not need the density ρ, since $\rho = m/V$. We are left with m, V, and P. Then we find experimentally that, as far as mechanics is concerned, if any two of these properties are fixed in value, the value of the third is always fixed. For a given mass of water at a given pressure, the volume is always the same; or if the volume and mass are fixed, we can no longer arbitrarily choose the pressure. Only two of the three variables of state are *independent* variables.

In what follows we shall assume that a definite mass has been taken—say one kilogram. Then the pressure and the volume are not independently variable in mechanics. The value of the volume is determined by the value of the pressure, or vice versa. This dependence can be expressed by saying that V is a function of P, which is written

$$V = f(P) \qquad \text{or} \qquad F(P, V) = 0 \tag{1.9}$$

According to this equation, if the pressure is held constant, the volume of our kilogram of water should also remain constant.

Our specification of the properties of the water has so far been restricted to mechanical variables. When we try to verify eq. (1.9), we shall find that on some days it appears to hold, but on other days it fails badly. The equation fails, for example, when somebody opens a window and lets in a blast of *cold* air, or when somebody lights a *hot* flame near our equipment. A new variable, a *thermal* variable, has been added to the mechanical ones. If the pressure is held constant, the volume of our kilogram of water is greater on the *hot* days than on the *cold* days.

The earliest devices for measuring "degrees of hotness" were based on exactly this sort of observation of the changes in volume of a liquid.[1] In 1631, the French physician Jean Rey used a glass bulb and stem partly filled with water to follow the progress of fevers in his patients. In 1641, Ferdinand II, Grand Duke of Tuscany, invented an alcohol-in-glass "thermoscope." Scales were added by marking equal divisions between the volumes at "coldest winter cold" and "hottest summer heat." A calibration based on two fixed points was introduced in 1688 by Dalencé, who chose the melting point of snow as $-10°$, and the melting point of butter as $+10°$. In 1694

---

[1] A detailed historical account is given by D. Roller in No. 3 of the Harvard Case Histories in Experimental Science, *The Early Development of the Concepts of Temperature and Heat* (Cambridge, Mass.: Harvard Univ. Press, 1950).

Rinaldi took the boiling point of water as the upper fixed point. If one adds the requirement that both the melting point of ice and the boiling point of water are to be taken at a constant pressure of one atmosphere, the fixed points are precisely defined.

7. Definition of temperature. We have seen how our sensory perception of relative "degrees of hotness" came to be roughly correlated with volume readings on constant-pressure *thermometers*. We have not yet demonstrated, however, that these readings in fact measure one of the variables that define the state of a thermodynamic system.

Let us consider, for example, two blocks of lead with known masses. At equilibrium the state of block I can be specified by the independent variables P_1 and V_1. Similarly P_2 and V_2 specify the state of block II. If we bring the two blocks together and wait until equilibrium is again attained, *i.e.*, until P_1, V_1, P_2, and V_2 have reached constant values, we shall discover as an experimental fact that P_1, V_1, P_2, and V_2 are no longer all independent. They are now connected by a relation, the equilibrium condition, which may be written

$$F(P_1, V_1, P_2, V_2) = 0$$

Furthermore, it is found *experimentally* that two bodies separately in equilibrium with the same third are also in equilibrium with each other. That is, if

$$F(P_1, V_1, P_3, V_3) = 0$$

and

$$F(P_2, V_2, P_3, V_3) = 0$$

it necessarily follows that

$$F(P_1, V_1, P_2, V_2) = 0$$

It is apparent that these equations can be satisfied if the function F has the special form

$$F(P_1, V_1, P_2, V_2) = f(P_1, V_1) - f(P_2, V_2) = 0 \tag{1.10}$$

Thus F is the difference of two functions each containing properties pertaining to one body only. The function $f(P, V)$ defined in this way is called the *empirical temperature* t. This definition of t is sometimes called the *Zeroth Law of Thermodynamics*. From eq. (1.10) the condition for thermal equilibrium between two systems is therefore

$$f(P_1, V_1) = f(P_2, V_2) = t_1 = t_2 \tag{1.11}$$

It may be noted that, strictly speaking, the temperature is defined only for a state of equilibrium. The state of our one kilogram of water, or lead, is now specified in terms of three *thermodynamic variables*, P, V, and t, of which only two are independent.

8. The equation of state. The properties of a system may be classified as *extensive* or *intensive*. Extensive properties are additive; their value for the whole system is equal to the sum of their values for the individual parts.

Sometimes they are called *capacity factors*. Examples are the volume and the mass. Intensive properties, or *intensity factors*, are not additive. Examples are temperature and pressure. The temperature of any small part of a system in equilibrium is the same as the temperature of the whole.

If P and V are chosen as independent variables, the temperature is some function of P and V. Thus

$$t = f(P, V) \tag{1.12}$$

For any fixed value of t, this equation defines an *isotherm* of the body under consideration. The state of a body in thermal equilibrium can be fixed by specifying any two of the three variables, pressure, volume, and temperature.

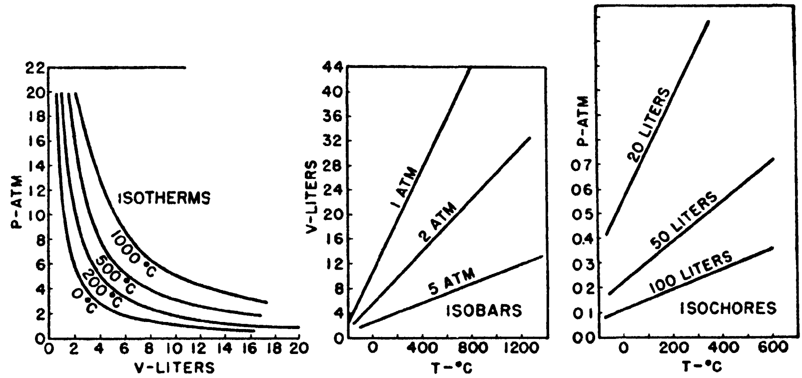


Fig. 1.2. Isotherms, isobars, and isochores for one gram of hydrogen.

The third variable can then be found by solving the equation. Thus, by analogy with eq. (1.12) we may have:

$$V = f'(t, P) \tag{1.13}$$

$$P = f''(t, V) \tag{1.14}$$

Equations such as (1.12), (1.13), (1.14) are called *equations of state*.

Geometrically considered, the state of a body in equilibrium can be represented by a point in the PV plane, and its isotherm by a curve in the PV plane connecting points at constant temperature. Alternatively, the state can be represented by a point in the Vt plane or the Pt plane, the curves connecting equilibrium points in these planes being called the *isobars* (constant pressure) and *isochores* or *isometrics* (constant volume) respectively. Examples of these curves for one gram of hydrogen gas are shown in Fig. 1.2.

We have already seen how eq. (1.12) can be the basis for a quantitative measure of temperature. For a liquid-in-glass thermometer, P is constant, and the change in volume measures the change in temperature. The Celsius (centigrade) calibration calls the melting point of ice at 1 atm pressure 0°C, and the boiling point of water at 1 atm pressure 100°C. The reading at other temperatures depends on the *coefficient of thermal expansion* α of the thermometric fluid,

$$\alpha = \frac{1}{V_0}\left(\frac{\partial V}{\partial t}\right)_P \tag{1.15}$$

where V_0 is the volume at 0°C and at the pressure of the measurements. If α is a constant over the temperature range in question, the volume increases linearly with temperature:

$$V_t = V_0 + \alpha t V_0 \tag{1.16}$$

This is approximately true for mercury, but may be quite far from true for other substances. Thus, although many substances could theoretically be used as thermometers, the readings of these various thermometers would in general agree only at the two fixed points chosen by convention.

9. Gas thermometry: the ideal gas. Gases such as hydrogen, nitrogen, oxygen, and helium, which are rather difficult to condense to liquids, have been found to obey approximately certain simple laws which make them especially useful as thermometric fluids.

In his book, *On the Spring of the Air*, Robert Boyle[2] reported in 1660 experiments confirming Torricelli's idea that the barometer was supported by the pressure of the air. An alternative theory proposed that the mercury column was held up by an invisible rigid thread in its interior. In answering this, Boyle placed air in the closed arm of a U-tube, compressed it by adding mercury to the other arm, and observed that the volume of gas varied inversely as the pressure. He worked under conditions of practically constant temperature.

Thus, at any constant temperature, he found

$$PV = \text{constant} \tag{1.17}$$

If the gas at constant pressure is used as a thermometer, the volume of the gas will be a function of the temperature alone.

By measuring the volume at 0°C and at 100°C a mean value of α can be calculated from eq. (1.16),

$$V_{100} = V_0(1 + 100\bar{\alpha}) \quad \text{or} \quad \bar{\alpha} = \frac{V_{100} - V_0}{100 V_0}$$

The measurements on gases published by Joseph Gay-Lussac in 1802, extending earlier work by Charles (1787), showed that this value of $\bar{\alpha}$ was a constant for "permanent" gases. Gay-Lussac found (1808) the value to be $\frac{1}{267}$. By a much better experimental procedure, Regnault (1847) obtained $\frac{1}{273}$. For every one-degree rise in temperature the fractional increase in the gas volume is $\frac{1}{273}$ of the volume at 0°C.

---

[2] *Robert Boyle's Experiments in Pneumatics*, Harvard Case Histories in Experimental Science No. 1 (Cambridge, Mass.: Harvard Univ. Press, 1950) is a delightful account of this work.

Later and more refined experiments revealed that the closeness with which the laws of Boyle and Gay-Lussac are obeyed varies from gas to gas. Helium obeys most closely, whereas carbon dioxide, for example, is relatively disobedient. It has been found that the laws are more nearly obeyed the lower the pressure of the gas.

It is very useful to introduce the concept of an *ideal gas*, one that follows the laws perfectly. The properties of such a gas usually can be obtained by extrapolation of values measured with real gases to zero pressure. Examples are found in some modern redeterminations of the coefficient $\bar{\alpha}$ shown plotted in Fig. 1.3. The extrapolated value at zero pressure is

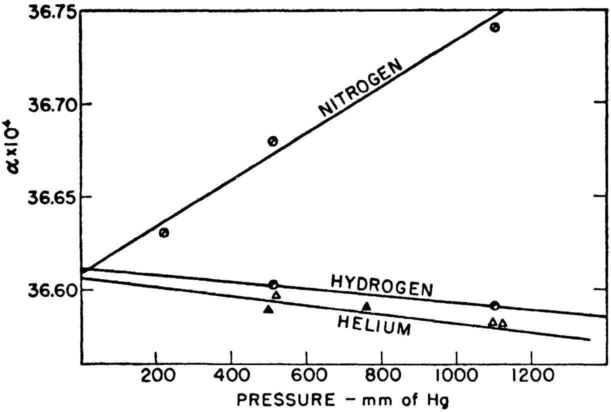


Fig. 1.3. Extrapolation of thermal expansion coefficients to zero pressure.

$$\alpha_0 = 36.608 \times 10^{-4}, \quad \text{or} \quad 1/\alpha_0 = 273.16$$

We may use such carefully measured values to define an *ideal gas temperature scale*, by introducing a new temperature,

$$T = t + \frac{1}{\alpha_0} = t + (273.16 \pm 0.01) \tag{1.18}$$

The new temperature T is called the *absolute temperature* (°K); the zero on this scale represents the limit of the thermal contraction of an ideal gas.

From eq. (1.16),

$$V_{T,P_0} = V_0\alpha_0 T = \frac{V_0 T}{273.16} = \frac{V_0 T}{T_0} \tag{1.19}$$

where V_0 is now the volume of gas at 0°C and standard atmospheric pressure P_0, and V_{T,P_0} is the volume at P_0 and any other temperature T. The temperature of the ice point on the absolute scale is written as T_0 (273.16°). Boyle's Law—eq. (1.17)—states that for a gas at temperature T

$$PV = P_0 V_{T,P_0}$$

Combining with eq. (1.19), we obtain

$$PV = \frac{P_0V_0}{T_0}T = C \cdot T \tag{1.20}$$

The value of the constant C depends on the amount of gas taken, but for a given volume of gas, it is the same for all ideal gases. Thus for 1 cc of gas at 1 atm pressure, $PV = T/273$.

For chemical purposes, the most significant volume is that of a mole of gas, a molecular weight in grams. In conformity with the hypothesis of Avogadro, this volume is the same for all ideal gases, being 22,414 cc at 0°C and 1 atm. Per mole, therefore,

$$PV = RT \tag{1.21}$$

where $R = 22{,}414/273.16 = 82.057$ cc atm per °C.

For n moles,

$$PV = nRT = \frac{m}{M}RT \tag{1.22}$$

where m is the mass of gas of molecular weight M. In all future discussions the volume V will be taken as the molar volume unless otherwise specified.

It is often useful to have the gas constant in other units. A pressure of 1 atm corresponds to 76.00 cm of mercury. A pressure of 1 atm in units of dynes cm^{-2} is 76.00 $\rho_{\text{Hg}}g_0$, where ρ_{Hg} is the density of mercury at 0°C and 1 atm, and g_0 is the standard gravitational acceleration. Thus 1 atm $= 76.00 \times 13.595 \times 980.665 = 1.0130 \times 10^6$ dyne cm^{-2}. The gas constant $R = 82.057 \times 1.0130 \times 10^6 = 8.3144 \times 10^7$ ergs deg^{-1} $\text{mole}^{-1} = 8.3144$ joules deg^{-1} mole^{-1}.

10. Relationships of pressure, volume, and temperature. The pressure, volume, temperature (PVT) relationships for gases, liquids, and solids would preferably all be succinctly summarized in the form of equations of state of the general form of eqs. (1.12), (1.13), and (1.14). Only in the case of gases has there been much progress in the development of these state equations. They are obtained not only by correlation of empirical PVT data, but also from theoretical considerations based on atomic and molecular structure. These theories are farthest advanced for gases, but more recent developments in the theory of liquids and solids give promise that suitable state equations may eventually be available in these fields also.

The ideal gas equation $PV = RT$ describes the PVT behavior of real gases only to a first approximation. A convenient way of showing the deviations from ideality is to write for the real gas:

$$PV = zRT \tag{1.23}$$

The factor z is called the *compressibility factor*. It is equal to PV/RT. For an ideal gas $z = 1$, and departure from ideality will be measured by the deviation of the compressibility factor from unity. The extent of deviations from ideality depends on the temperature and pressure, so z is a function of T and P. Some compressibility factor curves are shown in Fig. 1.4; these are determined from experimental measurements of the volumes of the gases at different pressures.

Useful PVT data for many substances are contained in the tabulated values at different pressures and temperatures of thermal expansion coefficients α [eq. (1.15)] and compressibilities β.[3] The *compressibility*[4] is defined by

$$\beta = -\frac{1}{V_0}\left(\frac{\partial V}{\partial P}\right)_T \qquad (1.24)$$

The minus sign is introduced because $(\partial V/\partial P)_T$ is itself negative, the volume decreasing with increasing pressure.

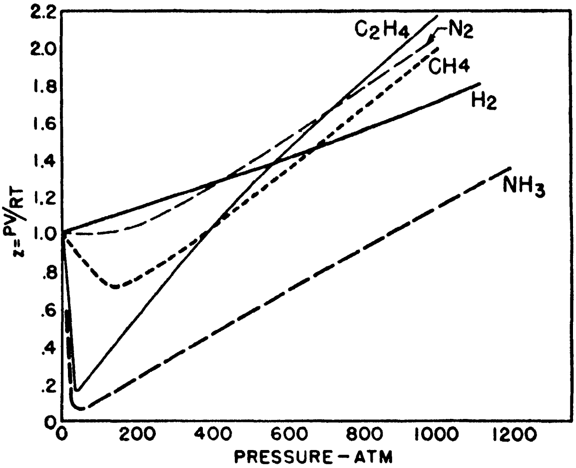


Fig. 1.4. Compressibility factors at 0°C.

Since $V = f(P, T)$, a differential change in volume can be written[5]:

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \qquad (1.25)$$

For a condition of constant volume, $V =$ constant, $dV = 0$, and

$$0 = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

Hence,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{-(\partial V/\partial T)_P}{(\partial V/\partial P)_T}. \qquad (1.26)$$

---

[3] See, for example, *International Critical Tables* (New York: McGraw-Hill, 1933); also J. H. Perry, ed., *Chemical Engineers' Handbook* (New York: McGraw-Hill, 1950), pp. 200, 205.

[4] Be careful not to confuse *compressibility* with *compressibility factor*. They are two distinctly different quantities.

[5] Granville, Smith, Longley, *Calculus* (Boston: Ginn, 1934), p. 412.

Or, from eqs. (1.15) and (1.24), $(\partial P/\partial T)_V = \alpha/\beta$. The variation of P with T can therefore readily be calculated if we know α and β.

An interesting example is suggested by a common laboratory accident, the breaking of a mercury-in-glass thermometer by overheating. If a thermometer is exactly filled with mercury at 50°C, what pressure will be developed within the thermometer if it is heated to 52°C? For mercury, $\alpha = 1.8 \times 10^{-4}$ deg^{-1}, $\beta = 3.9 \times 10^{-6}$ atm^{-1}. Therefore $(\partial P/\partial T)_V = \alpha/\beta = 46$ atm per deg. For $\Delta T = 2°$, $\Delta P = 92$ atm. It is apparent why even a little overheating will break the usual thermometer.

11. Law of corresponding states. If a gas is cooled to a low enough temperature and then compressed, it can be liquefied. For each gas there is a characteristic temperature above which it cannot be liquefied, no matter how great the applied pressure. This temperature is called the *critical temperature* T_c, and the pressure that just suffices to liquefy the gas at T_c is called the *critical pressure* P_c. The volume occupied at T_c and P_c is the *critical volume* V_c. A gas below the critical temperature is often called a *vapor*. The critical constants for various gases are collected in Table 1.1.

TABLE 1.1

CRITICAL POINT DATA AND VAN DER WAALS CONSTANTS

Formula	T_c (°K)	P_c (atm)	V_c (cc/mole)	a (l^2 atm/mole^2)	b (cc/mole)
He	5.3	2.26	57.6	0.0341	23.7
H_2	33.3	12.8	65.0	0.244	26.6
N_2	126.1	33.5	90.0	1.39	39.1
CO	134.0	35.0	90.0	1.49	39.9
O_2	153.4	49.7	74.4	1.36	31.8
C_2H_4	282.9	50.9	127.5	4.47	57.1
CO_2	304.2	73.0	95.7	3.59	42.7
NH_3	405.6	111.5	72.4	4.17	37.1
H_2O	647.2	217.7	45.0	5.46	30.5
Hg	1823.0	200.0	45.0	8.09	17.0

The ratios of P, V, and T to the critical values P_c, V_c, and T_c are called the *reduced* pressure, volume, and temperature. These reduced variables may be written

$$P_R = \frac{P}{P_c}; \quad V_R = \frac{V}{V_c}; \quad T_R = \frac{T}{T_c} \tag{1.27}$$

To a fairly good approximation, especially at moderate pressures, all gases obey the same equation of state when described in terms of the reduced variables, P_R, V_R, T_R, instead of P, V, T. If two different gases have identical values for two reduced variables, they therefore have approximately identical values for the third: They are then said to be in *corresponding states*, and

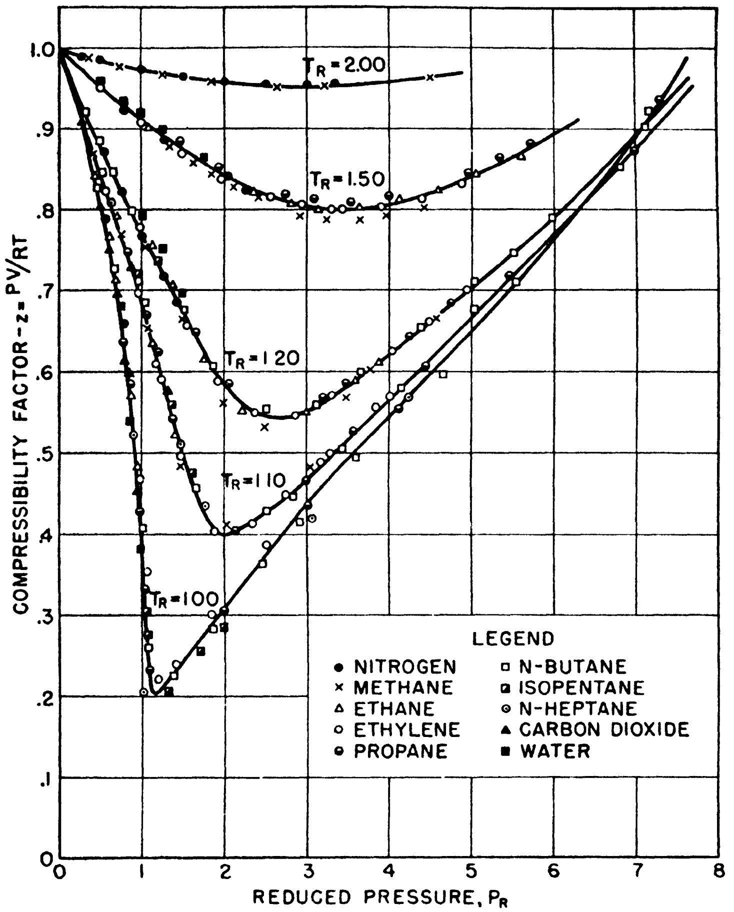


Fig. 1.5. Compressibility factor as function of reduced state variables. [From Gouq-Jen Su, *Ind. Eng. Chem.*, *38*, 803 (1946).]

this approximation is called the *Law of Corresponding States.* This is equivalent to saying that the compressibility factor z is the same function of the reduced variables for all gases. This rule is illustrated in Fig. 1.5 for a number of different gases, where $z = PV/RT$ is plotted at various reduced temperatures, against the reduced pressure.

12. Equations of state for gases. If the equation of state is written in terms of reduced variables as $F(P_R, V_R) = T_R$, it is evident that it contains at least two independent constants, characteristic of the gas in question, for example P_c and V_c. Many equations of state, proposed on semi-empirical grounds, serve to represent the PVT data more accurately than does the ideal gas equation. Several of the best known of these also contain two added constants. For example:

Equation of van der Waals:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{1.28}$$

Equation of Berthelot:

$$\left(P + \frac{A}{TV^2}\right)(V - B) = RT \tag{1.29}$$

Equation of Dieterici:

$$P(V - b')\, e^{a'/RTV} = RT \tag{1.30}$$

Van der Waals' equation provides a reasonably good representation of the *PVT* data of gases in the range of moderate deviations from ideality. For example, consider the following values in liter atm of the *PV* product for carbon dioxide at 40°C, as observed experimentally and as calculated from the van der Waals equation:

P, atm	1	10	50	100	200	500	1100
PV, obs.	25.57	24.49	19.00	6.93	10.50	22.00	40.00
PV, calc.	25.60	24.71	19.75	8.89	14.10	29.70	54.20

The constants *a* and *b* are evaluated by fitting the equation to experimental *PVT* measurements, or more usually from the critical constants of the gas. Some values for van der Waals' *a* and *b* are included in Table 1.1. Berthelot's equation is somewhat better than van der Waals' at pressures not much above one atmosphere, and is preferred for general use in this range.

Equations (1.28), (1.29), and (1.30) are all written for one mole of gas. For *n* moles they become:

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

$$\left(P + \frac{n^2A}{TV^2}\right)(V - nB) = nRT$$

$$P(V - nb')\, e^{na'/RTV} = nRT$$

The way in which the constants in these equations are evaluated from critical data will now be described, using the van der Waals equation as an example.

13. The critical region. The behavior of a gas in the neighborhood of its critical region was first studied by Thomas Andrews in 1869, in a classic series of measurements on carbon dioxide. Results of recent determinations of these *PV* isotherms around the critical temperature of 31.01°C are shown in Fig. 1.6.

Consider the isotherm at 30.4°, which is below T_c. As the vapor is compressed the *PV* curve first follows *AB*, which is approximately a Boyle's law isotherm. When the point *B* is reached, liquid is observed to form by the appearance of a meniscus between vapor and liquid. Further compression

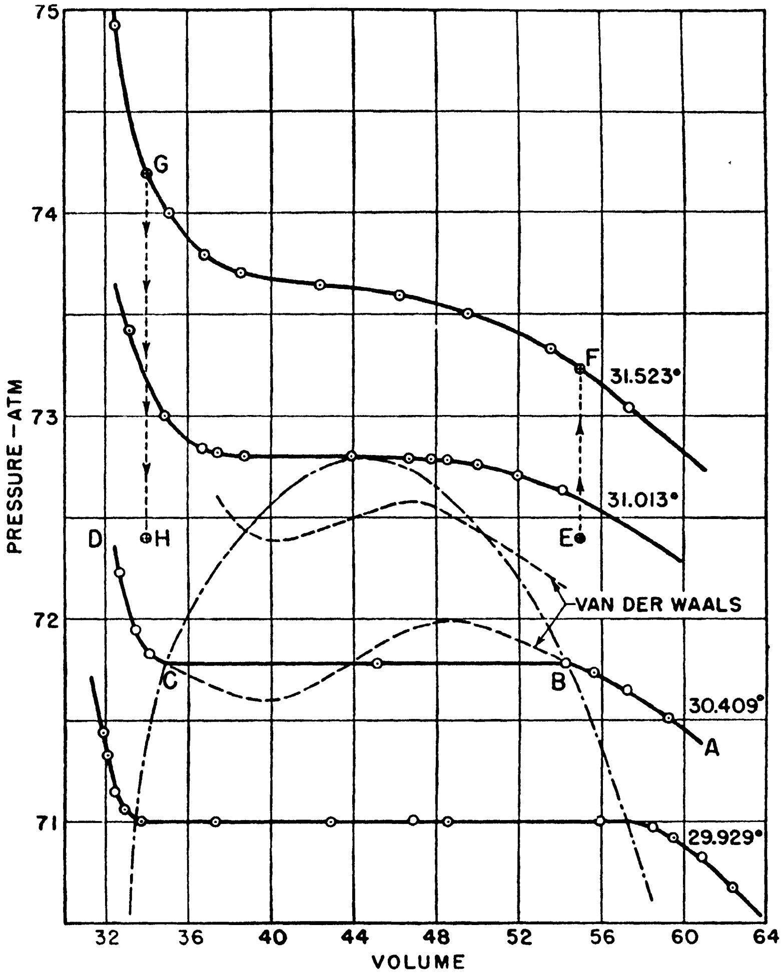


Fig. 1.6. Isotherms of carbon dioxide near the critical point.

then occurs at constant pressure until the point *C* is reached, at which all the vapor has been converted into liquid. The curve *CD* is the isotherm of liquid carbon dioxide, its steepness indicating the low compressibility of the liquid.

As isotherms are taken at successively higher temperatures the points of discontinuity *B* and *C* are observed to approach each other gradually, until at 31.01°C they coalesce, and no gradual formation of a liquid is observable. This isotherm corresponds to the critical temperature of carbon dioxide. Isotherms above this temperature exhibit no formation of a liquid no matter how great the applied pressure.

Above the critical temperature there is no reason to draw any distinction between liquid and vapor, since there is a complete *continuity of states*. This may be demonstrated by following the path *EFGH*. The vapor at point *E*, at a temperature below T_c, is warmed at constant volume to point *F*, above T_c. It is then compressed along the isotherm *FG*, and finally cooled at constant volume along *GH*. At the point *H*, below T_c, the carbon dioxide exists as a liquid, but at no point along this path are two phases, liquid and vapor, simultaneously present. One must conclude that the transformation from vapor to liquid occurs smoothly and continuously.

14. The van der Waals equation and liquefaction of gases. The van der Waals equation provides a reasonably accurate representation of the *PVT* data of gases under conditions that deviate only moderately from ideality. When an attempt is made to apply the equation to gases in states departing greatly from ideality, it is found that, although a quantitative representation of the data is not obtained, an interesting qualitative picture is still provided. Typical of such applications is the example shown in Fig. 1.6, where the van der Waals isotherms, drawn as dashed lines, are compared with the experimental isotherms for carbon dioxide in the neighborhood of the critical point. The van der Waals equation provides an adequate representation of the isotherms for the homogeneous vapor and even for the homogeneous liquid.

As might be expected, the equation cannot represent the discontinuities arising during liquefaction. Instead of the experimental straight line, it exhibits a maximum and a minimum within the two-phase region. We note that as the temperature gradually approaches the critical temperature, the maximum and the minimum gradually approach each other. At the critical point itself they have merged to become a point of inflection in the *PV* curve. The analytical condition for a maximum is that $(\partial P/\partial V) = 0$ and $(\partial^2 P/\partial V^2) < 0$; for a minimum, $(\partial P/\partial V) = 0$ and $(\partial^2 P/\partial V^2) > 0$. At the point of inflection, both the first and the second derivatives vanish, $(\partial P/\partial V) = 0 = (\partial^2 P/\partial V^2)$.

According to van der Waals' equation, therefore, the following three equations must be satisfied simultaneously at the critical point ($T = T_c$, $V = V_c$, $P = P_c$):

$$P_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2}$$

$$\left(\frac{\partial P}{\partial V}\right) = 0 = -\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right) = 0 = \frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4}$$

When these equations are solved for the critical constants we find

$$T_c = \frac{8a}{27bR}; \quad V_c = 3b; \quad P_c = \frac{a}{27b^2} \tag{1.31}$$

The values for the van der Waals constants are usually calculated from these equations.

In terms of the reduced variables of state, P_R, V_R, and T_R, one obtains from eq. (1.31):

$$P = \frac{a}{27b^2}P_R; \quad V = 3b\,V_R; \quad T = \frac{8a}{27Rb}T_R$$

The van der Waals equation then reduces to

$$\left(P_R + \frac{3}{V_R{}^2}\right)\left(V_R - \frac{1}{3}\right) = \frac{8}{3}T_R \tag{1.32}$$

As was pointed out previously, it is evident that a reduced equation of state similar to (1.32) can be obtained from any equation of state containing no more than two arbitrary constants, such as a and b. The Berthelot equation is usually used in the following form, applicable at pressures of the order of one atmosphere:

$$PV = nRT\left[1 + \frac{9}{128}\frac{P_R}{T_R}\left(1 - \frac{6}{T_R{}^2}\right)\right] \tag{1.33}$$

15. Other equations of state. In order to represent the behavior of gases with greater accuracy, especially at high pressures or near their condensation temperatures, it is necessary to use expressions having more than two adjustable parameters. Typical of such expressions is the very general *virial equation* of Kammerlingh-Onnes:

$$PV = RT + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} + \ldots$$

The factors $B(T)$, $C(T)$, $D(T)$, etc., are functions of the temperature, called the second, third, fourth, etc., virial coefficients. An equation like this, though difficult to use, can be extended to as many terms as are needed to reproduce the experimental PVT data with any desired accuracy.

One of the best of the empirical equations is that proposed by Beattie and Bridgeman in 1928.[6] This equation contains five constants in addition to R, and fits the PVT data over a wide range of pressures and temperatures, even near the critical point, to within 0.5 per cent.

16. Heat. The experimental observations that led to the concept of temperature led also to the concept of heat. Temperature, we recall, has been defined only in terms of the equilibrium condition that is reached when two bodies are placed in contact. A typical experiment might be the introduction of a piece of metal at temperature T_2 into a vessel of water at temperature T_1. To simplify the problem, let us assume that: (1) the system is isolated completely from its surroundings; (2) the change in temperature of the container itself may be neglected; (3) there is no change in the state of aggregation of either body, *i.e.*, no melting, vaporization, or the like. The end result is that

---

[6] J. A. Beattie and O. C. Bridgeman, *Proc. Am. Acad. Arts Sci.*, *63*, 229–308 (1928). J. A. Beattie, *Chem. Rev.*, *44*, 141–192 (1949).

the entire system finally reaches a new temperature T, somewhere between T_1 and T_2. This final temperature depends on certain properties of the water and of the metal. It is found experimentally that the temperatures can always be related by an equation having the form

$$C_2(T_2 - T) = C_1(T - T_1) \tag{1.34}$$

Here C_1 and C_2 are functions of the mass and constitution of the metal and of the water respectively. Thus, a gram of lead would cause a smaller temperature change than a gram of copper; 10 grams of lead would produce 10 times the temperature change caused by one gram.

Equation (1.34) has the form of an equation of conservation, such as eq. (1.8). Very early in the development of the subject it was postulated that when two bodies at different temperatures are placed in contact, something flows from the hotter to the colder. This was originally supposed to be a weightless material substance, called *caloric*. Lavoisier, for example, in his *Traité elémentaire de Chimie* (1789), included both caloric and light among the chemical elements.

We now speak of a flow of *heat* q, given by

$$q = C_2(T_2 - T) = C_1(T - T_1) \tag{1.35}$$

The coefficients C are called the *heat capacities* of the bodies. If the heat capacity is reckoned for one gram of material, it is called the *specific heat*; for one mole of material, the *molar heat capacity*.

The unit of heat was originally defined in terms of just such an experiment in *calorimetry* as has been described. The *gram calorie* was the heat that must be absorbed by one gram of water to raise its temperature 1°C. It followed that the specific heat of water was 1 cal per °C.

More careful experiments showed that the specific heat was itself a function of the temperature. It therefore became necessary to redefine the calorie by specifying the range over which it was measured. The standard was taken to be the *15° calorie*, probably because of the lack of central heating in European laboratories. This is the heat required to raise the temperature of a gram of water from 14.5° to 15.5°C. Finally another change in the definition of the calorie was found to be desirable. Electrical measurements are capable of greater precision than calorimetric measurements. The Ninth International Conference on Weights and Measures (1948) therefore recommended that the *joule* (*volt coulomb*) be used as the unit of heat. The *calorie*, however, is still popular among chemists, and the National Bureau of Standards uses a *defined calorie* equal to exactly 4.1840 joules.

The specific heat, being a function of temperature, should be defined precisely only in terms of a differential heat flow dq and temperature change dT. Thus, in the limit, eq. (1.35) becomes

$$dq = C\,dT, \quad \text{or} \quad C = \frac{dq}{dT} \tag{1.36}$$

The heat added to a body in raising its temperature from T_1 to T_2 is therefore

$$q = \int_{T_1}^{T_2} C\, dT \tag{1.37}$$

Since C depends on the exact process by which the heat is transferred, this integral can be evaluated only when the process is specified.

If our calorimeter had contained ice at 0°C instead of water, the heat added to it would not have raised its temperature until all the ice had melted. Such heat absorption or evolution accompanying a change in state of aggregation was first studied quantitatively by Joseph Black (1761), who called it *latent heat*. It may be thought of as somewhat analogous to potential energy. Thus we have latent heat of fusion, latent heat of vaporization, or latent heat accompanying a change of one crystalline form to another, for example rhombic to monoclinic sulfur.

17. Work in thermodynamic systems. In our discussion of the transfer of heat we have so far carefully restricted our attention to the simple case in which the system is completely isolated and is not allowed to interact mechanically with its surroundings. If this restriction does not apply, the system may either do work on its surroundings or have work done on itself. Thus, in certain cases, only a part of the heat added to a substance causes its temperature to rise, the remainder being used in the work of expanding the substance. The amount of heat that must be added to produce a certain temperature change depends on the exact process by which the change is effected.

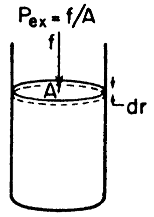


Fig. 1.7. Work in expansion.

A differential element of work may be defined by reference to eq. (1.3) as $dw = f\,dr$, the product of a displacement and the component of force in the same direction. In the case of a simple thermodynamic system, a fluid confined in a cylinder with a movable piston (assumed frictionless), the work done by the fluid against the external force on the piston (see Fig. 1.7) in a differential expansion dV would be

$$dw = \frac{f}{A} A\, dr = P_{\text{ex}}\, dV \tag{1.38}$$

Note that the work is done against the external pressure P_{ex}.

If the pressure is kept constant during a finite expansion from V_1 to V_2,

$$w = \int_{V_1}^{V_2} P_{\text{ex}}\, dV = P_{\text{ex}}(V_2 - V_1) = P_{\text{ex}}\, \Delta V \tag{1.39}$$

If a finite expansion is carried out in such a way that each successive state is an equilibrium state, it can be represented by a curve on the PV diagram, since then we always have $P_{ex} = P$. This is shown in (a), Fig. 1.8. In this case,

$$dw = P\,dV \tag{1.40}$$

On integration,

$$w = \int_A^B P\,dV \tag{1.41}$$

The value of the integral is given by the area under the PV curve. Only when equilibrium is always maintained can the work be evaluated from functions of the state of the substance itself, P and V, for only in this case does $P = P_{ex}$.

It is evident that the work done in going from point 1 to point 2 in the PV diagram, or from one *state* to another, depends upon the particular path that is traversed. Consider, for example, two alternate paths from A to B in (b), Fig. 1.8. More work will be done in going by the path ADB than by the path ACB, as is evident from the greater area under curve ADB. If we proceed from state A to state B by path ADB and return to A along BCA, we shall have completed a *cyclic process*. The net work done by the system during this cycle is seen to be equal to the difference between the areas under the two paths, which is the shaded area in (b), Fig. 1.8.

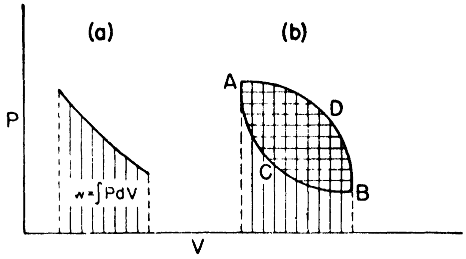


Fig. 1.8. Indicator diagrams for work.

It is evident, therefore, that in going from one state to another both the work done by a system and the heat added to a system depend on the particular path that is followed. The reason why alternate paths are possible in (b), Fig. 1.8 is that for any given volume, the fluid may exert different pressures depending on the temperature that is chosen.

18. Reversible processes. The paths followed in the PV diagrams of Fig. 1.8 belong to a special class, of great importance in thermodynamic arguments. They are called *reversible paths*. A reversible path is one connecting intermediate states all of which are equilibrium states. A process carried out along such an equilibrium path will be called a *reversible process*.

In order, for example, to expand a gas reversibly, the pressure on the piston must be released so slowly, in the limit infinitely slowly, that at every instant the pressure everywhere within the gas volume is exactly the same and is just equal to the opposing pressure on the piston. Only in this case can the state of the gas be represented by the variables of state, P and V

Geometrically speaking the state is represented by a point in the PV plane. The line joining such points is a line joining points of equilibrium.

Consider the situation if the piston were drawn back suddenly. Gas would rush in to fill the space, pressure differences would be set up throughout the gas volume, and even a condition of turbulence might ensue. The state of the gas under such conditions could no longer be represented by the two variables, P and V. Indeed a tremendous number of variables would be required, corresponding to the many different pressures at different points throughout the gas volume. Such a rapid expansion is a typical *irreversible process*; the intermediate states are no longer equilibrium states.

It will be recognized immediately that reversible processes are never realizable in actuality since they must be carried out infinitely slowly. All naturally occurring processes are therefore irreversible. The reversible path is the limiting path that is reached as we carry out an irreversible process under conditions that approach more and more closely to equilibrium conditions. We can define a reversible path exactly and calculate the work done in moving along it, even though we can never carry out an actual change reversibly. It will be seen later that the conditions for reversibility can be closely approximated in certain experiments.

19. Maximum work. In (b), Fig. 1.8, the change from A to B can be carried out along different reversible paths, of which two (ACB and ADB) are drawn. These different paths are possible because the volume V is a function of the temperature T, as well as of the pressure P. If one particular temperature is chosen and held constant throughout the process, only one reversible path is possible. Under such an *isothermal condition* the work obtained in going from A to B via a path that is reversible is the *maximum work* possible for the particular temperature in question. This is true because in the reversible case the expansion takes place against the maximum possible opposing force, which is one exactly in equilibrium with the driving force. If the opposing force, *e.g.*, pressure on a piston, were any greater, the process would occur in the reverse direction; instead of expanding and doing work the gas in the cylinder would have work done upon it and would be compressed.

20. Thermodynamics and thermostatics. From the way in which the variables of state have been defined, it would appear that thermodynamics might justly be called the study of equilibrium conditions. The very nature of the concepts and operations that have been outlined requires this restriction. Nowhere does *time* enter as a variable, and therefore the question of the rate of physicochemical processes is completely outside the scope of this kind of thermodynamic discussion. It would seem to be an unfortunate accident of language that this equilibrium study is called *thermodynamics*; a better term would be *thermostatics*. This would leave the term *thermodynamics* to cover the problems in which time occurs as a variable, *e.g.*, thermal conductivity, chemical reaction rates, and the like. The analogy with dynamics and statics as the two subdivisions of mechanics would then be preserved.

Although the thermodynamics we shall employ will be really a thermostatics, *i.e.*, a thermodynamics of reversible (equilibrium) processes, it should be possible to develop a much broader study that would include irreversible processes as well. Some progress along these lines has been made and the field should be a fruitful one for future investigation.[7]

PROBLEMS

1. The coefficient of thermal expansion of ethanol is given by $\alpha = 1.0414 \times 10^{-3} + 1.5672 \times 10^{-6}t + 5.148 \times 10^{-8}t^2$, where t is the centigrade temperature. If 0° and 50° are taken as fixed points on a centigrade scale, what will be the reading of the alcohol thermometer when an ideal gas thermometer reads 30°C?

2. In a series of measurements by J. A. Beattie, the following values were found for α of nitrogen:

P_0 (cm) . . .	99.828	74.966	59.959	44.942	33.311
$\alpha \times 10^3$, °K^{-1} . .	3.6740	3.6707	3.6686	3.6667	3.6652

Calculate from these data the melting point of ice on the absolute ideal gas scale.

3. An evacuated glass bulb weighs 37.9365 g. Filled with dry air at 1 atm pressure and 25°C, it weighs 38.0739 g. Filled with a mixture of methane and ethane it weighs 38.0347 g. Calculate the percentage of methane in the gas mixture.

4. An oil bath maintained at 50°C loses heat to its surroundings at the rate of 1000 calories per minute. Its temperature is maintained by an electrically heated coil with a resistance of 50 ohms operated on a 110-volt line. A thermoregulator switches the current on and off. What percentage of the time will the current be turned on?

5. Calculate the work done in accelerating a 2000 kg car from rest to a speed of 50 km per hr, neglecting friction.

6. A lead bullet is fired at a wooden plank. At what speed must it be traveling to melt on impact, if its initial temperature is 25° and heating of the plank is neglected? The melting point of lead is 327° and its specific heat is 0.030 cal deg^{-1} g^{-1}.

7. What is the average power production in watts of a man who burns 2500 kcal of food in a day?

8. Show that $\left(\frac{\partial P}{\partial V}\right)_T = -\frac{(\partial P/\partial T)_V}{(\partial V/\partial T)_P}$.

---

[7] See, for example, P. W. Bridgman, *The Nature of Thermodynamics* (New Haven: Yale Univ. Press, 1941); K. G. Denbigh, *The Thermodynamics of the Steady State* (London: Methuen, 1951).

9. Calculate the pressure exerted by 10 g of nitrogen in a closed 1-liter vessel at 25°C using (a) the ideal gas equation, (b) van der Waals' equation.

10. Use Berthelot's equation to calculate the pressure exerted by 0.1 g of ammonia, NH_3, in a volume of 1 liter at −20°C.

11. Evaluate the constants a' and b' in Dieterici's equation in terms of the critical constants P_c, V_c, T_c of a gas.

12. Derive an expression for the coefficient of thermal expansion α for a gas that follows (a) the ideal gas law, (b) the van der Waals equation.

13. The gas densities (g per liter) at 0°C and 1 atm of (a) CO_2 and (b) SO_2 are (a) 1.9769 and (b) 2.9269. Calculate the molar volumes of the gases and compare with the values given by Berthelot's equation.

14. The density of solid aluminum at 20°C is 2.70 g per cc; of the liquid at 660°C, 2.38 g per cc. Calculate the work done on the surroundings when 10 kg of Al are heated under atmospheric pressure from 20° to 660°C.

15. One mole of an ideal gas at 25°C is held in a cylinder by a piston at a pressure of 100 atm. The piston pressure is released in three stages: first to 50 atm, then to 20 atm, and finally to 10 atm. Calculate the work done by the gas during these irreversible isothermal expansions and compare it with that done in an isothermal reversible expansion from 100 to 10 atm at 25°C.

16. Two identical calorimeters are prepared, containing equal volumes of water at 20.0°. A 5.00-g piece of Al is dropped into calorimeter A, and a 5.00-g piece of alloy into calorimeter B. The equilibrium temperature in A is 22.0°, that in B is 21.5°. Take the specific heat of water to be independent of temperature and equal to 4.18 joule deg^{-1}. If the specific heat of Al is 0.887 joule deg^{-1}, estimate the specific heat of the alloy.

17. According to Hooke's Law the restoring force f on a stretched spring is proportional to the displacement r ($f = -\kappa r$). How much work must be expended to stretch a 10.0-cm-long spring by 10 per cent, if its force constant $\kappa = 10^5$ dynes cm^{-1}?

18. A kilogram of ammonia is compressed from 1000 liters to 100 liters at 50°. Calculate the minimum work that must be expended assuming (a) ideal gas, (b) van der Waals' equation.

REFERENCES

BOOKS

1. Berry, A. J., *Modern Chemistry* (Historical Development) (London: Cambridge, 1948).
2. Epstein, P. S., *Textbook of Thermodynamics* (New York: Wiley, 1937).
3. Guggenheim, E. A., *Modern Thermodynamics by the Methods of Willard Gibbs* (London: Methuen, 1933).
4. Keenan, J. G., *Thermodynamics* (New York: Wiley, 1941).

5. Klotz, I. M., *Chemical Thermodynamics* (New York: Prentice-Hall, 1950).
6. Lewis, G. N., and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances* (New York: McGraw-Hill, 1923).
7. MacDougall, F. H., *Thermodynamics and Chemistry* (New York: Wiley, 1939).
8. Planck, M., *Treatise on Thermodynamics* (New York: Dover, 1945).
9. Roberts, J. K., *Heat and Thermodynamics* (London: Blackie, 1951).
10. Rossini, F. D., *Chemical Thermodynamics* (New York: Wiley, 1950).
11. Sears, F. W., *An Introduction to Thermodynamics, The Kinetic Theory of Gases, and Statistical Mechanics* (Boston: Addison-Wesley, 1950).
12. Zemansky, M. W., *Heat and Thermodynamics* (New York: McGraw-Hill, 1951).

ARTICLES

1. Birkhoff, G. D., *Science in Progress*, vol. IV, 120–149 (New Haven: Yale Univ. Press, 1945), "The Mathematical Nature of Physical Theories."
2. Brescia, F., *J. Chem. Ed., 24*, 123–128 (1947), "The Critical Temperature."
3. Reilly, D., *J. Chem. Ed., 28*, 178–183 (1951), "Robert Boyle and His Background."
4. Roseman, R., and S. Katzoff, *J. Chem. Ed., 11*, 350–354 (1934), "The Equation of State of a Perfect Gas."
5. Woolsey, G., *J. Chem. Ed., 16*, 60–66 (1939), "Equations of State."

CHAPTER 2

The First Law of Thermodynamics

1. The history of the First Law. The First Law of Thermodynamics is an extension of the principle of the conservation of mechanical energy. This extension became natural when it was realized that work could be converted into heat, the expenditure of a fixed amount of work always giving rise to the production of the same amount of heat. To give the law an analytical formulation, it was only necessary to define a new energy function that included the heat.

The first quantitative experiments on this subject were carried out by Benjamin Thompson, a native of Woburn, Massachusetts, who became Count Rumford of The Holy Roman Empire. Commissioned by the King of Bavaria to supervise the boring of cannon at the Munich Arsenal, he became impressed by the tremendous generation of heat during this operation. He suggested (1798) that the heat arose from the mechanical energy expended, and was able to estimate the amount of heat produced by a horse working for an hour; in modern units his value would be 0.183 calorie per joule. The reaction at the time to these experiments was that the heat was produced owing to a lower specific heat of the metal in the form of fine turnings. Thus when bulk metal was reduced to turnings it had to release heat. Rumford then substituted a blunt borer, producing just as much heat with very few turnings. The adherents of the caloric hypothesis thereupon shifted their ground and claimed that the heat arose from the action of air on the metallic surfaces. Then, in 1799, Sir Humphry Davy provided further support for Rumford's theory by rubbing together two pieces of ice by clockwork in a vacuum and noting their rapid melting, showing that, even in the absence of air, this latent heat could be provided by mechanical work.

Nevertheless, the time did not become scientifically ripe for a mechanical theory of heat until the work of Dalton and others provided an atomic theory of matter, and gradually an understanding of heat in terms of molecular motion. This development will be considered in some detail in Chapter 7.

James Joule, at the age of twenty, began his studies in 1840 in a laboratory provided by his father in a Manchester brewery. In 1843, he published his results on the heating effect of the electric current. In 1849, he carefully determined the mechanical equivalent of heat by measuring the work input and the temperature rise in a vessel of water vigorously stirred with paddle wheels. His value, converted into our units, was 0.241 calorie per joule; the accepted modern figure is 0.239. Joule converted electric energy and mechanical energy into heat in a variety of ways: electric heating, mechanical stirring, compression of gases. By every method he found very nearly the same value for the conversion factor, thus clearly demonstrating that a given amount of work always produced the same amount of heat, to within the experimental error of his measurements.

2. Formulation of the First Law. The interconversion of heat and work having been demonstrated, it is possible to define a new function called the *internal energy* E. In any process the change in internal energy ΔE, in passing from one state A to another B, is equal to the sum of the heat added to the system q and the work done on the system $-w$. (Note that by convention work *done by* the system is called *positive*, $+w$.) Thus, $\Delta E = q - w$. Now the first law of thermodynamics states that this difference in energy ΔE depends only on the final state B and the initial state A, and not on the path between A and B.

$$\Delta E = E_B - E_A = q - w \tag{2.1}$$

Both q and w depend upon the path, but their difference $q - w$ is independent of the path. Equation (2.1) therefore defines a new *state function E*. Robert Mayer (1842) was probably the first to generalize the energy in this way.

For a differential change eq. (2.1) becomes

$$dE = dq - dw \tag{2.2}$$

The energy function is undetermined to the extent of an arbitrary additive constant; it has been defined only in terms of the difference in energy between one state and another. Sometimes, as a matter of convenience, we may adopt a conventional standard state for a system, and set its energy in this state equal to zero. For example, we might choose the state of the system at 0°K and 1 atm pressure as our standard. Then the energy E in any other state would be the change in energy in going from the standard state to the state in question.

The First Law has often been stated in terms of the universal human experience that it is impossible to construct a perpetual motion machine, that is, a machine that will continuously produce useful work or energy from nothing. To see how this experience is embodied in the First Law, consider a cyclic process from state A to B and back to A again. If perpetual motion were ever possible, it would sometimes be possible to obtain a net increase in energy $\Delta E > 0$ by such a cycle. That this is impossible can be ascertained from eq. (2.1), which indicates that for any such cycle $\Delta E = (E_B - E_A) + (E_A - E_B) = 0$. A more general way of expressing this fact is to say that for any cyclic process the integral of dE vanishes:

$$\oint dE = 0 \tag{2.3}$$

3. The nature of internal energy. On page 6 we restricted the systems under consideration to those in a state of rest in the absence of gravitational or electromagnetic fields. With these restrictions, changes in the internal energy E include changes in the potential energy of the system, and energy associated with the addition or subtraction of heat. The potential energy changes may be considered in a broad sense to include also the energy changes caused by the rearrangements of molecular configurations that take place during changes in state of aggregation, or in chemical reactions.

If the system were moving, the kinetic energy would have to be added to E. If the restriction on electromagnetic fields were removed, the definition of E would have to be expanded to include the electromagnetic energy. Similarly, if gravitational effects were of interest, as in centrifugal operations, the energy of the gravitational field would have to be included in or added to E before applying the First Law.

In view of these facts, it has been remarked that even if somebody did invent a perpetual motion machine, we should simply invent a new variety of energy to explain it, and so preserve the validity of the First Law. From this point of view, the First Law is essentially a definition of a function called the *energy*. What gives the Law real meaning and usefulness is the practical fact that a very small number of different kinds of energy suffice to describe the physical world.

In anticipation of future discussions, it may be mentioned that experimental proof of the interconversion of mass and energy has been provided by the nuclear physicists. The First Law should therefore become a law of the conservation of mass-energy, and the extension of thermodynamics along these lines is beginning to be studied. The changes in mass theoretically associated with the energy changes in chemical reactions are so small that they lie just outside the range of our present methods of measurement. Thus they need not be considered in ordinary chemical thermodynamics.

4. Properties of exact differentials. We have seen in Section 1–17 that the work done by a system in going from one state to another is a function of the path between the states, and that $\oint dw$ is not in general equal to zero. The reason was readily apparent when the reversible process was considered. Then, $\int_A^B dw = \int_A^B P\,dV$. The differential expression $P\,dV$ cannot be integrated when only the initial and final states are known, since P is a function not only of the volume V but also of the temperature T, and this temperature may also change along the path of integration. On the other hand, $\int_A^B dE$ can always be carried out, giving $E_B - E_A$, since E is a function of the state of the system alone, and is not dependent on the path by which that state is reached or on the previous history of the system.

Mathematically, therefore, we distinguish two classes of differential expressions. Those such as dE are called *exact differentials* since they are obtained by differentiation of some state function such as E. Those such as dq or dw are *inexact differentials*, since they cannot be obtained by differentiation of a function of the state of the system alone. Conversely, dq or dw cannot be integrated to yield a q or w. The First Law states that although

dq and dw are not exact differentials, their difference $dE = dq - dw$ is an exact differential.

The following statements are mathematically completely equivalent:

(1) The function E is a function of the state of a system.
(2) The differential dE is an exact differential.
(3) The integral of dE about a closed path $\oint dE$ is equal to zero.

As an important corollary of the fact that it is an exact differential, dE may be written[1]

$$dE = \left(\frac{\partial E}{\partial x}\right)_y dx + \left(\frac{\partial E}{\partial y}\right)_x dy \tag{2.4}$$

where x and y are any other variables of state of the system, for instance any two of P, T, V. Thus, for example,

$$dE = \left(\frac{\partial E}{\partial V}\right)_T dV + \left(\frac{\partial E}{\partial T}\right)_V dT \tag{2.5}$$

A further useful property of exact differential expressions is the *Euler reciprocity relation*. If an exact differential is written $dE = M\,dV + N\,dT$, then

$$\left(\frac{\partial M}{\partial T}\right)_V = \left(\frac{\partial N}{\partial V}\right)_T \tag{2.6}$$

This can be seen immediately from the typical case of eq. (2.5), whence eq. (2.6) becomes $(\partial^2 E/\partial V \partial T) = (\partial^2 E/\partial T \partial V)$ since the order of differentiation is immaterial.

5. Adiabatic and isothermal processes. Two kinds of processes occur frequently both in laboratory experiments and in thermodynamic arguments. An *isothermal process* is one that occurs at constant temperature, $T =$ constant, $dT = 0$. To approach isothermal conditions, reactions are often carried out in thermostats. In an *adiabatic process*, heat is neither added to nor taken from the system; *i.e.*, $q = 0$. For a differential adiabatic process, $dq = 0$, and therefore from eq. (2.2) $dE = -dw$. For an adiabatic reversible change in volume, $dE = -P\,dV$. Adiabatic conditions can be approached by careful thermal insulation of the system. High vacuum is the best insulator against heat conduction. Highly polished walls minimize radiation. These principles are combined in Dewar vessels of various types.

6. The heat content or enthalpy. No mechanical work is done during a process carried out at constant volume, since $V =$ constant, $dV = 0$, $w = 0$. It follows that the increase in energy equals the heat absorbed at constant volume.

$$\Delta E = q_V \tag{2.7}$$

If pressure is held constant, as for example in experiments carried out under atmospheric pressure, $\Delta E = E_2 - E_1 = q - w = q - P(V_2 - V_1)$ or

---

[1] See, *e.g.*, Granville, Smith, Longley, *Calculus* (Boston: Ginn, 1934), p. 412.

$(E_2 + PV_2) - (E_1 + PV_1) = q_P$, where q_P is the heat absorbed at constant pressure. We now define a new function, called the *enthalpy* or *heat content*[2] by

$$H = E + PV \tag{2.8}$$

Then

$$\Delta H = H_2 - H_1 = q_P \tag{2.9}$$

The increase in enthalpy equals the heat absorbed at constant pressure.

It will be noted that the enthalpy H, like the energy E, is a function of the state of the system alone, and is independent of the path by which that state is reached. This fact follows immediately from the definition in eq. (2.8), since E, P, and V are all state functions.

7. Heat capacities. Heat capacities may be measured either at constant volume or at constant pressure. From the definitions in eqs. (1.36), (2.7), and (2.9):

$$\text{heat capacity at constant volume:}\quad C_V = \frac{dq_V}{dT} = \left(\frac{\partial E}{\partial T}\right)_V \tag{2.10}$$

$$\text{heat capacity at constant pressure:}\quad C_P = \frac{dq_P}{dT} = \left(\frac{\partial H}{\partial T}\right)_P \tag{2.11}$$

The capital letters C_V and C_P are used to represent the heat capacities per mole. Unless otherwise specified, all thermodynamic quantities that are extensive in character will be referred to the molar basis.

The heat capacity at constant pressure C_P is always larger than that at constant volume C_V, because at constant pressure part of the heat added to a substance is used in the work of expanding it, whereas at constant volume all of the added heat produces a rise in temperature. An important equation for the difference $C_P - C_V$ can be obtained as follows:

$$C_P - C_V = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_V \tag{2.12}$$

Since,

$$dE = \left(\frac{\partial E}{\partial V}\right)_T dV + \left(\frac{\partial E}{\partial T}\right)_V dT$$

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial E}{\partial T}\right)_V$$

Substituting this value in eq. (2.12), we find

$$C_P - C_V = \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P \tag{2.13}$$

The term $P(\partial V/\partial T)_P$ may be seen to represent the contribution to the specific heat C_P caused by the expansion of the system against the *external*

---

[2] Note carefully that *heat content H* and *heat capacity dq/dT* are two entirely different functions. The similarity in nomenclature is unfortunate, and the term *enthalpy* is therefore to be preferred to *heat content.*

pressure P. The other term $(\partial E/\partial V)_T(\partial V/\partial T)_P$, is the contribution from the work done in expansion against the internal cohesive or repulsive forces of the substance, represented by a change of the energy with volume at constant temperature. The term $(\partial E/\partial V)_T$ is called the *internal pressure*.[3] In the case of liquids and solids, which have strong cohesive forces, this term is large. In the case of gases, on the other hand, the term $(\partial E/\partial V)_T$ is usually small compared with P.

In fact, the first attempts to measure $(\partial E/\partial V)_T$ for gases failed to detect it at all. These experiments were carried out by Joule in 1843.

8. The Joule experiment. Joule's drawing of his apparatus is reproduced in Fig. 2.1, and he described the experiment as follows.[4]

> I provided another copper receiver (E) which had a capacity of 134 cubic inches. . . . I had a piece D attached, in the center of which there was a bore $\frac{1}{8}$ of an inch diameter, which could be closed perfectly by means of a proper stopcock. . . .
>
> Having filled the receiver R with about 22 atmospheres of dry air and having exhausted the receiver E by means of an air pump, I screwed them together and put them into a tin can containing $16\frac{1}{2}$ lb. of water. The water was first thoroughly stirred, and its temperature taken by the same delicate thermometer which was made use of in the former experiments on mechanical equivalent of heat. The stopcock was then opened by means of a proper key, and the air allowed to pass from the full into the empty receiver until equilibrium was established between the two. Lastly, the water was again stirred and its temperature carefully noted.

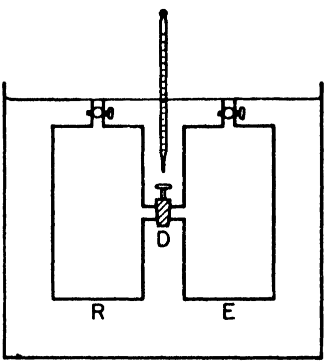


Fig. 2.1. The Joule experiment.

Joule then presented a table of experimental data, showing that there was no measurable temperature change, and arrived at the conclusion that "no change of temperature occurs when air is allowed to expand in such a manner as not to develop mechanical power" (*i.e.*, so as to do no external work).

The expansion in Joule's experiment, with the air rushing from R into the evacuated vessel E, is a typical irreversible process. Inequalities of temperature and pressure arise throughout the system, but eventually an equilibrium state is reached. There has been no change in the internal energy of the gas since no work was done by or on it, and it has exchanged no heat with the surrounding water (otherwise the temperature of the water would have changed). Therefore $\Delta E = 0$. Experimentally it is found that $\Delta T = 0$. It may therefore be concluded that the internal energy must depend only on the temperature and not on the volume. More mathematically expressed:

---

[3] Note that just as $\partial E/\partial r$, the derivative of the energy with respect to a displacement, is a force, the derivative with respect to volume, $\partial E/\partial V$, is a force per unit area or a pressure.

[4] *Phil. Mag.*, 1843, p. 263.

Since $$dE = \left(\frac{\partial E}{\partial V}\right)_T dV + \left(\frac{\partial E}{\partial T}\right)_V dT = 0$$

and $$dT = 0 \quad \text{while} \quad dV > 0$$

it follows that $$\left(\frac{\partial E}{\partial V}\right)_T = 0$$

Joule's experiment, however, was not capable of detecting small effects, since the heat capacity of his water calorimeter was extremely large compared with that of the gas used.

9. The Joule-Thomson experiment. William Thomson (Lord Kelvin) suggested a better procedure, and working with Joule, carried out a series of experiments between 1852 and 1862. Their apparatus is shown schematically in Fig. 2.2. The principle involved throttling the gas flow from the high pressure *A* to the low pressure *C* side by interposing a porous plug *B*. In their first trials, this plug consisted of a silk handkerchief; in later work, porous meerschaum was used. In this way, by the time the gas emerges into *C* it has already reached equilibrium and its temperature can be measured directly. The entire system is thermally insulated, so that the process is an adiabatic one, and $q = 0$.

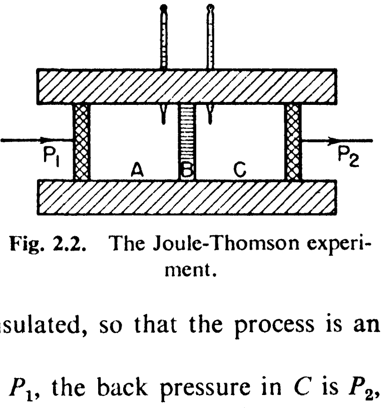


Fig. 2.2. The Joule-Thomson experiment.

Suppose that the fore pressure in *A* is P_1, the back pressure in *C* is P_2, and the volumes per mole of gas at these pressures are V_1 and V_2, respectively. The work per mole done *on* the gas in forcing it through the plug is then P_1V_1, and the work done *by* the gas in expanding on the other side is P_2V_2. The net work done *by* the gas is therefore $w = P_2V_2 - P_1V_1$.

It follows that a Joule-Thomson expansion occurs at constant enthalpy, since

$$\Delta E = E_2 - E_1 = q - w = 0 - w$$
$$E_2 - E_1 = P_1V_1 - P_2V_2$$
$$E_2 + P_2V_2 = E_1 + P_1V_1$$
$$H_2 = H_1$$

The Joule-Thomson coefficient, $\mu_{J.T.}$, is defined as the change of temperature with pressure at constant enthalpy:

$$\mu_{J.T.} = \left(\frac{\partial T}{\partial P}\right)_H \tag{2.14}$$

This quantity is measured directly from the temperature change ΔT of the gas as it undergoes a pressure drop ΔP through the porous plug. Some experimental values of the J.-T. coefficients, which are functions of temperature and pressure, are collected in Table 2.1.

TABLE 2.1

JOULE-THOMSON COEFFICIENTS FOR CARBON DIOXIDE*

μ (°C per atm)

Temperature (°K)	Pressure (atm)						
	0	1	10	40	60	80	100
220	2.2855	2.3035					
250	1.6885	1.6954	1.7570				
275	1.3455	1.3455	1.3470				
300	1.1070	1.1045	1.0840	1.0175	0.9675		
325	0.9425	0.9375	0.9075	0.8025	0.7230	0.6165	0.5220
350	0.8195	0.8150	0.7850	0.6780	0.6020	0.5210	0.4340
380	0.7080	0.7045	0.6780	0.5835	0.5165	0.4505	0.3855
400	0.6475	0.6440	0.6210	0.5375	0.4790	0.4225	0.3635

* From John H. Perry, *Chemical Engineers' Handbook* (New York: McGraw-Hill, 1941). Rearranged from *Int. Crit. Tables*, vol. 5, where further data may be found.

A positive μ corresponds to cooling on expansion, a negative μ to warming. Most gases at room temperatures are cooled by a J.-T. expansion. Hydrogen, however, is warmed if its initial temperature is above −80°C, but if it is first cooled below −80°C it can then be cooled further by a J.-T. effect. The temperature −80°C at which $\mu = 0$ is called *the Joule-Thomson inversion temperature for hydrogen.* Inversion temperatures for other gases, except helium, lie considerably higher.

10. Application of the First Law to ideal gases. An analysis of the theory of the Joule-Thomson experiment must be postponed until the Second Law of Thermodynamics has been studied in the next chapter. It may be said, however, that the porous-plug experiments showed that Joule's original conclusion that $(\partial E/\partial V)_T = 0$ for all gases was too broad. Real gases may have a considerable internal pressure and work must be done against the cohesive forces when they expand.

An ideal gas may now be defined in thermodynamic terms as follows:

(1) The internal pressure $(\partial E/\partial V)_T = 0$.
(2) The gas obeys Boyle's Law, $PV =$ constant at constant T.

It follows from eq. (2.5) that the energy of an ideal gas is a function of its temperature alone. Thus $dE = (\partial E/\partial T)_V\, dT = C_V\, dT$ and $C_V = dE/dT$. The heat capacity of an ideal gas also depends only on its temperature. These conclusions greatly simplify the thermodynamics of ideal gases, so that many thermodynamic discussions are carried on in terms of the ideal gas model. Some examples follow:

Difference in heat capacities. When eq. (2.13) is applied to an ideal gas, it becomes

$$C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P$$

Then, since

$$PV = RT$$

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

and

$$C_P - C_V = R \tag{2.15}$$

Heat capacities are usually given in units of calories per degree per mole, and, in these units,

$$R = 8.3144/4.1840$$

$$= 1.9872 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

Temperature changes. Since $dE = C_V\, dT$

$$\Delta E = E_2 - E_1 = \int_{T_1}^{T_2} C_V\, dT \tag{2.16}$$

Likewise for an ideal gas:

$$dH = C_P\, dT$$

and

$$\Delta H = H_2 - H_1 = \int_{T_1}^{T_2} C_P\, dT \tag{2.17}$$

Isothermal volume or pressure change. For an isothermal change in an ideal gas, the internal energy remains constant. Since $dT = 0$ and $(\partial E/\partial V)_T = 0$,

$$dE = dq - PdV = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV = 0$$

and

$$dq = dw = P\, dV$$

Since

$$P = \frac{RT}{V}$$

$$\int_1^2 dq = \int_1^2 dw = \int_1^2 RT\frac{dV}{V}$$

or

$$q = w = RT \ln\frac{V_2}{V_1} = RT \ln\frac{P_1}{P_2} \tag{2.18}$$

Since the volume change is carried out reversibly, P always having its equilibrium value RT/V, the work in eq. (2.18) is the maximum work done in an expansion, or the minimum work needed to effect a compression. The equation tells us that the work required to compress a gas from 10 atm to 100 atm is just the same as that required to compress it from 1 atm to 10 atm.

Reversible adiabatic expansion. In this case, $dq = 0$, and $dE = -dw = -P\,dV$.

From eq. (2.16)
$$dw = -C_V\,dT \tag{2.19}$$

For a finite change
$$w = -\int_1^2 C_V\,dT \tag{2.20}$$

We may write eq. (2.19) as $C_V\,dT + P\,dV = 0$

Whence
$$C_V\frac{dT}{T} + R\frac{dV}{V} = 0 \tag{2.21}$$

Integrating between T_1 and T_2, and V_1 and V_2, the initial and final temperatures and volumes, we have
$$C_V \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1} = 0 \tag{2.22}$$

This integration assumes that C_V is a constant, not a function of T.

We may substitute for R from eq. (2.15), and using the conventional symbol γ for the heat capacity ratio C_P/C_V we find

$$(\gamma - 1)\ln\frac{V_2}{V_1} + \ln\frac{T_2}{T_1} = 0$$

Therefore,
$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1} \tag{2.23}$$

Since, for an ideal gas,
$$\frac{T_1}{T_2} = \frac{P_1V_1}{P_2V_2},$$
$$P_1V_1^{\gamma} = P_2V_2^{\gamma} \tag{2.24}$$

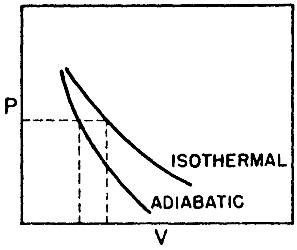


Fig. 2.3. Isothermal and adiabatic expansions.

It has been shown, therefore, that for a reversible adiabatic expansion of an ideal gas
$$PV^{\gamma} = \text{constant} \tag{2.25}$$

We recall that for an isothermal expansion $PV =$ constant.

These equations are plotted in Fig. 2.3. A given pressure fall produces a lesser volume increase in the adiabatic case, owing to the attendant fall in temperature during the adiabatic expansion.

11. Examples of ideal-gas calculations. Let us take 10 liters of gas at 0° and 10 atm. We therefore have $100/22.414 = 4.457$ moles. We shall calculate the final volume and the work done in three different expansions to a final pressure of 1 atm. The heat capacity is assumed to be $C_V = \frac{3}{2}R$, independent of temperature.

Isothermal reversible expansion. In this case the final volume
$$V_2 = P_1V_1/P_2 = (10)(10)/(1) = 100 \text{ liters}$$

The work done by the gas in expanding equals the heat absorbed by the gas from its environment. From eq. (2.18), for n moles,

$$\begin{aligned} q = w &= nRT \ln \frac{V_2}{V_1} \\ &= (4.457)(8.314)(273.2)(2.303) \log (10) \\ &= 23{,}310 \text{ joules} \end{aligned}$$

Adiabatic reversible expansion. The final volume is calculated from eq. (2.24), with

$$\gamma = \frac{C_P}{C_V} = \frac{(\frac{3}{2}R + R)}{\frac{3}{2}R} = \frac{5}{3}$$

Thus $$V_2 = \left(\frac{P_1}{P_2}\right)^{1/\gamma} V_1 = (10)^{3/5} \cdot 10 = 39.8 \text{ liters}$$

The final temperature is obtained from $P_2V_2 = nRT_2$:

$$T_2 = \frac{P_2V_2}{nR} = \frac{(1)(39.8)}{(4.457)(0.08205)} = 108.8^\circ\text{K}$$

For an adiabatic process, $q = 0$, and $\Delta E = q - w = -w$. Also, since C_V is constant, eq. (2.16) gives

$$\Delta E = nC_V\Delta T = n\tfrac{3}{2}R(T_2 - T_1) = -9125 \text{ joules}$$

The work done by the gas on expansion is therefore 9125 joules.

Irreversible adiabatic expansion. Suppose the pressure is suddenly released to 1 atm and the gas expands adiabatically against this constant pressure. Since this is not a reversible expansion, eq. (2.24) cannot be applied. Since $q = 0$, $\Delta E = -w$. The value of ΔE depends only on initial and final states:

$$\Delta E = -w = nC_V(T_2 - T_1)$$

Also, for a constant pressure expansion, we have from eq. (1.39),

$$w = P_2(V_2 - V_1) = P_2\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$$

Equating the two expressions for w, we obtain

$$-C_V(T_2 - T_1) = P_2\left(\frac{RT_2}{P_2} - \frac{RT_1}{P_1}\right)$$

The only unknown is T_2:

$$-\frac{3}{2}R(T_2 - 273.2) = 1\left(\frac{RT_2}{1} - \frac{R273.2}{10}\right)$$

$$T_2 = 174.8^\circ\text{K}$$

Then $$\begin{aligned} -\Delta E = w &= -\tfrac{3}{2}Rn(174.8 - 273.2) \\ &= 5470 \text{ joules} \end{aligned}$$

Note that there is considerably less cooling of the gas and less work done in the irreversible adiabatic expansion than in the reversible expansion.

12. Thermochemistry—heats of reaction. Thermochemistry is the study of the heat effects accompanying chemical reactions, the formation of solutions, and changes in state of aggregation such as melting or vaporization. Physicochemical changes can be classified as *endothermic*, accompanied by the absorption of heat, or *exothermic*, accompanied by the evolution of heat.

A typical example of an exothermic reaction is the burning of hydrogen:

$$H_2 + \tfrac{1}{2}\,O_2 = H_2O\,(\text{gas}) + 57{,}780\ \text{cal at } 18^\circ\text{C}$$

A typical endothermic reaction would be the reverse of this, the decomposition of water vapor:

$$H_2O = H_2 + \tfrac{1}{2}\,O_2 - 57{,}780\ \text{cal at } 18^\circ\text{C}$$

Heats of reaction may be measured at constant pressure or at constant volume. An example of the first type of experiment is the determination of the heat evolved when the reaction takes place at atmospheric pressure in an open vessel. If the reaction is carried out in a closed autoclave or bomb, the constant-volume condition holds.

By convention, reaction heats are considered positive when heat is absorbed by the system. Thus an exothermic reaction has a negative "heat of reaction." From eq. (2.7) the heat of reaction at constant volume,

$$Q_V = \Delta E_V \tag{2.26}$$

From eq. (2.9) the heat of reaction at constant pressure,

$$Q_P = \Delta H_P = \Delta E + P\,\Delta V \tag{2.27}$$

The heat of reaction at constant volume is greater than that at constant pressure by an amount equal to the external work done by the system in the latter case. In reactions involving only liquids or solids ΔV is so small that usually $P\,\Delta V$ is negligible and $Q_V \approx Q_P$. For gas reactions, however, the $P\,\Delta V$ terms may be appreciable.

The heat change in a chemical reaction can best be represented by writing the chemical equation for the reaction, specifying the states of all the reactants and products, and then appending the heat change, noting the temperature at which it is measured. Since most reactions are carried out under essentially constant pressure conditions, ΔH is usually chosen to represent the heat of reaction. Some examples follow:

(1) $SO_2\,(1\ \text{atm}) + \tfrac{1}{2}\,O_2\,(1\ \text{atm}) = SO_3\,(1\ \text{atm})$
$\Delta H_{298} = -10{,}300\ \text{cal}$

(2) $CO_2\,(1\ \text{atm}) + H_2\,(1\ \text{atm}) = CO\,(1\ \text{atm}) + H_2O\,(1\ \text{atm})$
$\Delta H_{298} = 9860\ \text{cal}$

(3) $AgBr\,(\text{cryst}) + \tfrac{1}{2}\,Cl_2\,(1\ \text{atm}) = AgCl\,(\text{cryst}) + \tfrac{1}{2}\,Br_2\,(\text{liq})$
$\Delta H_{298} = -6490\ \text{cal}$

As an immediate consequence of the First Law, ΔE or ΔH for any chemical reaction is independent of the path; that is, independent of any intermediate reactions that may occur. This principle was first established experimentally by G. H. Hess (1840), and is called *The Law of Constant Heat Summation.* It is often possible, therefore, to calculate the heat of a reaction from measurements on quite different reactions. For example:

(1) $COCl_2 + H_2S = 2\,HCl + COS$ $\qquad \Delta H_{298} = -42{,}950$ cal
(2) $COS + H_2S = H_2O\,(g) + CS_2\,(l)$ $\qquad \Delta H_{298} = +3980$ cal
(3) $COCl_2 + 2\,H_2S = 2\,HCl + H_2O\,(g) + CS_2\,(l)$
$\qquad \Delta H_{298} = -38{,}970$ cal

13. Heats of formation. A convenient standard state for a substance may be taken to be the state in which it is stable at 25°C and 1 atm pressure; thus, oxygen as O_2 (g), sulfur as S (rhombic crystal), mercury as Hg (l), and so on. By convention, the enthalpies of the *chemical elements* in this standard state are set equal to zero. The standard enthalpy of any *compound* is then the heat of the reaction by which it is formed from its elements, reactants and products all being in the standard state of 25°C and 1 atm.

For example:

(1) $S + O_2 = SO_2$ $\qquad \Delta H^{\circ}_{298} = -70{,}960$ cal
(2) $2\,Al + \frac{3}{2}\,O_2 = Al_2O_3$ $\qquad \Delta H^{\circ}_{298} = -380{,}000$ cal

The superscript zero indicates we are writing a *standard* heat of formation with reactants and products at 1 atm; the absolute temperature is written as a subscript. Thermochemical data are conveniently tabulated as heats of formation. A few examples, selected from a recent compilation of the National Bureau of Standards,[5] are given in Table 2.2. The standard heat of any reaction at 25°C is then readily found as the difference between the standard heats of formation of the products and of the reactants.

TABLE 2.2
STANDARD HEATS OF FORMATION AT 25°C

Compound	State	$\Delta H^{\circ}_{298.16}$ (kcal/mole)	Compound	State	$\Delta H^{\circ}_{298.16}$ (kcal/mole)
H_2O	g	−57.7979	H_2S	g	−4.815
H_2O	l	−68.3174	H_2SO_4	l	−193.91
H_2O_2	g	−31.83	SO_2	g	−70.96
HF	g	−64.2	SO_3	g	−94.45
HCl	g	−22.063	CO	g	−26.4157
HBr	g	−8.66	CO_2	g	−94.0518
HI	g	+6.20	$SOCl_2$	l	−49.2
HIO_3	c	−57.03	S_2Cl_2	g	−5.70

---

[5] The Bureau is publishing a comprehensive collection of thermodynamic data, copies of which are to be deposited in every scientific library ("Selected Values of Chemical Thermodynamic Properties").

Many of our thermochemical data have been obtained from measurements of heats of combustion. If the heats of formation of all its combustion products are known, the heat of formation of a compound can be calculated from its heat of combustion. For example

$$
\begin{array}{llll}
(1) & C_2H_6 + \frac{7}{2}O_2 = 2\,CO_2 + 3\,H_2O\,(l) & \Delta H^\circ_{298} = -373.8 \text{ kcal} \\
(2) & C\,(\text{graphite}) + O_2 = CO_2 & \Delta H^\circ_{298} = -94.5 \text{ kcal} \\
(3) & H_2 + \frac{1}{2}O_2 = H_2O\,(l) & \Delta H^\circ_{298} = -68.3 \text{ kcal} \\
\hline
(4) & 2\,C + 3\,H_2 = C_2H_6 & \Delta H^\circ_{298} = -20.1 \text{ kcal}
\end{array}
$$

The data in Table 2.3 were obtained from combustion heats by F. D. Rossini and his co-workers at the National Bureau of Standards. The standard state of carbon has been taken to be graphite.

When changes in state of aggregation occur, the appropriate latent heat must be added. For example:

$$
\begin{array}{ll}
S\,(rh) + O_2 = SO_2 & \Delta H^\circ_{298} = -70.96 \text{ kcal} \\
S\,(rh) = S\,(\text{mono}) & \Delta H^\circ_{298} = -0.08 \text{ kcal} \\
S\,(\text{mono}) + O_2 = SO_2 & \Delta H^\circ_{298} = -70.88 \text{ kcal}
\end{array}
$$

14. Experimental measurements of reaction heats.[6] The measurement of the heat of a reaction consists essentially of a careful determination of the amount of the chemical reaction that produces a definite measured change in the calorimeter, and then the measurement of the amount of electrical energy required to effect exactly the same change. The change in question is usually a temperature change. A notable exception is in the ice calorimeter, in which one measures the volume change produced by the melting of ice, and thereby calculates the heat evolution from the known latent heat of fusion of ice.

The ΔH values in Table 2.3 were obtained by means of a combustion-bomb calorimeter. It is estimated that the limit of accuracy with the present apparatus and technique is 2 parts in 10,000. Measurements with a bomb calorimeter naturally yield ΔE values, which are converted to ΔH's via eq. (2.27).

A thermochemical problem of great interest in recent years has been the difference in the energies of various organic compounds, especially the hydrocarbons. It is evident that extremely precise work will be necessary to evaluate such differences from combustion data. For example, the heat contents of the five isomers of hexane differ by 1 to 5 kcal per mole, while the heats of combustion of the hexanes are around 1000 kcal per mole; even a 0.1 per cent uncertainty in the combustion heats would lead to about a 50 per cent uncertainty in the energy differences. Important information about such small

---

[6] Clear detailed descriptions of the experimental equipment and procedures can be found in the publications of F. D. Rossini and his group at the National Bureau of Standards, *J. Res. of N.B.S.*, *6*, 1 (1930); *13*, 469 (1934); *27*, 289 (1941).

TABLE 2.3

HEATS OF FORMATION OF GASEOUS HYDROCARBONS

Substance	*Formula*	ΔH°_{298} (cal/mole)
Paraffins:		
Methane	CH_4	−17,865 ± 74
Ethane	C_2H_6	−20,191 ± 108
Propane	C_3H_8	−24,750 ± 124
n-Butane	C_4H_{10}	−29,715 ± 153
Isobutane	C_4H_{10}	−31,350 ± 132
n-Pentane	C_5H_{12}	−34,739 ± 213
2-Methylbutane	C_5H_{12}	36,671 ± 153
Tetramethylmethane	C_5H_{12}	−39,410 ± 227
Monolefines:		
Ethylene	C_2H_4	12,556 ± 67
Propylene	C_3H_6	4956 ± 110
1-Butene	C_4H_8	383 ± 180
cis-2-Butene	C_4H_8	−1388 ± 180
trans-2-Butene	C_4H_8	−2338 ± 180
2-Methylpropene	C_4H_8	−3205 ± 165
1-Pentene	C_5H_{10}	−4644 ± 300
Diolefines:		
Allene	C_3H_4	46,046 ± 260
1,3-Butadiene	C_4H_6	26,865 ± 240
1,3-Pentadiene	C_5H_8	18,885 ± 300
1,4-Pentadiene	C_5H_8	25,565 ± 300
Acetylenes:		
Acetylene	C_2H_2	54,228 ± 235
Methylacetylene	C_3H_4	44,309 ± 240
Dimethylacetylene	C_4H_6	35,221 ± 355

energy differences can be obtained for unsaturated hydrocarbons by measurement of their heats of hydrogenation. This method has been developed to a high precision by G. B. Kistiakowsky and his co-workers at Harvard.[7]

It is evident that in calorimetric experiments—for example, in a determination of a heat of combustion—the chemical reaction studied may actually occur at a very elevated temperature. One measures, however, the net temperature rise after equilibrium has been reached, and this usually amounts to only a few degrees, owing to the high heat capacity of the calorimeter. Since ΔE or ΔH depends only on the initial and final states, one actually measures the ΔE or ΔH, therefore, at around 25°C, even though temperatures of over 2000°C may have been attained during the actual combustion process.

15. Heats of solution. In many chemical reactions, one or more of the reactants are in solution, and the investigation of heats of solution is an important branch of thermochemistry. It is necessary to distinguish the *integral heat of solution* and the *differential heat of solution*. The distinction

---

[7] Kistiakowsky, et al., *J. Am. Chem. Soc.*, *57*, 876 (1935).

between these two terms can best be understood by means of a practical example.

If one mole of alcohol (C_2H_5OH) is dissolved in nine moles of water, the final solution contains 10 moles per cent of alcohol. The heat absorbed is the integral heat of solution per mole of alcohol to form a solution of this final composition. If the mole of alcohol is dissolved in four moles of water, the integral heat of solution has a different value, corresponding to the formation of a 20 mole per cent solution. The difference between any two integral heats of solution yields a value for the integral *heat of dilution*. The example can be written in the form of thermochemical equations as follows:

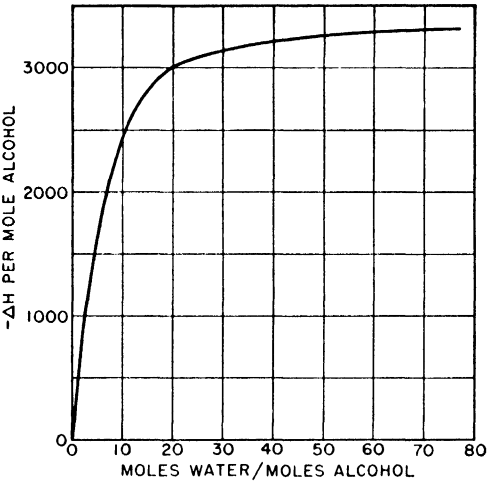


Fig. 2.4. Heat of solution of ethyl alcohol in water at 0°C.

(1) $C_2H_5OH + 9\ H_2O = C_2H_5OH$ (10 mole % solution)

$$\Delta H^\circ_{273} = -2300$$

(2) $C_2H_5OH + 4\ H_2O = C_2H_5OH$ (20% solution)

$$\Delta H^\circ_{273} = -1500$$

(3) C_2H_5OH (20% solution) + $5\ H_2O = C_2H_5OH$ (10% solution)

$$\Delta H^\circ_{273} = -800$$

The heat of dilution from 20 to 10 per cent amounts to −800 cal per mole.

It is evident that the heat evolved ($-\Delta H$) when a mole of alcohol is dissolved in water depends upon the final concentration of the solution. If one plots the measured integral heat of solution against the ratio moles water per mole alcohol (n_w/n_a), the curve in Fig. 2.4 is obtained. As the solution becomes more and more dilute, n_w/n_a approaches infinity. The asymptotic value of the heat of solution is called the *heat of solution at infinite dilution*, ΔH_∞. For alcohol in water at 0°C, this amounts to −3350 calories. The values of $\Delta H_{\text{solution}}$ generally become quite constant with increasing dilution, so that measured values in dilute solutions are usually close to ΔH_{∞}. Often one finds literature values for which the dilution is not specified. These are written, for aqueous solution, simply as in the following example:

$$\text{NaCl} + x\,\text{H}_2\text{O} = \text{NaCl (aq)} + 1260\ \text{cal}$$

In the absence of more detailed information, such values may be taken to give approximately the ΔH at infinite dilution.

The integral solution heats provide an average ΔH over a range of concentrations. For example, if alcohol is added to water to make a 50 mole per cent solution, the first alcohol added gives a heat essentially that for the solute dissolving in pure water, whereas the last alcohol is added to a solution of about 50 per cent concentration. For theoretical purposes, it is often necessary to know what the ΔH would be for the solution of solute in a solution of definite fixed concentration. Let us imagine a tremendous volume of solution of definite composition and add one more mole of solute to it. We can then suppose that this addition causes no detectable change in the concentration. The heat absorbed in this kind of solution process is the *differential heat of solution*. The same quantity can be defined in terms of a very small addition of δn moles of solute to a solution, the heat absorbed per mole being $\delta q/\delta n$ and the composition of the solution remaining unchanged. Methods of evaluating the differential heat will be considered in Chapter 6.

16. Temperature dependence of reaction heats. Reaction heats depend on the temperature and pressure at which they are measured. We may write the energy change in a chemical reaction as

$$\Delta E = E_{\text{products}} - E_{\text{reactants}}$$

Then
$$\left(\frac{\partial[\Delta E]}{\partial T}\right)_V = \left(\frac{\partial E_{\text{prod}}}{\partial T}\right)_V - \left(\frac{\partial E_{\text{react}}}{\partial T}\right)_V$$

From eq. (2.10),
$$\left(\frac{\partial[\Delta E]}{\partial T}\right)_V = C_{V\text{prod}} - C_{V\text{react}} = \Delta C_V \tag{2.28}$$

Similarly,
$$\left(\frac{\partial[\Delta H]}{\partial T}\right)_P = C_{P\text{prod}} - C_{P\text{react}} = \Delta C_P \tag{2.29}$$

Integrating, at a constant pressure of 1 atm, so that ΔH is the standard ΔH°, we obtain

$$\Delta H^\circ_{T_2} - \Delta H^\circ_{T_1} = \int_{T_1}^{T_2} \Delta C_P\, dT \tag{2.30}$$

These equations were first set forth by G. R. Kirchhoff in 1858. They state that the difference between the heats of reaction at T_1 and at T_2 is equal to the difference in the amounts of heat that must be added to reactants and products at constant pressure to raise them from T_1 to T_2. This conclusion is an immediate consequence of the First Law of Thermodynamics.

In order to apply eq. (2.30), expressions are required for the heat capacities of reactants and products over the temperature range of interest. Over a short range, these may often be taken as practically constant, and we obtain:

$$\Delta H^\circ_{T_2} - \Delta H^\circ_{T_1} = \Delta C_P(T_2 - T_1)$$

More generally, the experimental heat-capacity data will be represented by a power series:

$$C_P = a + bT + cT^2 + \ldots \tag{2.31}$$

Examples of such heat-capacity equations are given in Table 2.4. These three-term equations fit the experimental data to within about 0.5 per cent over a temperature range from 0°C to 1250°C. When the series expression for ΔC_P is substituted[8] in eq. (2.30), the integration can be carried out analytically. Thus at constant pressure, for the standard enthalpy change,

TABLE 2.4

HEAT CAPACITY OF GASES (273–1500°K)*

$C_P = a + bT + cT^2$ (C_P in calories per deg per mole)

Gas	a	$b \times 10^3$	$c \times 10^7$
H_2	6.9469	−0.1999	4.808
O_2	6.148	3.102	−9.23
Cl_2	7.5755	2.4244	−0.650
Br_2	8.4228	0.9739	−3.555
N_2	6.524	1.250	−0.01
CO	6.420	1.665	−1.96
HCl	6.7319	0.4352	3.697
HBr	6.5776	0.9549	1.581
H_2O	7.256	2.298	2.83
CO_2	6.214	10.396	−35.45
Benzene	−0.283	77.936	−262.96
n-Hexane	7.313	104.906	−323.97
CH_4	3.381	18.044	−43.00

* H. M. Spencer, *J. Am. Chem. Soc.*, *67*, 1858 (1945). Spencer and Justice, *ibid.*, *56*, 2311 (1934).

$$d(\Delta H^\circ) = \Delta C_P\, dT = (A + BT + CT^2 + \ldots)dT$$

$$\Delta H^\circ = \Delta H^\circ_0 + AT + \tfrac{1}{2} BT^2 + \tfrac{1}{3} CT^3 + \ldots \tag{2.32}$$

Here ΔH°_0 is the constant of integration.[9] Any one measurement of ΔH° at

---

[8] For a typical reaction, $\frac{1}{2} N_2 + \frac{3}{2} H_2 = NH_3$; $\Delta C_P = C_{P_{NH_3}} - \frac{1}{2} C_{P_{N_2}} - \frac{3}{2} C_{P_{H_2}}$.

[9] If the heat-capacity equations are valid to 0°K, we may note that at $T = 0$, $\Delta H^\circ = \Delta H^\circ_0$, so that the integration constant can be interpreted as the enthalpy change in the reaction at 0°K.

a known temperature T makes it possible to evaluate the constant ΔH°_0 in eq. (2.32). Then the ΔH° at any other temperature can be calculated from the equation. If the heat capacities are given in the form of a C_P vs. T curve, a graphical integration is often convenient.

Recently rather extensive *enthalpy tables* have become available, which give H as a function of T over a wide range of temperatures. The use of these tables makes direct reference to the heat capacities unnecessary.

16. Chemical affinity. Much of the earlier work on reaction heats was done by Julius Thomsen and Marcellin Berthelot, in the latter part of the nineteenth century. They were inspired to carry out a vast program of thermochemical measurements by the conviction that the heat of reaction was the quantitative measure of the *chemical affinity* of the reactants. In the words of Berthelot, in his *Essai de Mécanique chimique* (1878):

> Every chemical change accomplished without the intervention of an external energy tends toward the production of the body or the system of bodies that sets free the most heat.

This principle is incorrect. It would imply that no endothermic reaction could occur spontaneously, and it fails to consider the reversibility of chemical reactions. In order to understand the true nature of chemical affinity and of the driving force in chemical reactions, it is necessary to go beyond the First Law of Thermodynamics, and to investigate the consequences of the second fundamental law that governs the interrelations of work and heat.

PROBLEMS

1. Calculate ΔE and ΔH when 100 liters of helium at STP are heated to 100°C in a closed container. Assume gas is ideal with $C_V = \frac{3}{2}R$.

2. One mole of ideal gas at 25°C is expanded adiabatically and reversibly from 20 atm to 1 atm. What is the final temperature of the gas, assuming $C_V = \frac{3}{2}R$?

3. 100 g of nitrogen at 25°C are held by a piston under 30 atm pressure. The pressure is suddenly released to 10 atm and the gas adiabatically expands. If C_V for nitrogen $= 4.95$ cal per deg, calculate the final temperature of the gas. What are ΔE and ΔH for the change? Assume gas is ideal.

4. At its boiling point (100°C) the density of liquid water is 0.9584 g per cc; of water vapor, 0.5977 g per liter. Calculate the maximum work done when a mole of water is vaporized at the boiling point. How does this compare with the latent heat of vaporization of water?

5. If the Joule-Thomson coefficient is $\mu_{J.T.} = 1.084$ deg per atm and the heat capacity $C_P = 8.75$ cal per mole deg, calculate the change in enthalpy ΔH when 50 g of CO_2 at 25°C and 1 atm pressure are isothermally compressed to 10 atm pressure. What would the value be for an ideal gas?

6. Using the heat-capacity equation in Table 2.4, calculate the heat required to raise the temperature of one mole of HBr from 0° to 500°C.

7. In a laboratory experiment in calorimetry 100 cc of 0.500 *N* acetic acid are mixed with 100 cc of 0.500 *N* sodium hydroxide in a calorimeter. The temperature rises from 25.00° to 27.55°C. The effective heat capacity of the calorimeter is 36 cal per deg. The specific heat of 0.250 *N* sodium acetate solution is 0.963 cal deg^{-1} g^{-1} and its density, 1.034 g per cc. Calculate the heat of neutralization of acetic acid per mole.

8. Assuming ideal gas behavior, calculate the values of ΔE°_{298} for SO_3 (g), H_2O (g), and HCl (g) from the ΔH°_{298} values in Table 2.2.

9. From the heats of formation in Table 2.3, calculate ΔH°_{298} for the following cracking reactions:

$$C_2H_6 + H_2 = 2\,CH_4$$

$$n\text{-}C_4H_{10} + 3\,H_2 = 4\,CH_4$$

$$\text{iso-}C_4H_{10} + 3\,H_2 = 4\,CH_4$$

10. The heat of sublimation of graphite to carbon atoms has been estimated as 170 kcal per mole. The dissociation of molecular hydrogen into atoms, $H_2 = 2\,H$, has $\Delta H^\circ = 103.2$ kcal per mole. From these data and the value for the heat of formation of methane, calculate the ΔH° for C (g) + 4 H (g) = CH_4 (g). One fourth of this value is a measure of the "energy of the C—H bond" in methane.

11. Assuming that the energy of the C—H bond in ethane, C_2H_6, is the same as in methane (Problem 10) estimate the energy of the C—C bond in ethane from the heat of formation in Table 2.3.

12. When *n*-hexane is passed over a chromia catalyst at 500°C, benzene is formed: C_6H_{14} (g) = C_6H_6 (g) + 4 H_2, $\Delta H^\circ_{298} = 59.78$ kcal per mole. Calculate ΔH° for the reaction at 500°C (Table 2.4).

13. Derive a general expression for ΔH° of the water gas reaction ($H_2 + CO_2 = H_2O + CO$) as a function of temperature. Use it to calculate ΔH° at 500°K and 1000°K.

14. From the curve in Fig. 2.4, estimate the heat evolved when 1 kg of a 10 per cent (by weight) solution of ethanol in water is blended with 1 kg of a 75 per cent solution of ethanol in water.

15. If a compound is burned under adiabatic conditions so that all the heat evolved is utilized in heating the product gases, the maximum temperature attained is called the adiabatic flame temperature. Calculate this temperature for the burning of ethane with twice the amount of air (80 per cent N_2, 20 per cent O_2) needed for complete combustion to CO_2 and H_2O. Use heat capacities in Table 2.4, but neglect the terms cT^2.

16. Show that for a van der Waals gas, $(\partial E/\partial V)_T = a/V^2$.

17. Show that $(\partial E/\partial P)_V = \beta C_V/\alpha$.

REFERENCES

BOOKS

See Chapter 1, p. 25.

ARTICLES

1. Parks, G. S., *J. Chem. Ed.*, *26*, 262–66 (1949), "Remarks on the History of Thermochemistry."
2. Menger, K., *Am. J. Phys. 18*, 89 (1950), "The Mathematics of Elementary Thermodynamics."
3. Sturtevant, J. M., Article on "Calorimetry" in *Physical Methods of Organic Chemistry*, vol. 1, 311–435, edited by A. Weissberger (New York: Interscience, 1945).

CHAPTER 3

The Second Law of Thermodynamics

1. The efficiency of heat engines. The experiments of Joule helped to disprove the theory of "caloric" by demonstrating that heat was not a "substance" conserved in physical processes, since it could be generated by mechanical work. The reverse transformation, the conversion of heat into useful work, had been of greater interest to the practical engineer ever since the development of the steam engine by James Watt in 1769. Such an engine operates essentially as follows: A source of heat (*e.g.*, a coal or wood fire) is used to heat a "working substance" (*e.g.*, steam), causing it to expand through an appropriate valve into a cylinder fitted with a piston. The expansion drives the piston forward, and by suitable coupling mechanical work can be obtained from the engine. The working substance is cooled by the expansion, and this cooled working substance is withdrawn from the cylinder through a valve. A flywheel arrangement returns the piston to its original position, in readiness for another expansion stroke. In simplest terms, therefore, any such heat engine withdraws heat from a heat source, or hot reservoir, converts some of this heat into work, and discards the remainder to a heat sink or cold reservoir. In practice there are necessarily frictional losses of work in the various moving components of the engine.

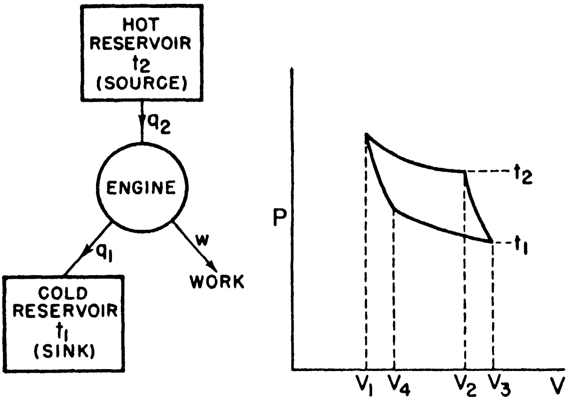
The first theoretical discussions of these engines were expressed in terms of the caloric hypothesis. The principal problem was to understand the factors governing the *efficiency* e of the engine, which was measured by the ratio of useful work output w to the heat input q_2.

$$e = \frac{w}{q_2} \tag{3.1}$$

A remarkable advance towards the solution of this problem was made in 1824 by a young French engineer, Sadi Carnot, in a monograph, *Réflexions sur la Puissance motrice du Feu.*

2. The Carnot cycle. The Carnot cycle represents the operation of an idealized engine in which heat is transferred from a hot reservoir at temperature t_2, is partly converted into work, and partly discarded to a cold reservoir at temperature t_1. (Fig. 3.1a.) The working substance through which these operations are carried out is returned at the end to the same state that it initially occupied, so that the entire process constitutes a complete cycle. We have written the temperatures as t_1 and t_2 to indicate that they are empirical temperatures, measured on any convenient scale whatsoever. The various steps in the cycle are carried out reversibly.

To make the operation more definite, we may consider the working substance to be a gas, and the cyclic process may be represented by the indicator



(a) (b)

Fig. 3.1. The essential features of the heat engine (a) and the Carnot cycle for its operation shown on an indicator diagram (b).

diagram of Fig. 3.1b. The steps in the working of the engine for one complete cycle are then:

(1) Withdrawal of heat $= q_2$ from a hot reservoir at temperature t_2 by the isothermal reversible expansion of the gas from V_1 to V_2. Work done by gas $= w_1$.
(2) Adiabatic reversible expansion from V_2 to V_3, during which $q = 0$, gas does work $= w_2$ and cools from t_2 to t_1.
(3) Isothermal reversible compression at t_1 from V_3 to V_4. Work done by the gas $= -w_3$. Heat $= q_1$ absorbed by the cold reservoir at t_1.
(4) Adiabatic reversible compression from V_4 to V_1, gas warming from t_1 to t_2. Work done by gas $= -w_4$, $q = 0$.

The First Law of Thermodynamics requires that for the cyclic process $\Delta E = 0$. Now ΔE is the sum of all the heat added to the gas, $q = q_2 - q_1$, less the sum of all the work done by the gas, $w = w_1 + w_2 - w_3 - w_4$.

$$\Delta E = q - w = q_2 - q_1 - w = 0$$

The net work done by the engine is equal, therefore, to the heat taken from the hot reservoir less the heat that is returned to the cold reservoir: $w = q_2 - q_1$. The efficiency of the engine is:

$$e = \frac{w}{q_2} = \frac{q_2 - q_1}{q_2} \tag{3.2}$$

Since every step in this cycle is carried out reversibly, the maximum possible work is obtained for the particular working substance and temperatures considered.[1]

Consider now another engine operating, for example, with a different working substance. Let us assume that this second engine, working between the same two empirical temperatures t_2 and t_1, is more efficient than engine 1; that is, it can deliver a greater amount of work, $w' > w$, from the same amount of heat q_2 taken from the hot reservoir. (See Fig. 3.1a.) It could accomplish this only by discarding less heat, $q_1' < q_1$, to the cold reservoir.

Let us now imagine that, after the completion of a cycle by this supposedly more efficient engine, the original engine is run in reverse. It therefore acts as a *heat pump.* Since the original Carnot cycle is reversible, all the heat and work terms are changed in sign but not in magnitude. The heat pump takes in q_1 of heat from the cold reservoir, and by the expenditure of work $= w$ delivers q_2 of heat to the hot reservoir.

$$\begin{array}{lrl}
\text{For the first process (engine 2)} & w' = & q_2 - q_1' \\
\text{For the second process (engine 1)} & -w = & -q_2 + q_1 \\
\cline{3-3}
\text{Therefore, the net result is:} & w' - w = & q_1 - q_1'
\end{array}$$

Since $w' > w$, and $q_1 > q_1'$, the net result of the combined operation of these two engines is that an amount of heat, $q = q_1 - q_1'$, has been abstracted from a heat reservoir at constant temperature t_1 and an amount of work $w'' = w' - w$ has been obtained from it, without any other change whatsoever taking place.

In this result there is nothing contrary to the First Law of Thermodynamics, for energy has been neither created nor destroyed. The work done would be equivalent to the heat extracted from the reservoir. Nevertheless, in all of human history, nobody has ever observed the isothermal conversion of heat into work without any concomitant change in the system. Think what it would imply. It would not be necessary for a ship to carry fuel: this wonderful device would enable it to use a small fraction of the immense thermal energy of the ocean to turn its propellers and run its dynamos. Such a continuous extraction of useful work from the heat of our environment has been called "perpetual motion of the second kind," whereas the production of work from nothing at all was called "perpetual motion of the first kind." The impossibility of the latter is postulated by the First Law of Thermodynamics; the impossibility of the former is postulated by the Second Law.

If the supposedly more efficient Carnot engine delivered the same amount of work w as the original engine, it would need to withdraw less heat $q_2' < q_2$

---

[1] In the isothermal steps, the maximum work is obtained on expansion and the minimum work done in compression of the gas (cf. p. 23). In the adiabatic steps $\Delta E = -w$, and the work terms are constant once the initial and final states are fixed.

from the hot reservoir. Then the result of running engine 2 forward and engine 1 in reverse, as a heat pump, would be

$$\begin{array}{lrcl} (2) & w = & q_2' - q_1' \\ (1) & -w = & -q_2 + q_1 \\ \hline & q_2 - q_2' = & q_1 - q_1' = q \end{array}$$

This amounts to the transfer of heat q from the cold reservoir at t_1 to the hot reservoir at t_2 without any other change in the system.

There is nothing in this conclusion contrary to the First Law, but it is even more obviously contrary to human experience than is perpetual motion of the second kind. We know that heat always flows from the hotter to the colder region. If we place a hot body and a cold body together, the hot one never grows hotter while the cold one becomes colder. We know in fact that considerable work must be expended to refrigerate something, to pump heat out of it. Heat never flows uphill, *i.e.*, against a temperature gradient, of its own accord.

3. The Second Law of Thermodynamics. This Second Law may be expressed precisely in various equivalent forms. For example:

The principle of Thomson. It is impossible by a cyclic process to take heat from a reservoir and convert it into work without, in the same operation, transferring heat from a hot to a cold reservoir.

The principle of Clausius. It is impossible to transfer heat from a cold to a warm reservoir without, in the same process, converting a certain amount of work into heat.

Returning to Carnot's cycle, we have seen that the supposition that one reversible cycle may exist that is more efficient than another has led to results contradicting human experience as embodied in the Second Law of Thermodynamics. We therefore conclude that *all reversible Carnot cycles operating between the same initial and final temperatures must have the same efficiency.* Since the cycles are reversible, this efficiency is the maximum possible. It is completely independent of the working substance and is a function only of the working temperatures:

$$e = f'(t_1, t_2)$$

4. The thermodynamic temperature scale. The principle of Clausius may be rephrased as "heat never flows spontaneously, *i.e.*, without the expenditure of work, from a colder to a hotter body." This statement contains essentially a definition of temperature, and we may recall that the temperature concept was first introduced as a result of the observation that all bodies gradually reach a state of thermal equilibrium.

Lord Kelvin was the first to use the Second Law to define a thermodynamic temperature scale, which is completely independent of any thermometric substance. The Carnot theorem on the efficiency of a reversible cycle may be written: Efficiency (independent of working substance) $= (q_2 - q_1)/q_2 = f'(t_1, t_2)$, or $1 - q_1/q_2 = f'(t_1, t_2)$. Therefore

$$\frac{q_1}{q_2} = f(t_1, t_2) \tag{3.3}$$

We have written $f'(t_1, t_2)$ and $f(t_1, t_2) = 1 - f'(t_1, t_2)$ to indicate unspecified functions of t_1 and t_2.

Consider two Carnot cycles such that: $q_1/q_2 = f(t_1, t_2)$; $q_2/q_3 = f(t_2, t_3)$. They must be equivalent to a third cycle, operating between t_1 and t_3, with $q_1/q_3 = f(t_1, t_3)$. Therefore

$$\frac{q_1}{q_2} = \frac{f(t_1, t_3)}{f(t_2, t_3)} = f(t_1, t_2)$$

But, if this condition is satisfied, we can write: $f(t_1, t_3) = F(t_1)/F(t_3)$: $f(t_2, t_3) = F(t_2)/F(t_3)$. That is, the efficiency function, $f(t_1, t_2)$, is the quotient of a function of t_1 alone and a function of t_2 alone. It follows that

$$\frac{q_1}{q_2} = \frac{F(t_1)}{F(t_2)} \tag{3.4}$$

Lord Kelvin decided to use eq. (3.4) as the basis of a *thermodynamic temperature scale*. He took the functions $F(t_1)$ and $F(t_2)$ to have the simplest possible form, namely, T_1 and T_2. Thus a temperature ratio on the Kelvin scale was defined as equal to the ratio of the heat absorbed to the heat rejected in the working of a reversible Carnot cycle.

$$\frac{q_2}{q_1} = \frac{T_2}{T_1} \tag{3.5}$$

The efficiency of the cycle, eq. (3.2), then becomes

$$e = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} \tag{3.6}$$

The zero point of the thermodynamic scale is physically fixed as the temperature of the cold reservoir at which the efficiency becomes equal to unity, *i.e.*, the heat engine is perfectly efficient. From eq. (3.6), in the limit as $T_1 \to 0$, $e \to 1$.

The efficiency calculated from eq. (3.6) is the *maximum thermal efficiency* that can be approached by a heat engine. Since it is calculated for a reversible Carnot cycle, it represents an ideal that actual irreversible cycles can never achieve. Thus with a heat source at 120°C and a sink at 20°C, the maximum thermal efficiency is 100/393 = 25.4 per cent. If the heat source is at 220° and the sink still at 20°, the efficiency is raised to 200/493 = 40.6 per cent. It is easy to see why the trend in power plant design has been to higher temperatures for the heat source. In practice, the efficiency of steam engines seldom exceeds 80 per cent of the theoretical value. Steam turbines generally can operate somewhat closer to their maximum thermal efficiencies, since they have fewer moving parts and consequently lower frictional losses.

5. Application to ideal gases. Temperature on the Kelvin, or thermodynamic, scale has been denoted by the symbol T, which is the same symbol used previously for the absolute ideal gas scale. It can be shown that these scales are indeed numerically the same by running a Carnot cycle with an ideal gas as the working substance.

Applying eqs. (2.18) and (2.20) to the four steps:

(1) Isothermal expansion: $w_1 = q_2 = RT_2 \ln V_2/V_1$

(2) Adiabatic expansion: $w_2 = \int_{T_1}^{T_2} C_V\, dT;\ q = 0$

(3) Isothermal compression: $-w_3 = -q_1 = -RT_1 \ln V_4/V_3$

(4) Adiabatic compression: $-w_4 = \int_{T_1}^{T_2} C_V\, dT;\ q = 0$

By summation of these terms, the net work obtained is $w = w_1 + w_2 - w_3 - w_4 = RT_2 \ln V_2/V_1 + RT_1 \ln V_4/V_3$.

Since, from eq. (2.22), $V_2/V_1 = V_3/V_4$,

$$w = R(T_2 - T_1) \ln \frac{V_2}{V_1}$$

$$e = \frac{w}{q_2} = \frac{T_2 - T_1}{T_2}$$

Comparison with eq. (3.6) completes the proof of the identity of the ideal gas and thermodynamic temperature scales.

6. Entropy. Equation (3.6) for a reversible Carnot cycle operating between T_2 and T_1 irrespective of the working substance may be rewritten

$$\frac{q_2}{T_2} - \frac{q_1}{T_1} = 0 \qquad (3.7)$$

Now it can be shown that *any cyclic process can be broken down into a number of Carnot cycles*. Consider the perfectly general ABA of Fig. 3.2. The area of the figure has been divided into a number of Carnot cycles by the crosshatched system of isothermals and adiabatics. The outside boundaries of these little cycles form the heavy zigzag curve which follows quite closely the path of the general cycle ABA. The inside portions of the little Carnot cycles cancel out, since each section is traversed once in the forward direction and once in the reverse direction. For example, consider the isothermal xy which belongs to an

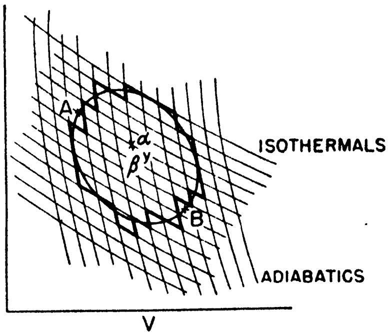


Fig. 3.2. General cycle broken down into Carnot cycles.

expansion in the small cycle β, and to a compression in the small cycle α, all the work and heat terms arising from it thereby being canceled.

If eq. (3.7) is now applied to all these little Carnot cycles, we have for the zigzag segments $\sum q/T = 0$. As the Carnot cycles are made smaller and smaller, the boundary curve approaches more and more closely to that for the general cyclic process ABA. In the limit, for differential Carnot cycles, the area enclosed by the crooked boundary becomes identical with the area of the cycle ABA. We can then replace the summation of finite terms by the integration of differentials and obtain[2]

$$\oint \frac{dq}{T} = 0 \tag{3.8}$$

This equation holds true for any *reversible* cyclic process whatsoever.

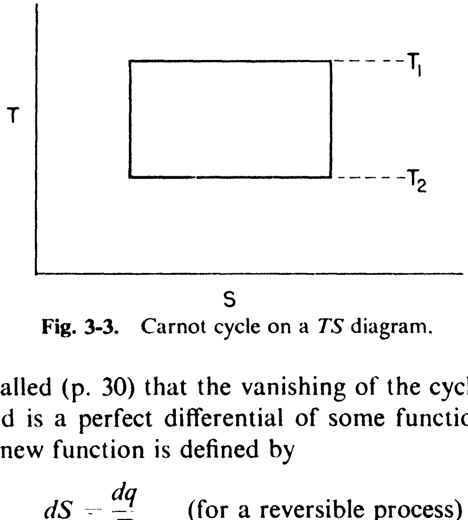


Fig. 3-3. Carnot cycle on a *TS* diagram.

It may be recalled (p. 30) that the vanishing of the cyclic integral means that the integrand is a perfect differential of some function of the state of the system. This new function is defined by

$$dS = \frac{dq}{T} \quad \text{(for a reversible process)} \tag{3.9}$$

Thus,

$$\oint dS = \int_A^B dS + \int_B^A dS$$
$$= S_B - S_A + S_A - S_B = 0$$

The function S was first introduced by Clausius in 1850, and is called the *entropy*. Equation (3.9) indicates that when the inexact differential expression dq is multiplied by $1/T$, it becomes an exact differential; the factor $1/T$ is called an *integrating multiplier*. The integral $\int_A^B dq_{\text{rev}}$ is dependent on the path, whereas $\int_A^B dq_{\text{rev}}/T$ is independent of the path. This, in itself, is an alternative statement of the Second Law of Thermodynamics.

It is interesting to consider the *TS* diagram in Fig. 3.3, which is analogous to the *PV* diagram of Fig. 1.8. In the *PV* case, the area under the curve is a

---

[2] See P. S. Epstein, *Textbook of Thermodynamics* (New York: Wiley, 1938), p. 57.

measure of the work done in traversing the indicated path. In the *TS* diagram, the area under the curve is a measure of the heat added to the system. Temperature and pressure are intensity factors; entropy and volume are capacity factors. The products $P\,dV$ and $T\,dS$ both have the dimensions of energy.

7. The inequality of Clausius. Equation (3.8) was obtained for a reversible cycle. Clausius showed that for a cycle into which irreversibility enters at any stage, the integral of dq/T is always less than zero.

$$\oint \frac{dq}{T} < 0 \tag{3.10}$$

The proof is evident from the fact that the efficiency of an irreversible Carnot cycle is always less than that of a reversible cycle operating between the same two temperatures. For the irreversible case, we therefore conclude from eq. (3.6) that

$$\frac{q_2 - q_1}{q_2} < \frac{T_2 - T_1}{T_2}$$

Then, instead of eq. (3.7), we find that

$$\frac{q_2}{T_2} - \frac{q_1}{T_1} < 0$$

This relation is extended to the general cycle, by following the argument based on Fig. (3.2). Instead of eq. (3.8), which applies to the reversible case, we obtain the inequality of Clausius, given by eq. (3.10).

8. Entropy changes in an ideal gas. The calculation of entropy changes in an ideal gas is particularly simple because in this case $(\partial E/\partial V)_T = 0$, and heat or work terms due to cohesive forces need not be considered at any point. For a reversible process in an ideal gas, the First Law requires that

$$dq = dE + P\,dV = C_V\,dT + \frac{RT\,dV}{V}$$

Therefore, $$dS = \frac{dq}{T} = \frac{C_V\,dT}{T} + \frac{R\,dV}{V} \tag{3.11}$$

On integration, $\Delta S = S_2 - S_1 = \int_1^2 C_V\,d\ln T + \int_1^2 R\,d\ln V$

If C_V is independent of temperature,

$$\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \tag{3.12}$$

For the special case of a temperature change at constant volume, the increase in entropy with increase in temperature is therefore

$$\Delta S = C_V \ln \frac{T_2}{T_1} \tag{3.13}$$

If the temperature of one mole of ideal gas with $C_V = 3$ is doubled, the entropy is increased by $3 \ln 2 = 2.08$ calories per degree, or 2.08 *entropy units* (eu).

For the case of an isothermal expansion, the entropy increase becomes

$$\Delta S = R \ln \frac{V_2}{V_1} = R \ln \frac{P_1}{P_2} \tag{3.14}$$

If one mole of ideal gas is expanded to twice its original volume, its entropy is increased by $R \ln 2 = 1.38$ eu.

9. Entropy changes in isolated systems. The change in entropy in going from a state A to a state B is always the same, irrespective of the path between A and B, since the entropy is a function of the state of the system alone. It makes no difference whether the path is reversible or irreversible. Only in case the path is reversible, however, is the entropy change given by

$$\Delta S = S_B - S_A = \int \frac{dq}{T} \tag{3.15}$$

In order to evaluate the entropy change for an irreversible process, it is necessary to devise a reversible method for going from the same initial to the same final state, and then to apply eq. (3.15).

In any completely isolated system we are restricted to adiabatic processes, since no heat can either enter or leave such a system.[3] For a *reversible* process in an isolated system, therefore, $dq = 0$ and $dS = dq/T = 0$, or $S =$ constant. If one part of the system increases in entropy, the remaining part must decrease by an exactly equal amount.

A fundamental example of an irreversible process is the transfer of heat from a hot to a colder body. We can make use of an ideal gas to carry out the transfer reversibly, and thereby calculate the entropy change. The gas is placed in thermal contact with the hot body at T_2 and expanded reversibly and isothermally until it takes up heat equal to q. To simplify the argument, it is assumed that the bodies have heat capacities so large that changes in their temperatures on adding or withdrawing heat q are negligible. The gas is then removed from contact with the hot reservoir and allowed to expand reversibly and adiabatically until its temperature falls to T_1. Next it is placed in contact with the colder body at T_1 and compressed isothermally until it gives up heat equal to q.

The hot reservoir has now lost entropy $= q/T_2$, whereas the cold reservoir has gained entropy $= q/T_1$. The net entropy change of the reservoirs has therefore been $\Delta S = q/T_1 - q/T_2$. Since $T_2 > T_1$, $\Delta S > 0$, and the entropy has increased. The entropy of the ideal gas, however, has decreased by an exactly equal amount, so that for the entire isolated system of ideal gas plus heat reservoirs, $\Delta S = 0$ for the reversible process. If the heat transfer had

---

[3] The completely isolated system is, of course, a figment of imagination. Perhaps our whole universe might be considered as an isolated system, but no small section of it can be rigorously isolated. As usual, the precision and sensitivity of our experiments must be allowed to determine how the system is to be defined.

been carried out irreversibly, for example by placing the two bodies in direct thermal contact and allowing heat q to flow along the finite temperature gradient thus established, there would have been no compensating entropy decrease. The entropy of the isolated system would have increased during the irreversible process, by the amount $\Delta S = q/T_1 - q/T_2$.

We shall now prove that *the entropy of an isolated system always increases during an irreversible process.* The proof of this theorem is based on the inequality of Clausius. Consider in Fig. (3.4) a perfectly general irreversible process in an isolated system, leading from state A to state B. It is represented by the dashed line. Next consider that the system is returned to its initial state A by a reversible path represented by the solid line from B to A. During this reversible process, the system need not be isolated, and can exchange heat and work with its environment. Since the entire cycle is in part irreversible, eq. (3.10) applies, and

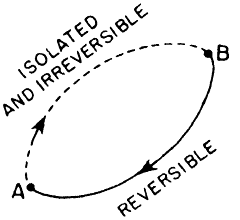


Fig. 3.4. A cyclic process.

$$\oint \frac{dq}{T} < 0$$

Writing the cycle in terms of its two sections, we obtain

$$\int_A^B \frac{dq_{\text{irrev}}}{T} + \int_B^A \frac{dq_{\text{rev}}}{T} < 0 \qquad (3.16)$$

The first integral is equal to zero, since during the process $A \to B$ the system is by hypothesis isolated and therefore no transfer of heat is possible. The second integral, from eq. (3.15), is equal to $S_A - S_B$. Therefore eq. (3.16) becomes

$$S_A - S_B < 0, \quad \text{or} \quad S_B - S_A > 0$$

We have therefore proved that the entropy of the final state B is always greater than that of the initial state A, if A passes to B by an irreversible process in an isolated system.

Since all naturally occurring processes are irreversible, any change that actually occurs spontaneously in nature is accompanied by a net increase in entropy. This conclusion led Clausius to his famous concise statement of the laws of thermodynamics. "The energy of the universe is a constant; the entropy of the universe tends always towards a maximum."

This increasing tendency of the entropy has also been expressed as a principle of the degradation of energy, by which it becomes less available for useful work. Thus temperature differences tend to become leveled out, mountains tend to become plains, fuel supplies become exhausted, and work is frittered away into heat by frictional losses. Interesting philosophical discussions have arisen from the entropy concept, notably the suggestion of Sir Arthur Eddington that, because of its continuously increasing character, "entropy is time's arrow"; that is, the constantly increasing entropy of the universe is the physical basis of our concept of time. The "meaning" of entropy will be displayed in another aspect when we discuss its statistical interpretation.

10. Change of entropy in changes of state of aggregation. As an example of a change in state of aggregation we may take the melting of a solid. At a fixed pressure, the melting point is a definite temperature T_m at which solid and liquid are in equilibrium. In order to change some of the solid to liquid, heat must be added to the system. As long as both solid and liquid are present, this added heat does not change the temperature of the system, but is absorbed by the system as the *latent heat of fusion* λ_f of the solid. Since the change occurs at constant pressure, the latent heat, by eq. (2.9), equals the difference in enthalpy between liquid and solid. Per mole of substance,

$$\lambda_f = \Delta H_f = H_{\text{liquid}} - H_{\text{solid}}$$

At the melting point, liquid and solid exist together in equilibrium. The addition of a little heat would melt some of the solid, the removal of a little heat would solidify some of the liquid, but the equilibrium between solid and liquid would be maintained. The latent heat is necessarily a *reversible heat,* because the process of melting follows a path consisting of successive equilibrium states. We can therefore evaluate the entropy of fusion ΔS_f by a direct application of the relation $\Delta S = q_{\text{rev}}/T$, which applies to any reversible isothermal process.

$$S_{\text{liquid}} - S_{\text{solid}} = \Delta S_f = \frac{\Delta H_f}{T_f} \tag{3.17}$$

For example,[4] ΔH_f for ice is 1430 cal per mole, so that $\Delta S_f = 1430/273.2 = 5.25$ cal deg^{-1} mole^{-1}.

By an exactly similar argument the entropy of vaporization ΔS_v, the latent heat of vaporization ΔH_v, and the boiling point T_b are related by

$$S_{\text{vapor}} - S_{\text{liquid}} = \Delta S_v = \frac{\Delta H_v}{T_b} \tag{3.18}$$

A similar equation holds for a change from one form of a polymorphic solid to another, if the change occurs at a T and P at which the two forms are in equilibrium, and if there is a latent heat λ associated with the transformation. For example, grey tin and white tin are in equilibrium at 13°C and 1 atm, and $\lambda = 500$ cal. Then $\Delta S_t = 500/286 = 1.75$ cal deg^{-1} mole^{-1}.

11. Entropy and equilibrium. Now that the entropy function has been defined and a method outlined for the evaluation of entropy changes, we have gained a powerful tool for our attack on the fundamental problem of

---

[4] Further typical data are shown in Table 14.1 in sec. 14.8.

physicochemical equilibrium. In our introductory chapter, the position of equilibrium in purely mechanical systems was shown to be the position of minimum potential energy. What is the criterion for equilibrium in a thermodynamic system?

Any spontaneously occurring change in an isolated system is accompanied by an increase in entropy. From the First Law of Thermodynamics we know that energy can be neither created nor destroyed, so that the internal energy of an isolated system must be constant. The only way such a system could gain or lose energy would be by some interaction with its surroundings, but the absence of any such interaction is just what we mean when we say that the system is "isolated"—no work is done on it; no heat flows across its boundaries. If we restrict work to PV work (expansion or compression), and exclude linear or surface effects, it follows also that the volume of an isolated system must remain constant. An isolated system may be defined, therefore, as a system of constant energy and constant volume. The first sentence of this paragraph can thus be rephrased: In a system at constant E and V, any spontaneous change is accompanied by an increase in entropy.

Now a system is said to be at equilibrium when it has no further tendency to change its properties. The entropy of an isolated system will increase until no further spontaneous changes can occur. When the entropy reaches its maximum, the system no longer changes: the equilibrium has been attained. A criterion for *thermodynamic equilibrium* is therefore the following: *In a system at constant energy and volume, the entropy is a maximum. At constant E and V, the S is a maximum.*

If instead of a system at constant E and V, a system at constant S and V is considered, the equilibrium criterion takes the following form: *At constant S and V, the E is a minimum.* This is just the condition applicable in ordinary mechanics, in which thermal effects are excluded.

The drive, or perhaps better the drift, of physicochemical systems toward equilibrium is therefore compounded of two factors. One is the tendency toward minimum energy, the bottom of the potential energy curve. The other is the tendency toward maximum entropy. Only if E is held constant can S achieve its maximum; only if S is held constant can E achieve its minimum. What happens when E and S are forced to strike a compromise?

12. The free energy and work functions. Chemical reactions are rarely studied under constant entropy or constant energy conditions. Usually the physical chemist places his systems in thermostats and investigates them under conditions of approximately constant temperature and pressure. Sometimes changes at constant volume and temperature are followed, for example, in bomb calorimeters. It is most desirable, therefore, to obtain criteria for thermodynamic equilibrium that will be applicable under these practical conditions.

To this end, two new functions have been invented, defined by the following equations:

$$A = E - TS \tag{3.19}$$

$$F = H - TS \tag{3.20}$$

A is called the *work function*; F is called the *free energy*.[5] Both A and F, by their definitions in terms of state functions, are themselves functions of the state of the system alone.

For a change *at constant temperature*,

$$\Delta A = \Delta E - T\,\Delta S \tag{3.21}$$

If this change is carried out reversibly, $T\,\Delta S = q$, and $\Delta A = \Delta E - q$ or

$$-\Delta A = w_{\max} \tag{3.22}$$

The work is the maximum obtainable since the process is reversible. When the system isothermally performs maximum work $w_{\max}$, its work function decreases by ΔA. In any naturally occurring process, which is more or less irreversible, the work obtained is always less than the decrease in A.

From eqs. (3.19) and (3.20), since $H = E + PV$,

$$F = A + PV \tag{3.23}$$

For a change *at constant pressure*,

$$\Delta F = \Delta A + P\,\Delta V \tag{3.24}$$

From eqs. (3.22) and (3.24), *at constant temperature and pressure*,

$$-\Delta F = w_{\max} - P\,\Delta V \tag{3.25}$$

The decrease in free energy equals the maximum work less the work done by the expansion of the system at constant pressure. This work of expansion is always equal to $P(V_2 - V_1) = P\,\Delta V$ no matter how the change occurs, reversibly or irreversibly, provided the external pressure is kept constant. The *net work* over and above this is given by $-\Delta F$ *for a reversible process.* For an irreversible process the net work is always less than $-\Delta F$. It may be zero as, for example, in a chemical reaction carried out in such a way that it yields no net work. Thus the combustion of gasoline in an automobile engine yields net work, but burning the same gasoline in a calorimeter yields none. The value of ΔF for the change is the same in either case, provided the initial and final states are the same.

A helpful interpretation of the entropy can be obtained in terms of the new functions A and F. From eqs. (3.19) and (3.20), we can write for a change *at constant temperature*,

$$\Delta A = \Delta E - T\,\Delta S \tag{3.21}$$

$$\Delta F = \Delta H - T\,\Delta S \tag{3.26}$$

---

[5] Sometimes A is called the *Helmholtz free energy*, and F the *Gibbs free energy* or *thermodynamic potential.*

The change in the work function in an isothermal process equals the change in the energy minus a quantity $T\,\Delta S$ that may be called *the unavailable energy*. Similarly, the change in free energy equals the total change in enthalpy minus the unavailable energy.

13. Free energy and equilibrium. The free energy function F may be used to define a condition for equilibrium in a form that is more directly applicable to experimental situations than the criteria in terms of the entropy. We have seen that for a *reversible* process occurring at constant temperature and pressure the net work done by the system is equal to the decrease in free energy. For a differential change, therefore, under these reversible (*i.e.*, equilibrium) conditions *at constant temperature and pressure*,

$$dF = -dw_{\text{net}} \tag{3.27}$$

Now most chemical laboratory experiments are carried out under such conditions that no work is obtained from the system or added to the system except the ordinary PV work,[6] so that $dw_{\text{net}} = 0$. In these cases the equilibrium criterion becomes simply:

At constant T and P, $$dF = 0 \tag{3.28}$$

This may be stated as follows: *Any change in a system at equilibrium at constant temperature and pressure is such that the free energy remains constant.*

Thus we have obtained an answer to the question of how the drive toward maximum entropy and the drive toward minimum energy reach a compromise as a system tends toward equilibrium. From eq. (3.26) it is evident that an increase in S and a decrease in H both tend to lower the free energy. Therefore the third criterion for equilibrium can be written: *at constant T and P, the F is a minimum.* A similar discussion of eq. (3.19) provides the equilibrium condition at constant temperature and volume: *at constant T and V, the A is a minimum.* These are the equilibrium conditions that are of greatest use in most chemical applications.

14. Pressure dependence of the free energy. From eq. (3.20), $F = H - TS = E + PV - TS$. Differentiating, we obtain

$$dF = dE + P\,dV + V\,dP - T\,dS - S\,dT$$

Since

$$dE = T\,dS - P\,dV$$

$$dF = V\,dP - S\,dT \tag{3.29}$$

Therefore,

$$\left(\frac{\partial F}{\partial P}\right)_T = V \tag{3.30}$$

For an isothermal change from state (1) to state (2):

$$F_2 - F_1 = \Delta F = \int_1^2 dF = \int_1^2 V\,dP \tag{3.31}$$

---

[6] Notable exceptions are experiments with electrochemical cells, in which electric work may be exchanged with the system. A detailed discussion is given in Chapter 15.

In order to integrate this equation, the variation of V with P must be known for the substance being studied. Then if the free energy is known at one pressure, it can be calculated for any other pressure. If a suitable equation of state is available, it can be solved for V as a function of P, and eq. (3.31) can be integrated after substituting this $f(P)$ for V. In the simple case of the *ideal gas*, $V = RT/P$, and

$$F_2 - F_1 = \Delta F = RT \ln \frac{P_2}{P_1} \tag{3.32}$$

This gives the increase in free energy on compression, or decrease on expansion. For example, if one mole of an ideal gas is compressed isothermally at 300°K to twice its original pressure, its free energy is increased by $1.98 \times 300 \ln 2 = 413$ calories.

15. Temperature dependence of free energy. From eq. (3.29), at constant pressure,

$$\left(\frac{\partial F}{\partial T}\right)_P = -S \tag{3.33}$$

To integrate this equation, we must know S as a function of temperature. This question is considered in the next section. An alternative expression can be obtained by combining eq. (3.33) with eq. (3.20):

$$\left(\frac{\partial F}{\partial T}\right)_P = \frac{F - H}{T} \tag{3.34}$$

For isothermal changes in a system, the variation of ΔF with temperature[7] is then

$$\left(\frac{\partial \Delta F}{\partial T}\right)_P = -\Delta S = \frac{\Delta F - \Delta H}{T} \tag{3.35}$$

This is called the *Gibbs-Helmholtz equation*. It permits us to calculate the change in enthalpy ΔH from a knowledge of ΔF and the temperature coefficient of ΔF. Since

$$\frac{d}{dT}\left(\frac{\Delta F}{T}\right) = \frac{1}{T}\frac{d(\Delta F)}{dT} - \frac{\Delta F}{T^2}$$

the Gibbs-Helmholtz equation can be written in the alternative forms:

$$\left[\frac{\partial}{\partial T}\left(\frac{\Delta F}{T}\right)\right]_P = \frac{-\Delta H}{T^2}$$

$$\text{Or,} \qquad \left[\frac{\partial(\Delta F/T)}{\partial(1/T)}\right]_P = \Delta H \tag{3.36}$$

---

[7] For example the free energy change ΔF of a chemical reaction might be studied at a series of different constant temperatures, always under the same constant pressure. The equation predicts how the observed ΔF depends on the temperature at which the reaction is studied.

Thus the slope of the plot of $\Delta F/T$ vs. $1/T$ is ΔH, the change in enthalpy. Important applications of these equations to chemical reactions will be considered in the next chapter. They are especially important because many chemical processes are carried out in thermostats under practically constant atmospheric pressure.

16. Variation of entropy with temperature and pressure. Besides its usefulness in the formulation of equilibrium conditions, the free-energy function can be used to derive important relations between the other thermodynamic variables. Consider, for example, the mathematical identity

$$\frac{\partial}{\partial P}\left(\frac{\partial F}{\partial T}\right)_P = \frac{\partial}{\partial T}\left(\frac{\partial F}{\partial P}\right)_T$$

By virtue of eqs. (3.30) and (3.33), this identity yields an expression for the pressure coefficient of the entropy:[8]

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad (3.37)$$

Thus *at constant temperature*, $dS = -(\partial V/\partial T)_P dP$, so that

$$\Delta S = -\int_{P_1}^{P_2}\left(\frac{\partial V}{\partial T}\right)_P dP = -\int_{P_1}^{P_2} \alpha V_0\, dP \qquad (3.38)$$

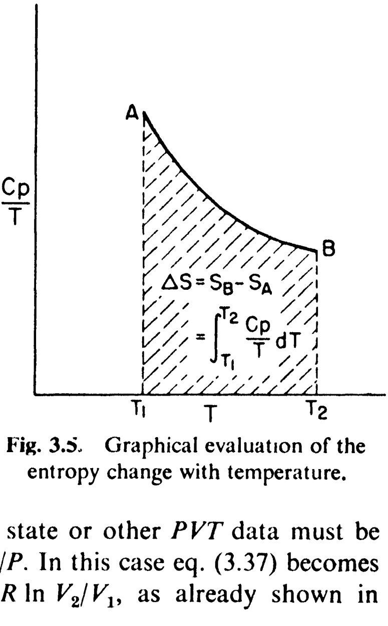


Fig. 3.5. Graphical evaluation of the entropy change with temperature.

To evaluate this integral, the equation of state or other *PVT* data must be available. For an ideal gas, $(\partial V/\partial T)_P = R/P$. In this case eq. (3.37) becomes $dS = -R\, d\ln P$, or $\Delta S = R\ln P_1/P_2 = R\ln V_2/V_1$, as already shown in Section 3.8.

The temperature variation of the entropy can be calculated as follows: At constant pressure,

$$dS = \frac{dq}{T} = \frac{dH}{T} = \frac{C_P\, dT}{T} \qquad (3.39)$$

At constant volume,

$$dS = \frac{dq}{T} = \frac{dE}{T} = \frac{C_V\, dT}{T} \qquad (3.40)$$

Thus at constant pressure,

$$S = \int C_P\, d\ln T + \text{const}$$

$$S = \int \frac{C_P}{T} dT + \text{const}; \qquad \Delta S = \int_{T_1}^{T_2} \frac{C_P}{T} dT \qquad (3.41)$$

---

[8] Alternatively, apply Euler's rule to eq. (3.29).

When C_P is known as a function of T, the entropy change is evaluated by the integration in eq. (3.41). This integration is often conveniently carried out graphically, as in Fig. 3.5: if C_P/T is plotted against T, the area under the curve is a measure of the entropy change. The entropy change is also the area under the curve of C_P vs. $\ln T$.

17. The entropy of mixing. Consider two gases at a pressure P. If these gases are brought together at constant temperature and pressure, they will become mixed spontaneously by interdiffusion. The spontaneous process will be associated with an increase in entropy. This entropy of mixing is of interest in a number of applications, and it can be calculated as follows.

In the final mixture of gases the partial pressure of gas (1) is $P_1 = X_1P$, of gas (2), $P_2 = X_2P$, where X_1 and X_2 are the mole fractions.[9] The ΔS of mixing is equal to the ΔS required to expand each gas from its initial pressure P to its partial pressure in the gas mixture. On the basis of one mole of ideal gas mixture,

$$\Delta S = X_1R\ln\frac{P}{P_1} + X_2R\ln\frac{P}{P_2}$$

$$= X_1R\ln\frac{1}{X_1} + X_2R\ln\frac{1}{X_2}$$

$$\Delta S = -R(X_1\ln X_1 + X_2\ln X_2)$$

This result can be extended to any number of gases in a mixture, yielding

$$\Delta S = -R\sum_i X_i\ln X_i \tag{3.42}$$

The equation is only approximately valid for liquid and solid solutions.

Let us calculate the entropy of mixing of the elements in air, taking the composition to be 79 per cent N_2, 20 per cent O_2, and 1 per cent argon.

$$\Delta S = -R(0.79\ln 0.79 + 0.20\ln 0.20 + 0.01\ln 0.01)$$

$$= 1.10 \text{ cal per deg per mole of mixture}$$

18. The calculation of thermodynamic relations. One great utility of thermodynamics is that it enables us by means of a few simple paper-and-pencil operations to avoid many tedious and difficult laboratory experiments. The general aim is to reduce the body of thermodynamic data to relations in terms of readily measurable functions. Thus the coefficients $(\partial V/\partial T)_P$, $(\partial P/\partial T)_V$, and $(\partial V/\partial P)_T$ can usually be measured by straightforward experiments. The results are often expressed implicitly in the equation of state for the substance, of the general form $f(P, V, T) = 0$.

The heat capacity at constant pressure C_P is usually measured directly and C_V can then be calculated from it and the equation of state. Thermodynamics itself does not provide any theoretical interpretation of heat

---

[9] See Chapter 6, Section 1..

capacities, the magnitudes of which depend on the structures and constitutions of the substances considered.

The basic thermodynamic relations may be reduced to a few fundamental equations:

(1) $H = E + PV$
(2) $A = E - TS$
(3) $F = E + PV - TS$
(4) $dE = T\,dS - P\,dV$
(5) $dH = T\,dS + V\,dP$
(6) $dA = -S\,dT - P\,dV$
(7) $dF = -S\,dT + V\,dP$

Since dA and dF are perfect differentials, they obey the Euler condition eq. (2.6), and therefore from (6) and (7)

(8) $(\partial S/\partial V)_T = (\partial P/\partial T)_V$
(9) $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$

By the definition of the heat capacities,

(10) $C_P = (dq/dT)_P = T(\partial S/\partial T)_P$
(11) $C_V = (dq/dT)_V = T(\partial S/\partial T)_V$

These eleven equations are the starting point for the evaluation of all others.[10]

The relation $dE = T\,dS - P\,dV$ may be considered as a convenient expression of the combined First and Second Laws of Thermodynamics. By differentiating it with respect to volume at constant temperature, $(\partial E/\partial V)_T = T(\partial S/\partial V)_T - P$. Then, since $(\partial S/\partial V)_T = (\partial P/\partial T)_V$,

$$\left(\frac{\partial E}{\partial V}\right)_T + P = T\left(\frac{\partial P}{\partial T}\right)_V \tag{3.43}$$

This equation has often been called a *thermodynamic equation of state*, since it provides a relationship among P, T, V, and the energy E that is valid for all substances. To be sure, all thermodynamic equations are in a sense equations of state, since they are relations between state variables, but equations like eq. (3.43) are particularly useful because they are closely related to the ordinary PVT data.

It is now possible by means of eq. (3.43) to prove the statement in the previous chapter that a gas that obeys the equation $PV = RT$ has a zero internal pressure, $(\partial E/\partial V)_T$. For such a gas $T(\partial P/\partial T)_V = RT/V = P$, so that $(\partial E/\partial V)_T = P - P = 0$.

An equation similar to eq. (3.43) can be obtained in terms of the enthalpy instead of the energy:

$$\left(\frac{\partial H}{\partial P}\right)_T - V = -T\left(\frac{\partial V}{\partial T}\right)_P \tag{3.44}$$

---

[10] A. Tobolsky, *J. Chem. Phys.*, *10*, 644 (1942), gives a useful general method.

An important application of this equation is the theoretical discussion of the Joule-Thomson experiment. Since

$$\mu_{J.T.} = \left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T$$

it follows from eq. (3.44) that

$$\mu_{J.T.} = \frac{T(\partial V/\partial T)_P - V}{C_P} \tag{3.45}$$

It is apparent that the Joule-Thomson effect can be either a warming or a cooling of the substance, depending on the relative magnitudes of the two terms in the numerator of eq. (3.45). In general, a gas will have one or more *inversion points* at which the sign of the coefficient changes as it passes through zero. The condition for an inversion point is that

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

A coefficient of thermal expansion is defined by

$$\alpha = \frac{1}{V_0}\left(\frac{\partial V}{\partial T}\right)_P$$

so that the Joule-Thomson coefficient vanishes when $V = \alpha V_0 T$. For an ideal gas this is always true (Law of Gay-Lussac) so that $\mu_{J.T.}$ is always zero in this case. For other equations of state, it is possible to derive $\mu_{J.T.}$ from eq. (3.45) without direct measurement, if C_P data are available.

These considerations are very important in the design of equipment for the liquefaction of gases. Usually, the gas is cooled by doing external work in an adiabatic expansion until it is below its inversion point, after which further cooling is accomplished by a Joule-Thomson expansion. A further discussion of the methods used for attaining very low temperatures will be postponed till the next chapter. We shall then see that these low-temperature studies have an important bearing on the problem of chemical equilibrium.

PROBLEMS

1. A steam engine operates between 120° and 30°C. What is the minimum amount of heat that must be withdrawn from the hot reservoir to obtain 1000 joules of work?

2. Compare the maximum thermal efficiencies of heat engines operating with (a) steam between 130°C and 40°C, (b) mercury vapor between 380°C and 50°C.

3. A cooling system is designed to maintain a refrigerator at −20°C in a room at ambient temperature of 25°C. The heat transfer into the refrigerator is estimated as 10^4 joules per min. If the refrigerating unit is assumed to operate at 50 per cent of its maximum thermal efficiency, estimate the power (in watts) required to operate the unit.

4. Prove that it is impossible for two reversible adiabatics on a P-V diagram to intersect.

5. One mole of an ideal gas is heated at constant pressure from 25° to 300°C. Calculate the entropy change ΔS if $C_V = \frac{3}{2}R$.

6. Find the increase in E, H, S, A, and F in expanding 1.0 liter of an ideal gas at 25°C to 100 liter at the same temperature.

7. Ten grams of carbon monoxide at 0°C are adiabatically and reversibly compressed from 1 atm to 20 atm. Calculate ΔE, ΔH, ΔS for the change in the gas. Assume $C_V = 4.95$ cal per deg mole and ideal gas behavior. Would it be possible to calculate ΔF from the data provided?

8. At −5°C the vapor pressure of ice is 3.012 mm and that of supercooled liquid water is 3.163 mm. Calculate the ΔF per mole for the transition water → ice at −5°C.

9. One mole of an ideal gas, initially at 100°C and 10 atm, is adiabatically expanded against a constant pressure of 5 atm until equilibrium is reattained. If $C_V = 4.50 + 0.005T$ calculate ΔE, ΔH, ΔS for the change in the gas.

10. Calculate ΔS when 10 g of ice at 0°C are added to 50 g of water at 40°C in an isolated system. The latent heat of fusion of ice is 79.7 cal per g; the specific heat of water, 1.00 cal per g deg.

11. The following data are available for water: latent heat of vaporization 9630 cal per mole; latent heat of fusion 1435 cal per mole. Molar heat capacities: solid, $C_P = 0.50 + 0.030\,T$; liquid, $C_P = 18.0$; vapor, $C_P = 7.256 + 2.30 \times 10^{-3}T + 2.83 \times 10^{-7}T^2$. Calculate ΔS when one mole of water at 100°K is heated at constant pressure of 1 atm to 500°K.

12. Derive an expression for the Joule-Thomson coefficient of a van der Waals gas.

13. Calculate the ΔS per liter of solution when pure N_2, H_2, and NH_3 gases are mixed to form a solution having the final composition 20 per cent N_2, 50 per cent H_2, and 30 per cent NH_3 (at S.T.P.).

14. Prove that a gas that obeys Boyle's Law and has zero internal pressure follows the equation of state, $PV = RT$.

15. For each of the following processes, state which of the quantities ΔE, ΔH, ΔS, ΔF, ΔA are equal to zero.

(a) An ideal gas is taken around a Carnot cycle.
(b) H_2 and O_2 react to form H_2O in a thermally isolated bomb.
(c) A nonideal gas is expanded through a throttling valve.
(d) Liquid water is vaporized at 100°C and 1 atm pressure.

16. Derive the expression $(\partial H/\partial P)_T = T(\partial S/\partial P)_T + V$.

17. Derive: $(\partial C_P/\partial P)_T = -T(\partial^2 V/\partial T^2)_P$.

18. Evaluate the following coefficients for (a) an ideal gas; (b) a van der Waals gas: $(\partial^2 P/\partial T^2)_V$; $(\partial E/\partial P)_T$; $(\partial P/\partial V)_S$; $(\partial^2 V/\partial T^2)_P$.

19. Derive expressions for: (a) $(\partial A/\partial P)_T$ in terms of P and V; (b) $(\partial F/\partial T)_P$ in terms of A and T.

20. Bridgman obtained the following volumes for methanol under high pressure, relative to a volume = 1.0000 at 0°C and 1 kg per cm^2:

P, kg/cm^2	1	500	1000	2000	3000	4000	5000
Vol. at 20°	1.0238	0.9823	0.9530	0.9087	0.8792	0.8551	0.8354
Vol. at 50°	1.0610	1.0096	0.9763	0.9271	0.8947	0.8687	0.8476

Use these data to estimate the ΔS when 1 mole of methanol at 35°C and 1 kg per cm^2 pressure is compressed isothermally to 5000 kg per cm^2.

REFERENCES

BOOKS

See Chapter 1, p. 25.

ARTICLES

1. Buchdahl, H. A., *Am. J. Phys.*, *17*, 41–46 (1949), "Principle of Caratheodory."
2. Crawford, F. H., *Am. J. Phys.*, *17*, 1–5 (1949), "Jacobian Methods in Thermodynamics."
3. Darrow, K. K., *Am. J. Phys.*, *12*, 183–96 (1944), "Concept of Entropy."
4. Dyson, F. J., *Scientific American*, *191*, 58–63 (1954), "What is Heat?"
5. LaMer, V. K., O. Foss, and H. Reiss, *Ann. N. Y. Acad. Sci.*, *51*, 605–26 (1949), "Thermodynamic Theory of J. N. Brønsted."

CHAPTER 4

Thermodynamics and Chemical Equilibrium

1. Chemical affinity. The problem of chemical affinity may be summarized in the question, "What are the factors that determine the position of equilibrium in chemical reactions?"

The earliest reflections on this subject were those of the ancient alchemists, who endowed their chemicals with almost human natures, and answered simply that reactions occurred when the reactants loved each other. Robert Boyle, in *The Sceptical Chymyst* (1661), commented upon these theories without enthusiasm: "I look upon amity and enmity as affections of intelligent beings, and I have not yet found it explained by any, how those appetites can be placed in bodies inanimate and devoid of knowledge or of so much as sense."

Isaac Newton's interest in gravitational attractions led him to consider also the problem of chemical interaction, which he thought might spring from the same causes. Thus in 1701, he surveyed some of the existing experimental knowledge, as follows:

> When oil of vitriol is mix'd with a little water . . . in the form of spirit of vitriol, and this spirit being poured upon iron, copper, or salt of tartar, unites with the body and lets go the water, doth not this show that the acid spirit is attracted by the water, and more attracted by the fix'd body than by the water, and therefore lets go the water to close with the fix'd body? And is it not also from a natural attraction that the spirits of soot and sea-salt unite and compose the particles of sal-ammoniac . . . and that the particles of mercury uniting with the acid particles of spirit of salt compose mercury sublimate, and with particles of sulphur, compose cinnaber . . . and that in subliming cinnaber from salt of tartar, or from quick lime, the sulphur by a stronger attraction of the salt or lime lets go the mercury, and stays with the fix'd body?

Such considerations achieved a more systematic form in the early "Tables of Affinity," such as that of Etienne Geoffroy in 1718, which recorded the order in which acids would expel weaker acids from combination with bases.

Claude Louis de Berthollet, in 1801, pointed out in his famous book, *Essai de statique chimique*, that these tables were wrong in principle, since the quantity of reagent present plays a most important role, and a reaction can be reversed by adding a sufficient excess of one of the products. While serving as scientific adviser to Napoleon with the expedition to Egypt in 1799, he noted the deposition of sodium carbonate along the shores of the salt lakes there. The reaction $Na_2CO_3 + CaCl_2 = CaCO_3 + 2\ NaCl$ as carried out in the laboratory was known to proceed to completion as the $CaCO_3$ was precipitated. Berthollet recognized that, under the peculiar conditions of large excess of sodium chloride that occurred in the evaporating brines, the reaction could be reversed, converting the limestone into sodium carbonate.

Berthollet, unfortunately, pushed his theorizing too far, and finally maintained that the actual *composition* of chemical compounds could be changed by varying the proportions of the reaction mixture. In the ensuing controversy with Louis Proust the Law of Definite Proportions was well established, but Berthollet's ideas on chemical equilibrium, the good with the bad, were discredited, and consequently neglected for some fifty years.[1]

It is curious that the correct form of what we now know as the *Law of Chemical Equilibrium* was arrived at as the result of a series of studies of chemical reaction rates, and not of equilibria at all. In 1850, Ludwig Wilhelmy investigated the hydrolysis of sugar with acids and found that the rate was proportional to the concentration of sugar remaining undecomposed. In 1862, Marcellin Berthelot and Péan de St. Gilles reported similar results in their famous paper[2] on the hydrolysis of esters, data from which are shown in Table 4.1. The effect on the products of varying the concentrations of the reactants is readily apparent.

TABLE 4.1

DATA OF BERTHELOT AND ST. GILLES ON THE REACTION $C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

(*One mole* of acetic acid is mixed with varying amounts of alcohol, and the amount of ester present at equilibrium is found)

Moles of Alcohol	*Moles of Ester Produced*	*Equilibrium Constant* $K = \frac{[EtAc][H_2O]}{[EtOH][HAc]}$
0.05	0.049	2.62
0.18	0.171	3.92
0.50	0.414	3.40
1.00	0.667	4.00
2.00	0.858	4.52
8.00	0.966	3.75

In 1863, the Norwegian chemists C. M. Guldberg and P. Waage expressed these relations in a very general form and applied the results to the problem of chemical equilibrium. They recognized that chemical equilibrium is a dynamic and not a static condition. It is characterized not by the cessation of all reaction but by the fact that the rates of the forward and reverse reactions have become the same.

Consider the general reaction, $A + B \rightleftharpoons C + D$. According to the "law of mass action," the rate of the forward reaction is proportional to the

---

[1] We now recognize many examples of definite departures from stoichiometric composition in various inorganic compounds such as metallic oxides and sulfides, which are appropriately called "berthollide compounds."

[2] *Ann. chim. phys.*, [3] *65*, 385 (1862).

concentrations of A and of B. If these are written as (A) and (B), $V_{\text{forward}} = k_{\text{f}}(A)(B)$. Similarly, $V_{\text{backward}} = k_{\text{b}}(C)(D)$. At equilibrium, therefore, $V_{\text{forward}} = V_{\text{backward}}$ so that

$$k_{\text{f}}(A)(B) = k_{\text{b}}(C)(D)$$

Thus,

$$\frac{(C)(D)}{(A)(B)} = \frac{k_{\text{f}}}{k_{\text{b}}} = K$$

More generally, if the reaction is $aA + bB = cC + dD$, at equilibrium

$$\frac{(C)^c(D)^d}{(A)^a(B)^b} = K \tag{4.1}$$

Equation (4.1) is a statement of Guldberg and Waage's *Law of Chemical Equilibrium.* The constant K is called the *equilibrium constant* of the reaction. It provides a quantitative expression for the dependence of chemical affinity on the concentrations of reactants and products. By convention, the concentration terms for the reaction products are always placed in the numerator of the expression for the equilibrium constant.

Actually, this work of Guldberg and Waage does not constitute a general proof of the equilibrium law, since it is based on a very special type of rate equation, which is certainly not always obeyed, as we shall see when we take up the study of chemical kinetics. Their recognition that chemical affinity is influenced by two factors, the "concentration effect" and what might be called the "specific affinity," depending on the chemical nature of the reacting species, their temperature, and pressure, was nevertheless very important. The equilibrium law will subsequently be derived from thermodynamic principles.

2. Free energy and chemical affinity. The free-energy function described in Chapter 3 provides the true measure of chemical affinity under conditions of constant temperature and pressure. The free-energy change in a chemical reaction can be defined as $\Delta F = F_{\text{products}} - F_{\text{reactants}}$. When the free-energy change is zero, there is no net work obtainable by any change or reaction at constant temperature and pressure. The system is in a state of equilibrium. When the free-energy change is positive for a proposed reaction, net work must be put into the system to effect the reaction, otherwise it cannot take place. When the free-energy change is negative, the reaction can proceed spontaneously with the accomplishment of useful net work. The larger the amount of this work that can be accomplished, the farther removed is the reaction from equilibrium. For this reason, $-\Delta F$ has often been called the *driving force* of the reaction. From the statement of the equilibrium law, it is evident that this driving force depends on the concentrations of the reactants and products. It also depends on their specific chemical constitution, and on the temperature and pressure, which determine the molar free-energy values of reactants and products.

If we consider a reaction at constant temperature, *e.g.*, one conducted in a thermostat, $-\Delta F = -\Delta H + T\,\Delta S$. The driving force is seen to be made up of two parts, a $-\Delta H$ term and a $T\,\Delta S$ term. The $-\Delta H$ term is the reaction heat at constant pressure, and the $T\,\Delta S$ term is the heat change when the process is carried out reversibly. The difference is the amount of reaction heat that can be converted into useful net work, *i.e.*, total heat minus unavailable heat.

If a reaction at constant volume and temperature is considered, the decrease in the work function, $-\Delta A = -\Delta E + T\,\Delta S$, should be used as the proper measure of the affinity of the reactants, or the driving force of the reaction. The constant volume condition is much less usual in laboratory practice.

It is now apparent why the principle of Berthelot and Thomsen (p. 45) was wrong. They considered only one of the two factors that make up the driving force of a chemical reaction, namely, the heat of reaction. They neglected the $T\,\Delta S$ term. The reason for the apparent validity of their principle was that for many reactions the ΔH term far outweighs the $T\,\Delta S$ term. This is especially so at low temperatures; at higher temperatures the $T\,\Delta S$ term naturally increases.

The fact that the driving force for a reaction is large (ΔF is a large negative quantity) does not mean that the reaction will necessarily occur under any given conditions. An example is a bulb of hydrogen and oxygen on the laboratory shelf. For the reaction, $H_2 + \frac{1}{2}\,O_2 = H_2O\,(g)$, $\Delta F_{298} = -54{,}638$ cal. Despite the large negative ΔF, the reaction mixture can be kept for years without any detectable formation of water vapor. If, after ten years on the shelf, a pinch of platinum-sponge catalyst is added, the reaction takes place with explosive violence. The necessary affinity was certainly there, but the *rate* of attainment of equilibrium depended on entirely different factors.

Another example is the resistance to oxidation of such extremely active metals as aluminum and magnesium. $2\,Mg + O_2(1\text{ atm}) = 2\,MgO\,(c)$; $\Delta F_{298} = -136{,}370$ cal. In this case, after the metal is exposed to air it becomes covered with a very thin layer of oxide and further reaction occurs at an immeasurably slow rate since the reactants must diffuse through the oxide film. Thus the equilibrium condition is never attained. The incendiary bomb and the thermit reaction, on the other hand, remind us that the large $-\Delta F$ for this reaction is a valid measure of the great affinity of the reactants.

3. Free-energy and cell reactions. Reactions occurring in electrochemical cells with the production of electric energy are of especial interest in the discussion of free-energy changes, since they can be carried out under conditions that are almost ideally reversible. This practical reversibility is achieved by balancing the electromotive force of the cell by an opposing emf which is imperceptibly less than that of the cell. Such a procedure can be accomplished with the laboratory potentiometer, in which an external source of emf, such as a battery, is balanced against the standard cell. The arrangement for this "compensation method" is shown in Fig. 4.1. When the opposing emf's are balanced by adjustment of the slide wire S, there is no detectable deflection of the galvanometer G.

An electrochemical cell converts chemical free energy into electric free energy. The electric energy is given by the product of the emf of the cell times the amount of electricity flowing through it. Michael Faraday showed, in 1834, that a given amount of electricity was always produced by or would produce the same amount of chemical reaction. For one chemical equivalent of reaction the associated amount of electricity is called the Faraday, $\mathcal{F}$, and is equal to 96,519 coulombs. Thus the electric energy available per mole of reaction equals $z\mathcal{E}\mathcal{F}$, where z is the number of equivalents per mole and $\mathcal{E}$ is the emf of the cell. A convenient energy unit is therefore the volt-coulomb or joule.

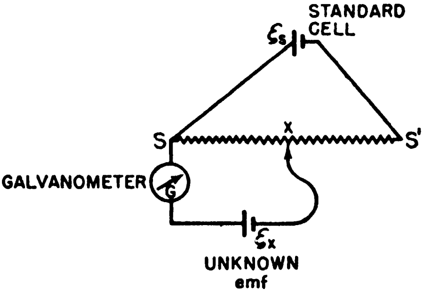


Fig. 4.1. Compensation method for measuring the emf of a cell without drawing current from it. When there is no deflection of galvanometer $\mathcal{E}_x = (SX/SS')\mathcal{E}_s$.

When the reaction is carried out reversibly, this energy is the maximum available, or the net work w'. If the reaction is carried out at a finite rate, some of the energy is expended in overcoming the electric resistance of the cell, appearing as heat. This Joule heat, I^2R, is the electrical analogue of the frictional heat produced in irreversible mechanical processes. We may now write, if $\mathcal{E}$ is the reversible emf,

$$-\Delta F = z\mathcal{E}\mathcal{F} \tag{4.2}$$

This equation provides a direct method for evaluating the free-energy change in the cell reaction. If we know the temperature coefficient of the emf of the cell, we can also calculate ΔH and ΔS for the reaction by means of eq. (3.35), which on combination with eq. (4.2) yields the relations

$$\Delta H = -z\mathcal{F}\left(\mathcal{E} - T\frac{d\mathcal{E}}{dT}\right); \qquad \Delta S = z\mathcal{F}\frac{d\mathcal{E}}{dT} \tag{4.3}$$

In a later chapter, devoted to electrochemistry, we shall see that it is possible to carry out many changes by means of reversible cells, and thereby to evaluate ΔF and ΔH for the changes from measurements of the emf and its temperature coefficient.

A cell that is occasionally used as a laboratory standard of emf is the Clark cell shown in Fig. 4.2. The reaction in this cell is $Zn + Hg_2SO_4 = ZnSO_4 + 2\,Hg$, or more simply, $Zn + 2\,Hg^+ = Zn^{++} + 2\,Hg$. The emf of the cell is 1.4324 volts at 15°C and the temperature coefficient $d\mathcal{E}/dT = -0.00119$ volt per degree. It can therefore be calculated that for the cell reaction $\Delta F = (-1.4324 \times 2 \times 96{,}519 = -276{,}510$ joule. From eq. (4.3), $\Delta S = (-0.00119 \times 2 \times 96{,}519) = -229.7$ joule deg^{-1} mole^{-1}. Whence, $\Delta H = \Delta F + T\,\Delta S = -276{,}510 - 66{,}200 = -342{,}710$ joule. The value of ΔH obtained from thermochemical data is $-339{,}500$, in good agreement with the electrochemical value.

Since the temperature coefficient is negative, heat is given up to the surroundings during the working of this cell, and the net work obtainable, $-\Delta F$, is less than the heat of the reaction. There are other cells for which the temperature coefficient is positive. These cells absorb heat from the environment, and their work output, under reversible conditions, is greater than the heat of the reaction.

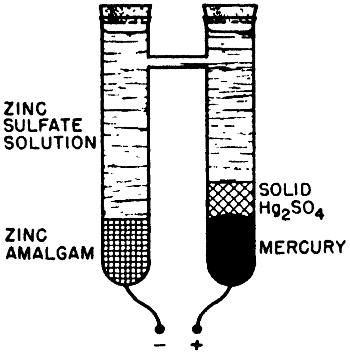


Fig. 4.2. A typical electrochemical cell: the Clark cell.

These relationships, discovered theoretically by Willard Gibbs in 1876, were first applied to experimental cases by Helmholtz in 1882. Before that time it was thought, reasoning from the First Law, that the maximum work output that could be achieved was the conversion of all of the heat of reaction into work. The Gibbs-Helmholtz treatment shows clearly that the work output is governed by the value of ΔF for the cell reaction, not by that of ΔH The working cell can either reversibly absorb heat from or furnish heat to its environment. This reversible heat change then appears as the $T\,\Delta S$ term in the free-energy expression.

4. Standard free energies. In Chapter 2 (p. 39) the definition of standard states was introduced in order to simplify calculations with energies and enthalpies. Similar conventions are very helpful for use with free-energy data. Various choices of the standard state have been made, one that is frequently used being the state of the substance under one atmosphere pressure. This is a useful definition for gas reactions; for reactions in solution, other choices of standard state may be more convenient and will be introduced as needed. A superscript zero will be used to indicate a standard state of 1 atm pressure. The absolute temperature will be written as a subscript.

The most stable form of an *element* in the standard state (1 atm pressure) and at a temperature of 25°C will by convention be assigned a free energy of zero.

The standard free energy of formation of a compound is the free energy of the reaction by which it is formed from its elements, when all the reactants and products are in the standard state. For example:

$$H_2\,(1\text{ atm}) + \tfrac{1}{2}\,O_2\,(1\text{ atm}) = H_2O\,(\text{g; 1 atm}) \qquad \Delta F^\circ_{298} = -54{,}638$$

$$S\,(\text{rhombic crystal}) + 3\,F_2\,(1\text{ atm}) = SF_6\,(\text{g; 1 atm}) \qquad \Delta F^\circ_{298} = -235{,}000$$

In this way it is possible to make tabulations of standard free energies such as that given by Latimer,[3] examples from which are collected in Table 4.2. Some of these free-energy values are determined directly from reversible cell emf's but most are obtained by other methods to be described later.

TABLE 4.2

STANDARD FREE ENERGIES OF FORMATION OF CHEMICAL COMPOUNDS AT 25°C

Compound	*State*	ΔF°_{298} *(kcal/mole)*	*Compound*	*State*	ΔF°_{298} *(kcal/mole)*
AgCl	c	−26.22	H_2O	g	−54.638
AgI	c	−15.81	H_2O_2	g	−24.73
$CaCl_2$	aq	−195.36	H_2O_2	l	−28.23
$CaCO_3$	c	−207.22	H_2S	g	−7.87
CH_4	g	- 12.09	NaCl	c	−91.70
C_2H_2	g	50.0	NH_3	g	−3.94
C_2H_4	g	16.28	N_2O	g	24.93
C_2H_6	g	−7.79	NO	g	20.66
CO	g	−32.79	NO_2	g	12.27
CO_2	g	−94.24	N_2O_4	g	23.44
CuO	c	−30.4	O_3	g	39.4
Cu_2O	c	−35.15	SO_2	g	−71.74
H_2O	l	−56.693	HCOOH	l	−86.4

Free-energy equations can be added and subtracted just as thermochemical equations are, so that the free energy of any reaction can be calculated from the sum of the free energies of the products minus the sum of the free energies of the reactants.

$$\Delta F^\circ = \sum F^\circ_{\text{products}} - \sum F^\circ_{\text{reactants}}$$

If we adopt the convention that moles of products are positive and moles of reactants negative in the summation, this equation can be written concisely as

$$\Delta F^\circ = \sum n_i F_i^\circ \tag{4.4}$$

For example:

$$Cu_2O\,(c) + NO\,(g) = 2\,CuO\,(c) + \tfrac{1}{2}\,N_2\,(g)$$

From Table 4.2,

$$\Delta F^\circ = 2\,(-30.4) + \tfrac{1}{2}\,(0) - 20.66 - (-35.15) = -46.31 \quad \text{kcal}$$

5. Free energy and equilibrium constant of ideal gas reactions. Many important applications of equilibrium theory are in the field of homogeneous gas reactions, that is, reactions taking place entirely between gaseous products and reactants. To a good approximation in many such cases, the gases may be considered to obey the ideal gas laws.

The variation at constant temperature of the free energy of an ideal gas

---

[3] W. M. Latimer, *The Oxidation States of the Elements*, 2nd ed. (New York: Prentice-Hall, 1952).

is given from eq. (3.29) as $dF = V\,dP = RT\,d\ln P$. Integrating from F° and P°, the free energy and pressure in the chosen standard state, to F and P, the values in any other state, $F - F^\circ = RT\ln(P/P^\circ)$. Since $P^\circ = 1$ atm, this becomes

$$F - F^\circ = RT\ln P \tag{4.5}$$

Equation (4.5) gives the free energy of one mole of an ideal gas at pressure P and temperature T, minus its free energy in a standard state at $P = 1$ atm and temperature T.

If an ideal mixture of ideal gases is considered, Dalton's Law of Partial Pressures must be obeyed, and the total pressure is the sum of the pressures that the gases would exert if each one occupied the entire volume by itself. These pressures are called the *partial pressures* of the gases in the mixture, $P_1, P_2 \ldots P_n$. Thus if n_i is the number of moles of gas i in the mixture,

$$P = \sum P_i = \frac{RT}{V}\sum n_i \tag{4.6}$$

For each individual gas i in the mixture eq. (4.5) can be written

$$F_i - F_i^\circ = RT\ln P_i \tag{4.7}$$

For n_i moles, $n_i(F_i - F_i^\circ) = RTn_i\ln P_i$. For a chemical reaction, therefore, from eq. (4.4),

$$\Delta F - \Delta F^\circ = RT\sum n_i \ln P_i \tag{4.8}$$

If we now consider the pressures P_i to be the equilibrium pressures in the gas mixture, ΔF must equal zero for the reaction at equilibrium. Thus we obtain the important relation

$$-\Delta F^\circ = RT\sum n_i \ln P_i^{\text{eq}} \tag{4.9}$$

or

$$\sum n_i \ln P_i^{\text{eq}} = -\frac{\Delta F^\circ}{RT}$$

Since ΔF° is a function of the temperature alone, the left side of this expression is equal to a constant at constant temperature. For a typical reaction, $aA + bB = cC + dD$, the summation can be written out as

$$\sum n_i \ln P_i^{\text{eq}} = \ln\frac{(P_C^{\text{eq}})^c\,(P_D^{\text{eq}})^d}{(P_A^{\text{eq}})^a\,(P_B^{\text{eq}})^b}$$

This expression is simply the logarithm of the equilibrium constant in terms of partial pressures, K_p. Equation (4.9) therefore becomes

$$-\Delta F^\circ = RT\ln K_p \tag{4.10}$$

The analysis in this section has now established two important results. The constancy of the expression

$$K_p = \frac{P_C^{\,c}P_D^{\,d}}{P_A^{\,a}P_B^{\,b}} \tag{4.11}$$

at equilibrium has been proved by thermodynamic arguments. This constitutes a thermodynamic proof of the Law of Chemical Equilibrium. Second, an explicit expression has been derived, eq. (4.10), which relates the equilibrium constant to the *standard* free-energy change in the chemical reaction. We are now able, from thermodynamic data, to calculate the equilibrium constant, and thus the concentration of products from any given concentration of reactants. This was one of the fundamental problems that chemical thermodynamics aimed to answer.

Sometimes the equilibrium constant is expressed explicitly in terms of concentrations c_i. For an ideal gas $P_i = n_i(RT/V) = c_iRT$. Substituting in eq. (4.11), we find

$$K_p = \frac{c_C{}^c c_D{}^d}{c_A{}^a c_B{}^b}(RT)^{c+d-a-b}$$

$$K_p = K_c(RT)^{\Delta n} \tag{4.12}$$

Here K_c is the equilibrium constant in terms of concentrations (*e.g.*, moles per liter) and Δn is the number of moles of products less that of reactants in the stoichiometric equation for the reaction.

Another way of expressing the concentrations of the reacting species is in terms of mole fractions. The mole fraction of component i in a mixture is defined by

$$X_i = \frac{n_i}{\sum n_i} \tag{4.13}$$

It is the number of moles of a component i in the mixture divided by the total number of moles of all the components. It follows that $P_i = X_iP$. Therefore the equilibrium constant in terms of the mole fractions is

$$K_x = \frac{X_C{}^c X_D{}^d}{X_A{}^a X_B{}^b} = K_pP^{-\Delta n} \tag{4.14}$$

Since K_p for ideal gases is independent of pressure, it is evident that K_x is a function of pressure except when $\Delta n = 0$. It is thus a "constant" only with respect to variations of the X's at constant T and P.

6. The measurement of homogeneous gas equilibria. The experimental methods for measuring gaseous equilibria can be classified as either static or dynamic.

In the static method, known amounts of the reactants are introduced into suitable reaction vessels, which are closed and kept in a thermostat until equilibrium has been attained. The contents of the vessels are then analyzed in order to determine the equilibrium concentrations. If the reaction proceeds very slowly at temperatures below those chosen for the experiment, it is sometimes possible to "freeze the equilibrium" by chilling the reaction vessel rapidly. The vessel may then be opened and the contents analyzed chemically.

This was the procedure used by Max Bodenstein[4] in his classic investigation of the hydrogen-iodine equilibrium: $H_2 + I_2 = 2\ HI$. The reaction products were treated with an excess of standard alkali; iodide and iodine were determined by titration, and the hydrogen gas was collected and its volume measured. For the formation of hydrogen iodide, $\Delta n = 0$; there is no change in the number of moles during the reaction. Therefore $K_p = K_c = K_x$.

If the initial numbers of moles of H_2 and I_2 are a and b, respectively, they will be reduced to $a - x$ and $b - x$ with the formation of $2x$ moles of HI. The total number of moles at equilibrium is therefore $a + b + c$, where c is the initial number of moles of HI.

Accordingly the equilibrium constant can be written

$$K_p = K_x = \frac{(c + 2x)^2}{(a - x)(b - x)}$$

The $(a + b + c)$ terms required to convert "number of moles" into "mole fraction" have been canceled out between numerator and denominator. In a run at 448°C, Bodenstein mixed 22.13 cc at STP of H_2 with 16.18 of I_2, and found 25.72 cc of HI at equilibrium. Hence

$$K = \frac{25.72^2}{(22.13 - 12.86)(16.18 - 12.86)} = 21.5$$

In the dynamic method for studying equilibria, the reactant gases are passed through a thermostated hot tube at a rate slow enough to allow complete attainment of equilibrium. This condition can be tested by making runs at successively lower flow rates, until there is no longer any change in the observed extent of reaction. The effluent gases are rapidly chilled and then analyzed. Sometimes a catalyst is included in the hot zone to speed the attainment of equilibrium. This is a safer method if a suitable catalyst is available, since it minimizes the possibility of any back reaction occurring after the gases leave the reaction chamber. The catalyst changes the rate of a reaction, not the position of final equilibrium.

These flow methods were extensively used by W. Nernst and F. Haber (around 1900) in their pioneer work on technically important gas reactions. An example is the "water-gas equilibrium," which has been studied both with and without an iron catalyst.[5] The reaction is

$$H_2 + CO_2 = H_2O + CO, \quad \text{and} \quad K_p = \frac{P_{H_2O}P_{CO}}{P_{H_2}P_{CO_2}}$$

If we consider an original mixture containing a moles of H_2, b moles of CO_2, c moles of H_2O, and d moles of CO, the analysis of the data is as follows.

---

[4] *Z. physik. Chem.*, *22*, 1 (1897); *29*, 295 (1899).

[5] *Z. anorg. Chem.*, *38*. 5 (1904).

		At Equilibrium		
Constituent	*Original Moles*	*Moles*	*Mole Fraction*	*Partial Pressure*
H_2	a	$a - x$	$a - x/(a + b + c + d)$	$[(a - x)/n]P$
CO_2	b	$b - x$	$b - x/(a + b + c + d)$	$[(b - x)/n]P$
H_2O	c	$c + x$	$(c + x)/(a + b + c + d)$	$[(c + x)/n]P$
CO	d	$d + x$	$(d + x)/(a + b + c + d)$	$[(d + x)/n]P$
Total Moles at Equilibrium			$a + b + c + d = n$	

Substituting the partial pressure expressions, we obtain

$$K_p = \frac{(c + x)(d + x)}{(a - x)(b - x)}$$

The values for the equilibrium composition, obtained by analysis of the product gases, have been used to calculate the constants in Table 4.3.

TABLE 4.3

THE WATER GAS EQUILIBRIUM $H_2 + CO_2 = H_2O + CO$; temperature 986°C

Initial Composition (moles per cent)		Equilibrium Composition (moles per cent)			K_p
CO_2	H_2	CO_2	H_2	$CO = H_2O$	
10.1	89.9	0.69	80.52	9.40	1.59
30.1	69.9	7.15	46.93	22.96	1.57
49.1	51.9	21.44	22.85	27.86	1.58
60.9	39.1	34.43	12.68	26.43	1.61
70.3	29.7	47.51	6.86	22.82	1.60

It is often possible to calculate the equilibrium constant for a reaction from the known values of the constants of other reactions. This is a principle of great practical utility. For example, from the dissociation of water vapor and the water-gas equilibrium one can calculate the equilibrium constant for the dissociation of carbon dioxide.

$$\begin{aligned}
H_2O &= H_2 + \tfrac{1}{2} O_2 & K_p &= P_{H_2}P_{O_2}^{1/2}/P_{H_2O} \\
CO_2 + H_2 &= H_2O + CO & K_p' &= P_{H_2O}P_{CO}/P_{CO_2}P_{H_2} \\
CO_2 &= CO + \tfrac{1}{2} O_2 & K_p'' &= P_{CO}P_{O_2}^{1/2}/P_{CO_2}
\end{aligned}$$

It is apparent that $K_p'' = K_p'K_p$.

7. The principle of Le Chatelier. The effects of such variables as pressure, temperature, and concentration on the position of chemical equilibrium have been succinctly summarized by Henry Le Chatelier (1888). "Any change in one of the variables that determine the state of a system in equilibrium causes a shift in the position of equilibrium in a direction that tends to counteract the change in the variable under consideration." This is a principle of broad and general utility, and it can be applied not only to chemical equilibria but to equilibrium states in any physical system. It is indeed possible that it can be applied also with good success in the psychological, economic, and sociological fields.

The principle indicates, for example, that if heat is evolved in a chemical reaction, increasing the temperature tends to reverse the reaction; if the volume decreases in a reaction, increasing the pressure shifts the equilibrium position farther toward the product side. Quantitative expressions for the effect of variables such as temperature and pressure on the position of equilibrium will now be obtained by thermodynamic methods.

8. Pressure dependence of equilibrium constant. The equilibrium constants K_p and K_c are independent of the pressure for ideal gases; the constant K_x is pressure-dependent. Since $K_x = K_p P^{-\Delta n}$, $\ln K_x = \ln K_p - \Delta n \ln P$.

$$\frac{d \ln K_x}{dP} = \frac{-\Delta n}{P} = -\frac{\Delta V}{RT} \tag{4.15}$$

When a reaction occurs without any change in the total number of moles of gas in the system, $\Delta n = 0$. An example is the previously considered water gas reaction. In these instances the constant K_p is the same as K_x or K_c, and for ideal gases the position of equilibrium does not depend on the total pressure. When Δn is not equal to zero, the pressure dependence of K_x is given by eq. (4.15). When there is a decrease in the mole number ($\Delta n < 0$) and thus a decrease in the volume, K_x increases with increasing pressure. If there is an increase in n and V ($\Delta n > 0$), K_x decreases with increasing pressure.

An important class of reactions for which $\Delta n \neq 0$ is that of dissociation-association equilibria. An extensively studied example is the dissociation of nitrogen tetroxide into the dioxide, $N_2O_4 = 2\,NO_2$. In this case, $K_p = P^2_{NO_2}/P_{N_2O_4}$. If one mole of N_2O_4 is dissociated at equilibrium to a fractional extent a, $2a$ moles of NO_2 are produced. The total number of moles at equilibrium is then $(1 - a) + 2a = 1 + a$. It follows that

$$K_x = \frac{[2a/(1+a)]^2}{(1-a)/(1+a)} = \frac{4a^2}{1-a^2}$$

Since for this reaction $\Delta n = +1$,

$$K_p = K_x P = \frac{4a^2}{1-a^2} P$$

When a is small compared to unity, this expression predicts that the degree of dissociation a shall vary inversely as the square root of the pressure.

Experimentally it is found that N_2O_4 is appreciably dissociated even at room temperatures. As a result, the observed pressure is greater than that predicted by the ideal gas law for a mole of N_2O_4, since each mole yields $1 + a$ moles of gas after dissociation. Thus $P\,(\text{ideal}) = RT/V$, whereas $P\,(\text{observed}) = (1 + a)RT/V$. Hence $a = (V/RT)(P_{\text{obs}} - P_{\text{ideal}})$.

This behavior provides a very simple means for measuring a. For example, in an experiment at 318°K and 1 atm pressure, a is found to be 0.38. Therefore $K_x = 4(0.38)^2/(1 - 0.38^2) = 0.67$. At 10 atm pressure, $K_x = 0.067$ and a is 0.128.

Among the most interesting dissociation reactions are those of the elementary gases. The equilibrium constants for a few of these are collected in Table 4.4.

TABLE 4.4

EQUILIBRIUM CONSTANTS OF DISSOCIATION REACTIONS

Temp. (°K)	K_p				
	$O_2 = 2\,O$	$H_2 = 2\,H$	$N_2 = 2\,N$	$Cl_2 = 2\,Cl$	$Br_2 = 2\,Br$
600	1.4×10^{-37}	3.6×10^{-33}	1.3×10^{-56}	4.8×10^{-16}	6.18×10^{-12}
800	9.2×10^{-27}	1.2×10^{-23}	5.1×10^{-41}	1.04×10^{-10}	1.02×10^{-7}
1000	3.3×10^{-20}	7.0×10^{-18}	1.3×10^{-31}	2.45×10^{-7}	3.58×10^{-5}
1200	8.0×10^{-16}	5.05×10^{-14}	2.4×10^{-25}	2.48×10^{-5}	1.81×10^{-3}
1400	1.1×10^{-12}	2.96×10^{-11}	7.5×10^{-21}	8.80×10^{-4}	3.03×10^{-2}
1600	2.5×10^{-10}	3.59×10^{-9}	1.8×10^{-17}	1.29×10^{-2}	2.55×10^{-1}
1800	1.7×10^{-8}	1.52×10^{-7}	7.6×10^{-15}	0.106	
2000	5.2×10^{-7}	3.10×10^{-6}	9.8×10^{-13}	0.570	

9. Effect of an inert gas on equilibrium. In reactions in which there is no change in the total number of moles, $\Delta n = 0$, and the addition of an inert gas cannot affect the composition of the equilibrium mixture. If, however, $\Delta n \neq 0$, the inert gas must be included in calculating the mole fractions and the total pressure P. Let us consider as an example the technically important gas reaction, $SO_2 + \frac{1}{2}\,O_2 = SO_3$. In this case $\Delta n = -\frac{1}{2}$, and $K_p = K_x P^{-1/2}$. Let the initial reactant mixture contain a moles of SO_2, b moles of O_2, and c moles of inert gas, for example N_2. If y moles of SO_3 are formed at equilibrium, the equilibrium mole fractions are

$$X_{SO_2} = \frac{a - y}{n}; \quad X_{O_2} = \frac{b - (y/2)}{n}; \quad X_{SO_3} = \frac{y}{n}$$

Here n is the total number of moles at equilibrium: $n = a + b + c - (y/2)$. The equilibrium constant,

$$K_x = K_p P^{1/2} = \frac{y/n}{[(a - y)/n]\{[b - (y/2)]/n\}^{1/2}} = \frac{y n^{1/2}}{[a - y][b - (y/2)]^{1/2}}$$

It follows that
$$\frac{y}{a-y} = K_p\sqrt{\frac{[b-(y/2)]P}{n}}$$

$$\frac{n_{\mathrm{SO_3}}}{n_{\mathrm{SO_2}}} = K_p\sqrt{\frac{n_{\mathrm{O_2}}}{n}P}$$

where $n_{\mathrm{SO_3}}$, $n_{\mathrm{SO_2}}$, $n_{\mathrm{O_2}}$, n are the equilibrium mole numbers.

Let us now consider three cases. (1) If the pressure is increased by compressing the system without addition of gas from outside, n is constant, and as P increases, $n_{\mathrm{SO_3}}/n_{\mathrm{SO_2}}$ also increases. (2) If an inert gas is added at constant volume, both n and P increase in the same ratio, so that the equilibrium conversion of SO_2 to SO_3, $n_{\mathrm{SO_3}}/n_{\mathrm{SO_2}}$ remains unchanged. (3) If an inert gas is added at constant pressure, n is increased while P remains constant, and this dilution of the mixture with the inert gas decreases the extent of conversion $n_{\mathrm{SO_3}}/n_{\mathrm{SO_2}}$.

This reaction is exothermic, and therefore increasing the temperature decreases the formation of products. The practical problem is to run the reaction at a temperature high enough to secure a sufficiently rapid velocity, without reaching so high a temperature that the equilibrium lies too far to the left. In practice, a temperature around 500°C is chosen, with a platinum or vanadium-pentoxide catalyst to accelerate the reaction. The equilibrium constant from 700° to 1200°K is represented quite well by the equation $\ln K_p = (22{,}600/RT) - (21.36/R)$. At 800°K, therefore, $K_p = 33.4$.

Let us now consider two different gas mixtures, the first containing 20 per cent SO_2 and 80 per cent O_2 at 1 atm pressure, and a second containing in addition a considerable admixture of nitrogen, *e.g.*, 2 per cent SO_2, 8 per cent O_2, 90 per cent N_2, at 1 atm pressure. Letting y = moles SO_3 at equilibrium, we obtain:

I

$$K_x = K_pP^{1/2} = 33.4$$
$$= \frac{\dfrac{y}{1-(y/2)}}{\dfrac{0.2-y}{1-(y/2)}\left[\dfrac{0.8-(y/2)}{1-(y/2)}\right]^{1/2}}$$
$$y^3 - 2.000y^2 + 0.681y - 0.0641 = 0$$
$$y = 0.190$$

95% conversion of SO_2 to SO_3

II

$$K_x = K_pP^{1/2} = 33.4$$
$$= \frac{\dfrac{y}{1-(y/2)}}{\dfrac{0.02-y}{1-(y/2)}\left[\dfrac{0.08-(y/2)}{1-(y/2)}\right]^{1/2}}$$
$$y^3 - 0.1985y^2 + 6.81 \times 10^{-3}y - 64.06 \times 10^{-6} = 0$$
$$y = 0.0180$$

90% conversion of SO_2 to SO_3

The cubic equations that arise in problems like these are probably best solved by successive approximations. Beginning with a reasonable value guessed for the percentage conversion, a sufficiently accurate solution can usually be obtained after three or four trials.

10. Temperature dependence of the equilibrium constant. An expression for the variation of K_p with temperature is derived by combining eqs. (4.10) and (3.36). Since

$$-\Delta F^\circ = RT \ln K_p \tag{4.10}$$

and

$$\left[\frac{\partial}{\partial T}\left(\frac{\Delta F^\circ}{T}\right)\right]_p = \frac{-\Delta H^\circ}{T^2} \tag{3.36}$$

therefore

$$\left(\frac{\partial \ln K_p}{\partial T}\right)_p = \frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2} \tag{4.16}$$

It is apparent that if the reaction is endothermic (ΔH° positive) the equilibrium constant increases with temperature; if the reaction is exothermic (ΔH° negative) the equilibrium constant decreases as the temperature is raised.

Equation (4.16) can also be written:

$$\frac{d \ln K_p}{d(1/T)} = \frac{-\Delta H^\circ}{R} \tag{4.17}$$

Thus if ln K_p is plotted against $1/T$, the slope of the curve at any point is equal to $-\Delta H^\circ/R$. As an example of this treatment, the data for the variation with temperature of the $2\,HI = H_2 + I_2$ equilibrium are plotted in Fig. 4.3. The curve is almost a straight line, indicating that ΔH° is approximately constant for the reaction over the experimental temperature range. The value calculated from the slope at 400°C is $\Delta H^\circ = 7080$ cal.

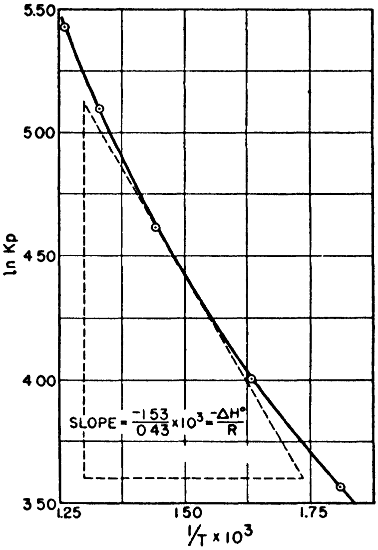


Fig. 4.3. The variation with temperature of $K_p = P_{H_2}P_{I_2}/P_{HI}^2$. (Data of Bodenstein.)

It is also possible to measure the equilibrium constant at one temperature and with a value of ΔH° obtained from thermochemical data to calculate the constant at other temperatures. Equation (4.16) can be integrated, giving

$$\ln \frac{K_p(T_2)}{K_p(T_1)} = \int_{T_1}^{T_2} \frac{\Delta H^\circ}{RT^2}\, dT$$

Since, over a short temperature range, ΔH° may often be taken as approximately constant, one obtains

$$\ln \frac{K_p(T_2)}{K_p(T_1)} = \frac{-\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{4.18}$$

If the variations of the heat capacities of the reactants and products are known as functions of temperature, an explicit expression for the temperature dependence of ΔH° can be derived from Kirchhoff's equation (2.29). This expression for ΔH° as a function of temperature can then be substituted into eq. (4.16), whereupon integration yields an explicit equation for K_p as a function of temperature. This has the form

$$\ln K_p = -\Delta H^\circ_0/RT + A \ln T + BT + CT^2 \ . \ . \ . + I \qquad (4.19)$$

In this case, as usual, the value of the integration constant I can be determined if the value of K_p is known at any one temperature, either experimentally or by calculation from ΔF°. It will be recalled that one value of ΔH° is needed to determine ΔH°_0, the integration constant of the Kirchhoff equation.

To summarize, from a knowledge of the heat capacities of the reactants and products, and of one value each for ΔH° and K_p, it is possible to calculate the equilibrium constant at any temperature.

As an example, consider the calculation of the constant for the water-gas reaction as a function of the temperature.

$$CO + H_2O\,(g) = H_2 + CO_2; \qquad K_p = \frac{P_{H_2} P_{CO_2}}{P_{CO} P_{H_2O}}$$

From Table 4.2, the standard free-energy change at 25°C is:

$$\Delta F^\circ_{298} = -94{,}240 - (-54{,}640 - 32{,}790) = -6810$$

Thus $$\ln K_{p298} = \frac{6810}{298R} = 11.48, \quad \text{or} \quad K_{p298} = 9.55 \times 10^4$$

From the enthalpies of formation on page 39,

$$\Delta H^\circ_{298} = -94{,}050 - (-57{,}800 - 26{,}420) = -9830$$

The heat capacity table on page 44 yields for this reaction

$$\Delta C_P = C_{PCO_2} + C_{PH_2} - C_{PCO} - C_{PH_2O}$$
$$= -0.515 + 6.23 \times 10^{-3}T - 29.9 \times 10^{-7}T^2$$

From eq. (2.32),

$$\Delta H^\circ = \Delta H^\circ_0 - 0.515T + 3.12 \times 10^{-3}T^2 - 10.0 \times 10^{-7}T^3$$

Substituting $\Delta H^\circ = -9830$, $T = 298$°K, and solving for ΔH°_0, we get $\Delta H^\circ_0 = -9921$. Then the temperature dependence of the equilibrium constant, eq. (4.19), becomes

$$\ln K_p = \frac{9921}{RT} - \frac{0.515}{R}\ln T + \frac{3.12 \times 10^{-3}}{R}T - \frac{10.0 \times 10^{-7}}{2R}T^2 + I$$

By inserting the value of ln K_p at 298°K, the integration constant can be evaluated as $I = -3.97$. The final expression for K_p as a function of temperature is, therefore,

$$\ln K_p = -3.97 + \frac{4990}{T} - 0.259 \ln T + 1.56 \times 10^{-3}T - 2.53 \times 10^{-7}T^2$$

For example, at 800°K, $\ln K_p = 1.63$, $K_p = 5.10$.

11. Equilibrium constants from thermal data. We have now seen how a knowledge of the heat of reaction and of the temperature variation of the heat capacities of reactants and products allows us to calculate the equilibrium constant at any temperature, provided there is a single experimental measurement of either K_p or ΔF° at some one temperature. If an independent method is available for finding the integration constant I in eq. (4.19), it will be possible to calculate K_p without any recourse to experimental measurements of the equilibrium or of the free-energy change. This calculation would be equivalent to the evaluation of the entropy change, ΔS°, from thermal data alone, *i.e.*, heats of reaction and heat capacities. If we know ΔS° and ΔH°, K_p can be found from $\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ$.

From eq. (3.41), the entropy per mole of a substance at temperature T is given by

$$S = \int_0^T C_P \, d \ln T + S_0$$

where S_0 is the entropy at 0°K.[6] If any changes of state occur between the temperature limits, the associated entropy changes should be added. For a gas at temperature T the general expression for the entropy therefore becomes

$$S = \int_0^{T_f} C_{P\text{cryst}} \, d \ln T + \frac{\Delta H_{\text{fus}}}{T_f} + \int_{T_f}^{T_b} C_{P\text{liq}} \, d \ln T + \frac{\Delta H_{\text{vap}}}{T_b} + \int_{T_b}^{T} C_{P\text{gas}} \, d \ln T + S_0 \qquad (4.20)$$

All these terms can be measured except the constant S_0. The evaluation of this constant becomes possible by virtue of the third fundamental law of thermodynamics.

12. The approach to absolute zero. The laws of thermodynamics are inductive in character. They are broad generalizations having an experimental basis in certain human frustrations. Our failure to invent a perpetual-motion machine has led us to postulate the First Law of Thermodynamics. Our failure ever to observe a spontaneous flow of heat from a cold to a hotter body or to obtain perpetual motion of the second kind has led to the statement of the Second Law. The Third Law of Thermodynamics can be based on our failure to attain the absolute zero of temperature. A detailed study of refrigeration principles indicates that the absolute zero can never be reached.

---

[6] Be careful not to confuse S°, the entropy in the standard state of 1 atm pressure, and S_0, the entropy at 0°K.

Most cryogenic systems have depended on the cooling of a gas by an adiabatic expansion. This effect was first described by Clément and Désormes in 1819. If a container of compressed air is vented to the atmosphere, the outrushing gas must do work to push back the gas ahead of it. If the process is carried out rapidly enough, it is essentially adiabatic, and the gas is cooled by the expansion.

To obtain continuous refrigeration, some kind of cyclic process must be devised; simply opening a valve on a tank of compressed gas is obviously unsatisfactory.[7] Two methods of controlled expansion can be utilized: (1) a Joule-Thomson expansion through a throttling valve; (2) an expansion against a constraining piston. In the latter case, the gas does work against the external force and also against its internal cohesive forces. In the Joule-Thomson case, only the internal forces are operative, and these change in sign as the gas passes through an *inversion point.* It was shown on page 66 that in order to obtain cooling $\mu_{J.T.} = (1/C_P)[T(\partial V/\partial T)_P - V]$ must be positive.

In 1860, Sir William Siemens devised a countercurrent heat exchanger, which greatly enhanced the utility of the Joule-Thomson method. This was applied in the Linde process for the production of liquid air. Chilled compressed gas is cooled further by passage through a throttling valve. The expanded gas passes back over the inlet tube, cooling the unexpanded gas. When the cooling is sufficient to cause condensation, the liquid air can be drawn off at the bottom of the apparatus. Liquid nitrogen boils at 77°K, liquid oxygen at 90°K, and they are easily separated by fractional distillation.

In order to liquefy hydrogen, it is necessary to chill it below its Joule-Thomson inversion temperature at 193°K; the Linde process can then be used to bring it below its critical temperature at 33°K. The production of liquid hydrogen was first achieved in this way by James Dewar in 1898.

The boiling point of hydrogen is 22°K. In 1908, Kammerlingh-Onnes, founder of Leiden's famous cryogenic laboratory, used liquid hydrogen to cool helium below its inversion point at 100°K, and then liquefied it by an adaptation of the Joule-Thomson principle. Temperatures as low as 0.84°K have been obtained with liquid helium boiling under reduced pressures. This temperature is about the limit of this method, since enormous pumps become necessary to carry off the gaseous helium.

Let us consider more carefully this cooling produced by evaporating liquid from a thermally isolated system. The change in state, liquid → vapor, is a change from the liquid, a state of low entropy and low energy, to the vapor, a state of higher entropy and higher energy. The increase in entropy on evaporation can be equated to $\Delta H_{\text{vap}}/T$. Since the system is thermally

---

[7] This method is used, however, in a laboratory device for making small quantities of "dry ice," solid carbon dioxide.

isolated, the necessary heat of vaporization can come only from the liquid itself. Thus the temperature of the liquid must fall as the adiabatic evaporation proceeds.

In 1926, a new refrigeration principle was proposed independently by W. F. Giauque[8] and P. Debye. This is the *adiabatic demagnetization method.* Certain rare earth salts have a high *paramagnetic susceptibility*;[9] *i.e.*, in a magnetic field they tend to become highly magnetized, but when the field is removed, they lose their magnetism immediately. In 1933, Giauque performed the following experiment. A sample of gadolinium sulfate was cooled to 1.5°K in a magnetic field of 8000 oersteds, and then thermally isolated. The field was suddenly shut off. The salt lost its magnetism spontaneously. Since this was a spontaneous process, it was accompanied by an increase in the entropy of the salt. The magnetized state is a state of lower energy and lower entropy than the demagnetized state. The change, magnetized → demagnetized, is therefore analogous to the change, liquid → vapor, discussed in the preceding paragraph. If the demagnetization occurs in a thermally isolated system, the temperature of the salt must fall.

When the field was turned off in Giauque's experiment, the temperature fell to 0.25°K. In 1950, workers at Leiden[10] reached a temperature of 0.0014°K by this method. Even the measurement of these low temperatures is a problem of some magnitude. The helium vapor-pressure thermometer is satisfactory down to about 1°K. Below this, the Curie-Weiss expression for the paramagnetic susceptibility, $\chi = \text{const}/T$, can be used to define a temperature scale.

The fact that we have approached to within a few thousandths of a degree of absolute zero does not mean that the remaining step will soon be taken. On the contrary, it is the detailed analysis of these low-temperature experiments that indicates most definitely that zero degrees Kelvin is absolutely unattainable.

The Third Law of Thermodynamics will, therefore, be postulated as follows: "It is impossible by any procedure, no matter how idealized, to reduce the temperature of any system to the absolute zero in a finite number of operations."[11]

13. The Third Law of Thermodynamics. How does the Third Law answer the question of the value of the entropy of a substance at $T = 0°K$, the integration constant S_0 in eq. (4.20)? Since absolute zero is unattainable, it would be more precise to ask what is the limit of S as T approaches 0.

Consider a completely general process, written as $a \rightarrow b$. This may be a chemical reaction, a change in temperature, a change in the magnetization,

---

[8] *J. Am. Chem. Soc.*, *49*, 1870 (1927).

[9] Cf. Sec. 11–20.

[10] D. de Klerk, M. J. Steenland, and C. J. Gorter, *Physica*, *16*, 571 (1950).

[11] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (London: Cambridge, 1940), p. 224.

or the like. The entropies of the system in the two different states a and b can be written as:

$$S_a = S_{a0} + \int_0^T C_a \, d\ln T$$

$$S_b = S_{b0} + \int_0^T C_b \, d\ln T \tag{4.21}$$

S_{a0} and S_{b0} are the limiting entropy values as T approaches zero.

Let us start with the system a at a temperature T' and allow the process $a \rightarrow b$ to take place *adiabatically and reversibly*, the final temperature being T''. The entropy must remain constant, so that $S_a = S_b$, or

$$S_{a0} + \int_0^{T'} C_a \, d\ln T = S_{b0} + \int_0^{T''} C_b \, d\ln T$$

In order for the temperature T'' in the final state to equal zero, it would be necessary to have

$$S_{b0} - S_{a0} = \int_0^{T'} C_a \, d\ln T \tag{4.22}$$

As $T \rightarrow 0$, $C_a \rightarrow 0$. Now if $S_{b0} > S_{a0}$ it is possible to choose an initial T' that satisfies this equation, since the integral is a positive quantity. In this way the process $a \rightarrow b$ could be used to reach the absolute zero starting from this T'. This conclusion, however, would be a direct contradiction of the Third Law, the principle of the unattainability of absolute zero. The only escape is to declare that S_{b0} *cannot* be greater than S_{a0}. Then there can be no T' that satisfies the condition (4.22). The same reasoning, based upon the reverse process $b \rightarrow a$, can be used to show that S_{a0} cannot be greater than S_{b0}.

Since S_{a0} can be neither greater than nor less than S_{b0}, it must be equal to S_{b0}. In order to conform with the principle of the unattainability of absolute zero, therefore, it is necessary to have

$$S_{a0} = S_{b0} \qquad \text{or} \qquad \Delta S_0 = 0 \tag{4.23}$$

This equation indicates that for any change in a thermodynamic system the limiting value of ΔS as one approaches absolute zero is equal to zero. The change in question may be a chemical reaction, a change in physical state such as magnetized $\rightleftharpoons$ demagnetized, or in general any change that can in principle be carried out reversibly. This requirement of a possible reversible process is necessary, since otherwise there would be no way of evaluating the ΔS for the change being considered.[12] The statement in eq. (4.23) is the

---

[12] This restriction may be a little too severe. In one-component systems, changes of one polymorphic crystal to another may also have $\Delta S_0 = 0$. Examples are white tin → grey tin, diamond → graphite, monoclinic sulfur → rhombic sulfur, zinc blende → wurtzite. The heat capacity of the metastable form can be measured at low temperatures, and by extrapolation to 0°K and assuming $S_0 = 0$, it is possible to obtain a "Third-Law entropy," as defined in the next section.

famous *heat theorem* first proposed by Walther Nernst in 1906. It has served as a useful statement of the Third Law of Thermodynamics.

Certain types of systems therefore do not fall within the scope of eq. (4.23). For example, any reaction that changed the identity of the chemical elements, *i.e.*, nuclear transmutation, would not be included, since there is no thermodynamic method of calculating ΔS for such a change. This restriction, of course, does not affect chemical thermodynamics in any way, since the nuclei of the elements retain their identities in any chemical change.

Another class of changes that must be excluded from eq. (4.23) comprises those in which the system passes from a metastable to a more stable state. Such changes are essentially irreversible and can proceed in one direction only, namely, toward the more stable states. Certain systems can become "frozen" in nonequilibrium states at low temperatures. Examples are glasses, which can be regarded as supercooled liquids, and solid solutions and alloys, in which there is a residual entropy of mixing. At sufficiently low temperatures, the glass is metastable with respect to the crystalline silicates of which it is composed, and the solid solutions are less stable than a mixture of pure crystalline metals. Yet the rate of attainment of equilibrium becomes so slow in the very cold solids that transformations to the more stable states do not occur. Such systems have an extra entropy, which can be considered as an entropy of mixing, and this may persist at the lowest temperatures attainable experimentally. This fact does not contradict eq. (4.23) because a change such as "metastable glass → crystalline silicates" cannot be carried out by a reversible isothermal path. Hence these metastable states are said to be "nonaccessible," and the changes do not lie within the scope of eq. (4.23). These cases will be discussed later from a statistical point of view in Chapter 12.

14. Third-law entropies. Only changes or differences in entropy have any physical meaning in thermodynamics. When we speak of the entropy of a substance at a certain temperature, we really mean the difference between its entropy at that temperature and its entropy at some other temperature, usually 0°K. Since the chemical elements are unchanged in any physicochemical process, we can assign any arbitrary values to their entropies at 0°K without affecting in any way the values of ΔS for any chemical change. It is most convenient, therefore, to take the value of S_0 for all the *chemical elements* as equal to zero. This is a convention first proposed by Max Planck in 1912.

It then follows, from eq. (4.23), that the entropies of all pure *chemical compounds* in their stable states at 0°K are also zero, because for their formation from the elements, $\Delta S_0 = 0$. This formulation is equivalent to setting the constant S_0 in eq. (4.20) equal to zero.

It is now possible to use heat-capacity data extrapolated to 0°K to determine so-called *third-law entropies*, which can be used in equilibrium calculations. As an example, the determination of the standard entropy, S°_{298}, for

TABLE 4.5

EVALUATION OF ENTROPY OF HYDROGEN CHLORIDE FROM HEAT-CAPACITY MEASUREMENTS

Contribution	*cal/deg mole*
1. Extrapolation from 0–16°K (Debye Theory, Sec. 13–23)	0.30
2. $\int C_P\, d \ln T$ for Solid I from 16°–98.36°	7.06
3. Transition, Solid I → Solid II, 2843/98.36	2.89
4. $\int C_P\, d \ln T$ for Solid II from 98.36°–158.91°	5.05
5. Fusion, 476.0/158.91	3.00
6. $\int C_P\, d \ln T$ for Liquid from 158.91°–188.07°	2.36
7. Vaporization, 3860/188.07	20.52
8. $\int C_P\, d \ln T$ for Gas from 188.07°–298.15°K	3.22
	$S^\circ_{298.15} = 44.40 \pm 0.10$

hydrogen chloride gas is shown in Table 4.5. The value $S^\circ_{298} = 44.4$ eu is that for HCl at 25°C and 1 atm pressure. A small correction due to nonideality of the gas raises the figure to 44.7. A number of third-law-entropies are collected in Table 4.6.

TABLE 4.6

THIRD-LAW ENTROPIES

(Substances in the Standard State at 25°C)

Substance	S°_{298} (*cal/deg mole*)	*Substance*	S°_{298} (*cal/deg mole*)
	Gases		
H_2	31.2	CO_2	51.1
D_2	34.4	H_2O	45.2
He	29.8	NH_3	46.4
N_2	45.8	SO_2	59.2
O_2	49.0	CH_4	44.5
Cl_2	53.2	C_2H_2	48.0
HCl	44.7	C_2H_4	52.5
CO	47.3	C_2H_6	55.0
	Liquids		
Mercury	17.8	Benzene	41.9
Bromine	18.4	Toluene	52.4
Water	16.8	Diethylether	60.5
Methanol	30.3	*n*-Hexane	70.6
Ethanol	38.4	Cyclohexane	49.2
	Solids		
C (diamond)	0.6	K	16.5
C (graphite)	1.4	I_2	14.0
S (rhombic)	7.6	NaCl	17.2
S (monoclinic)	7.8	KCl	19.9
Ag	10.2	KBr	22.5
Cu	8.0	KI	23.4
Fe	6.7	AgCl	23.4
Na	12.3	Hg_2Cl_2	46.4

The standard entropy change ΔS° in a chemical reaction can be calculated immediately, if the standard entropies of products and reactants are known.

$$\Delta S^\circ = \sum n_i S_i^\circ$$

One of the most satisfactory experimental checks of the Third Law is provided by the comparison of ΔS° values obtained in this way from low-temperature heat capacity measurements, with ΔS° values derived either from measured equilibrium constants and reaction heats or from the temperature coefficients of cell emf's—eq. (4.3). Examples of such comparisons are shown in Table 4.7. The Third Law is now considered to be on a firm experimental basis. Its full meaning will become clearer when its statistical interpretation is considered in a later chapter.

The great utility of Third Law measurements in the calculation of chemical equilibria has led to an intensive development of low-temperature heat-capacity techniques, using liquid hydrogen as a refrigerant. The experimental procedure consists essentially in a careful measurement of the temperature rise that is caused in an insulated sample by a carefully measured energy input.

We have now seen how thermodynamics has been able to answer the old question of chemical affinity by providing a quantitative method for calculating (from thermal data alone) the position of equilibrium in chemical reactions.

TABLE 4.7

CHECKS OF THE THIRD LAW OF THERMODYNAMICS

Reaction	Temp. (°K)	Third Law ΔS° (cal/deg mole)	Experimental ΔS°	Method
$Ag\ (c) + \frac{1}{2} Br_2\ (l) = AgBr\ (c)$	265.9	-3.01 ± 0.40	-3.02 ± 0.10	emf
$Ag\ (c) + \frac{1}{2} Cl_2\ (g) = AgCl\ (c)$	298.16	-13.85 ± 0.25	-13.73 ± 0.10	emf
$Zn\ (c) + \frac{1}{2} O_2\ (g) = ZnO\ (c)$	298.16	-24.07 ± 0.25	-24.24 ± 0.05	K and ΔH
$C + \frac{1}{2} O_2\ (g) = CO\ (g)$	298.16	-20.01 ± 0.40	-21.38 ± 0.05	K and ΔH
$CaCO_3\ (c) = CaO\ (c) + CO_2\ (g)$	298.16	38.40 ± 0.20	38.03 ± 0.20	K and ΔH

15. General theory of chemical equilibrium: the chemical potential. We have so far confined our attention to equilibria involving ideal gases. The relations discovered are of great utility, and are accurate enough for the discussion of most homogeneous gas equilibria. Some gas reactions, however, are carried out under such conditions that the ideal gas laws are no longer a good approximation. Examples include the high-pressure syntheses of ammonia and methanol. In addition, there are the great number of chemical reactions that occur in condensed phases such as liquid or even solid solutions. In order to treat these reactions especially, a more general equilibrium theory will be needed.

The composition of a system in which a chemical reaction is taking place is continually changing, and the state of the system is not defined by specifying merely the pressure, volume, and temperature. In order to discuss the changes of composition it is necessary to introduce, in addition to P, V, and T, new variables that are a measure of the amount of each chemical constituent of the system. As usual, the mole will be chosen as the chemical measure, with the symbols $n_1, n_2, n_3 \ldots n_i$ representing the number of moles of constituent 1, 2, 3, or i.

It then follows that each thermodynamic function depends on these n_i's as well as on P, V, and T. Thus, $E = E(P, V, T, n_i)$; $F = F(P, V, T, n_i)$, etc. Consequently, a perfect differential, for example of the free energy, becomes

$$dF = \left(\frac{\partial F}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial F}{\partial P}\right)_{T,n_i} dP + \sum \left(\frac{\partial F}{\partial n_i}\right)_{T,P,n_j} dn_i \tag{4.24}$$

By eq. (3.29) $dF = -S\,dT + V\,dP$ for any system of constant composition, *i.e.*, when all $dn_i = 0$. Therefore

$$dF = -S\,dT + V\,dP + \sum \left(\frac{\partial F}{\partial n_i}\right)_{T,P,n_j} dn_i \tag{4.25}$$

The coefficient $(\partial F/\partial n_i)_{T,P,n_j}$, first introduced by Gibbs, has been given a special name because of its great importance in chemical thermodynamics. It is called the *chemical potential*, and is written as

$$\mu_i = \left(\frac{\partial F}{\partial n_i}\right)_{T,P,n_j} \tag{4.26}$$

It is the change of the free energy with change in number of moles n_i of component i, the temperature, the pressure, and the number of moles of all other components in the system being kept constant. Using the new symbol, eq. (4.25) becomes

$$dF = -S\,dT + V\,dP + \sum_i \mu_i\,dn_i \tag{4.27}$$

At constant temperature and pressure,

$$dF = \sum \mu_i\,dn_i \tag{4.28}$$

The condition for equilibrium, $dF = 0$, then becomes

$$\sum_i \mu_i\,dn_i = 0 \tag{4.29}$$

For an ideal gas, the chemical potential is simply the free energy per mole at pressure P_i. Therefore from eq. (4.7),

$$\mu_i - \mu_i^\circ = RT \ln P_i \tag{4.30}$$

The value of μ_i for the ideal gas is the same whether the ideal gas is pure gas at a pressure P_i or is in an ideal gas mixture[13] at partial pressure P_i. If,

---

[13] This statement is a definition of an ideal gas mixture. To be precise, one must distinguish an ideal gas mixture from a mixture of ideal gases. There might be specific interactions between two ideal gases that would cause their mixture to deviate from ideality.

however, the gas mixture is not ideal, this identity no longer holds true. Various interaction forces come into operation, and the evaluation of μ_i becomes a separate experimental problem in each case.

16. The fugacity. Because relations such as eq. (4.30) lead to equations of such simple form in the development of the theory of chemical equilibrium, it is convenient to introduce a new function, called the *fugacity* of the substance, that preserves the form of eq. (4.30) even for nonideal systems. Therefore we write

$$d\mu = V\,dP = RT\,d\ln f, \quad \text{and} \quad \mu_i - \mu_i^\circ = RT\ln\frac{f_i}{f_i^\circ}$$

where f_i is the fugacity of the substance, and f_i° is its fugacity in the standard state. It now becomes desirable to change the definition of the standard state so that instead of the state of unit pressure, it becomes the state of unit fugacity, $f_i^\circ = 1$. Then

$$\mu_i - \mu_i^\circ = RT\ln f_i \tag{4.31}$$

Now the treatment of equilibrium in Section 4–5 can be carried through in terms of the fugacity and chemical potential. This leads to an expression for the equilibrium constant which is true in general, not only for real (nonideal) gases but also for substances in any state of aggregation whatsoever:

$$K_f = \frac{f_C{}^c f_D{}^d}{f_A{}^a f_B{}^b}$$

$$-\Delta\mu^\circ = RT\ln K_f \tag{4.32}$$

The fugacity of a pure gas or of a gas in a mixture can be evaluated if sufficiently detailed *PVT* data are available. This discussion will be limited to an illustration of the method for determining the fugacity of a pure gas. In this case,

$$dF = d\mu = V\,dP \tag{4.33}$$

If the gas is ideal, $V = RT/P$. For a nonideal gas, this is no longer true. We may write $a = V_{\text{ideal}} - V_{\text{real}} = (RT/P) - V$, whence $V = (RT/P) - a$. Substituting this expression into eq. (4.33), we find

$$RT\,d\ln f = dF = d\mu = RT\,d\ln P - a\,dP$$

The equation is integrated from $P = 0$ to P.

$$RT\int_{f,P=0}^{f} d\ln f = RT\int_{P=0}^{P} d\ln P - \int_0^P a\,dP$$

As its pressure approaches zero, a gas approaches ideality, and for an ideal gas the fugacity equals the pressure, $f = P$ [cf. eqs. (4.30 and (4.31)]. The lower limits of the first two integrals must therefore be equal, so that we obtain

$$RT\ln f = RT\ln P - \int_0^P a\,dP \tag{4.34}$$

This equation enables us to evaluate the fugacity at any pressure and temperature, provided *PVT* data for the gas are available. If the deviation from ideality of the gas volume is plotted against *P*, the integral in eq. (4.34) can be evaluated graphically. Alternatively, an equation of state can be used to calculate an expression for *a* as a function of *P*, making it possible to evaluate the integral by analytical methods.

The fugacity may be thought of as a sort of idealized pressure, which measures the true *escaping tendency* of a gas. In Chapter 1, it was pointed out that the deviations of gases from ideality are approximately determined by their closeness to the critical point. This behavior is confirmed by the fact that at the same reduced pressures all gases have approximately the same ratio of fugacity to pressure. The ratio of fugacity to pressure is called the *activity coefficient*, $\gamma = f/P$. Figure 4.4 shows a family of curves[14] relating the activity coefficient of a gas to its reduced pressure P_R at various values of the reduced temperature T_R. To the approximation that the law of corresponding states is valid, all gases have the same value of γ when they are in corresponding states, *i.e.*, at equal P_R and T_R. This is a very useful principle,

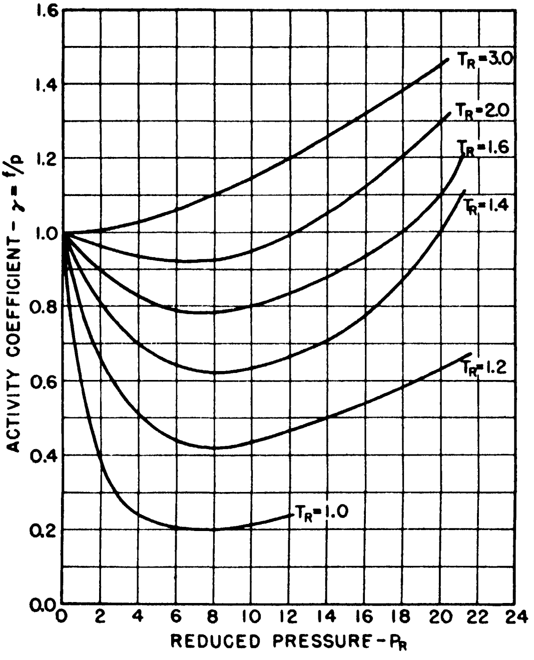


Fig. 4.4. Variation of activity coefficient with reduced pressure at various reduced temperatures.

---

[14] Newton, *Ind. Eng. Chem.*, *27*, 302 (1935). Graphs for other ranges of P_R and T_R are included in this paper.

for it allows us to estimate the fugacity of a gas solely from a knowledge of its critical constants.

17. Use of fugacity in equilibrium calculations. Among the industrially important gas reactions that are carried out under high pressures is the synthesis of ammonia: $\frac{1}{2}\ N_2 + \frac{3}{2}\ H_2 = NH_3$. This reaction has been carefully investigated up to 1000 atm by Larson and Dodge.[15] The per cent of NH_3 in equilibrium with a three-to-one H_2-N_2 mixture at 450°C and various total pressures is shown in Table 4.8. In the third column of the table are the values of $K_p = P_{NH_3}/P_{N_2}{}^{1/2}P_{H_2}{}^{3/2}$ calculated from these data.

Since K_p for ideal gases should be independent of the pressure, these results indicate considerable deviations from ideality at the higher pressures. Let us therefore calculate the equilibrium constant K_f using Newton's graphs to obtain the fugacities. We are therefore adopting the approximation that the fugacity of a gas in a mixture is determined only by the temperature and by the total pressure of the gas mixture.

Consider the calculation of the activity coefficients at 450°C (723°K) and 600 atm.

	P_c	T_c	P_R	T_R	γ
N_2	33.5	126	17.9	5.74	1.35
H_2	12.8	33.3	46.8	21.7	1.19
NH_3	111.5	405.6	5.38	1.78	0.85

The activity coefficients γ are read from the graphs, at the proper values of reduced pressure P_R and reduced temperature T_R. (Only the NH_3 values are found in Fig. 4.4; the complete graphs must be consulted for the other gases.)

TABLE 4.8

EQUILIBRIUM IN THE AMMONIA SYNTHESIS AT 450°C WITH 3:1 RATIO OF H_2 TO N_2

Total Pressure (atm)	Per cent NH_3 at Equilibrium	K_p	K_γ	K_f
10	2.04	0.00659	0.995	0.00655
30	5.80	0.00676	0.975	0.00659
50	9.17	0.00690	0.945	0.00650
100	16.36	0.00725	0.880	0.00636
300	35.5	0.00884	0.688	0.00608
600	53.6	0.01294	0.497	0.00642
1000	69.4	0.02328	0.434	0.01010

Since the fugacity $f = \gamma P$, we can write in general $K_f = K_\gamma K_p$, where in this case $K_\gamma = \gamma_{NH_3}/\gamma_{N_2}{}^{1/2}\gamma_{H_2}{}^{3/2}$. The values of K_γ and K_f are shown in Table 4.8. There is a marked improvement in the constancy of K_f as compared with K_p. Only at 1000 atm does the approximate treatment of the fugacities appear to fail. To carry out an exact thermodynamic treatment, it

---

[15] *J. Am. Chem. Soc.*, *45*, 2918 (1923); *46*, 367 (1924).

would be necessary to calculate the fugacity of each gas in the particular mixture under study. This would require very extensive *PVT* data on the mixture.

Often, knowing ΔF° for the reaction, we wish to calculate the equilibrium concentrations in a reaction mixture. The procedure is to obtain K_f from $-\Delta F^\circ = RT \ln K_f$, to estimate K_γ from the graphs, and then to calculate the partial pressures from $K_p = K_f/K_\gamma$.

PROBLEMS

1. The emf of the cadmium-calomel cell in which the reaction is $Cd + Hg_2^{++} = Cd^{++} + 2\,Hg$, can be represented by: $\mathscr{E} = 0.6708 - 1.02 \times 10^{-4}(t - 25) - 2.4 \times 10^{-6}(t - 25)^2$, where t is the centigrade temperature. Calculate ΔF, ΔS, and ΔH for the cell reaction at 45°C.

2. From the standard free energies in Table 4.2 calculate ΔF° and K_p at 25°C for the following reactions:

$$\text{(a)}\ N_2O + 4\,H_2 = 2\,NH_3 + H_2O\,(g)$$
$$\text{(b)}\ H_2O_2\,(g) = H_2O\,(g) + \tfrac{1}{2}\,O_2$$
$$\text{(c)}\ CO + H_2O\,(l) = HCOOH\,(l)$$

3. At 900°K the reaction $C_2H_6 = C_2H_4 + H_2$ has $\Delta H^\circ = 34.42$, $\Delta F^\circ = 5.35$ kcal. Calculate the per cent H_2 present at equilibrium if pure C_2H_6 is passed over a dehydrogenation catalyst at this temperature and 1 atm pressure. Estimate the per cent H_2 at equilibrium at 1000°K.

4. If an initial mixture of 10 per cent C_2H_4, 10 per cent C_2H_6, and 80 per cent N_2 is passed over the catalyst at 900°K and 1 atm, what is the per cent composition of effluent gas at equilibrium? What if the same mixture is used at 100 atm? (Cf. data in Problem 3.)

5. The equilibrium $LaCl_3\,(s) + H_2O\,(g) = LaOCl\,(s) + 2\,HCl\,(g)$. [*J. Am. Chem. Soc.*, *74*, 2349 (1952)] was found to have $K_p = 0.63$ at 804°K, and 0.125 at 733°K. Estimate ΔH for the reaction. If the equilibrium HCl vapor pressure at 900°K is 2.0 mm estimate the equilibrium H_2O vapor pressure.

6. From the data in Table 4.4, calculate the heat of dissociation of O_2 into 2 O at 1000°K. Similarly, calculate ΔH°_{1000} for $H_2 = 2\,H$. Assuming atomic H and O are ideal gases with $C_P = \frac{5}{2}R$, and using the C_P's for H_2 and O_2 in Table 2.4, calculate ΔH°_{298} for $2\,H + O = H_2O\,(g)$. The heat of formation of $H_2O\,(g)$ is -57.80 kcal. One-half the heat calculated in this problem is a measure of the "strength of the O—H bond" in water.

7. For the reaction $N_2O_4 = 2\,NO_2$, calculate K_p, K_x, K_c at 25°C. and 1 atm from the free energies of formation of the compounds (Table 4.2).

8. PCl_5 vapor decomposes on heating according to $PCl_5 = PCl_3 + Cl_2$. The density of a sample of partially dissociated PCl_5 at 1 atm and 230°C was found to be 4.80 g per liter. Calculate the degree of dissociation α and ΔF° for the dissociation at 230°C.

9. The following results were obtained for the degree of dissociation of CO_2 ($CO_2 = CO + \frac{1}{2} O_2$) at 1 atm:

°K	1000	1400	2000
α	2.0×10^{-7}	1.27×10^{-4}	1.55×10^{-2}

What is ΔS° for the reaction at 1400°K?

10. The free energy of formation of H_2S is given by $\Delta F^\circ = -19{,}200 + 0.94T \ln T - 0.00165T^2 - 0.00000037T^3 + 1.65T$. $H_2 + \frac{1}{2} S_2\,(g) = H_2S\,(g)$. If H_2S at 1 atm is passed through a tube heated to 1200°K, what is per cent H_2 in the gas at equilibrium?

11. Jones and Giauque obtained the following values for C_p of nitromethane.[16]

°K	15	20	30	40	50	60	70	80	90	100
C_p	0.89	2.07	4.59	6.90	8.53	9.76	10.70	11.47	12.10	12.62
°K	120	140	160	180	200	220	240	260	280	300
C_p	13.56	14.45	15.31	16.19	17.08	17.98	18.88	25.01	25.17	25.35

The melting point is 244.7°K, heat of fusion 2319 cal per mole. The vapor pressure of the liquid at 298.1°K is 3.666 cm. The heat of vaporization at 298.1°K is 9147 cal per mole. Calculate the Third-Law entropy of CH_3NO_2 gas at 298.1°K and 1 atm pressure (assuming ideal gas behavior).

12. Using the Third-Law entropies in Table 4.6 and the standard heats of formation calculate the equilibrium constants at 25°C of the following reactions:

$$H_2 + Cl_2 = 2\,HCl$$

$$CH_4 + 2\,O_2 = CO_2 + 2\,H_2O\,(g)$$

$$2\,Ag\,(s) + Cl_2 = 2\,AgCl\,(s)$$

13. For the reaction $CO + 2\,H_2 = CH_3OH\,(g)$, $\Delta F^\circ = -3220$ cal at 700°K. Calculate the per cent CH_3OH at equilibrium with a 2 : 1 mixture of $H_2 + CO$ at a pressure of 600 atm using (a) ideal gas law, (b) Newton's fugacity charts.

14. At high temperature and pressure, a quite good equation of state for gases is $P(V - b) = RT$. Calculate the fugacity of N_2 at 1000 atm and 1000°C according to this equation, if $b = 39.1$ cc per mole.

15. Show that

$$\mu_i = \left(\frac{\partial F}{\partial n_i}\right)_{T,P,n_j} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j} = \left(\frac{\partial E}{\partial n_i}\right)_{S,V,n_j}$$

16. Amagat measured the molar volume of CO_2 at 60°C.

Pressure, atm	13.01	35.42	53.65	74.68	85.35
Volume, cc	2000.0	666.7	400.0	250.0	200.0

---

[16] *J. Am. Chem. Soc.*, *69*, 983 (1947).

Calculate the activity coefficient $\gamma = f/P$ for CO_2 at 60°C and pressures of 10, 20, 40, and 80 atm.

17. When *n*-pentane is passed over an isomerization catalyst at 600°K, the following reactions occur:

$$\text{(A)}\ CH_3CH_2CH_2CH_2CH_3 = CH_3CH(CH_3)CH_2CH_3 \qquad \text{(B)}$$
$$= C(CH_3)_4 \qquad \text{(C)}$$

The free energies of formation at 600°K are: (A) 33.79, (B) 32.66, (C) 35.08 kcal per mole. Calculate the composition of the mixture when complete equilibrium is attained.

18. For the reaction $3\,CuCl\,(g) = Cu_3Cl_3\,(g)$, Brewer and Lofgren [*J. Am. Chem. Soc.*, *72*, 3038 (1950)] found $\Delta F° = -126{,}400 - 12.51T\log T + 104.7\,T$. What are the $\Delta H°$ and $\Delta S°$ of reaction at 2000°K? What is the equilibrium mole fraction of trimer in the gas at 1 atm and 2000°K?

REFERENCES

BOOKS

1. Kubaschewski, O., and E. L. Evans, *Metallurgical Thermochemistry* (London: Butterworth, 1951).
2. Putnam, P. C., *Energy in the Future* (New York: Van Nostrand, 1953).
3. Squire, C. F., *Low Temperature Physics* (New York: McGraw-Hill, 1953).
4. Wenner, R. R., *Thermochemical Calculations* (New York: McGraw-Hill, 1941).

Also see Chapter 1, p. 25.

ARTICLES

1. *Chem. Revs.*, *39*, 357–481 (1946), "Symposium on Low Temperature Research."
2. Daniels, F., *Scientific American*, *191*, 58–63 (1954), "High Temperature Chemistry."
3. Huffman, H. M., *Chem. Revs.*, *40*, 1–14 (1947), "Low Temperature Calorimetry."
4. Lemay, P., and R. Oesper, *J. Chem. Ed.*, *23*, 158–65, 230–36 (1946), "Claude Berthollet "
5. Oesper, R., *J. Chem. Ed.*, *21*, 263–64 (1944), "H. Kammerlingh-Onnes."
6. Urey, H. C., *J. Chem. Soc.*, 562–81 (1947), "Thermodynamic Properties of Isotopic Substances."
7. Walden, P., *J. Chem. Ed.*, *31*, 27–33 (1954), "Beginnings of the Doctrine of Chemical Affinity."
8. Watson, R. G., *Research*, *7*, 34–40 (1954), "Electrochemical Generation of Electricity."

CHAPTER 5

Changes of State

1. Phase equilibria. Among the applications of thermodynamics is the study of the equilibrium conditions for changes such as the melting of ice, the solution of sugar, the vaporization of benzene, or the transformation of monoclinic to rhombic sulfur. Certain fundamental principles are applicable to all such phenomena, which are examples of "changes in state of aggregation" or "phase changes."

The word *phase* is derived from the Greek φασις, meaning "appearance." If a system is "uniform throughout, not only in chemical composition, but also in physical state,"[1] it is said to be homogeneous, or to consist of only one phase. Examples are a volume of air, a noggin of rum, or a cake of ice. Mere difference in shape or in degree of subdivision is not enough to determine a new phase. Thus a mass of cracked ice is still only one phase.[2]

A system consisting of more than one phase is called *heterogeneous*. Each physically or chemically different, homogeneous, and mechanically separable part of a system constitutes a distinct phase. Thus a glassful of water with cracked ice in it is a two-phase system. The contents of a flask of liquid benzene in contact with benzene vapor and air is a two-phase system; if we add a spoonful of sugar (practically insoluble in benzene) we obtain a three-phase system: a solid, a liquid, and a vapor phase.

In systems consisting entirely of gases, only one phase can exist at equilibrium, since all gases are miscible in all proportions (unless, of course, a chemical reaction intervenes, *e.g.*, $NH_3 + HCl$). With liquids, depending on their mutual miscibility, one, two, or more phases can arise. Many different solid phases can coexist.

2. Components. The composition of a system may be completely described in terms of the "components" that are present in it. The ordinary meaning of the word "component" is somewhat restricted in this technical usage. We wish to impose a requirement of economy on our description of the system. This is done by using the *minimum* number of chemically distinct constituents necessary to describe the composition of each phase in the system. The constituents so chosen are the *components*. If the concentrations of the components are stated for each phase, then the concentrations in each phase of any and all substances present in the system are uniquely fixed. This definition may be expressed more elegantly by saying that the com-

---

[1] J. Willard Gibbs.

[2] This is because we are assuming, at this stage in our analysis, that a variable surface area has no appreciable effect on the properties of a substance.

ponents are those constituents whose concentrations may be *independently varied* in the various phases.

Consider, for example, a system consisting of liquid water in contact with its vapor. We know that water is composed of hydrogen and oxygen, but these elements are always present in fixed and definite proportions. The system therefore contains one component only.

Another example is the system consisting of calcium carbonate, calcium oxide, and carbon dioxide. A chemical reaction between these compounds is possible, $CaCO_3 = CaO + CO_2$. In this case, three phases are present, gaseous CO_2, solid $CaCO_3$ and CaO. Two components are required in order to describe the composition of all of these phases, the most suitable choice being CaO and CO_2.

A less obvious example is the system formed by water and two salts without a common ion, *e.g.*, H_2O, NaCl, KBr. As a result of interaction between ions in solution four different salts, or their hydrates, may occur in solid phases, namely NaCl, KBr, NaBr, KCl. In order to specify the composition of all possible phases, four components are necessary, consisting of water and three of the possible salts. This fixes the concentrations of three of the four ions in any phase, and the fourth is fixed by the requirement of over-all electrical neutrality.

Careful examination of each individual system is necessary in order to decide the best choice of components. It is generally wise to choose as components those constituents that cannot be converted into one another by reactions occurring within the system. Thus $CaCO_3$ and CaO would be a possible choice for the $CaCO_3 = CaO + CO_2$ system, but a poor choice because the concentrations of CO_2 would have to be expressed by negative quantities. While the *identity* of the components is subject to some degree of choice, the *number* of components is always definitely fixed for any given case.

Even the last statement should perhaps be modified, because the actual choice of the number of components depends on how precisely one wishes to describe a system. In the water system, there is always some dissociation of water vapor into hydrogen and oxygen. At moderate temperatures, this dissociation is of no consequence in any experimental measurements, and to consider it in deciding the number of components would be unduly scrupulous.[3] The precision with which experimental data on the system can be obtained should be allowed to decide borderline cases.

3. Degrees of freedom. For the complete description of a system, the numerical values of certain variables must be reported. These variables are

---

[3] It is worth noting that the mere dissociation of water into hydrogen and oxygen does not create new components, because the proportion of H_2 to O_2 is always fixed at 2:1, since we exclude the possibility that additional H_2 or O_2 can be added to the system. The reason why an extra component, either H_2 or O_2, might conceivably be required is that H_2 and O_2 dissolve to different extents in the water, so that their ratio is no longer fixed at 2:1 in each phase.

chosen from among the "state functions" of the system, such as pressure, temperature, volume, energy, entropy, and the concentrations of the various components in the different phases. Values for all of the possible variables need not be explicitly stated, for a knowledge of some of them definitely determines the values of the others. For any complete description, however, at least one capacity factor is required, since otherwise the mass of the system is undetermined, and one is not able, for example, to distinguish between a system containing a ton of water and one containing a few drops.

An important feature of equilibria between phases is that they are independent of the actual amounts of the phases that may be present.[4] Thus the vapor pressure of water above liquid water in no way depends on the volume of the vessel or on whether a few milliliters or many gallons of water are in equilibrium with the vapor phase. Similarly, the concentration of a saturated solution of salt in water is a fixed and definite quantity, regardless of whether a large or a small excess of undissolved salt is present.

In discussing phase equilibria, we therefore need not consider the capacity factors, which express the absolute bulk of any phase. We consider only the intensity factors, such as temperature, pressure, and concentrations. Of these variables a certain number may be independently varied, but the rest are fixed by the values chosen for the independent variables and by the thermodynamic requirements for equilibrium. The number of the intensive state variables that can be independently varied without changing the number of phases is called the *number of degrees of freedom* of the system, or sometimes the *variance*.

For example, the state of a certain amount of a pure gas may be specified completely by any two of the variables, pressure, temperature, and density. If any two of these are known, the third can be calculated. This is therefore a system with two degrees of freedom, or a bivariant system.

In the system "water—water vapor," only one variable need be specified to determine the state. At any given temperature, the pressure of vapor in equilibrium with liquid water is fixed in value. This system has one degree of freedom, or is said to be univariant.

4. Conditions for equilibrium between phases. In a system containing several phases, certain thermodynamic requirements for the existence of equilibrium may be derived.

For thermal equilibrium it is necessary that the temperatures of all the phases be the same. Otherwise, heat would flow from one phase to another. This intuitively recognized condition may be proved by considering two phases α and β at temperatures T^α, T^β. The condition for equilibrium at constant volume and composition is given on p. 59 as $dS = 0$. Let S^α and S^β be the entropies of the two phases, and suppose there were a transfer of heat δq from α to β at equilibrium.

---

[4] This statement is proved in the next Section. It is true as long as surface area variations are left out of consideration. (See Chapter 16.)

Then $$dS = dS^\alpha + dS^\beta = 0 \quad \text{or} \quad -\frac{\delta q}{T^\alpha} + \frac{\delta q}{T^\beta} = 0$$

whence $$T^\alpha = T^\beta \tag{5.1}$$

For mechanical equilibrium it is necessary that the pressures of all the phases be the same. Otherwise, one phase would increase in volume at the expense of another. This condition may be derived from the equilibrium condition at constant over-all volume and temperature, $dA = 0$. Suppose one phase expanded into another by δV. Then

$$P^\alpha \, \delta V - P^\beta \, \delta V = 0$$

or $$P^\alpha = P^\beta \tag{5.2}$$

In addition to the conditions given by eqs. (5.1) and (5.2), a condition is needed that expresses the requirements of chemical equilibrium. Let us consider the system with phases α and β maintained at constant temperature and pressure, and denote by n_i^α, n_i^β, the numbers of moles of some particular component i in the two phases. From eq. (3.28) the equilibrium condition becomes $dF = 0$, or

$$dF^\alpha + dF^\beta = 0 \tag{5.3}$$

Suppose that a process occurred by which δn_i moles of component i were taken from phase α and added to phase β. (This process might be a chemical reaction or a change in aggregation-state.) Then, by virtue of eq. (4.28), eq. (5.3) becomes

$$-\mu_i^\alpha \, \delta n_i + \mu_i^\beta \, \delta n_i = 0$$

or $$\mu_i^\alpha = \mu_i^\beta \tag{5.4}$$

This is the general condition for equilibrium with respect to transport of matter between phases, including chemical equilibrium between phases. For any component i in the system, the value of the chemical potential μ_i must be the same in every phase.

An important symmetry between the various equilibrium conditions is apparent in the following summary:

Capacity factor	*Intensity factor*	*Equilibrium condition*
S	T	$T^\alpha = T^\beta$
V	P	$P^\alpha = P^\beta$
n_i	μ_i	$\mu_i^\alpha = \mu_i^\beta$

5. The phase rule. Between 1875 and 1878, Josiah Willard Gibbs, Professor of Mathematical Physics at Yale University, published in the *Transactions of the Connecticut Academy of Sciences* a series of papers entitled "On the Equilibrium of Heterogeneous Substances." In these papers Gibbs disclosed the entire science of heterogeneous equilibrium with a beauty and preciseness never before and seldom since seen in thermodynamic studies.

Subsequent investigators have had little to do save to provide experimental illustrations for Gibbs's equations.

The Gibbs phase rule provides a general relationship among the degrees of freedom of a system f, the number of phases p, and the number of components c. This relationship always is

$$f = c - p + 2 \tag{5.5}$$

The derivation proceeds as follows:

The number of degrees of freedom is equal to the number of intensive variables required to describe a system, minus the number that cannot be independently varied. The state of a system containing p phases and c components is specified at equilibrium if we specify the temperature, the pressure, and the amounts of each component in each phase. The total variables required in order to do this are therefore $pc + 2$.

Let n_i^α denote the number of moles of a component i in a phase α. Since the size of the system, or the actual amount of material in any phase, does not affect the equilibrium, we are really interested in the relative amounts of the components in the different phases and not in their absolute amounts. Therefore, instead of the mole numbers n_i^α, the mole fractions X_i^α should be used. These are given by

$$X_i^\alpha = \frac{n_i^\alpha}{\sum\limits_j n_j^\alpha}$$

For each phase, the sum of the mole fractions equals unity.

$$X_1^\alpha + X_2^\alpha + X_3^\alpha + \dots + X_c^\alpha = 1$$

or

$$\sum_i X_i^\alpha = 1 \tag{5.6}$$

If all but one mole fraction are specified, that one can be calculated from eq. (5.6). If there are p phases, there are p equations similar to eq. (5.6), and therefore p mole fractions that need not be specified since they can be calculated. The total number of independent variables to be specified is thus $pc + 2 - p$ or $p(c - 1) + 2$.

At equilibrium, the eqs. (5.4) impose a set of further restraints on the system by requiring that the chemical potentials of each component be the same in every phase. These conditions are expressed by a set of equations such as:

$$\begin{aligned} \mu_1^\alpha &= \mu_1^\beta = \mu_1^\gamma = \dots \\ \mu_2^\alpha &= \mu_2^\beta = \mu_2^\gamma = \dots \\ \mu_c^\alpha &= \mu_c^\beta = \mu_c^\gamma = \dots \end{aligned} \tag{5.7}$$

Each equality sign in this set of equations signifies a condition imposed on the system, decreasing its variance by one. Inspection shows that there are therefore $c(p - 1)$ of these conditions.

The degrees of freedom equal the total required variables minus the restraining conditions. Therefore

$$f = p(c - 1) + 2 - c(p - 1)$$

$$f = c - p + 2 \tag{5.8}$$

6. Systems of one component—water. In the remainder of this chapter, systems of one component will be considered. These systems comprise the study of the conditions of equilibrium in changes in the state of aggregation of pure substances.

From the phase rule, when $c = 1$, $f = 3 - p$, and three different cases are possible:

$p = 1, f = 2$	bivariant system
$p = 2, f = 1$	univariant system
$p = 3, f = 0$	invariant system

These situations may be illustrated by the water system, with its three familiar phases, ice, water, and steam. Since the maximum number of degrees of freedom is two, any one-component system can be represented by a two-dimensional diagram. The most convenient variables are the pressure and the temperature. The water system is shown in Fig. 5.1.

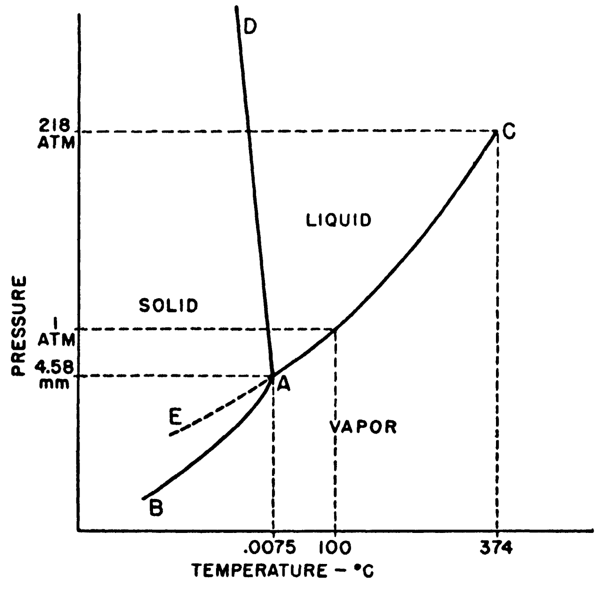


Fig. 5.1. The water system—schematic. (Not drawn to scale.)

The diagram is divided into three areas, the fields of existence of ice, water, and steam. Within these single-phase areas, the system is bivariant, and pressure and temperature may be independently varied.

Separating the areas are lines connecting the points at which two phases may coexist at equilibrium. Thus the curve *AC* dividing the liquid from the vapor region is the familiar vapor-pressure curve of liquid water. At any given temperature there is one and only one pressure at which water vapor is in equilibrium with liquid water. The system is univariant, having one degree of freedom. The curve *AC* has a natural upper limit at the point *C*, which is the critical point, beyond which the liquid phase is no longer distinguishable from the vapor phase.

Similarly, the curve *AB* is the sublimation-pressure curve of ice, giving the pressure of water vapor in equilibrium with solid ice, and dividing the ice region from the vapor region.

The curve *AD* divides the solid-ice region from the liquid-water region. It shows how the melting temperature of ice or the freezing temperature of water varies with the pressure. It is still an open question whether such curves, at sufficiently high pressures, ever have a natural upper limit beyond which solid and liquid are indistinguishable.

These three curves intersect at a point *A*, at which solid, liquid, and vapor are simultaneously at equilibrium. This point, which occurs at 0.0075°C and 4.579 mm pressure, is called a *triple point*. Since three phases coexist, the system is invariant. There are no degrees of freedom and neither pressure nor temperature can be altered even slightly without causing the disappearance of one of the phases.

It should be noted that this triple point is not the same as the ordinary melting point of ice, which by definition is the temperature at which ice and water are in equilibrium under an applied pressure of 1 atm or 760 mm. This temperature is, by definition, 0°C.

Liquid water may be cooled below its freezing point without solidifying. In *AE* we have drawn the vapor-pressure curve of this *supercooled* water, which is a continuous extension of curve *AC*. It is shown as a dotted line on the diagram since it represents a *metastable* system. Note that the metastable vapor pressure of supercooled water is higher than the vapor pressure of ice.

The slope of the curve *AD*, the melting-point curve, is worth remarking. It shows that the melting point of ice is decreased by increasing pressure. This is a rather unusual behavior; only bismuth and antimony among common substances behave similarly. These substances expand on freezing. Therefore the Le Chatelier principle demands that increasing the pressure should lower the melting point. The popularity of ice skating and the flow of glaciers are among the consequences of the peculiar slope of the melting point curve for ice. For most substances, the density of the solid is greater than that of the liquid, and by Le Chatelier's principle, increase in pressure raises the melting point.

7. The Clapeyron-Clausius equation. There are two fundamental theoretical equations that govern much of the field of phase equilibrium. The first is the Gibbs phase rule, which determines the general pattern of the phase diagram. The second is the Clapeyron-Clausius equation, which determines the slopes of the lines in the diagram. It is a quantitative expression for the Le Chatelier principle as it applies to heterogeneous systems. First proposed by the French engineer Clapeyron in 1834, it was placed on a firm thermodynamic foundation by Clausius, some thirty years later.

From eq. (5.4) the condition for equilibrium of a component i between two phases, α and β, is $\mu_i^\alpha = \mu_i^\beta$. For a system of one component, the chemical potentials μ are identical with the free energies per mole F, so that $F^\alpha = F^\beta$ at equilibrium. Consider two different equilibrium states, at slightly separated temperatures and pressures:

(1) $T, P, F^\alpha = F^\beta$.
(2) $T + dT, P + dP, F^\alpha + dF^\alpha = F^\beta + dF^\beta$.

It follows that $dF^\alpha = dF^\beta$. The change in F with T and P is given by eq. (3.29), $dF = V\,dP - S\,dT$. Therefore, $V^\alpha\,dP - S^\alpha\,dT = V^\beta\,dP - S^\beta\,dT$, or

$$\frac{dP}{dT} = \frac{S^\beta - S^\alpha}{V^\beta - V^\alpha} = \frac{\Delta S}{\Delta V} \tag{5.9}$$

If the heat of the phase transformation is λ, ΔS is simply λ/T where T is the temperature at which the phase change is occurring. The Clapeyron-Clausius equation is now obtained as

$$\frac{dP}{dT} = \frac{\lambda}{T\,\Delta V} \tag{5.10}$$

This equation is applicable to any change of state: fusion, vaporization, sublimation, and changes between crystalline forms, provided the appropriate latent heat is employed.

In order to integrate the equation exactly, it would be necessary to know both λ and ΔV as functions of temperature and pressure.[5] The latter corresponds to a knowledge of the densities of the two phases over the desired temperature range. In most calculations over short temperature ranges, however, both λ and ΔV may be taken as constants.

In the case of the change "liquid ⇌ vapor," several approximations are possible, leading to a simpler equation than eq. (5.10),

$$\frac{dP}{dT} = \frac{\lambda_{\text{vap}}}{T_b(V_g - V_l)} \tag{5.11}$$

Neglecting the volume of the liquid compared with that of the vapor, and assuming ideal gas behavior for the latter, one obtains

$$\frac{d\ln P}{dT} = \frac{\lambda_{\text{vap}}}{RT^2} \tag{5.12}$$

---

[5] A good discussion of the temperature variation of λ is given by Guggenheim, *Modern Thermodynamics*, p. 57. The variation with pressure of λ and ΔV is much less than that with temperature.

A similar equation would be a good approximation for the sublimation curve.

Just as was shown for eq. (3.36), this may also be written

$$\frac{d \ln P}{d(1/T)} = -\frac{\lambda}{R} \tag{5.13}$$

If the logarithm of the vapor pressure is plotted against $1/T$, the slope of the curve at any point multiplied by $-R$ yields a value for the heat of vaporization. In many cases, since λ is effectively constant over short temperature ranges, a straight-line plot is obtained. This fact is useful to remember in extrapolating vapor pressure data.

When λ is taken as constant, the integrated form of eq. (5.12) is

$$\ln \frac{P_2}{P_1} = -\frac{\lambda}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{5.14}$$

An approximate value for λ_{vap} can often be obtained from *Trouton's Rule* (1884):

$$\frac{\lambda_{\text{vap}}}{T_b} \approx 22 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

The rule is followed fairly well by many nonpolar liquids (Sec. 14–8). It is equivalent to the statement that the entropy of vaporization is approximately the same for all such liquids.

8. Vapor pressure and external pressure. It is of interest to consider the effect of an increased hydrostatic pressure on the vapor pressure of a liquid. Let us suppose that an external hydrostatic pressure P_e is imposed on a liquid of molar volume V_l. Let the vapor pressure be P, and the molar volume of the vapor V_g. Then at equilibrium at constant temperature:

$$dF_{\text{vap}} = dF_{\text{liq}} \quad \text{or} \quad V_g\, dP = V_l\, dP_e$$

or

$$\frac{dP}{dP_e} = \frac{V_l}{V_g} \tag{5.15}$$

This is sometimes called the *Gibbs equation*. If the vapor is an ideal gas, this equation becomes

$$RT\left(\frac{d \ln P}{dP_e}\right) = V_l$$

Since the molar volume of the liquid does not vary greatly with pressure, this equation may be integrated approximately, assuming constant V_l:

$$\ln \frac{P_1}{P_2} = \frac{V_l(P_{e1} - P_{e2})}{RT} \tag{5.16}$$

In theory, one can measure the vapor pressure of a liquid under an applied hydrostatic pressure in only two ways: (1) with an atmosphere of "inert" gas; (2) with an ideal membrane semipermeable to the vapor. In practice, the inert gas will dissolve in the liquid, so that the application of the Gibbs equation to the problem is dubious. The second case is treated in the theory of osmotic pressure.

As an example of the use of eq. (5.16), let us calculate the vapor pressure of mercury under an external pressure of 1000 atm at 100°C. The density is 13.352 g cm^{-3}; hence $V_l = M/\rho = 200.61/13.352 = 15.025$ cm^3, and

$$\ln \frac{P_1}{P_2} = \frac{15.025(1000 - 1)}{82.05 \times 373.2} = 0.4902$$

Therefore, $P_1/P_2 = 1.633$. The vapor pressure at 1 atm is 0.273 mm, so that the calculated vapor pressure at 1000 atm is 0.455 mm.

9. Experimental measurement of vapor pressure. Many different experimental arrangements have been employed in vapor-pressure measurements. One of the most convenient static methods is the Smith-Menzies isoteniscope shown in Fig. 5.2. The bulb and short attached U-tube are filled with the liquid to be studied, which is allowed to boil vigorously until all air is removed from the sample side of the U-tube. At each temperature the external pressure is adjusted until the arms of the differential U-tube manometer are level, and the pressure and temperature are then recorded.

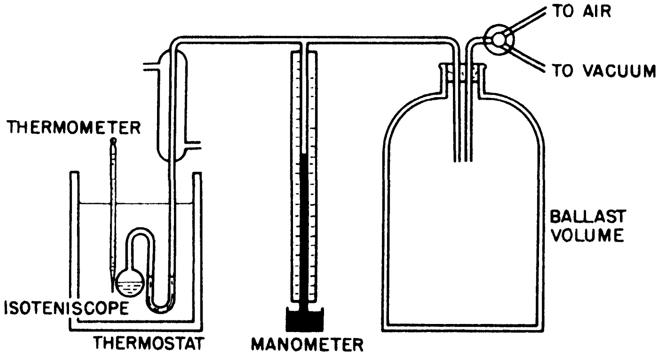


Fig. 5.2. Vapor pressure measurement with isoteniscope.

The gas-saturation method was used extensively by Ramsay and Young. An inert gas is passed through the liquid maintained in a thermostat. The volume of gas used is measured, and its final vapor content or the loss in weight of the substance being studied is determined. If care is taken to ensure saturation of the flowing gas, the vapor pressure of the liquid may readily be calculated.

Some experimentally measured vapor pressures are collected[6] in Table 5.1.

---

[6] A very complete compilation is given by D. R. Stull, *Ind. Eng. Chem.*, *39*, 517–550 (1947).

TABLE 5.1

TYPICAL VAPOR PRESSURE DATA

Temp. (°C)	Vapor Pressure in Millimeters of Mercury						
	CCl_4	CH_3COOH	C_2H_5OH	$(C_2H_5)_2O$	C_7H_{16}	$C_6H_5{\cdot}CH_3$	H_2O
0	—	—	12.2	185.3	11.45	—	4.579
10	—	--	23.6	291.7	20.5	—	9.209
20	91	11.7	43.9	442.2	35.5	—	17.535
30	143.0	20.6	78.8	647.3	58.35	36.7	31.824
40	215.8	34.8	135.3	921.3	92.05	59.1	55.324
50	317.1	56.6	222.2	1277	140.9	92.6	92.51
60	450.8	88.9	352.7	—	208.9	139.5	149.38
70	622.3	136.0	542.5	—	302.3	202.4	233.7
80	843	202.3	812.6	—	426.6	289.7	355.1
90	1122	293.7	1187	—	588.8	404.6	525.76
100	1463	417.1	—	—	795.2	557.2	760.00

10. Solid-solid transformations—the sulfur system. Sulfur provides the classical example of a one-component system displaying a solid-solid transformation. The phenomenon of *polymorphism*, discovered by Mitscherlich in 1821, is the occurrence of the same chemical substance in two or more different crystalline forms. In the case of elements, it is called *allotropy*.

Sulfur occurs in a low-temperature rhombic form and a high-temperature monoclinic form. The phase diagram for the system is shown in Fig. 5.3. The pressure scale in this diagram has been made logarithmic in order to bring the interesting low-pressure regions into prominence.

The curve *AB* is the vapor-pressure curve of solid rhombic sulfur. At point *B* it intersects the vapor-pressure curve of monoclinic sulfur *BE*, and also the transformation curve for rhombic-monoclinic sulfur, *BD*. This intersection determines the triple point *B*, at which rhombic and monoclinic sulfur and sulfur vapor coexist. Since there are three phases and one component, $f = c - p + 2 = 3 - 3 = 0$, and point *B* is an invariant point. It occurs at 0.01 mm pressure and 95.5°C.

The density of monoclinic sulfur is less than that of rhombic sulfur, and therefore the transition temperature ($S_r \rightleftharpoons S_m$) increases with increasing pressure.

Monoclinic sulfur melts under its own vapor pressure of 0.025 mm at 120°C, the point *E* on the diagram. From *E* to the critical point *F* there extends the vapor-pressure curve of liquid sulfur *EF*. Also from *E*, there extends the curve *ED*, the melting-point curve of monoclinic sulfur. The density of liquid sulfur is less than that of the monoclinic solid, the usual situation in a solid-liquid transformation, and hence *ED* slopes to the right as shown. The point *E* is a triple point, S_m-S_{liq}-S_{vap}.

The slope of *BD* is greater than that of *ED*, so that these curves intersect at *D*, forming a third triple point on the diagram, S_r-S_m-S_{liq}. This occurs at 155° and 1290 atm. At pressures higher than this, rhombic sulfur is again the stable solid form, and *DG* is the melting-point curve of rhombic sulfur in this high-pressure region. The range of stable existence of monoclinic sulfur is confined to the totally enclosed area *BED*.

Besides the stable equilibria represented by the solid lines, a number of metastable equilibria are easily observed. If rhombic sulfur is heated quite rapidly, it will pass by the transition point *B* without change and finally melt

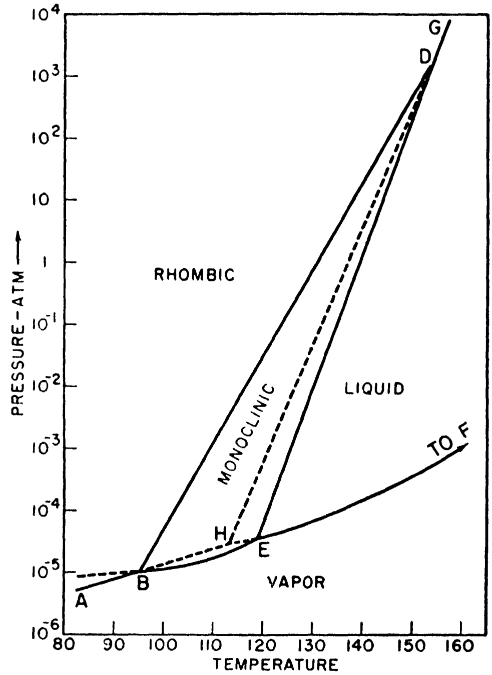


Fig. 5.3. The sulfur system.

to liquid sulfur at 114°C (point *H*). The curve *BH* is the metastable vapor-pressure curve of rhombic sulfur, and the curve *EH* is the metastable vapor pressure curve of supercooled liquid sulfur. Extending from *H* to *D* is the metastable rhombic melting-point curve. Point *H* is a metastable triple point, S_r-S_{liq}-S_{vap}.

All these metastable equilibria are quite easily studied because of the extreme sluggishness that characterizes the rate of attainment of equilibrium between solid phases.

In this discussion of the sulfur system, the well-known equilibrium between S_λ and S_μ in liquid sulfur has not been taken into consideration. If this occurrence of two distinct forms of liquid sulfur is considered, the sulfur system can no longer be treated as a simple one-component system, but becomes a "pseudobinary" system.[7]

11. Enantiotropism and monotropism. The transformation of monoclinic to rhombic sulfur under equilibrium conditions of temperature and pressure is perfectly reversible. This fact is, of course, familiar, since the transformation curve represents a set of stable equilibrium conditions. Such a change between two solid forms, occurring in a region of the phase diagram where both are stable, is called an *enantiotropic change.*

On the other hand, there are cases in which the transformation of one solid form to another is irreversible. The classical example occurs in the phosphorus system, in the relations between white (cubic) phosphorus and violet (hexagonal) phosphorus. When white phosphorus is heated, transformation into violet phosphorus occurs at an appreciable rate at temperatures above 260°; but solid violet phosphorus is never observed to change into solid white phosphorus under any conditions. In order to obtain white phosphorus, it is necessary to vaporize the violet variety, whereupon the vapor condenses to white phosphorus.

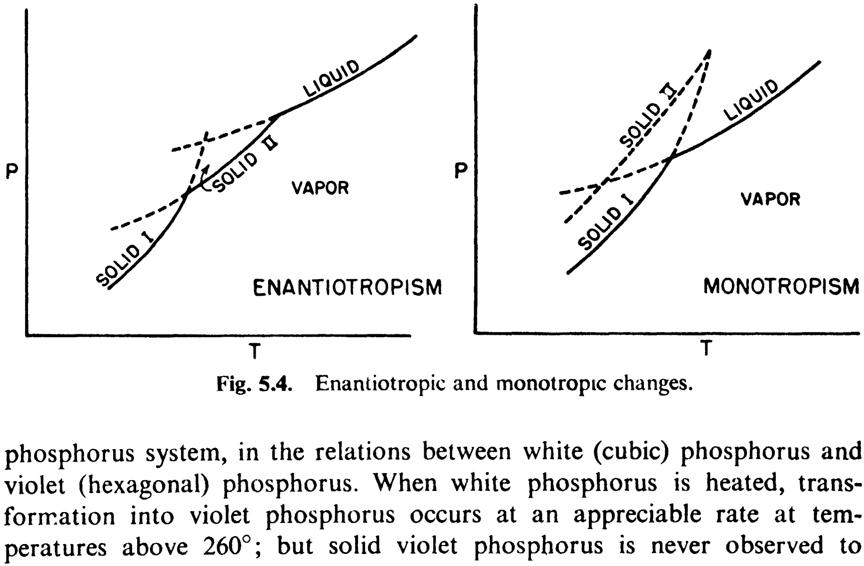


Fig. 5.4. Enantiotropic and monotropic changes.

Such an irreversible solid-state transformation is called a *monotropic change.* It may be characterized by saying that one form is metastable with respect to the other at all temperatures up to its melting point. The situation is shown schematically in Fig. 5.4. The transition point (metastable) between the two solid forms in this case lies above the melting point of either form.

---

[7] If S_λ and S_μ came to equilibrium quickly when the T or P of the liquid was changed, the sulfur system would still have only one component (unary system) as explained in footnote 3. If S_λ and S_μ were present in fixed proportions, which did not change with T and P, because the time of transformation was very long compared with the time of the experiment, the sulfur system would have two components (binary system). In fact it appears that the time of transformation is roughly comparable with the time of most experiments, so that the observed behavior is partly unary and partly binary, being called "pseudobinary."

Actually, the phosphorus case is complicated by the occurrence of several molecular species, P_2, P_4, P_6, and so on, so that considerations based on a one-component system must be applied with caution.

12. Second-order transitions. The usual change of state (solid to liquid, liquid to vapor, etc.) is called a *first-order transition*. At the transition temperature T_t at constant pressure, the free energies of the two forms are equal, but there is a discontinuous change in the slope of the F vs. T curve for the substance at T_t. Since $(\partial F/\partial T) = -S$, there is therefore a break in the S vs. T curve, the value of ΔS at T_t being related to the observed latent heat for the transition by $\Delta S = \lambda/T_t$. There is also a discontinuous change in volume ΔV, since the densities of the two forms are not the same.

A number of transitions have been studied in which no latent heat or density change can be detected. Examples are the transformation of certain metals from ferromagnetic to paramagnetic solids at their Curie points, the transition of some metals at low temperatures to a condition of electric superconductivity, and the transition observed in helium from one liquid form to another.[8] In these cases, there is a change in slope, but no discontinuity, in the S vs. T curve at T_t. As a result, there is a break ΔC_p in the heat capacity curve, since $C_p = T(\partial S/\partial T)_P$. Such a change is called a *second-order transition*.

13. High-pressure studies. It is only a truism that our attitude toward the physical world is conditioned by the scale of magnitudes provided in our terrestrial environment. We tend, for example, to classify pressures or temperatures as high or low by comparing them with the fifteen pounds per square inch and 70°F of a spring day in the laboratory, despite the fact that almost all the matter in the universe exists under conditions very different from these. Thus, even at the center of the earth, by no means a large astronomical body, the pressure is around 1,200,000 atm, and substances at this pressure would have properties quite unlike those to which we are accustomed. At the center of a comparatively small star, like our sun, the pressure would be around ten billion atmospheres.

The pioneer work of Gustav Tammann on high-pressure measurements has been greatly extended over the past twenty years by P. W. Bridgman and his associates at Harvard. Pressures up to 400,000 atm have been achieved and methods have been developed for measuring the properties of substances at 100,000 atm.[9]

The attainment of such pressures has been made possible by the construction of pressure vessels of alloys such as Carboloy, and by the use of a multiple-chamber technique. The container for the substance to be studied is enclosed in another vessel, and pressure is applied both inside and outside the inner container, usually by means of hydraulic presses. Thus although

---

[8] W. H. Keesom, *Helium* (Amsterdam: Elsevier, 1942).

[9] For details see P. W. Bridgman, *The Physics of High Pressures* (London: Bell & Co., 1949), and his review article, *Rev. Mod. Phys.*, *18*, 1 (1946).

the absolute pressure in the inner vessel may be 100,000 atm, the pressure differential that its walls must sustain is only 50,000 atm.

High-pressure measurements on water yielded some of the most interesting results, which are shown in the phase diagram of Fig. 5.5. The melting point of ordinary ice (ice I) falls on compression, until a value of −22.0°C is reached at 2040 atm. Further increase in pressure results in the transformation of ice I into a new modification, ice III, whose melting point increases with pressure. Altogether six different polymorphic forms of ice have been found. There are six triple points shown on the water diagram. Ice VII is an extreme high-pressure form not shown on the diagram; at a pressure of around 20,000 atm, liquid water freezes to ice VII at about 100°C. Ice IV is not shown. Its existence was indicated by the work of Tammann, but it was not confirmed by Bridgman.

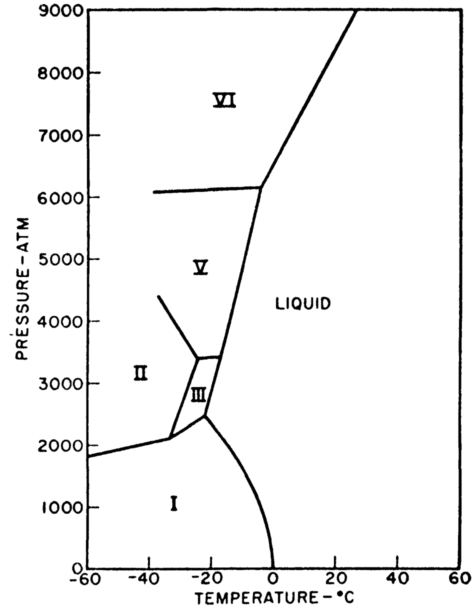


Fig. 5.5. Water system at high pressures.

PROBLEMS

1. From the following data, roughly sketch the phase diagram for carbon dioxide: critical point at 31°C and 73 atm; triple point (solid-liquid-vapor) at −57° and 5.3 atm; solid is denser than liquid at the triple point. Label all regions on the diagram.

2. Roughly sketch the phase diagram of acetic acid, from the data:

(a) The low-pressure α form melts at 16.6°C under its own vapor pressure of 9.1 mm.

(b) There is a high-pressure β form that is denser than the α, but both α and β are denser than the liquid.

(c) The normal boiling point of liquid is 118°C.

(d) Phases α, β, liquid are in equilibrium at 55°C and 2000 atm.

3. Sketch the liquid-solid regions of the phase diagram of urethane. There are three solid forms, α, β, γ. The triple points and the volume changes ΔV in cc per kg at the triple points are as follows:

(*a*) liq, α, β	$P = 2270$ atm	$t = 66°C$	ΔV: $(l - \alpha) = 25.3$ $(l - \beta) = 35.5$ $(\alpha - \beta) = 10.2$
(*b*) liq, β, γ	$P = 4090$ atm	$t = 77°C$	ΔV: $(l - \beta) = 18.4$ $(l - \gamma) = 64.0$ $(\beta - \gamma) = 45.6$
(*c*) α, β, γ	$P = 3290$ atm	$t = 25.5°C$	ΔV: $(\alpha - \beta) = 9.2$ $(\beta - \gamma) = 48.2$ $(\alpha - \gamma) = 57.4$

4. The density ρ of ice at 1 atm and 0°C is 0.917 g per cc. Water under the same conditions has $\rho = 1.000$ g per cc. Estimate the melting point of ice under a pressure of 400 atm assuming that ρ for both ice and water is practically constant over the temperature and pressure range.

5. Bridgman found the following melting points t (°C) and volume changes on melting ΔV (cc per g) for Na:

P, kg/cm^2	1	2000	4000	6000
t	97.6	114.2	129.8	142.5
ΔV	0.0279	0.0236	0.0207	0.0187

Estimate the heat of fusion of sodium at 3000 atm.

6. Estimate the vapor pressure of mercury at 25°C assuming that the liquid obeys Trouton's rule. The normal boiling point is 356.9°C.

7. The vapor pressure of solid iodine is 0.25 mm and its density 4.93 at 20°C. Assuming the Gibbs equation to hold, calculate the vapor pressure of iodine under a 1000-atm argon pressure.

8. In a determination of the vapor pressure of ethyl acetate by the gas saturation method 100 liters of nitrogen (STP) were passed through a saturator containing ethyl acetate at 0°C, which lost a weight of 12.8 g. Calculate vapor pressure at 0°C.

9. The vapor pressures of liquid gallium are as follows:

t, °C	1029	1154	1350
P, mm	0.01	0.1	1.0

Calculate $\Delta H°$, $\Delta F°$, and $\Delta S°$ for the vaporization of gallium at 1154°C.

10. At 25°C, the heat of combustion of diamond is 94.484 kcal per mole and that of graphite is 94.030. The molar entropies are 0.5829 and 1.3609 cal per deg mole, respectively. Find the ΔF for the transition graphite → diamond at 25°C and 1 atm. The densities are 3.513 g per cc for diamond and 2.260

for graphite. Estimate the pressure at which the two forms would be in equilibrium at 25°C. You may assume the densities to be independent of pressure.

11. Sketch graphs of F, S, V, C_P against T at constant P, and P at constant T, for typical first- and second-order phase transitions.

12. From the data in Table 5.1, plot $\log P$ vs. T^{-1} for water and calculate the latent heats of vaporization of water at 20° and at 80°C.

REFERENCES

BOOKS

1. Bridgman, P. W., *The Physics of High Pressures* (London: Bell, 1949).
2. Findlay, A., *The Phase Rule* (New York: Dover, 1945).
3. Marsh, J. S., *Principles of Phase Diagrams* (New York: McGraw-Hill, 1935).
4. Ricci, J. E., *The Phase Rule and Heterogeneous Equilibrium* (New York: Van Nostrand, 1951).
5. Tammann, G., *The States of Aggregation* (New York: Van Nostrand, 1925).
6. Wheeler, L. P., *Josiah Willard Gibbs* (New Haven: Yale Univ. Press, 1953).

ARTICLES

1. Bridgman, P. W., *Science in Progress*, vol. III, 108–46 (New Haven: Yale Univ. Press, 1942), "Recent Work in the Field of High Pressures."
2. Garner, W. E., *J. Chem. Soc.*, 1961–1973 (1952), "The Tammann Memorial Lecture."
3. Staveley, L. A. K., *Quart. Rev.*, *3*, 65–81 (1949), "Transitions in Solids and Liquids."
4. Swietoslawski, W., *J. Chem. Ed.*, *23*, 183–85 (1946), "Phase Rule and the Action of Gravity."
5. Ubbelohde, A. R., *Quart. Rev.*, *4*, 356–81 (1950), "Melting and Crystal Structure."

CHAPTER 6

Solutions and Phase Equilibria

1. The description of solutions. As soon as systems of two or more components are studied, the properties of solutions must be considered, for a solution is by definition any phase containing more than one component. This phase may be gaseous, liquid, or solid. Gases are in general miscible in all proportions, so that all mixtures of gases, at equilibrium, are solutions. Liquids often dissolve a wide variety of gases, solids, or other liquids, and the composition of these liquid solutions can be varied over a wide or narrow range depending on the particular solubility relationships in the individual system. Solid solutions are formed when a gas, a liquid, or another solid dissolves in a solid. They are often characterized by very limited concentration ranges, although pairs of solids are known, for example copper and nickel, that are mutually soluble in all proportions.

It is often convenient in discussing solutions to call some components the solvents and others the solutes. It should be recognized, however, that the only distinction between solute and solvent is a verbal one, although the solvent is usually taken to be the constituent present in excess.

The concentration relations in solutions are expressed in a variety of units. The more important of these are summarized in Table 6.1.

TABLE 6.1

CONCENTRATION OF SOLUTIONS

Name	*Symbol*	*Definition*
Molar	c	Moles of solute in 1 liter solution
Molal	m	Moles of solute in 1000 g solvent
Volume molal	m'	Moles of solute in 1 liter solvent
Weight per cent	%	Grams of solute in 100 g solution
Mole fraction	X	Moles of solute divided by total number of moles of all components

2. Partial molar quantities: partial molar volume. The equilibrium properties of solutions are described in terms of the thermodynamic state functions, such as P, T, V, E, S, F, H. One of the most important problems in the theory of solutions is how these properties depend on the concentrations of the various components. In discussing this question, it will be assumed that the solution is kept at constant over-all pressure and temperature.

Consider a solution containing n_A moles of A and n_B moles of B. Let the volume of the solution be V, and assume that this volume is so large that the addition of one extra mole of A or of B does not change the concentration of the solution to an appreciable extent. The change in volume caused by adding one mole of A to this large amount of solution is then called the *partial molar volume* of A in the solution at the specified pressure, temperature, and concentration, and is denoted by the symbol $\bar{V}_A$. It is the change of volume V, with moles of A, n_A, at constant temperature, pressure; and moles of B, and is therefore written as

$$\bar{V}_A = \left(\frac{\partial V}{\partial n_A}\right)_{T,P,n_B} \tag{6.1}$$

One reason for introducing such a function is that the volume of a solution is not, in general, simply the sum of the volumes of the individual components. For example, if 100 ml of alcohol are mixed at 25°C with 100 ml of water, the volume of the solution is not 200 ml, but about 190 ml. The volume change on mixing depends on the relative amount of each component in the solution.

If dn_A moles of A and dn_B moles of B are added to a solution, the increase in volume at constant temperature and pressure is given by the complete differential,

$$dV = \left(\frac{\partial V}{\partial n_A}\right)_{n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{n_A} dn_B$$

or

$$dV = \bar{V}_A\, dn_A + \bar{V}_B\, dn_B \tag{6.2}$$

This expression can be integrated, which corresponds physically to increasing the volume of the solution without changing its composition, $\bar{V}_A$ and $\bar{V}_B$ hence being held constant.[1] The result is

$$V = \bar{V}_A n_A + \bar{V}_B n_B \tag{6.3}$$

This equation tells us that the volume of the solution equals the number of moles of A times the partial molar volume of A, plus the number of moles of B times the partial molar volume of B.

On differentiation, eq. (6.3) yields

$$dV = \bar{V}_A\, dn_A + n_A\, d\bar{V}_A + \bar{V}_B\, dn_B + n_B\, d\bar{V}_B$$

By comparison with eq. (6.2), it follows that

$$n_A\, d\bar{V}_A + n_B\, d\bar{V}_B = 0$$

or

$$d\bar{V}_A = -\frac{n_B}{n_A}\, d\bar{V}_B \tag{6.4}$$

Equation (6.4) is one example of the *Gibbs-Duhem equation*. This particular application is in terms of the partial molar volumes, but any other

---

[1] Mathematically, the integration is equivalent to the application of Euler's theorem to the homogeneous differential expression. See D. V. Widder, *Advanced Calculus* (New York: Prentice-Hall, 1947), p. 15.

partial molar quantity may be substituted for the volume. These partial molar quantities can be defined for any extensive state function. For example:

$$\bar{S}_A = \left(\frac{\partial S}{\partial n_A}\right)_{T,P,n_B} \qquad \bar{H}_A = \left(\frac{\partial H}{\partial n_A}\right)_{T,P,n_B} \qquad \bar{F}_A = \left(\frac{\partial F}{\partial n_A}\right)_{T,P,n_B}$$

The partial molar quantities are themselves intensity factors, since they are capacity factors per mole. The partial molar free energy is the chemical potential μ.

All the thermodynamic relations derived in earlier chapters can be applied to the partial molar quantities. For example:

$$\left(\frac{\partial \bar{F}_A}{\partial P}\right)_T = \left(\frac{\partial \mu_A}{\partial P}\right)_T = \bar{V}_A, \quad \left(\frac{\partial \mu_A}{\partial T}\right)_P = -\bar{S}_A, \quad \left(\frac{\partial \bar{H}_A}{\partial T}\right)_P = \bar{C}_{PA} \qquad (6.5)$$

The general thermodynamic theory of solutions is expressed in terms of these partial molar functions and their derivatives just as the theory for pure substances is based on the ordinary thermodynamic functions.

3. The determination of partial molar quantities. The evaluation of the partial quantities will now be described, using the partial molar volume as an example. The methods for $\bar{H}_A$, $\bar{S}_A$, $\bar{F}_A$, and so on, are exactly similar.

The partial molar volume $\bar{V}_A$, defined by eq. (6.1), is equal to the slope of the curve obtained when the volume of the solution is plotted against the *molal* concentration of A. This follows since the molal concentration m_A is the number of moles of A in a *constant* quantity, namely 1000 grams, of solvent B.

The determination of partial molar volumes by this slope method is rather inaccurate; the *method of intercepts* is therefore usually preferred. To employ this method, a quantity is defined, called the *molar volume of the solution* v, which is the volume of the solution divided by the total number of moles of the various constituents. For a two-component solution:

$$v = \frac{V}{n_A + n_B}$$

Then,

$$V = v\,(n_A + n_B)$$

and

$$\bar{V}_A = \left(\frac{\partial V}{\partial n_A}\right)_{n_B} = v + (n_A + n_B)\left(\frac{\partial v}{\partial n_A}\right)_{n_B} \qquad (6.6)$$

Now the derivative with respect to mole number of A, n_A, is transformed into a derivative with respect to mole fraction of B, X_B.

$$\left(\frac{\partial v}{\partial n_A}\right)_{n_B} = \frac{dv}{dX_B}\left(\frac{\partial X_B}{\partial n_A}\right)_{n_B}$$

since

$$X_B = \frac{n_B}{n_A + n_B}, \qquad \left(\frac{\partial X_B}{\partial n_A}\right)_{n_B} = -\frac{n_B}{(n_A + n_B)^2}$$

Thus eq. (6.6) becomes: $\bar{V}_A = v - \dfrac{n_B}{n_A + n_B} \dfrac{dv}{dX_B}$

$$\bar{V}_A = v - X_B \frac{dv}{dX_B} \tag{6.7}$$

The application of this equation is illustrated in Fig. 6.1, where v for a solution is plotted against the mole fraction. The slope S_1S_2 is drawn tangent to the curve at point P, corresponding to a definite mole fraction X_B'. The line A_1A_2 is drawn through P parallel to O_1O_2. Therefore the distance $O_1A_1 = v'$, the molar volume corresponding to X_B'. The distance S_1A_1 is equal to the slope at X_B' multiplied by X_B', *i.e.*, to the term in eq. (6.7), $X_B(dv/dX_B)$. It follows that $O_1S_1 = O_1A_1 - S_1A_1$ equals $\bar{V}_A$, the partial molar volume of A in the solution. It can readily be shown that the intercept on the other axis, O_2S_2, is the partial molar volume of B, $\bar{V}_B$. This convenient intercept method is the one usually used to determine partial molar quantities. It is not restricted to volumes, but can be applied to any extensive state function, S, H, E, F, and so on, given the necessary data. It can also be applied to heats of solution, and the partial molar heats of solution so obtained are the same as the differential heats described in Chapter 2.

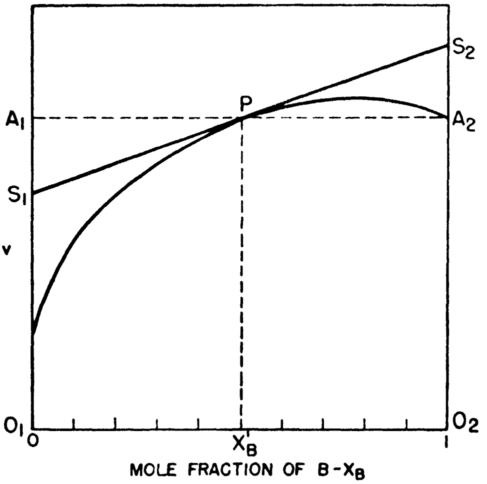


Fig. 6.1. Determination of partial molar volumes—intercept method.

If the variation with concentration of a partial molar quantity is known for one component in a binary solution, the Gibbs-Duhem equation (6.4) permits the calculation of the variation for the other component. This calculation can be accomplished by graphical integration of eq. (6.4). For example:

$$\int d\bar{V}_A = -\int \frac{n_B}{n_A} d\bar{V}_B = -\int \frac{X_B}{X_A} d\bar{V}_B$$

where X is the mole fraction. If X_B/X_A is plotted against $\bar{V}_B$, the area under the curve gives the change in $\bar{V}_A$ between the upper and lower limits of integration. The $\bar{V}_A$ of pure A is simply the molar volume of pure A, and this can be used as the starting point for the evaluation of $\bar{V}_A$ at any other concentration.

4. The ideal solution—Raoult's Law. The concept of the "ideal gas" has played a most important role in discussions of the thermodynamics of gases and vapors. Many cases of practical interest are treated adequately by means of the ideal gas approximations, and even systems deviating largely from ideality are conveniently referred to the norm of behavior set by the ideal case. It would be most helpful to find some similar concept to act as a guide in the theory of solutions, and fortunately this is indeed possible. Because they are very much more condensed than gases, liquid or solid solutions cannot be expected to behave ideally in the sense of obeying an equation of state such as the ideal gas law. Ideality in a gas implies a complete *absence* of cohesive forces; the internal pressure, $(\partial E/\partial V)_T = 0$. Ideality in a solution is defined by complete *uniformity* of cohesive forces. If there are two components A and B, the forces between A and A, B and B, and A and B are all the same.

A property of great importance in the discussion of solutions is the vapor pressure of a component above the solution. This partial vapor pressure may be taken as a good measure of the *escaping tendency* of the given species from the solution. The exact measure of this escaping tendency is the fugacity, which becomes equal to the partial pressure when the vapor behaves as an ideal gas. The tendency of a component to escape from solution into the vapor phase is a very direct reflection of the physical state of affairs within the solution,[2] so that by studying the escaping tendencies, or partial vapor pressures, as functions of temperature, pressure, and concentration, we obtain a description of the properties of the solution.

This method is a direct consequence of the relation between chemical potential and fugacity. If we have a solution, say of A and B, the chemical potential of A in the solution must be equal to the chemical potential of A in the vapor phase. This is related to the fugacity by eq. (4.31), since

$$\mu_A = \mu_A^\circ + RT \ln f_A \tag{6.8}$$

If we know the pressure, the temperature, and the chemical potentials of the various components, we then have a *complete* thermodynamic description of a system, except for the absolute amounts of the various phases. The partial vapor pressures are important because they are an approximate indication of the chemical potentials.

A solution is said to be ideal if the escaping tendency of each component

---

[2] One may think of an analogy in which a nation represents a solution and its citizens the molecules. If life in the nation is a good one, the tendency to emigrate will be low. This presupposes, of course, the absence of artificial barriers.

is proportional to the mole fraction of that component in the solution. It is helpful to look at this concept from a molecular point of view. Consider an ideal solution of A and B. The definition of ideality then implies that a molecule of A in the solution will have the same tendency to escape into the vapor whether it is surrounded entirely by other A molecules, entirely by B molecules, or partly by A and partly by B molecules. This means that the intermolecular forces between A and A, A and B, and B and B, are all essentially the same. It is immaterial to the behavior of a molecule what sort of neighbors it has. The escaping tendency of component A from such an ideal solution, as measured by its partial vapor pressure, is accordingly the same as that from pure liquid A, except that it is proportionately reduced on account of the lowered fraction of A molecules in the solution.

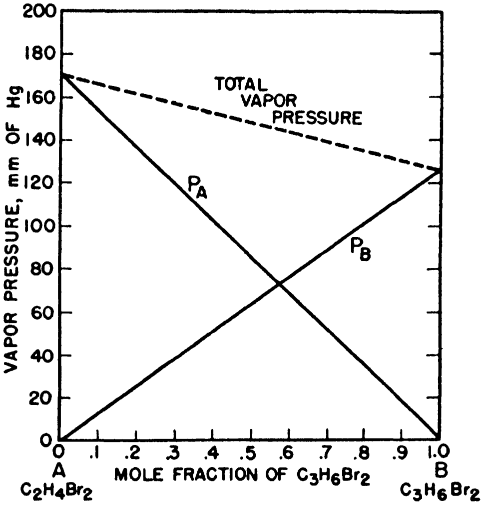


Fig. 6.2. Pressures of vapors above solutions of ethylene bromide and propylene bromide at 85°C. The solutions follow Raoult's Law.

This law of behavior for the ideal solution was first given by François Marie Raoult in 1886, being based on experimental vapor-pressure data. It can be expressed as

$$P_A = X_A P_A^\circ \tag{6.9}$$

Here P_A is the partial vapor pressure of A above a solution in which its mole fraction is X_A, and P_A° is the vapor pressure of pure liquid A at the same temperature.

If the component B added to pure A lowers the vapor pressure, eq. (6.9) can be written in terms of a *relative vapor pressure lowering*,

$$\frac{P_A^\circ - P_A}{P_A^\circ} = (1 - X_A) = X_B \tag{6.10}$$

This form of the equation is especially useful for solutions of a relatively involatile solute in a volatile solvent.

The vapor pressures of the system ethylene bromide—propylene bromide are plotted in Fig. 6.2. The experimental results almost coincide with the theoretical curves predicted by eq. (6.9). The agreement with Raoult's Law in this instance is very close.

Only in exceptional cases are solutions found that follow Raoult's Law closely over an extended range of concentrations. This is because ideality in solutions implies a complete similarity of interaction between the components, which can rarely be achieved.

This equality of interaction leads to two thermodynamic conditions: (1) there can be no heat of solution; (2) there can be no volume change on mixing. Hence, $\Delta V_{\text{solution}} = 0$ and $\Delta H_{\text{solution}} = 0$.

5. Equilibria in ideal solutions. If we wish to avoid the assumption that the saturated vapor above a solution behaves as an ideal gas, Raoult's Law may be written

$$f_A = X_A f_A^\circ \tag{6.11}$$

where f_A and f_A° are the fugacities of A in the solution, and in pure A. It is evident from eq. (6.8) that

$$d\mu = RT\, d\ln f_A = RT\, d\ln X_A \tag{6.12}$$

Then, following the sort of development given in Section 4–5, one obtains for the equilibrium constant in an ideal solution

$$-\Delta F^\circ = RT \ln K_x$$

with

$$K_x = \frac{X_C{}^c X_D{}^d}{X_A{}^a X_B{}^b} \tag{6.13}$$

for the typical case.

6. Henry's Law. Consider a solution of component B, which may be called the solute, in A, the solvent. If the solution is sufficiently diluted, a condition ultimately is attained in which each molecule of B is effectively completely surrounded by component A. The solute B is then in a uniform environment irrespective of the fact that A and B may form solutions that are far from ideal at higher concentrations.

In such a very dilute solution, the escaping tendency of B from its uniform environment is proportional to its mole fraction, but the proportionality constant k no longer is P_B°. We may write

$$P_B = kX_B \tag{6.14}$$

This equation was established and extensively tested by William Henry in 1803 in a series of measurements of the pressure dependence of the solubility of gases in liquids. Some results of this type are collected in Table 6.2. The k's are almost constant, so that Henry's Law is nearly but not exactly obeyed.

TABLE 6.2

THE SOLUBILITY OF GASES IN WATER (ILLUSTRATING HENRY'S LAW $P_B = kX_B$, THE GAS PRESSURE BEING IN ATM AND X_B BEING THE MOLE FRACTION)

Partial Pressure (atm)	Henry's Law Constant ($k \times 10^{-4}$)		
	N_2 at 19.4°	O_2 at 23°	H_2 at 23°
1.18	8.24	4.58	. . .
2.63	8.32	4.59	7.76
3.95	8.41	4.60	7.77
5.26	8.49	4.68	7.81
6.58	8.59	4.73	7.89
7.90	8.74	4.80	8.00
9.20	8.86	4.88	8.16

As an example, let us calculate the volume of oxygen (at STP) dissolved in 1 liter of water in equilibrium with air at 23°. From eq. (6.14) the mole fraction of O_2 is $X_B = P_B/k$. Since $P_B = 0.20$, and from the table $k = 4.58 \times 10^4$, $X_B = 4.36 \times 10^{-6}$. In 1 liter of H_2O there are $1000/18 = 55.6$ moles. Thus $X_B = n_B/(n_B + 55.6)$, or $n_B = 2.43 \times 10^{-4}$. This number of moles of oxygen equals 5.45 cc at STP.

Henry's Law is not restricted to gas-liquid systems, but is followed by a wide variety of fairly dilute solutions and by *all* solutions in the limit of extreme dilution.

7. Two-component systems. For systems of two components the phase rule, $f = c - p + 2$, becomes $f = 4 - p$. The following cases are possible:

$p = 1, \quad f = 3$ trivariant system
$p = 2, \quad f = 2$ bivariant system
$p = 3, \quad f = 1$ univariant system
$p = 4, \quad f = 0$ invariant system

The maximum number of degrees of freedom is three. A complete graphical representation of a two-component system therefore requires a three-dimensional diagram, with coordinates corresponding to pressure, temperature, and composition. Since a three-dimensional representation is usually inconvenient, one variable is held constant while the behavior of the other two is plotted. In this way, plane graphs are obtained showing pressure vs. composition at constant temperature, temperature vs. composition at constant pressure, or pressure vs. temperature at constant composition.

8. Pressure-composition diagrams. The example of a (P-X) diagram in Fig. 6.3a shows the system *ethylene bromide–propylene bromide*, which obeys Raoült's Law quite closely over the entire range of compositions. The straight upper line represents the dependence of the total vapor pressure above the solution on the mole fraction in the liquid. The curved lower line represents the dependence of the pressure on the composition of the vapor.

Consider a liquid of composition X_2 at a pressure P_2 (point C on the diagram). This point lies in a one-phase region, so there are three degrees of freedom. One of these degrees is used by the requirement of constant temperature for the diagram. Thus for any arbitrary composition X_2, the liquid solution at constant T can exist over a range of different pressures.

As the pressure is decreased along the dotted line of constant composition, nothing happens until the *liquidus curve* is reached at B. At this point liquid begins to vaporize. The vapor that is formed is richer than the liquid in the more volatile component, ethylene bromide. The composition of the first vapor to appear is given by the point A on the vapor curve.

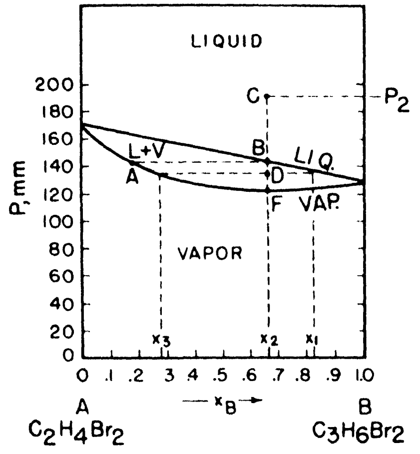


Fig. 6.3a. Pressure-composition (mole fraction) diagram for system obeying Raoult's Law.

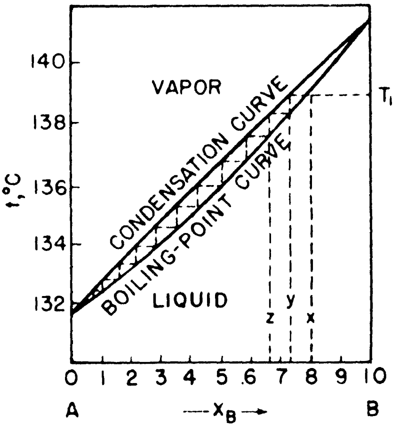


Fig. 6.3b. Temperature-composition diagram for system obeying Raoult's Law.

As the pressure is further reduced below B, a two-phase region on the diagram is entered. This represents the region of stable coexistence of liquid and vapor. The dotted line passing horizontally through a typical point D in the two-phase region is called a *tie line*; it connects the liquid and vapor compositions that are in equilibrium.

The over-all composition of the system is X_2. This is made up of liquid having a composition X_1 and vapor having a composition X_3. The relative amounts of the liquid and vapor phases required to yield the over-all composition are given by the *lever rule*: if (l) is the fraction of liquid and (v) the fraction[3] of vapor, $(l)/(v) = (X_3 - X_2)/(X_2 - X_1)$. This rule

---

[3] Since a mole fraction diagram is being used, (v) is the fraction of the total number of moles that is vapor. On a weight fraction diagram, (v) would be the weight fraction that is vapor.

is readily proved: It is evident that $X_2 = (l)X_1 + [1 - (l)]X_3$, or $(l) = (X_2 - X_3)/(X_1 - X_3)$. Similarly $(v) = 1 - (l) = (X_1 - X_2)/(X_1 - X_3)$. Hence $(l)/(v) = (X_3 - X_2)/(X_2 - X_1)$, the lever rule.

As the pressure is still further decreased along *BF* more and more liquid is vaporized till finally, at *F*, no liquid remains. Further decrease in pressure then proceeds in the one-phase, all-vapor region.

In the two-phase region, the system is bivariant. One of the degrees of freedom is used by the requirement of constant temperature; only one remains. When the pressure is fixed in this region, therefore, the compositions of *both* the liquid and the vapor phases are also definitely fixed. They are given, as has been seen, by the end points of the tie line.

9. Temperature-composition diagrams. The temperature-composition diagram of the liquid-vapor equilibrium is the boiling-point diagram of the solutions at the constant pressure chosen. If the pressure is one atmosphere, the boiling points are the *normal* ones.

The boiling-point diagram for a solution in which the solvent obeys Raoult's Law can be calculated if the vapor pressures of the pure components are known as functions of temperature (Fig. 6.3b). The two end points of the boiling-point diagram shown in Fig. 6.3b are the temperatures at which the pure components have a vapor pressure of 760 mm, *viz.*, 131.5°C and 141.6°C. The composition of the solution that boils anywhere between these two temperatures, say at 135°C, is found as follows:

According to Raoult's Law, letting X_A be the mole fraction of $C_2H_4Br_2$, $760 = P_A^\circ X_A + P_B^\circ(1 - X_A)$. At 135°, the vapor pressure of $C_2H_4Br_2$ is 835 mm, of $C_3H_6Br_2$, 652 mm. Thus, $760 = 835\ X_A + 652\,(1 - X_A)$, or $X_A = 0.590$, $X_B = 0.410$. This gives one intermediate point on the liquidus curve; the others are calculated in the same way.

The composition of the vapor is given by Dalton's Law:

$$X_A^{\text{vap}} = \frac{P_A}{760} = \frac{X_A^{\text{liq}} P_A^\circ}{760} = 0.59 \times \frac{835}{760} = 0.648$$

$$X_B^{\text{vap}} = \frac{P_B}{760} = \frac{X_B^{\text{liq}} P_B^\circ}{760} = 0.41 \times \frac{652}{760} = 0.352$$

The vapor-composition curve is therefore readily constructed from the liquidus curve.

10. Fractional distillation. The application of the boiling-point diagram to a simplified representation of distillation is shown in Fig. 6.3b. The solution of composition *X* begins to boil at temperature T_1. The first vapor that is formed has a composition *Y*, richer in the more volatile component. If this is condensed and reboiled, vapor of composition *Z* is obtained. This process is repeated until the distillate is composed of pure component *A*. In practical cases, the successive fractions will each cover a range of compositions, but the vertical lines in Fig. 6.3b, may be considered to represent average compositions within these ranges.

A fractionating column is a device that carries out automatically the successive condensations and vaporizations required for fractional distillation. An especially clear example of this is the "bubble-cap" type of column in Fig. 6.4. As the vapor ascends from the boiler, it bubbles through a film of liquid on the first plate. This liquid is somewhat cooler than that in the boiler, so that a partial condensation takes place. The vapor that leaves the first plate is therefore richer than the vapor from the boiler in the more volatile component. A similar enrichment takes place on each succeeding plate. Each attainment of equilibrium between liquid and vapor corresponds to one of the steps in Fig. 6.3b.

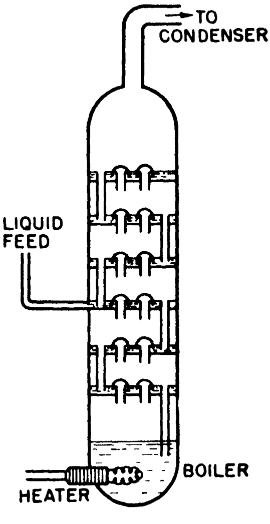


Fig. 6.4. Schematic drawing of bubble-cap column.

The efficiency of a distilling column is measured by the number of such equilibrium stages that it achieves. Each such stage is called a *theoretical plate*. In a well designed bubble-cap column, each unit acts very nearly as one theoretical plate. The performance of various types of packed columns is also described in terms of theoretical plates. The separation of liquids whose boiling points lie close together requires a column with a considerable number of theoretical plates. The number actually required depends on the *cut* that is taken from the head of the column, the ratio of distillate taken off to that returned to the column.[4]

11. Boiling-point elevation. If a small amount of a nonvolatile solute is dissolved in a volatile solvent, the solution being sufficiently dilute to behave ideally, the lowering of the vapor pressure can be calculated from eq. (6.10). As a consequence of the lowered vapor pressure, the boiling point of the solution is higher than that of the pure solvent. This fact is evident on inspection of the vapor pressure curves in Fig. 6.5.

The condition for equilibrium of a component A, the volatile solvent, between the liquid and vapor phases is simply $\mu_A{}^v = \mu_A{}^l$. From eq. (6.12), $\mu_A{}^l = \mu_A^{ol} + RT\ln X_A$, where μ_A^{ol} is the chemical potential of pure liquid A, *i.e.*, $\mu_A{}^l$ when $X_A = 1$. At the boiling point the pressure is 1 atm, so that $\mu_A{}^v = \mu_A^{ov}$, the chemical potential of pure A vapor at 1 atm. Therefore $(\mu_A{}^v = \mu_A{}^l)$ becomes $\mu_A^{ov} = \mu_A^{ol} + RT\ln X_A$. For the pure component A, the chemical potentials μ are identical with the molar free energies F. Hence,

$$F_A^{ov} - F_A^{ol} = RT\ln X_A$$

---

[4] For details of methods for determining the number of theoretical plates in a column, see C. S. Robinson and E. R. Gilliland, *Fractional Distillation* (New York: McGraw-Hill,

From eq. (3.36), $\partial(F/T)/\partial T = -H/T^2$, so that differentiating the above yields

$$H_A^{\circ v} - H_A^{\circ l} = -RT^2 \frac{d \ln X_A}{dT}$$

Since $H_A^{\circ v} - H_A^{\circ l}$ is the molar heat of vaporization, λ_{vap},

$$-d \ln X_A = \frac{\lambda_{\text{vap}}}{RT^2}\, dT$$

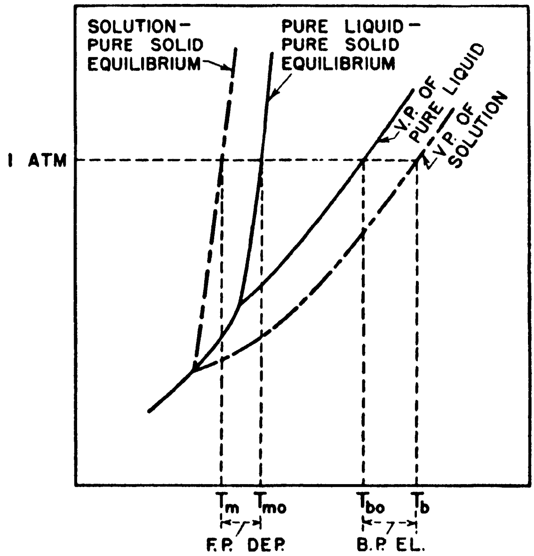


Fig. 6.5. Diagram showing the elevation of the boiling point caused by addition of a nonvolatile solute to a pure liquid.

Taking λ as constant over the temperature range, this equation is integrated between the limits set by the pure solvent ($X_A = 1$, $T = T_0$) and the solution ($X_A = X_A$, $T = T$)

$$-\int_1^{X_A} d \ln X_A = \frac{\lambda_{\text{vap}}}{R} \int_{T_0}^{T} \frac{dT}{T^2}$$

$$-\ln X_A = \frac{\lambda_{\text{vap}}}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) = \frac{\lambda_{\text{vap}}}{R} \left(\frac{T - T_0}{TT_0} \right)$$

When the boiling-point elevation is not large, TT_0 can be replaced by T_0^2. If X_B is the mole fraction of solute, the term on the left can be written $-\ln(1 - X_B)$, and then expanded in a power series. Writing ΔT_B for the boiling-point elevation, $T - T_0$, we obtain

$$\frac{\lambda\, \Delta T_B}{RT_0^2} = X_B + \frac{1}{2} X_B^2 + \frac{1}{3} X_B^3 + \ldots$$

When the solution is dilute, X_B is a small fraction whose higher powers may be neglected. Then,

$$\Delta T_B = \frac{RT_0^2}{\lambda_{\text{vap}}} X_B \tag{6.15}$$

In the dilute solutions for which eq. (6.15) is valid, it is also a good approximation to replace X_B by $(W_B M_A)/(W_A M_B)$; W_B, M_B, and W_A, M_A being the masses and molecular weights of solute and solvent. Then,

$$\Delta T_B = \frac{RT_0^2}{\lambda_{\text{vap}}} \cdot \frac{W_B M_A}{W_A M_B} = \frac{RT_0^2}{l_{\text{vap}}} \cdot \frac{W_B}{W_A M_B}$$

where l_{vap} is the latent heat of vaporization *per gram*. Finally $W_B/W_A M_B$ is set equal to $m/1000$, m being the weight molal concentration, moles of solute per 1000 grams of solvent. Thus,

$$\Delta T_B = \frac{RT_0^2}{l_{\text{vap}}} \cdot \frac{m}{1000} = K_B m \tag{6.16}$$

and K_B is called the *molal boiling-point elevation constant.*

For example, for water $T_0 = 373.2$, $l_{\text{vap}} = 538$ cal per g. Hence

$$K_B = \frac{(1.986)(373.2)^2}{(538)(1000)} = 0.514$$

For benzene, $K_B = 2.67$; for acetone, 1.67, etc.

The expression (6.16) is used frequently for *molecular-weight determination* from the boiling-point elevation. From K_B and the measured T_B, we calculate m, and then the molecular weight from $M_B = 1000\, W_B/mW_A$. For many combinations of solute and solvent, perfectly *normal* molecular weights are obtained. In certain instances, however, there is apparently an association or dissociation of the solute molecules in the solution. For example, the molecular weight of benzoic acid in acetone solution is found to be equal to the formula weight of 122.1. In 1 per cent solution in benzene, benzoic acid has an apparent molecular weight of 242. This indicates that the acid is to a considerable extent dimerized into double molecules. The extent of association is greater in more concentrated solutions, as is required by the Le Chatelier principle. From molecular-weight determinations at different concentrations, it is possible to calculate the equilibrium constant of the reaction $(C_6H_5COOH)_2 = 2\,C_6H_5COOH$.

12. Solid and liquid phases in equilibrium. The properties of solutions related to the vapor pressure are called *colligative* from the Latin, *colligatus, collected together*. They are properties which depend on the collection of particles present, that is, on the number of particles, rather than on the kind. A colligative property amenable to the same sort of treatment as the boiling-point elevation is the depression of the freezing point. That this also has its origin in the lowering of the vapor pressure in solutions can be seen by inspection of Fig. 6.5. The freezing point of pure solvent, T_{m_0} is lowered to T_m in the solution.

It should be understood that "freezing-point depression curve" and "solubility curve" are merely two different names for the same thing—that is, a temperature vs. composition curve for a solid-liquid equilibrium at some constant pressure, usually chosen as one atmosphere. Such a diagram is shown in Fig. 6.13 (p. 147) for the system benzene–chloroform. The curve *CE* may be considered to illustrate either (1) the depression of the freezing point of benzene by the addition of chloroform, or (2) the solubility of solid benzene in the solution. Both interpretations are fundamentally equivalent: in one case, we consider *T* as a function of *c*; in the other, *c* as a function of *T*. The lowest point *E* on the solid-liquid diagram is called the *eutectic point* (ευτηκτος, "easily melted").

In this diagram, the solid phases that separate out are shown as pure benzene (*A*) on one side and pure chloroform (*B*) on the other. It becomes evident in the next section that this is not exactly correct, since there is usually at least a slight solid solution of the second component *B* in the solid component *A*. Nevertheless the absence of any solid solution is in many cases a good enough approximation.

The equation for the freezing-point depression, or the solubility equation for ideal solutions, is derived by essentially the same method used for the boiling-point elevation. In order for a pure solid *A* to be in equilibrium with a solution containing *A*, it is necessary that the chemical potentials of *A* be the same in the two phases, $\mu_A{}^s = \mu_A{}^l$. From eq. (6.12) the chemical potential of component *A* in an ideal solution is $\mu_A{}^l = \mu_A^{ol} + RT \ln X_A$, where μ_A^{ol} is the chemical potential of pure liquid *A*. Thus the equilibrium condition can be written $\mu_A{}^s = \mu_A^{ol} + RT \ln X_A$. Now $\mu_A{}^s$ and μ_A^{ol} are simply the molar free energies of pure solid and pure liquid, hence

$$\frac{F_A{}^s - F_A{}^l}{RT} = \ln X_A \tag{6.17}$$

Since we have $\partial(F/T)/\partial T = -H/T^2$ from eq. (3.36), differentiation of eq. (6.17) with respect to *T* yields

$$\frac{H_A{}^l - H_A{}^s}{RT^2} = \frac{\lambda_{\text{fus}}}{RT^2} = \frac{d \ln X_A}{dT} \tag{6.18}$$

Integrating this expression from T_0, the freezing point of pure *A*, mole fraction unity, to *T*, the temperature at which pure solid *A* is in equilibrium with solution of mole fraction X_A, we obtain[5]

$$\frac{\lambda_{\text{fus}}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) = \ln X_A \tag{6.19}$$

---

[5] It is a good approximation to take λ_{fus} independent of *T* over moderate ranges of temperature.

This is the equation for the temperature variation of the solubility X_A of a pure solid in an ideal solution.

As an example, let us calculate the solubility of naphthalene in an ideal solution at 25°C. Naphthalene melts at 80°C, and its heat of fusion at the melting point is 4610 cal per mole. Thus, from eq. (6.19),

$$\frac{4610}{1.986}(353.2^{-1} - 298.2^{-1}) = 2.303 \log X_A$$

$$X_A = 0.298$$

This is the mole fraction of naphthalene in any ideal solution, whatever the solvent may be. Actually, the solution will approach ideality only if the solvent is rather similar in chemical and physical properties to the solute. Typical experimental values for the solubility X_A of naphthalene in various solvents at 25°C are as follows: chlorobenzene, 0.317; benzene, 0.296; toluene, 0.286; acetone, 0.224; hexane, 0.125.

The simplification of eq. (6.19) for dilute solutions follows from the same approximations used in the boiling-point elevation case. The final expression for the depression of the freezing point $\Delta T_F = T_0 - T$ is

$$\Delta T_F = K_F m$$

with

$$K_F = \frac{RT_0^2}{l_{\text{fus}}\,1000} \tag{6.20}$$

For example: water, $K_F = 1.855$; benzene, 5.12; camphor, 40.0, and so on. Because of its exceptionally large K_F, camphor is used in a micro method for molecular-weight determination by freezing-point depression.

13. The Distribution Law. The equilibrium condition for a component A distributed between two phases α and β is $\mu_A^\alpha = \mu_A^\beta$. From eq. (6.8), $f_A^\alpha = f_A^\beta$. If the solutions are ideal, Raoult's Law is followed, and $f_A = X_A f_A^\circ$, where f_A° is the fugacity of pure A (equal, if the vapor is an ideal gas, to the vapor pressure P_A°. Thus $X_A^\alpha f_A^\circ = X_A^\beta f_A^\circ$, or $X_A^\alpha = X_A^\beta$, and as long as the solutions are ideal, the solute A must be distributed equally between them.

If the solutions do not follow Raoult's Law, but are sufficiently dilute to follow Henry's Law, $f_A = k_A X_A$, and it follows that

$$\frac{X_A^\alpha}{X_A^\beta} = \frac{k_A^\alpha}{k_A^\beta} = K_D \tag{6.21}$$

The ratio of the Henry's Law constants, K_D, is called the *distribution constant* (or *distribution coefficient*). Thus K_D is a function of temperature and pressure. Equation (6.21) is one form of the *Nernst Distribution Law.*[6]

In a dilute solution, $X_A = n_A/(n_A + n_B) \approx n_A/n_B \approx c_A M_B/1000\,\rho_B$, where c_A is the ordinary molar concentration and M_B and ρ_B are the molecular weight and density of the solvent. With this approximation, the ratio

---

[6] W. Nernst, *Z. physik. Chem.*, *8*, 110 (1891).

of mole fractions is proportional to the ratio of molar concentrations, and eq. (6.21) becomes

$$\frac{c_A^{\alpha}}{c_A^{\beta}} = K_D' \tag{6.22}$$

A test of the Law in this form, for the distribution of iodine between water and carbon bisulfide may be seen in Table 6.3.

TABLE 6.3

DISTRIBUTION OF I_2 BETWEEN CS_2 AND H_2O AT 18°

c^{α} g I_2 per liter CS_2 .	174	129	66	41	7.6
c^{β} g I_2 per liter H_2O .	0.41	0.32	0.16	0.10	0.017
$K_D' = c^{\alpha}/c^{\beta}$ . .	420	400	410	410	440

If association, dissociation, or chemical reaction of the distributed component takes place in either phase, modification of the Distribution Law is required. For example, if a solute S is partly dimerized to S_2 molecules in both phases, there will be two distribution equations, one for monomer and one for dimer, but the two distribution constants will not be independent, being related through the dissociation constants of the dimers.

Solvent extraction is an important method for the isolation of pure organic compounds. Apparatus has been developed by L. C. Craig[7] at the Rockefeller Institute to carry out continuously hundreds of successive stages of extraction by the so-called "countercurrent distribution method."

14. Osmotic pressure. The classical trio of colligative properties, of which boiling-point elevation and freezing-point depression are the first two members, is completed by the phenomenon of osmotic pressure.

In 1748, the Abbé Nollet described an experiment in which a solution of "spirits of wine" was placed in a cylinder, the mouth of which was closed with an animal bladder and immersed in pure water. The bladder was observed to swell greatly and sometimes even to burst. The animal membrane is *semipermeable*; water can pass through it, but alcohol cannot. The increased pressure in the tube, caused by diffusion of water into the solution, was called the *osmotic pressure* (from the Greek, ωσμος—"impulse").

The first detailed quantitative study of osmotic pressure is found in a series of researches by W. Pfeffer, published in 1877. Ten years earlier, Moritz Traube had observed that colloidal films of cupric ferrocyanide acted as semipermeable membranes. Pfeffer deposited this colloidal precipitate within the pores of earthenware pots, by soaking them first in copper sulfate and then in potassium ferrocyanide solution. Some typical results of measurements using such artificial membranes are summarized in Table 6.4.

---

[7] L. C. Craig and D. Craig, "Extraction and Distribution," in *Techniques of Organic Chemistry*, ed. by A. Weissberger (New York: Interscience, 1950).

In 1885 J. H. van't Hoff pointed out that in dilute solutions the osmotic pressure Π obeyed the relationship $\Pi V = nRT$, or

$$\Pi = cRT \tag{6.23}$$

where $c = n/V$ is the concentration of solute in moles per liter. The validity of the equation can be judged by comparison of the calculated and experimental values of Π in Table 6.4.

TABLE 6.4

OSMOTIC PRESSURES OF SOLUTIONS OF SUCROSE IN WATER AT 20°

Molal Concentration (*m*)	Molar Concentration (*c*)	Observed Osmotic Pressure (atm)	Calculated Osmotic Pressure		
			Eq. (6.23)	Eq. (6.27)	Eq. (6.25)
0.1	0.098	2.59	2.36	2.40	2.44
0.2	0.192	5.06	4.63	4.81	5.46
0.3	0.282	7.61	6.80	7.21	7.82
0.4	0.370	10.14	8.90	9.62	10.22
0.5	0.453	12.75	10.9	12.0	12.62
0.6	0.533	15.39	12.8	14.4	15.00
0.7	0.610	18.13	14.7	16.8	17.40
0.8	0.685	20.91	16.5	19.2	19.77
0.9	0.757	23.72	18.2	21.6	22.15
1.0	0.825	26.64	19.8	24.0	24.48

The essential requirements for the existence of an osmotic pressure are two. There must be two solutions of different concentrations (or a pure solvent and a solution) and there must be a semipermeable membrane separating these solutions. A simple illustration can be found in the case of a gaseous solution of hydrogen and nitrogen. Thin palladium foil is appreciably permeable to hydrogen, but practically impermeable to nitrogen. If pure nitrogen is put on one side of a palladium barrier and a solution of nitrogen and hydrogen on the other side, the requirements for osmosis are satisfied. Hydrogen flows through the palladium from the hydrogen-rich to the hydrogen-poor side of the membrane. This flow continues until the chemical potential of the H_2, μ_{H_2} is the same on both sides of the barrier.

In this example, the nature of the semipermeable membrane is rather clear. Hydrogen molecules are catalytically dissociated into hydrogen atoms at the palladium surface, and these atoms, perhaps in the form of protons and electrons, diffuse through the barrier. A solution mechanism of some kind probably is responsible for many cases of semipermeability. For example, it seems reasonable that protein membranes, like those employed by Nollet, can dissolve water but not alcohol.

In other cases, the membrane may act as a sieve, or as a bundle of capillaries. The cross sections of these capillaries may be very small, so that they can be permeated by small molecules like water, but not by large molecules like carbohydrates or proteins.

Irrespective of the mechanism by which the semipermeable membrane operates, the final result is the same. Osmotic flow continues until the chemical potential of the diffusing component is the same on both sides of the barrier. If the flow takes place into a closed volume, the pressure therein necessarily increases. The final equilibrium osmotic pressure can be calculated by thermodynamic methods. It is the pressure that must be *applied to the solution* in order to prevent flow of solvent across the semipermeable membrane from the pure solvent into the solution. The same effect can be produced by applying a negative pressure or tension to the pure solvent.

15. Measurement of osmotic pressure. We are principally indebted to two groups of workers for precise measurements of osmotic pressure: H. N. Morse, J. C. W. Frazer, and their colleagues at Johns Hopkins, and the Earl of Berkeley and E. G. J. Hartley at Oxford.[8]

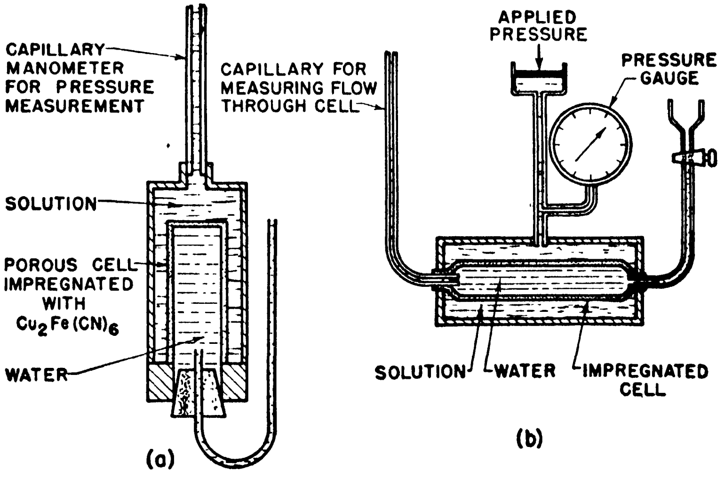


Fig. 6.6. Osmotic pressure measurements: (a) method of Frazer; (b) method of Berkeley and Hartley.

The method used by the Hopkins group is shown in (a), Fig. 6.6. The porous cell impregnated with copper ferrocyanide is filled with water and immersed in a vessel containing the aqueous solution. The pressure is measured by means of an attached manometer. The system is allowed to stand until there is no further increase in pressure. Then the osmotic pressure is just balanced by the hydrostatic pressure in the column of solution. The pressures studied extended up to several hundred atmospheres, and a

---

[8] An excellent detailed discussion of this work is to be found in J. C. W. Frazer's article, "The Laws of Dilute Solutions" in *A Treatise on Physical Chemistry*, 2nd ed., edited by H. S. Taylor (New York: Van Nostrand, 1931), pp. 353–414.

number of ingenious methods of measurement were developed. These included the calculation of the pressure from the change in the refractive index of water on compression, and the application of piezoelectric gauges.

The English workers used the apparatus shown schematically in (b), Fig. 6.6. Instead of waiting for equilibrium to be established and then reading the pressure, they applied an external pressure to the solution just sufficient to balance the osmotic pressure. This balance could be made very precisely by observing the level of liquid in the capillary tube, which would fall rapidly if there was any flow of solvent into the solution.

16. Osmotic pressure and vapor pressure. Consider a pure solvent A that is separated from a solution of B in A by a membrane permeable to A alone. At equilibrium an osmotic pressure Π has developed. The condition for equilibrium is that the chemical potential of A is the same on both sides of the membrane, $\mu_A{}^\alpha = \mu_A{}^\beta$. Thus the μ_A in the solution must equal that of the pure A. There are two factors tending to make the value of μ_A in the solution different from that in pure A. These factors must therefore have exactly equal and opposite effects on μ_A. The first is the change in μ_A produced by dilution of A in the solution. This change causes a lowering of μ_A equal to $\Delta\mu = RT \ln P_A/P_A^\circ$ [eq. (6.8) with $f = P$]. Exactly counteracting this is the increase in μ_A in the solution due to the imposed pressure Π. From eq. (6.5) $d\mu = \bar{V}\,dP$, so that $\Delta\mu = \int_0^\Pi \bar{V}_A\,dP$.

At equilibrium, therefore, in order that μ_A in solution should equal μ_A° in the pure liquid, $\int_0^\Pi \bar{V}_A\,dP = -RT \ln (P_A/P_A^\circ)$. If it is assumed that the partial molar volume $\bar{V}_A$ is independent of pressure, *i.e.*, the solution is practically incompressible,

$$\bar{V}_A \Pi = RT \ln \frac{P_A^\circ}{P_A} \tag{6.24}$$

The significance of this equation can be stated as follows: the osmotic pressure is the external pressure that must be applied to the solution to raise the vapor pressure of solvent A to that of pure A.

In most cases, also, the partial molar volume of solvent in solution $\bar{V}_A$ can be well approximated by the molar volume of the pure liquid V_A. In the special case of an ideal solution, eq. (6.24) becomes

$$\Pi V_A = -RT \ln X_A \tag{6.25}$$

By replacing X_A by $(1 - X_B)$ and expanding as in Section 6–11, the dilute solution formula is obtained:

$$\Pi V_A = RTX_B \tag{6.26}$$

Since the solution is dilute,

$$\Pi \approx \frac{RT}{V_A} \cdot \frac{n_B}{n_A} \approx RTm' \tag{6.27}$$

This is the equation used by Frazer and Morse as a better approximation than the van't Hoff equation (6.23). As the solution becomes very dilute, m' the volume molal concentration approaches c the molar concentration, and we find as the end product of the series of approximations

$$\Pi = RTc \tag{6.23}$$

The adequacy with which eqs. (6.23), (6.25), and (6.27) represent the experimental data can be judged from the comparisons in Table 6.4.[9]

17. Deviations from Raoult's Law. Only a very few of the many liquid solutions that have been investigated follow Raoult's Law over the complete range of concentrations. It is for this reason that the greatest practical application of the ideal equations is made in the treatment of dilute solutions, in which the solvent obeys Raoult's Law and the solute obeys Henry's Law. Nevertheless, one of the most instructive ways of qualitatively discussing the properties of nonideal solutions is in terms of their deviations from ideality. The first extensive series of vapor-pressure measurements, permitting such comparisons, were those made by Jan von Zawidski, around 1900.

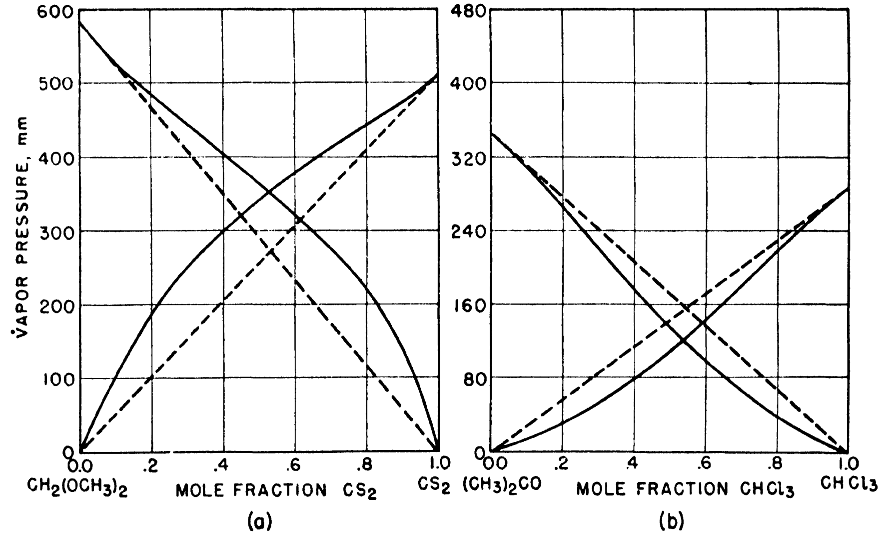


Fig. 6.7. (a) Positive deviation from Raoult's Law—the *PX* diagram of carbon bisulfide-methylal system. (b) Negative deviation from Raould's Law—the *PX* diagram of chloroform-acetone system.

Two general types of deviation were distinguished. An example exhibiting a *positive deviation* from Raoult's Law is the system carbon bisulfide-methylal, whose vapor-pressure–composition diagram is shown in (a), Fig. 6.7. An ideal solution would follow the dashed lines. The positive

---

[9] The osmotic pressures of solutions of high polymers and proteins provide some of the best data on their thermodynamic properties. A typical investigation is that of Shick, Doty, and Zimm, *J. Am. Chem. Soc.*, 72, 530 (1950).

deviation is characterized by vapor pressures higher than those calculated for ideal solutions.

The escaping tendencies of the components in the solution are accordingly higher than the escaping tendencies in the individual pure liquids. This effect has been ascribed to cohesive forces between unlike components smaller than those within the pure liquids, resulting in a trend away from complete miscibility. To put it naively, the components are happier by themselves than when they are mixed together; they are unsociable. These are metaphorical expressions; a scientific translation is obtained by equating a happy component to one in a state of low free energy. One would expect that this incipient immiscibility would be reflected in an increase in volume on mixing and also in an absorption of heat on mixing.

The other general type of departure from Raoult's Law is the *negative deviation*. This type is illustrated by the system chloroform–acetone in (b), Fig. 6.7. In this case, the escaping tendency of a component from solution is less than it would be from the pure liquid. This fact may be interpreted as being the result of greater attractive forces between the unlike molecules in solution than between the like molecules in the pure liquids. In some cases, actual association or compound formation may occur in the solution. As a result, in cases of negative deviation, a contraction in volume and an evolution of heat are to be expected on mixing.

In some cases of deviation from ideality, the simple picture of varying cohesive forces may not be adequate. For example, positive deviations are often observed in aqueous solutions. Pure water is itself strongly associated and addition of a second component may cause partial depolymerization of the water. This would lead to an increased partial vapor pressure.

A sufficiently great positive deviation from ideality may lead to a maximum in the PX diagram, and a sufficiently great negative deviation, to a minimum. An illustration of this behavior is shown in (a), Fig. 6.8. It is now no longer meaningful to say that the vapor is richer than the liquid in the "more volatile component." The following more general statement (Konovalov's Rule) is employed: the vapor is richer than the liquid with which it is in equilibrium in that component by addition of which to the system the vapor pressure is raised. At a maximum or minimum in the vapor-pressure curve, the vapor and the liquid must have the same composition.

18. Boiling-point diagrams. The PX diagram in (a), Fig. 6.8, has its counterpart in the boiling-point diagram in (b), Fig. 6.8. A minimum in the PX curve necessarily leads to a maximum in the TX curve. A well known example is the system $HCl–H_2O$, which has a maximum boiling point (at 760 mm) of 108.58° at a concentration of 20.222 per cent HCl.

A solution with the composition corresponding to a maximum or minimum point on the boiling-point diagram is called an *azeotropic solution* (*ζειν*, "to boil"; *ατροπος*, "unchanging"), since there is no change in composition on boiling. Such solutions cannot be separated by isobaric distillation. It was, in fact, thought at one time that they were real chemical compounds, but changing the pressure changes the composition of the azeotropic solution.

The distillation of a system with a maximum boiling point can be discussed by reference to (b), Fig. 6.8. If the temperature of a solution having the composition l is raised, it begins to boil at the temperature t_1. The first vapor that distills has the composition v, richer in component A than is the original liquid. The residual solution therefore becomes richer in B; and if the vapor is continuously removed the boiling point of the residue rises, as its composition moves along the liquidus curve from l toward m. If a fractional distillation is carried out, a final separation into pure A and the azeotropic solution is achieved. Similarly a solution of original composition l' can be separated into pure B and azeotrope.

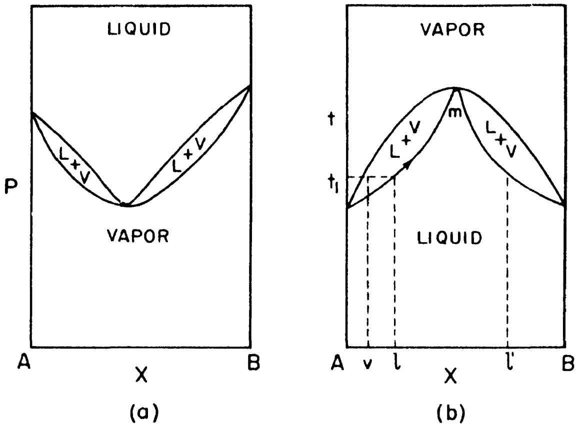


Fig. 6.8. Large negative deviation from Raoult's Law. The PX curve has a minimum; the TX curve has a maximum.

19. Partial miscibility. If the positive deviations from Raoult's Law become sufficiently large, the components may no longer form a continuous series of solutions. As successive portions of one component are added to the other, a limiting solubility is finally reached, beyond which two distinct liquid phases are formed. Usually, but not always, increasing temperature tends to promote solubility, as the thermal kinetic energy conquers the reluctance of the components to mix freely. In other words, the $T\,\Delta S$ term in $\Delta F = \Delta H - T\,\Delta S$ becomes more important. A solution that displays a large positive deviation from ideality at elevated temperatures therefore frequently splits into two phases when it is cooled.

A PC diagram for a partially miscible liquid system, such as aniline and water, is shown in (a), Fig. 6.9. The point x lies in the two-phase region and corresponds to a system of two liquid solutions, one a dilute solution of aniline in water having the composition y, and the other a dilute solution of water in aniline having the composition z. These are called ***conjugate solutions.*** The relative amounts of the two phases are given by the ratios of the distances along the tie line, xy/xz. Applying the phase rule to this two-phase region: since $p = 2$ and $c = 2$, the system is bivariant. Because of the requirement of constant temperature imposed on the *PC* diagram, only one degree of freedom remains. Once the pressure is fixed, the compositions of both phases are fixed, which is indeed what the diagram indicates. The over-all composition x is of course not fixed, since this depends on the relative amounts of the two conjugate solutions, with which the phase rule is not concerned.

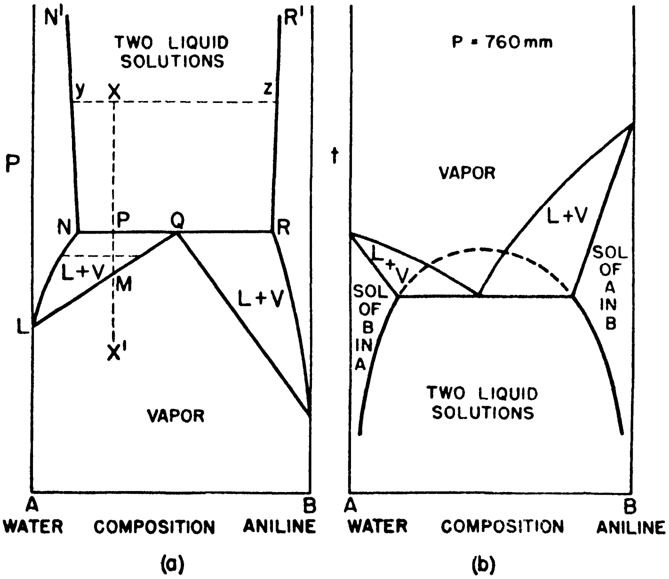


Fig. 6.9. Schematic diagrams for aniline-water system, showing limited solubility of liquids. (a) *PC* diagram. (b) *TC* diagram.

Let us follow the sequence of events as the pressure is gradually reduced along the line of constant composition, or *isopleth*, xx'.

At the point *P*, vapor having a composition corresponding to point *Q* begins to appear. There are now three phases coexisting in equilibrium, so that the system is invariant. If the volume available to the vapor is increased, the amount of the vapor phase will increase, at constant pressure, until all the aniline-rich solution, of composition *R*, has vaporized. When this process is complete, there will remain a vapor of composition *Q* and a solution of composition *N*, so that the system becomes univariant again as the pressure falls below that at *P*.

Since the vapor that is formed is richer in aniline, the composition of the residual solution becomes richer in water. The liquid composition moves along the line *NL*, and the vapor composition moves along *QL* until all the liquid has been transformed into vapor, at the point M. After this, further decrease in pressure proceeds at constant vapor composition along Mx'.

It may be noted that the two conjugate solutions N and R have the same total vapor pressure and the same vapor composition. It follows that the partial vapor pressure of component A above a dilute solution of A in B is the same as the vapor pressure of A above the dilute solution of B in A. For example, if benzene and water are mixed at 25°C, two immiscible layers are formed, one containing 0.09 per cent C_6H_6 and 99.91 per cent H_2O, the other 99.81 per cent C_6H_6 and 0.19 per cent H_2O. The partial pressure of benzene above either of these solutions is the same, namely 85 mm.

In (a), Fig. 6.9, the lines NN' and RR' are almost vertical, since the solubility limits are only slightly dependent on pressure. Change in temperature, on the other hand, may greatly affect the mutual solubility of two liquids. In (b), Fig. 6.9, the TC diagram for the water-aniline system is drawn for the constant pressure of one atmosphere (normal-boiling-point diagram). Increasing the temperature tends to close the *solubility gap*, the difference between the concentrations of the two conjugate solutions.

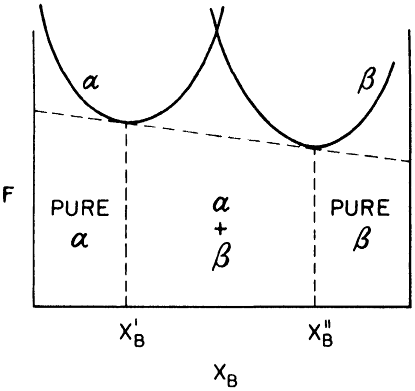


Fig. 6.10. Partial miscibility determined by free energy.

The interpretation of the solubility gap can be given in terms of the free energy of the system. At some constant temperature, let us plot the molar free energy of the system, defined as $\mathrm{F} = F/(n_A + n_B)$, against the mole fraction of B, X_B, for both the α and β phases. In Fig. 6.9b, for example, these phases would be the two immiscible liquid solutions. The diagram obtained, Fig. 6.10, is an exact analog of Fig. 6.1, which was used for the determination of partial molar volumes. In this case, the intercept of the common tangent to the two F vs. X curves gives the value of the partial molar free energies, or chemical potentials, of the two components. At this composition, therefore, $\mu_A^{\alpha} = \mu_A^{\beta}$, and $\mu_B^{\alpha} = \mu_B^{\beta}$, *i.e.*, the condition for equilibrium of components A and B between the two phases is fulfilled. The corresponding mole fractions represent the phase-boundary compositions; at any composition between X'_B and X''_B, the system will split into two distinct phases, since in this way it can reach its minimum free energy. For $X_B < X'_B$, however, pure phase α gives the lowest free energy, and for $X_B > X''_B$, pure phase β.

20. Condensed-liquid systems. In (b), Fig. 6.9, the variation of solubility with temperature is shown for only one pressure. At high enough temperatures boiling occurs, and it is therefore not possible to trace the ultimate course of the solubility curves. One might expect that the solubility gap would close completely if a high enough temperature could be reached before the onset of boiling. This expectation is represented by the dashed line in (b), Fig. 6.9.

A number of *condensed systems* have been studied, which illustrate complete liquid-liquid solubility curves. A classical example is the phenol-water system of Fig. 6.11 (a). At the temperature and composition indicated by the point x, two phases coexist, the conjugate solutions represented by y and z. The relative amounts of the two phases are proportional, as usual, to the segments of the tie line.

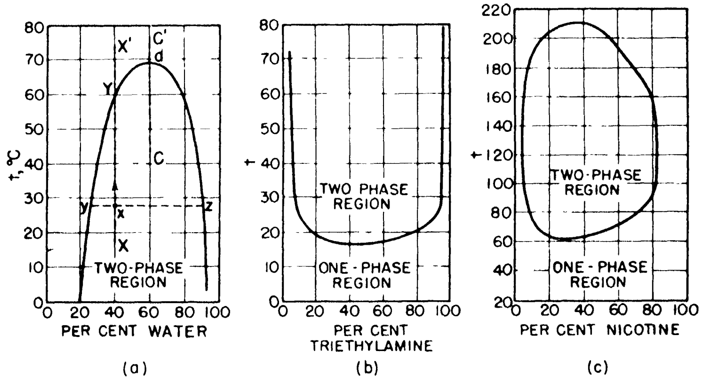


Fig. 6.11. Partial miscibility of two liquids. (a) phenol-water system. (b) triethylamine-water system. (c) nicotine-water system.

As the temperature is increased along the isopleth XX', the amount of the phenol-rich phase decreases and the amount of water-rich phase increases.

Finally at Y the compositions of the two phases become identical, the phenol-rich phase disappears completely, and at temperatures above Y there is only one solution.

This gradual disappearance of one solution is characteristic of systems having all compositions except one. The exception is the composition corresponding to the maximum in the TC curve. This composition is called the *critical composition* and the temperature at the maximum is the *critical solution temperature* or *upper consolute temperature*. If a two-phase system having the critical composition is gradually heated [line CC' in (a), Fig. 6.11] there is no gradual disappearance of one phase. Even in the immediate neighborhood of the maximum d, the ratio of the segments of the tie line remains practically constant. The compositions of the two conjugate solutions gradually approach each other until, at the point d, the boundary line between the two phases suddenly disappears and a single-phase system remains.

As the critical temperature is slowly approached from above, a most curious phenomenon is observed. Just before the single homogeneous phase passes over into two distinct phases, the solution is diffused by a pearly opalescence. This *critical opalescence* is believed to be caused by the scattering of light from small regions of slightly differing density, which are formed in the liquid in the incipient separation of the two phases.

Strangely enough, some systems exhibit a lower consolute temperature. At high temperatures, two partially miscible solutions are present, which become completely intersoluble when sufficiently cooled. An example is the triethylamine-water system in (b), Fig. 6.11, with a lower consolute temperature of 18.5° at 1 atm pressure. It is almost impossible to locate the critical composition exactly, since lowering the temperature a fraction of a degree greatly increases the solubility. This somewhat weird behavior suggests that large negative deviations from Raoult's Law (*e.g.*, compound formation) become sufficient at the lower temperatures to counteract the positive deviations responsible for the immiscibility.

Finally, systems have been found with both upper and lower consolute temperatures. These are most common at elevated pressures, and indeed one would expect all systems with a lower consolute temperature to display an upper one at sufficiently high temperature and pressure. An atmospheric-pressure example is the nicotine-water system of Fig. 6.11 (c). Having come to solutions of this type, we have run the gamut of deviations from ideality.

21. Thermodynamics of nonideal solutions: the activity. A complete thermodynamic description of a solution, except for its amount, can be expressed in terms of the temperature, the pressure, and the chemical potentials of the various components. All the other thermodynamic functions can be derived from these.

For a single pure ideal gas, the change in chemical potential is given from eq. (4.33) as $d\mu = RT\,d\ln P$. By integration we obtain $\mu = \mu^\circ + RT\ln P$, where μ° is the chemical potential of the gas at one atmosphere pressure. For a pure gas, this equation is identical with $F = F^\circ + RT\ln P$, where F is the free energy per mole.

If the gas is not ideal, the fugacity is *defined* by the equation $\mu = \mu^\circ + RT\ln f$. Such an equation holds also for any component in a mixture of gases (gaseous solution). The constant μ° is a function of temperature alone. It is the chemical potential of the gas in its standard state of unit fugacity, or the standard free energy of the gas.

The same equation is valid for a component in a liquid or solid solution, since at equilibrium the chemical potential must be the same in the condensed phase as in the vapor. For a component A,

$$\mu_A = \mu_A^\circ + RT\ln f_A \tag{6.8}$$

If the vapor above the solution can be considered to behave as an ideal gas, $f_A = P_A$, and $\mu_A = \mu_A^\circ + RT\ln P_A$. For an ideal solution, $P_A = X_A f_A^\circ = X_A P_A^\circ$, and therefore

$$\begin{aligned} \mu_A &= \mu_A^\circ + RT\ln f_A^\circ + RT\ln X_A \\ \mu_A &= \mu_A^\circ + RT\ln P_A^\circ + RT\ln X_A \end{aligned} \tag{6.28}$$

The two constant terms can be combined, giving

$$\mu_A = \mu_A^{\circ\prime} + RT\ln X_A \tag{6.29}$$

This is the expression for the chemical potential in an ideal solution, $\mu_A^{\circ\prime}$ being the chemical potential of A when $X_A = 1$; *i.e.*, of pure liquid A. It should be clearly understood that $\mu_A^{\circ\prime}$ is a function of both temperature and pressure, in contrast with μ_A° in eq. (6.8). This is because the vapor pressure of the pure liquid, P_A° in eq. (6.28), is a function of both temperature and over-all pressure (p. 107).

In the discussion of nonideal solutions we can always use the chemical potential, obtained from eq. (6.8) in terms of the partial vapor pressure or fugacity. Sometimes, however, it is convenient to introduce a new function, the *activity a*, which was invented by G. N. Lewis. It is defined as follows so as to preserve the form of eq. (6.29),

$$\mu_A = \mu_A^{\circ\prime} + RT\ln a_A \tag{6.30}$$

or

$$\mu_A = \mu_A^{\circ\prime} + RT\ln \gamma_A X_A$$

where $\gamma = a/X$ is called the *activity coefficient*.

One advantage of the activity coefficient is that it indicates at a glance the magnitude of the deviation from ideality in the solution. In terms of the activity, Raoult's Law becomes simply $a = X$, or $\gamma = 1$.

Comparing eq. (6.30) with eqs. (6.28) and (6.8), we find that

$$a_A = \frac{f_A}{f_A^\circ} \tag{6.31}$$

The activity is accordingly the ratio of the fugacity to the fugacity in the standard state. We have implicitly taken this standard state to be pure A, but other definitions might have been used. For a gas $f_A^\circ = 1$ and therefore $a_A = f_A$, the activity equals the fugacity.

Equation (6.31) provides the most direct method of determining the activity of a component in a solution. It is usually sufficiently accurate to ignore gas imperfections and set the fugacity ratio equal to the vapor pressure ratio, so that $a_A = P_A/P_A^\circ$.

Some activities calculated in this way from vapor-pressure data are collected in Table 6.5. Once the activity of one component has been obtained as a function of concentration, the activity of the other component in a binary solution can be calculated from the Gibbs-Duhem equation.

TABLE 6.5

ACTIVITIES OF WATER AND SUCROSE IN THEIR SOLUTIONS AT 50°C OBTAINED FROM VAPOR PRESSURE LOWERING AND THE GIBBS-DUHEM EQUATION

Mole Fraction of Water X_A	Activity of Water a_A	Mole Fraction of Sucrose X_B	Activity of Sucrose a_B
0.9940	0.9939	0.0060	0.0060
0.9864	0.9934	0.0136	0.0136
0.9826	0.9799	0.0174	0.0197
0.9762	0.9697	0.0238	0.0302
0.9665	0.9617	0.0335	0.0481
0.9559	0.9477	0.0441	0.0716
0.9439	0.9299	0.0561	0.1037
0.9323	0.9043	0.0677	0.1390
0.9098	0.8758	0.0902	0.2190
0.8911	0.8140	0.1089	0.3045

Corresponding with eq. (6.4) for the partial molar volumes, we have for the partial molar free energies or chemical potentials,

$$d\mu_A = -\frac{n_B}{n_A}\, d\mu_B$$

From eq. (6.30),

$$d \ln a_A = -\frac{X_B}{X_A}\, d \ln a_B$$

If a_B is known as a function of X_B, a_A can be obtained by a graphical integration.

Activities can also be calculated from any of the colligative properties related to the vapor pressure. The details of these calculations are to be found in various treatises on thermodynamics.[10]

22. Chemical equilibria in nonideal solutions. The activity function defined in eq. (6.30) is useful in discussing the equilibrium constants of reactions in solution. It is readily proved (cf. p. 76) that for the schematic reaction

$$aA + bB \rightleftharpoons cC + dD$$

$$K_a = \frac{a_C{}^c\, a_D{}^d}{a_A{}^a\, a_B{}^b} \tag{6.32}$$

and

$$\Delta\mu^\circ = -RT \ln K_a$$

In terms of activity coefficients and mole fractions,

$$K_a = \frac{\gamma_C{}^c\, \gamma_D{}^d}{\gamma_A{}^a\, \gamma_B{}^b} \cdot \frac{X_C{}^c\, X_D{}^d}{X_A{}^a\, X_B{}^b} = K_\gamma K_x$$

In an ideal solution, all the activity coefficients become equal to unity,

---

[10] G. N. Lewis and M. Randall, *Thermodynamics and Free Energy of Chemical Substances* (New York: McGraw-Hill, 1923), p. 278.

and the equilibrium constant is simply K_x. Extensive data on the activity coefficients of components in solutions of nonelectrolytes are not available, and the most important applications of eq. (6.32) have been made in electrolytic solutions, which will be discussed in Chapter 15.

23. Gas-solid equilibria. The varieties of heterogeneous equilibrium that have been considered so far have almost all been chosen from systems involving liquid and vapor phases only. Some systems of the solid-vapor and solid-liquid types will now be described. Most of the examples will be chosen from two-component systems, with only a brief introduction to three-component phase diagrams.

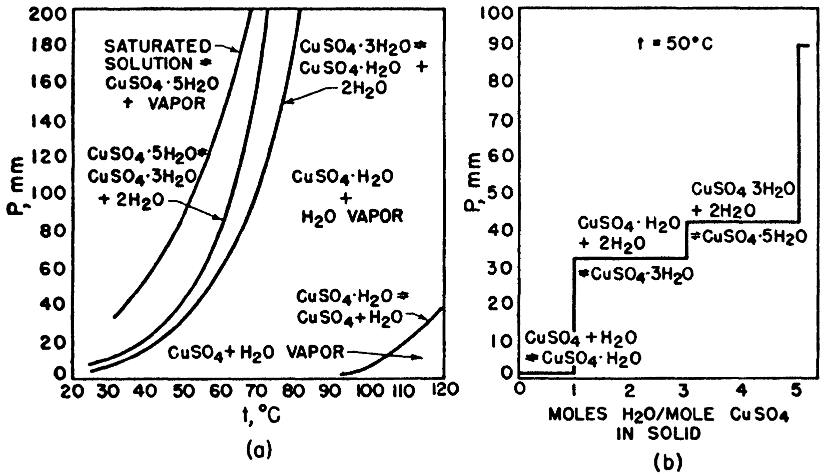


Fig. 6.12. The system $CuSO_4$–H_2O.

A two-component gas-solid system in which there is no appreciable solid-solution formation is exemplified by: $CaCO_3 \rightleftharpoons CaO + CO_2$. Since $c = 2$, the degrees of freedom are $f = 4 - p$. If the two solid phases are present, together with the gaseous phase CO_2, the system is univariant, $f = 4 - 3 = 1$. At a given temperature, the pressure of CO_2 has a fixed value. For example, if CO_2 is admitted to a sample of CaO at 700°C, there is no absorption of gas until a pressure of 25 mm is reached; then the CaO takes up CO_2 at constant pressure until it is completely converted into $CaCO_3$, whereupon further addition of CO_2 again results in an increase in pressure.

The pressure-temperature diagram for such a system is therefore similar to the vapor-pressure curve of a pure liquid or solid. The CO_2 pressure has been loosely called the "dissociation pressure of $CaCO_3$." Since the pressure has a definite value only when the vapor phase is in equilibrium with *both* solid phases, it is really necessary to speak of the "dissociation pressure in the system $CaCO_3$–CaO–CO_2."

The necessity of specifying both the solid phases is to be emphasized in systems formed by various salts, their hydrates, and water vapor. The case of copper sulfate–water is shown in (a), Fig. 6.12, on a *PT* diagram, and in (b), Fig. 6.12, on a *PC* diagram. As long as only the two phases are present, a salt hydrate can exist in equilibrium with water vapor at any temperature if the pressure of water vapor is (1) above the dissociation pressure to lower hydrate or anhydrous salt and (2) below the dissociation pressure of the next higher hydrate or the vapor pressure of the saturated solution. Statements in the older literature that a given hydrate "loses water at 110°C" are devoid of precise meaning.

When the pressure of water vapor falls below the dissociation pressure for the system, *efflorescence* occurs, as the hydrate loses water and its surface becomes covered with a layer of lower hydrate or anhydrous salt. When the vapor pressure exceeds that of the saturated aqueous solution, *deliquescence* occurs, and the surface of hydrate becomes covered with a layer of saturated solution.

24. Equilibrium constant in solid-gas reactions. The equilibrium constant for a reaction involving solid phases can be discussed conveniently by considering a typical reaction of this kind, the reduction of zinc oxide by carbon monoxide, $\mathrm{ZnO\ (s) + CO \rightarrow Zn\ (g) + CO_2}$.

The equilibrium constant in terms of activities can be written as follows:

$$K_a = \frac{a_{\mathrm{Zn}}a_{\mathrm{CO_2}}}{a_{\mathrm{ZnO}}a_{\mathrm{CO}}}, \quad \Delta F^\circ = -RT \ln K_a \tag{6.33}$$

The activity is the ratio of the fugacity under the experimental conditions to the fugacity in a standard state, f_A/f_A°. The standard state of a pure solid component is taken to be its state as a pure solid at one atmosphere pressure. The fugacity of the solid varies so slightly with pressure that over a considerable range of pressure, f_A/f_A° for a solid is effectively a constant equal to unity. Making this very good approximation, the expression in eq. (6.33) becomes

$$K_a = \frac{a_{\mathrm{Zn}}a_{\mathrm{CO_2}}}{a_{\mathrm{CO}}} = \frac{f_{\mathrm{Zn}}f_{\mathrm{CO_2}}}{f_{\mathrm{CO}}}$$

If the gases are considered to be ideal the activity ratio equals the partial pressure ratio, and $K_p = P_{\mathrm{Zn}}P_{\mathrm{CO_2}}/P_{\mathrm{CO}}$.

This discussion leads to the following general rule: no terms involving pure solid or liquid components need be included in equilibrium constants for solid-gas or liquid-gas reactions, unless very high precision is required, in which case there may be a small pressure correction to K_p or K_f.

Equilibrium data for the reduction of zinc oxide are given in Table 6.6.

25. Solid-liquid equilibria: simple eutectic diagrams. For two-component solid-liquid equilibria in which the liquids are completely intersoluble in all proportions and there is no appreciable solid-solid solubility, the simple

TABLE 6.6

THE EQUILIBRIUM $ZnO + CO \rightleftharpoons Zn + CO_2$ (TOTAL PRESSURE = 760 MM)

Temp. (°C)	Equilibrium Concentrations in Vapor		$K_p = P_{Zn}P_{CO_2}/P_{CO}$ (atm)
	Per cent CO	Per cent CO_2 = Per cent Zn	
427	99.98	0.01	1.00×10^{-8}
627	99.12	0.44	1.95×10^{-5}
827	91.76	4.12	1.84×10^{-3}
1027	66.92	16.54	4.08×10^{-2}
1227	30.84	34.58	3.87×10^{-1}
1427	9.8	45.1	2.07

diagram of Fig. 6.13 is obtained. Examples of systems of this type are collected in Table 6.7.

TABLE 6.7

SYSTEMS WITH SIMPLE EUTECTIC DIAGRAMS SUCH AS FIG. 6.13

Component *A*	M. pt. *A* (°C)	Component *B*	M. pt. *B* (°C)	Eutectic	
				°C	Mol per cent *B*
$CHBr_3$	7.5	C_6H_6	5.5	−26	50
$CHCl_3$	−63	$C_6H_5NH_2$	−6	−71	24
Picric acid	122	TNT	80	60	64
Sb	630	Pb	326	246	81
Cd	321	Bi	271	144	55
KCl	790	AgCl	451	306	69
Si	1412	Al	657	578	89
Be	1282	Si	1412	1090	32

Consider the behavior of a solution of composition *X* on cooling along the isopleth *XX'*. When point *P* is reached, pure solid *A* begins to separate from the solution. As a result, the residual solution becomes richer in the other component *B*, its composition falling along the line *PE*. At any point *Q* in the two-phase region, the relative amounts of pure *A* and residual solution are given as usual by the ratio of the tie-line segments. When point *R* is reached, the residual solution has the eutectic composition *E*. Further cooling now results in the simultaneous precipitation of a mixture of *A* and *B* in relative amounts corresponding to *E*.

The eutectic point is an invariant point on a constant pressure diagram; since three phases are in equilibrium, $f = c - p + 2 = 2 - p + 2 = 4 - 3 = 1$, and the single degree of freedom is used by the choice of the constant-pressure condition.

Microscopic examination of alloys often reveals a structure indicating that they have been formed from a melt by a cooling process similar to that considered along the isopleth XX' of Fig. 6.13. Crystallites of pure metal are found dispersed in a matrix of finely divided eutectic mixture. An example taken from the antimony-lead system is shown in the photomicrograph of Fig. 6.14.

26. Cooling curves. The method of cooling curves is one of the most useful for the experimental study of solid-liquid systems. A two-component system is heated until a homogeneous melt is obtained. A thermocouple, or other convenient device for temperature measurement, is immersed in the liquid, which is kept in a fairly well insulated container. As the system slowly cools, the temperature is recorded at regular time intervals. Examples of such curves for the system shown in Fig. 6.13 are drawn in Fig. 6.15.

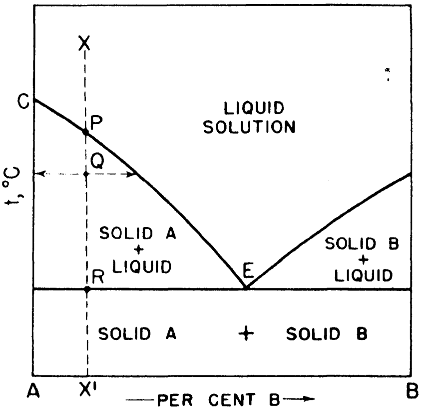


Fig. 6.13. Simple eutectic diagram for two components, A and B, completely intersoluble as liquids but with negligible solid-solid solubility.

The curve a for pure A exhibits a gradual decline until the melting point of A is reached. It then remains perfectly flat as long as solid and liquid A are both present, and resumes its decline only after all the liquid has solidified. The curve for cooling along the isopleth XX' is shown in b. The decline as the homogeneous melt is cooled becomes suddenly less steep when the temperature is reached corresponding to point P, where the first solid begins to

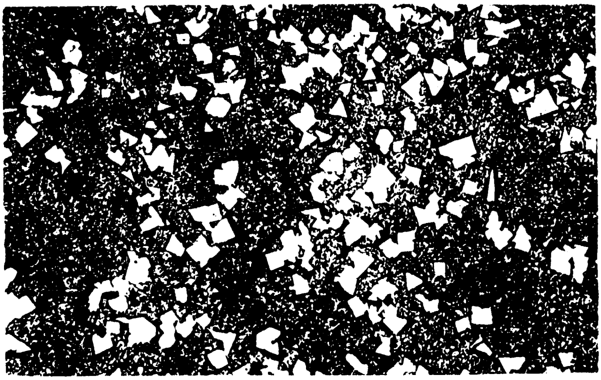


Fig. 6.14. Photomicrograph at 50× of 80 per cent Pb–20 per cent Sb, showing crystals of Sb in a eutectic matrix. (Courtesy Professor Arthur Phillips, Yale University.)

separate from the solution. This change of slope is a consequence of the liberation of latent heat of fusion during the solidification of *A*. The more gradual decline continues until the eutectic temperature is reached. Then the cooling curve becomes absolutely flat. This is because the eutectic point in a two-component system, just as the melting point of one component, is an invariant point at constant over-all pressure. If the composition of the system chosen initially happened to be the same as that of the eutectic, the cooling curve would be that drawn in *c*.

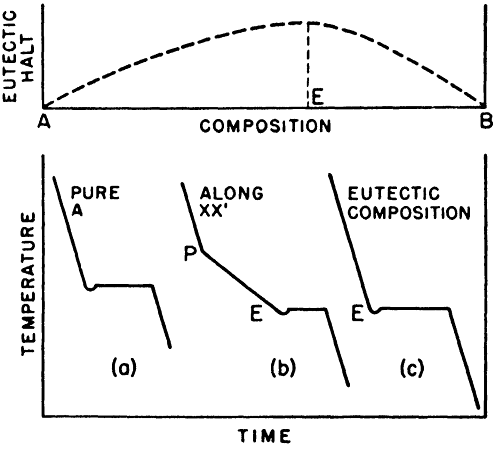


Fig. 6.15. Cooling curves for various compositions on the simple eutectic diagram of Fig. 6.13.

The duration of the constant-temperature period at the eutectic temperature is called the *eutectic halt*. This halt is a maximum for a melt having the eutectic composition.

Each cooling curve determination yields one point on the *TC* diagram (point of initial break in slope) in addition to a value for the eutectic temperature. By these methods, the entire diagram can be constructed.

27. Compound formation. If aniline and phenol are melted together in equimolar proportions, a definite compound crystallizes on cooling, $C_6H_5OH{\cdot}C_6H_5NH_2$. Pure phenol melts at 40°C, pure aniline at −6.1°C, and the compound melts at 31°C. The complete *TC* diagram for this system, in Fig. 6.16, is typical of many instances in which stable compounds occur as solid phases. The most convenient way of looking at such a diagram is to imagine it to be made up of two diagrams of the simple eutectic type placed side by side. In this case, one such diagram would be the phenol-compound diagram, and the other the aniline-compound diagram. The phases corresponding with the various regions of the diagram are labeled.

A maximum such as the point *C* is said to indicate the formation of a compound with a *congruent melting point*, since if a solid having the composition $C_6H_5OH{\cdot}C_6H_5NH_2$ is heated to 31°C, it melts to a liquid of identical composition. Compounds with congruent melting points are readily detected by the cooling-curve method. A liquid having the composition of the compound exhibits no eutectic halt, behaving in every respect like a single pure component.

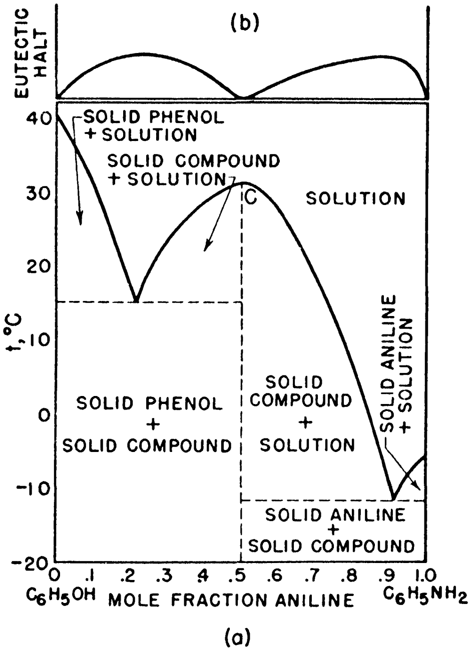


Fig. 6.16. The system phenol-aniline.

28. Solid compounds with incongruent melting points. In some systems, solid compounds are formed that do not melt to a liquid having the same composition, but instead decompose before such a melting point is reached. An example is the silica-alumina system (Fig. 6.17), which includes a compound, $3Al_2O_3{\cdot}SiO_2$, called *mullite*.

If a melt containing 40 per cent Al_2O_3 is prepared and cooled slowly, solid mullite begins to separate at about 1780°C. If some of this solid compound is removed and reheated along the line XX', it decomposes at 1800°C into solid corundum and a liquid solution (melt) having the composition P. Thus: $3Al_2O_3{\cdot}SiO_2 \rightarrow Al_2O_3 +$ solution. Such a change is called *incongruent* melting, since the composition of the liquid differs from that of the solid.

The point P is called the *incongruent melting point* or the *peritectic point* (τηκτος, "melting"; περι, "around"). The suitability of this name becomes evident if one follows the course of events as a solution with composition $3Al_2O_3{\cdot}SiO_2$ is gradually cooled along XX'. When the point M is reached, solid corundum (Al_2O_3) begins to separate from the melt, whose composition therefore becomes richer in SiO_2, falling along the line *MP*. When the temperature falls below that of the peritectic at *P*, the following change occurs: liquid + corundum → mullite. The solid Al_2O_3 that has separated

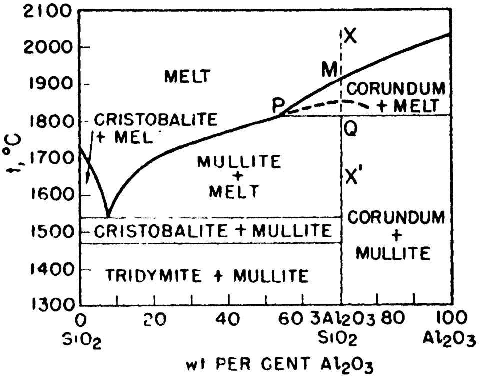


Fig. 6.17. System displaying peritectic.

reacts with the surrounding melt to form the compound mullite. If a specimen taken at a point such as *Q* is examined, the solid material is found to consist of two phases, a core of corundum surrounded by a coating of mullite. It was from this characteristic appearance that the term "peritectic" originated.

29. Solid solutions. Solid solutions are in theory no different from other kinds of solution: they are simply solid phases containing more than one

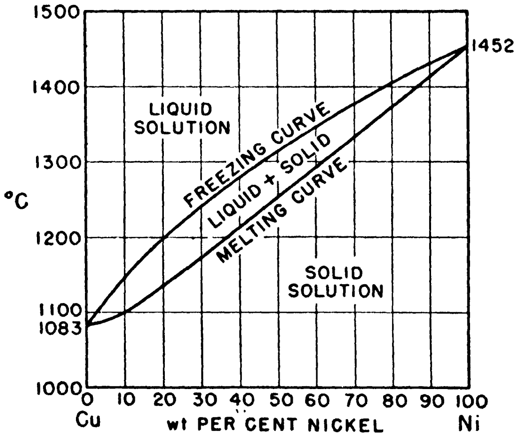


Fig. 6.18. The copper-nickel system—a continuous series of solid solutions.

component. The phase rule makes no distinction between the kind of phase (gas, liquid, or solid) that occurs, being concerned only with how many pure tin melts at 232°C and pure bismuth at 268°C, their eutectic being at 133°C and 42 per cent Sn. The Sn-Bi eutectic temperature is lowered by the addition of lead to a minimum at 96°C and a composition of 32 per cent Pb, 16 per cent Sn, 52 per cent Bi. This is the ternary eutectic point.

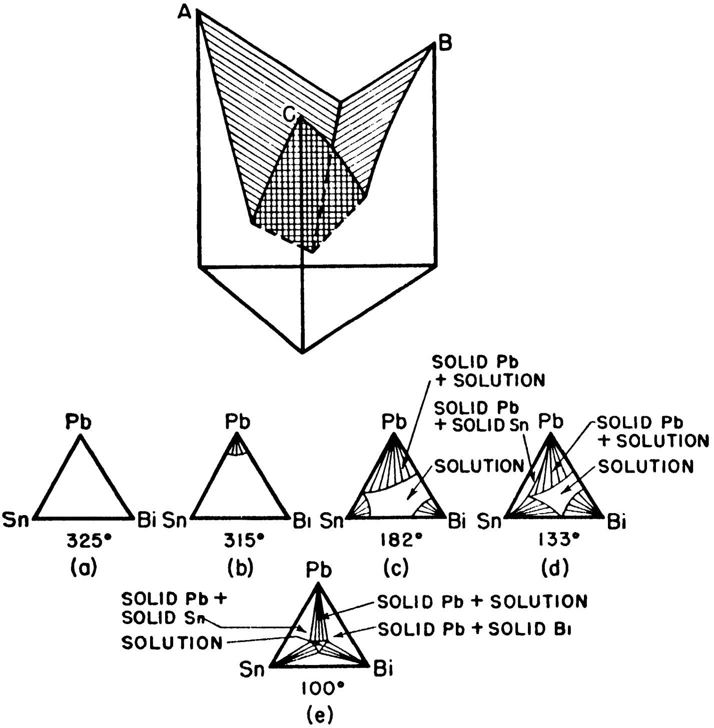


Fig. 6.22. The system Pb–Sn–Bi: three-dimensional diagram and isothermal sections.

Without using a solid model, the behavior of this system is best illustrated by a series of *isothermal sections*, shown in Fig. 6.22. Above 325°C (*a*), the melting point of pure lead, there is a single liquid solution. At around 315°C (*b*) the system consists of solid Pb and solution. The section at 182°C (c) indicates the binary eutectic of Sn and Pb. Below this temperature, solid Pb and solid Sn both separate from the solution. At 133°C the binary eutectic between Sn and Bi is reached (*d*). Finally, in (*e*) at 100°C there is shown a section slightly above the ternary eutectic.

The subject of ternary diagrams is an extended and very important one, and only a few of the introductory aspects have been mentioned. For further details some of the special treatises that are available should be consulted.[11]

---

[11] J. S. Marsh, *Principles of Phase Diagrams* (New York: McGraw-Hill, 1935); G. Massing, *Introduction to the Theory of Three Component-Systems* (New York: Reinhold, 1944).

PROBLEMS

1. Solutions are prepared at 25°C containing 1000 g of water and n moles of NaCl. The volume is found to vary with n as $V = 1001.38 + 16.6253n + 1.7738n^{3/2} + 0.1194n^2$. Draw a graph showing the partial molar volumes of H_2O and NaCl in the solution as a function of the molality from 0 to 2 molal.

2. In the *International Critical Tables* (vol. III, p. 58) there is an extensive table of densities of HNO_3—H_2O solutions. Use these data to calculate, by the graphical method of Fig. 6.1, the partial molar volumes of H_2O and HNO_3 in 10, 20, 30, and 40 per cent solutions at 25°.

3. When 2 g of nonvolatile hydrocarbon containing 94.4 per cent C is dissolved in 100 g benzene, the vapor pressure of benzene at 20°C is lowered from 74.66 mm to 74.01 mm. Calculate the empirical formula of the hydrocarbon.

4. Pure water is saturated with a 2 : 1 mixture of hydrogen and oxygen at a total pressure of 5 atm. The water is then boiled to remove all the gases. Calculate the per cent composition of the gases driven off (after drying). Use data from Table 6.2.

5. Water and nitrobenzene can be considered to be immiscible liquids. Their vapor pressures are: H_2O, 92.5 mm at 50°C; 760 mm at 100°C; $C_6H_5NO_2$, 22.4 mm at 100°C; 148 mm at 150°C. Estimate the boiling point of a mixture of water and nitrobenzene at 1 atm pressure. In a steam distillation at 1 atm how many grams of steam would be condensed to obtain one gram of nitrobenzene in the distillate?

6. The following data were obtained for the boiling points at 1 atm of solutions of CCl_4 in C_2Cl_4:

Mole fraction CCl_4 in liq. .	0.000	0.100	0.200	0.400	0.600	0.800	1.000
Mole fraction CCl_4 in vap. .	0.000	0.469	0.670	0.861	0.918	0.958	1.000
Boiling point °C . . .	120.8	108.5	100.8	89.3	83.5	79.9	76.9

If half of a solution 30 mole per cent in CCl_4 is distilled, what is the composition of the distillate? If a solution 50 mole per cent in CCl_4 is distilled until the residue is 20 mole per cent CCl_4, what is approximate composition of the distillate?

7. A compound insoluble in water is steam distilled at 97.0°C, the distillate containing 68 wt. per cent H_2O. The vapor pressure of water is 682 mm at 97°. What is the molecular weight of the compound?

8. When hexaphenylethane is dissolved in benzene, the f.pt. depression of a 2 per cent solution is 0.219°C; the b.pt. elevation is 0.135°. Calculate the heat of dissociation of hexaphenylethane into triphenylmethyl radicals.

9. Calculate the weight of (a) methanol, (b) ethylene glycol which, when dissolved in 4.0 liters of water, would just prevent the formation of ice at −10°C.

10. The solubility of picric acid in benzene is:

t, °C	5	10	15	20	25	35
g/100 g C_6H_6	3.70	5.37	7.29	9.56	12.66	21.38

The melting points of benzene and picric acid are 5.5° and 121.8°C. Calculate the heat of fusion of picric acid.

11. The osmotic pressure at 25°C of a solution of β-lactoglobulin containing 1.346 g protein per 100 cc solution was found to be 9.91 cm of water. Estimate the molecular weight of the protein.

12. For the ideal solutions of ethylene bromide and propylene bromide (p. 124), draw a curve showing how the mole fraction of $C_2H_4Br_2$ in the vapor varies with that in the liquid. Use this curve to estimate the number of theoretical plates required in a column in order to yield a distillate with mole fraction of $C_2H_4Br_2 = 0.9$ from a solution of mole fraction 0.1. Assume total reflux.

13. Calculate the distribution coefficient K for piperidine between water and benzene at 20°C, given:

g solute/100 cc water layer	0.635	1.023	1.635	2.694
g solute/100 cc benzene layer	0.550	0.898	1.450	2.325

14. A solution of 3.795 g sulfur in 100 g carbon bisulfide (b.pt. $CS_2 =$ 46.30°C; $\Delta H_{\text{vap}} = 6400$ cal per mole) boils at 46.66°C. What is the formula of the sulfur molecule in the solution?

15. The melting points and heats of fusion of *o*, *p*, *m* dinitrobenzenes are: 116.9°, 173.5°, 89.8°, and 3905, 3345, 4280 cal per mole [Johnston, *J. Phys. Chem.*, *29*, 882, 1041 (1925)]. Assuming the ideal solubility law, calculate the ternary eutectic temperature and composition for mixtures of *o*, *m*, *p* compounds.

16. The following boiling points are obtained for solutions of oxygen and nitrogen at 1 atm:

b.pt., °K	77.3	78.0	79.0	80.0	82.0	84.0	86.0	88.0	90.1
Mole % O in liq.	0	8.1	21.6	33.4	52.2	66.2	77.8	88.5	100
Mole % O in vap.	0	2.2	6.8	12.0	23.6	36.9	52.2	69.6	100

Draw the *TX* diagram. If 90 per cent of a mixture containing 20 per cent O_2 and 80 per cent N_2 is distilled, what will be the composition of the residual liquid and its b.pt.? Plot an activity a vs. mole fraction X diagram from the data.

17. For a two-component system (A, B) show that:

$$\log \gamma_A = \int_0^{X_B} \frac{\log \gamma_B}{(1 - X_B)^2}\, dX_B - \frac{X_B}{1 - X_B} \log \gamma_B$$

18. Pedder and Barratt [*J. Chem. Soc.*, 537 (1933)] measured the vapor pressures of potassium amalgams at 387.5°C, at which temperature the vapor pressure of K is 3.25 mm, of Hg 1280 mm.

Mole % K in liq.	41.1	46.8	50.0	56.1	63.0	72.0
P of Hg, mm	31.87	17.30	13.00	9.11	6.53	3.70
P of K, mm	0.348	0.68	1.07	1.69	2.26	2.95

Calculate the activity coefficients of K and Hg in the amalgams and plot them vs. the composition in the range studied.

19. The equilibrium pressures for the system $CaSO_4 \cdot 2\,H_2O = CaSO_4 + 2\,H_2O$, and the vapor pressures of pure water, at various temperatures are:

t, °C	50	55	60	65
$CaSO_4$ system, mm	80	109	149	204
H_2O, mm	92	118	149	188

The solubility of $CaSO_4$ in water is so low that the vapor pressure of the saturated solution can be taken to equal that of pure water.

(a) State what happens on heating the dihydrate in a previously evacuated sealed tube from 50 to 65°C. (b) What solid phase separates when a solution of $CaSO_4$ is evaporated at 65°, at 55°C? (c) What solid phase separates on evaporating at 55° if, when the solution becomes saturated, enough $CaCl_2$ is added to reduce its v.p. by 10 per cent?

20. Data for the Au-Te system:

wt. % Te	0	10	20	30	40	42	50	56.4	60	70	82.5	90	100
f.pt., °C	1063	940	855	710	480	447	458	464	460	448	416	425	453

Sketch the phase diagram. Label all regions carefully. Describe what happens when a melt containing 50 per cent Te is cooled slowly.

21. The dissociation pressure of galactose monohydrate is given by $\log_{10} P\,(\text{mm}) = 7.04 - 1780/T$. Calculate $\Delta F°$, $\Delta H°$, $\Delta S°$, at 25°C for the dissociation.

22. The solubility of glycine in liquid ammonia was found to be:

Moles per liter	0.20	0.65	2.52
t, °C	−77	−63	−45

Estimate the heat of solution per mole.

23. For the free energies of formation of Cu_2O and CuO the following equations are cited:

$$Cu_2O\!: \Delta F° = -40{,}720 + 1.17T \ln T - 1.545 \times 10^{-3}T^2 + 85.7T^{1/2} + 6.97T$$

$$CuO\!: \Delta F° = -37{,}680 + 1.75T \ln T - 2.73 \times 10^{-3}T^2 + 85.7T^{1/2} + 9.49T$$

What product is formed when O_2 at 10 mm pressure is passed over copper at 900°C?

REFERENCES

BOOKS

1. Brick, R. M., and A. Phillips, *Structure and Properties of Alloys* (New York: McGraw-Hill, 1949).

2. Carney, T. P., *Laboratory Fractional Distillation* (New York: Macmillan, 1949).
3. Guggenheim, E. A., *Mixtures* (New York: Oxford, 1952).
4. Hildebrand, J. H., and R. L. Scott, *Solubility of Nonelectrolytes* (New York: Reinhold, 1950).
5. Hume-Rothery, W., J. W. Christian, and W. B. Pearson, *Metallurgical Equilibrium Diagrams* (London: Inst. of Physics, 1952).
6. Shand, S. J., *Rocks for Chemists* (London: Murby, 1952).
7. Wagner, C., *Thermodynamics of Alloys* (Cambridge, Mass: Addison-Wesley, 1952).
8. Weissberger, A. (editor), *Physical Methods of Organic Chemistry*, vol. I (New York: Interscience, 1950). Articles on determination of melting point, boiling point, solubility, osmotic pressure.

ARTICLES

1. *Chem. Rev.*, *44*, 1–233 (1949), "Symposium on Thermodynamics of Solutions."
2. Fleer, K. B., *J. Chem. Ed.*, *22*, 588–92 (1945), "Azeotropism."
3. Hildebrand, J. H., *J. Chem. Ed.*, *25*, 74–77 (1948), "Ammonia as a Solvent."
4. Teller, A. J., *Chem. Eng.*, *61*, 168–88 (1954), "Binary Distillation."

CHAPTER 7

The Kinetic Theory

1. The beginning of the atom. Thermodynamics is a science that takes things more or less as it finds them. It deals with pressures, volumes, temperatures, and energies, and the relations between them, without seeking to elucidate further the nature of these entities. For thermodynamics, matter is a continuous substance, and energy behaves in many ways like an incompressible, weightless fluid. The analysis of nature provided by thermodynamics is very effective in a rather limited field. Almost from the beginning of human thought, however, man has tried to achieve an insight into the structure of things, and to find an indestructible reality beneath the ever-changing appearances of natural phenomena.

The best example of this endeavor has been the development of the atomic theory. The word atom is derived from the Greek *ατομος*, meaning "indivisible"; the atoms were believed to be the ultimate and eternal particles of which all material things were made. Our knowledge of Greek atomism comes mainly from the long poem of the Roman, Lucretius, *De Rerum Natura*—"Concerning the Nature of Things," written in the first century before Christ. Lucretius expounded the theories of Epicurus and of Democritus:

> The same letters, variously selected and combined
> Signify heaven, earth, sea, rivers, sun,
> Most having some letters in common.
> But the different subjects are distinguished
> By the arrangement of letters to form the words.
> So likewise in the things themselves,
> When the intervals, passages, connections, weights,
> Impulses, collisions, movements, order,
> And position of the atoms interchange,
> So also must the things formed from them change.

The properties of substances were determined by the form of their atoms. Atoms of iron were hard and strong with spines that locked them together into a solid; atoms of water were smooth and slippery like poppy seeds; atoms of salt were sharp and pointed and pricked the tongue; whirling atoms of air pervaded all matter.

Later philosophers were inclined to discredit the atomic theory. They found it hard to explain the many qualities of materials, color, form, taste, and odor, in terms of naked, colorless, tasteless, odorless atoms. Many followed the lead of Heraclitus and Aristotle, considering matter to be formed from the four "elements," earth, air, fire, and water, in varying proportions. Among the alchemists there came into favor the *tria prima* of Paracelsus (1493–1541), who wrote:

> Know, then, that all the seven metals are born from a threefold matter, namely, Mercury, Sulphur, and Salt, but with distinct and peculiar colorings.

Atoms were almost forgotten till the seventeenth century, as the alchemists sought the philosopher's stone by which the "principles" could be blended to make gold.

2. The renascence of the atom. The writings of Descartes (1596–1650) helped to restore the idea of a corpuscular structure of matter. Gassendi (1592–1655) introduced many of the concepts of the present atomic theory; his atoms were rigid, moved at random in a void, and collided with one another. These ideas were extended by Hooke, who first proposed (1678) that the "elasticity" of a gas was the result of collisions of its atoms with the retaining walls.

The necessary philosophic background for the rapid development of atomism was now provided by John Locke. In his *Essay on Human Understanding* (1690), he took up the old problem of how the atoms could account for all the qualities perceived by the senses in material things. The qualities of things were divided into two classes. The *primary qualities* were those of shape, size, motion, and situation. These were the properties inherent in the corpuscles or atoms that make up matter. *Secondary qualities*, such as color, odor, and taste, existed only in the mind of the observer. They arose when certain arrangements of the atoms of matter interacted with other arrangements of atoms in the sense organs of the observer.

Thus a "hot object" might produce a change in the size, motion, or situation of the corpuscles of the skin, which then produces in the mind the sensations of warmth or of pain. The consequences of Locke's empiricism have been admirably summarized by J. C. Gregory.[1]

> The doctrine of qualities was a curiously dichotomized version of perception. A snowflake, as perceived, was half in the mind and half out of it, for its shape was seen but its whiteness was only in the mind. . . . This had quick consequences for philosophy. . . . The division between science and philosophy began about the time of Locke, as the one turned, with its experimental appliances, to the study of the corpuscular mechanism, and the other explored the mind and its ideas. The severance had begun between science and philosophy and, although it only gradually progressed into the nineteenth century cleft between them, when the seventeenth century closed, physical science was taking the physical world for her domain, and philosophy was taking the mental world for hers.

In the early part of the eighteenth century, the idea of the atom became widely accepted. Newton wrote in 1718:

> It seems probable to me that God in the beginning formed matter in solid, massy, hard, impenetrable, movable particles, of such sizes and figures, and with such other properties, and in such proportion, as most conduced to the end for which He formed them.

---

[1] *A Short History of Atomism* (London: A. & C. Black, Ltd., 1931).

Newton suggested, incorrectly, that the pressure of a gas was due to repulsive forces between its constituent atoms. In 1738, Daniel Bernouilli correctly derived Boyle's Law by considering the collisions of atoms with the container wall.

3. Atoms and molecules. Boyle had discarded the alchemical notion of elements and defined them as substances that had not been decomposed in the laboratory. Until the work of Antoine Lavoisier from 1772 to 1783, however, chemical thought was completely dominated by the phlogiston theory of Georg Stahl, which was actually a survival of alchemical conceptions. With Lavoisier's work the elements took on their modern meaning, and chemistry became a quantitative science. The Law of Definite Proportions and The Law of Multiple Proportions had become fairly well established by 1808, when John Dalton published his *New System of Chemical Philosophy.*

Dalton proposed that the atoms of each element had a characteristic atomic weight, and that these atoms were the combining units in chemical reactions. This hypothesis provided a clear explanation for the Laws of Definite and Multiple Proportions. Dalton had no unequivocal way of assigning atomic weights, and he made the unfounded assumption that in the most common compound between two elements, one atom of each was combined. According to this system, water would be HO, and ammonia NH. If the atomic weight of hydrogen was set equal to unity, the analytical data would then give $O = 8$, $N = 4.5$, in Dalton's system.

At about this time, Gay-Lussac was studying the chemical combinations of gases, and he found that the ratios of the volumes of the reacting gases were small whole numbers. This discovery provided a more logical method for assigning atomic weights. Gay-Lussac, Berzelius, and others felt that the volume occupied by the atoms of a gas must be very small compared with the total gas volume, so that equal volumes of gas should contain equal numbers of atoms. The weights of such equal volumes would therefore be proportional to the atomic weights. This idea was received coldly by Dalton and many of his contemporaries, who pointed to reactions such as that which they wrote as $N + O = NO$. Experimentally the nitric oxide was found to occupy the same volume as the nitrogen and oxygen from which it was formed, although it evidently contained only half as many "atoms."[2]

Not till 1860 was the solution to this problem understood by most chemists, although half a century earlier it had been given by Amadeo Avogadro. In 1811, he published in the *Journal de physique* an article that clearly drew the distinction between the molecule and the atom. The "atoms" of hydrogen, oxygen, and nitrogen are in reality "molecules" containing two atoms each. Equal volumes of gases should contain the same number of molecules (Avogadro's Principle).

Since a molecular weight in grams (mole) of any substance contains the same number of molecules, according to Avogadro's Principle the molar

---

[2] The elementary corpuscles of compounds were then called "atoms" of the compound.

volumes of all gases should be the same. The extent to which real gases conform to this rule may be seen from the molar volumes in Table 7.1 calculated from the measured gas densities. For an ideal gas at 0°C and 1 atm, the molar volume would be 22,414 cc. The number of molecules in one mole is now called Avogadro's Number *N*.

TABLE 7.1

MOLAR VOLUMES OF GASES IN CC AT 0°C AND 1 ATM PRESSURE

Hydrogen	22,432	Argon	22,390
Helium	22,396	Chlorine	22,063
Methane	22,377	Carbon dioxide	22,263
Nitrogen	22,403	Ethane	22,172
Oxygen	22,392	Ethylene	22,246
Ammonia	22,094	Acetylene	22,085

The work of Avogadro was almost completely neglected until it was forcefully presented by Cannizzaro at the Karlsruhe Conference in 1860. The reason for this neglect was probably the deeply rooted feeling that chemical combination occurred by virtue of an affinity between unlike elements. After the electrical discoveries of Galvani and Volta, this affinity was generally ascribed to the attraction between unlike charges. The idea that two identical atoms of hydrogen might combine into the compound molecule H_2 was abhorrent to the chemical philosophy of the early nineteenth century.

4. The kinetic theory of heat. Even among the most primitive peoples the connection between heat and motion was known through frictional phenomena. As the kinetic theory became accepted during the seventeenth century, the identification of heat with the mechanical motion of the atoms or corpuscles became quite common.

Francis Bacon (1561–1626) wrote:

> When I say of motion that it is the genus of which heat is a species I would be understood to mean, not that heat generates motion or that motion generates heat (though both are true in certain cases) but that heat itself, its essence and quiddity, is motion and nothing else. . . . Heat is a motion of expansion, not uniformly of the whole body together, but in the smaller parts of it . . . the body acquires a motion alternative, perpetually quivering, striving, and struggling, and initiated by repercussion, whence springs the fury of fire and heat.

Although such ideas were widely discussed during the intervening years, the caloric theory, considering heat as a weightless fluid, was the working hypothesis of most natural philosophers until the quantitative work of Rumford and Joule brought about the general adoption of the mechanical theory. This theory was rapidly developed by Boltzmann, Maxwell, Clausius, and others, from 1860 to 1890.

According to the tenets of the kinetic theory, both temperature and pressure are thus manifestations of molecular motion. Temperature is a measure of the average translational kinetic energy of the molecules, and pressure arises from the average force resulting from repeated impacts of molecules with the containing walls.

5. The pressure of a gas. The simplest kinetic-theory model of a gas assumes that the volume occupied by the molecules may be neglected completely compared to the total volume. It is further assumed that the molecules behave like rigid spheres, with no forces of attraction or repulsion between them except during actual collisions.

In order to calculate the pressure in terms of molecular quantities, let us consider a volume of gas contained in a cubical box of side l. The velocity c of any molecule may be resolved into components u, v, and w, parallel to the three mutually perpendicular axes X, Y, and Z, so that its magnitude is given by

$$c^2 = u^2 + v^2 + w^2 \tag{7.1}$$

Collisions between a molecule and the walls are assumed to be perfectly elastic; the angle of incidence equals the angle of reflexion, and the velocity changes in direction but not in magnitude. At each collision with a wall that is perpendicular to X, the velocity component u changes sign from $+u$ to $-u$, or vice versa; the momentum component of the molecule accordingly changes from $\pm mu$ to $\mp mu$, where m is the mass of the molecule. The magnitude of the change in momentum is therefore $2\,mu$.

The number of collisions in unit time with the two walls perpendicular to X is equal to u/l, and thus the change in the X component of momentum in unit time is $2mu \cdot (u/l) = 2mu^2/l$.

If there are N molecules in the box, the change in momentum in unit time becomes $2(Nm\overline{(u^2)}/l)$, where $\overline{(u^2)}$ is the average value of the square of velocity component[3] u. This rate of change of momentum is simply the force exerted by the molecules colliding against the two container walls normal to X, whose area is $2l^2$. Since pressure is defined as the force normal to unit area,

$$P = \frac{2Nm\overline{(u^2)}}{2l^2 \cdot l} = \frac{Nm\overline{(u^2)}}{V}$$

Now there is nothing to distinguish the magnitude of one particular component from another in eq. (7.1) so that on the average $\overline{(u^2)} = \overline{(v^2)} = \overline{(w^2)}$. Thus $3\overline{(u^2)} = \overline{(c^2)}$ and the expression for the pressure becomes

$$P = \frac{Nm\overline{(c^2)}}{3V} \tag{7.2}$$

The quantity $\overline{(c^2)}$ is called the *mean square speed* of the molecules, and may be given the special symbol C^2. Then $C = \overline{(c^2)}^{1/2}$ is called the *root mean*

---

[3] Not to be confused with the square of the average value of the velocity component, which would be written $(\bar{u})^2$. In this derivation we are averaging u^2, not u.

square speed. The total translational kinetic energy E_K of the molecules is $\frac{1}{2}NmC^2$. Therefore from eq. (7.2):

$$PV = \tfrac{1}{3}NmC^2 = \tfrac{2}{3}E_K \qquad (7.3)$$

Since the total kinetic energy is a constant, unchanged by the elastic collisions, eq. (7.3) is equivalent to Boyle's Law.

If several different molecular species are present in a gas mixture, their kinetic energies are additive. From eq. (7.3), therefore, the total pressure is the sum of the pressures each gas would exert if it occupied the entire volume alone. This is Dalton's Law of Partial Pressures.[4]

6. Kinetic energy and temperature. The concept of temperature was first introduced in connection with the study of thermal equilibrium. When two bodies are placed in contact, energy flows from one to the other until a state of equilibrium is reached. The two bodies are then at the same temperature. We have found that the temperature can be measured conveniently by means of an ideal-gas thermometer, this empirical scale being identical with the thermodynamic scale derived from the Second Law.

A distinction was drawn in thermodynamics between mechanical work and heat. According to the kinetic theory, the transformation of mechanical work into heat is simply a degradation of large-scale motion into motion on the molecular scale. An increase in the temperature of a body is equivalent to an increase in the average translational kinetic energy of its constituent molecules. We may express this mathematically by saying that the temperature is a function of E_K alone, $T = f(E_K)$. We know that this function must have the special form $T = \frac{2}{3}E_K/R$, or

$$E_K = \tfrac{3}{2}RT \qquad (7.4)$$

so that eq. (7.3) may be consistent with the ideal-gas relation, $PV = RT$.

Temperature is thus not only a function of, but in fact proportional to, the average translational kinetic energy of the molecules. The kinetic-theory interpretation of absolute zero is thus the complete cessation of all molecular motion—the zero point of kinetic energy.[5]

The average translational kinetic energy may be resolved into components in the three *degrees of freedom* corresponding to velocities parallel to the three rectangular coordinates. Thus, for one mole of gas, where N is Avogadro's Number,

$$E_K = \tfrac{1}{2}NmC^2 = \tfrac{1}{2}Nm(\overline{u^2}) + \tfrac{1}{2}Nm(\overline{v^2}) + \tfrac{1}{2}Nm(\overline{w^2})$$

For each translational degree of freedom, therefore, from eq. (7.4),

$$E_K' = \tfrac{1}{2}Nm(\overline{u^2}) = \tfrac{1}{2}RT \qquad (7.5)$$

[4] $PV = \frac{2}{3}(E_{K1} + E_{K2} + \ldots)$; $P_1V = \frac{2}{3}E_{K1}$; $P_2V = \frac{2}{3}E_{K2}$; etc.
Therefore, $P = P_1 + P_2 + \ldots$, Dalton's Law.

[5] It will be seen later that this picture has been somewhat changed by quantum theory, which requires a small residual energy even at the absolute zero.

This is a special case of a more general theorem known as the Principle of the Equipartition of Energy.

7. Molecular speeds. Equation (7.3) may be written

$$C^2 = \frac{3P}{\rho} \tag{7.6}$$

where $\rho = Nm/V$ is the density of the gas. From eqs. (7.3) and (7.4) we obtain for the *root mean square speed C*, if M is the molecular weight,

$$C^2 = \frac{3RT}{Nm} = \frac{3RT}{M}$$

$$C = \left(\frac{3RT}{M}\right)^{1/2} \tag{7.7}$$

The *average speed* $\bar{c}$, as we shall see later, differs only slightly from the root mean square speed:

$$\bar{c} = \left(\frac{8RT}{\pi M}\right)^{1/2} \tag{7.8}$$

From eq. (7.6), (7.7), or (7.8), we can readily calculate average or root mean square speeds of the molecules of any gas at any temperature. Some results are shown in Table 7.2. The average molecular speed of hydrogen at 25°C is 1768 m per sec or 3955 mi per hr, about the speed of a rifle bullet. The average speed of a mercury vapor atom would be only about 400 mi per hr.

TABLE 7.2

AVERAGE SPEEDS OF GAS MOLECULES AT 0°C

Gas	*Meters/sec*	*Gas*	*Meters/sec*
Ammonia	582.7	Hydrogen	1692.0
Argon	380.8	Deuterium	1196.0
Benzene	272.2	Mercury	170.0
Carbon dioxide	362.5	Methane	600.6
Carbon monoxide	454.5	Nitrogen	454.2
Chlorine	285.6	Oxygen	425.1
Helium	1204.0	Water	566.5

We note that, in accordance with the principle of equipartition of energy, at any constant temperature the lighter molecules have the higher average speeds. This principle extends even to the phenomena of Brownian motion, where the dancing particles are some thousand times heavier than the molecules colliding with them, but nevertheless have the same average kinetic energy.

8. Molecular effusion. A direct experimental illustration of the different average speeds of molecules of different gases can be obtained from the phenomenon called *molecular effusion*. Consider the arrangement shown in (a), Fig. 7.1. Molecules from a vessel of gas under pressure are permitted to escape through a tiny orifice, so small that the distribution of the velocities of the gas molecules remaining in the vessel is not affected in any way; that is, no appreciable mass flow in the direction of the orifice is set up. The number of molecules escaping in unit time is then equal to the number that, in their random motion, happen to hit the orifice, and this number is proportional to the average molecular speed.

In (b), Fig. 7.1 is shown an enlarged view of the orifice, having an area ds. If all the molecules were moving directly perpendicular to the opening with their mean speed $\bar{c}$, in one second all those molecules would hit the opening that were contained in an element of volume of base ds and height $\bar{c}$, or volume $\bar{c}\,ds$, for a molecule at a distance $\bar{c}$ will just reach the orifice at the end of one second. If there are n molecules per cc, the number striking would be $n\bar{c}\,ds$. To a first approximation only one-sixth of all the molecules are moving toward the opening, since there are six different possible directions of translation corresponding to the three rectangular axes. The number of molecules streaming through the orifice would therefore be $\frac{1}{6}n\bar{c}\,ds$, or per unit area $\frac{1}{6}n\bar{c}$.

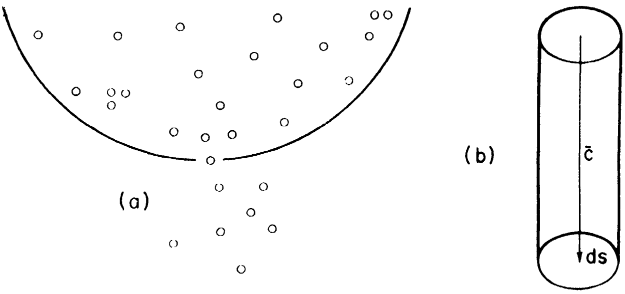


Fig. 7.1. Effusion of gases.

Actually, the problem is considerably more complicated, since half the molecules have a component of motion toward the area, and one must average over all the different possible directions of motion. This gives the result: number of molecules striking unit area per second = number of molecules effusing through unit area per second = $\frac{1}{4}n\bar{c}$.

It is instructive to consider how this result is obtained, since the averaging method is typical of many kinetic-theory calculations. This derivation will be the only one in the chapter that makes any pretense of exactitude, and may therefore serve also to inculcate a proper suspicion of the cursory methods used to obtain subsequent equations.

If the direction of the molecules is no longer normal to the wall, instead of the situation of Fig. 7.1, we have that of Fig. 7.2(a). For any given direction the number of molecules hitting ds in unit time will be those contained in a cylinder of base ds and slant height $\bar{c}$. The volume of this cylinder is $\bar{c}\cos\theta\,ds$, and the number of molecules in it is $n\bar{c}\cos\theta\,ds$.

The next step is to discover how many molecules out of the total have velocities in the specified direction. The velocities of the molecules will be referred to a system of polar coordinates [Fig. 7.2.(b)] with its origin at the wall of the vessel. We call such a representation a plot of the molecular velocities in "velocity space." The distance from the origin $\bar{c}$ defines the magnitude of the velocity, and the angles θ and ϕ represent its direction. Any particular direction from the origin is specified by the differential solid angle $d\omega$. The fraction of the total number of molecules having their velocities within this particular spread of directions is $d\omega/4\pi$ since 4π is the total solid angle subtended by the surface of a sphere. In polar coordinates this solid angle is given[6] by $\sin\theta\, d\theta\, d\phi$.

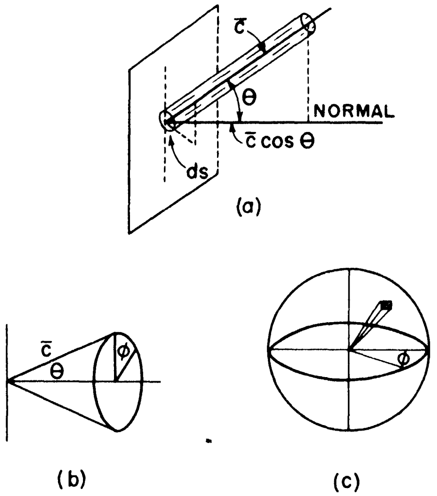


Fig. 7.2. Calculation of gaseous effusion. Element of solid angle is shown in (c).

The number of molecules hitting the surface ds in unit time from the given direction (θ, ϕ) becomes $(1/4\pi)n\bar{c}\cos\theta\sin\theta\, d\theta\, d\phi\, ds$. Or, for unit surface, it is $(1/4\pi)n\bar{c}\cos\theta\sin\theta\, d\theta\, d\phi$. In order to find the total number striking from all directions, dn'/dt, this expression must be integrated:

$$\frac{dn'}{dt} = \int_0^{\pi/2}\int_0^{2\pi} \frac{1}{4\pi}\, n\bar{c}\cos\theta\sin\theta\, d\phi\, d\theta$$

The limits of integration of ϕ are from 0 to 2π, corresponding to all the directions around the circle at any given θ. Then θ is integrated from 0 to $\pi/2$. The final result for the number of molecules striking unit area in unit time is then

$$\frac{dn'}{dt} = \tfrac{1}{4}\, n\bar{c} \tag{7.9}$$

The steps of the derivation may be reviewed by referring to Fig. 7.2.

If ρ is the gas density, the weight of gas that effuses in unit time is

$$\frac{dW}{dt} = \tfrac{1}{4}\,\rho\bar{c} \tag{7.10}$$

From eq. (7.8)

$$\frac{dW}{dt} = \rho\left(\frac{RT}{2\pi M}\right)^{1/2} \tag{7.11}$$

---

[6] G. P. Harnwell, *Principles of Electricity and Electromagnetism* (New York: McGraw-Hill, 1949), p. 649.

For the volume rate of flow, *e.g.*, cc per sec per cm²,

$$\frac{d\bar{V}}{dt} = \left(\frac{RT}{2\pi M}\right)^{1/2} \tag{7.12}$$

It follows that at constant temperature the rate of effusion varies inversely as the square root of the molecular weight. Thomas Graham (1848) was the first to obtain experimental evidence for this law, which is now named in his honor. Some of his data are shown in Table 7.3.

TABLE 7.3
THE EFFUSION OF GASES*

Gas	Relative Velocity of Effusion	
	Observed	Calculated from (7.12)
Air	(1)	(1)
Nitrogen	1.0160	1.0146
Oxygen	0.9503	0.9510
Hydrogen	3.6070	3.7994
Carbon dioxide	0.8354	0.8087

* *Source:* Graham, "On the Motion of Gases," *Phil. Trans. Roy. Soc.* (London), *136*, 573 (1846).

It appears from Graham's work, and also from that of later experimenters, that eq. (7.12) is not perfectly obeyed. It fails rapidly when one goes to higher pressures and larger orifices. Under these conditions the molecules can collide many times with one another in passing through the orifice, and a hydrodynamic flow towards the orifice is set up throughout the container, leading to the formation of a jet of escaping gas.[7]

It is evident from eq. (7.12) that the effusive-flow process provides a good method for separating gases of different molecular weights. By using permeable barriers with very fine pores, important applications have been made in the separation of isotopes. Because the lengths of the pores are considerably greater than their diameters, the flow of gases through such barriers does not follow the simple orifice-effusion equation. The dependence on molecular weight is the same, since each molecule passes through the barrier independently of any others.

9. Imperfect gases—van der Waals' equation, The calculated properties of the *perfect* gas of the kinetic theory are the same as the experimental properties of the *ideal* gas of thermodynamics. It might be expected then that extension and modification of the simplified model of the perfect gas should provide an explanation for observed deviations from ideal-gas behavior.

---

[7] For a discussion of jet flow, see H. W. Liepmann and A. E. Puckett, *Introduction to Aerodynamics of a Compressible Fluid* (New York: Wiley, 1947), pp. 32 *et seq.*

The first improvement of the model is to abandon the assumption that the volume of the molecules themselves can be completely neglected in comparison with the total gas volume. The effect of the finite volume of the molecules is to decrease the available void space in which the molecules are free to move. Instead of the V in the perfect gas equation, we must write $V - b$ where b is called the *excluded volume*. This is not just equal to the volume occupied by the molecules, but actually to four times that volume. This may be seen in a qualitative way by considering the two molecules of Fig. 7.3 (a), regarded as impenetrable spheres each with a diameter d. The centers of these two molecules cannot approach each other more closely than the distance d; the excluded volume for the pair is therefore a sphere of radius $d = 2r$ (where r is the radius of a molecule). This volume is $\frac{4}{3}\pi d^3 = 8 \, . \, \frac{4}{3}\pi r^3$ per pair, or $4 \, . \, \frac{4}{3}\pi r^3$ which equals $4V_m$ per molecule (where V_m is the volume of the molecule).

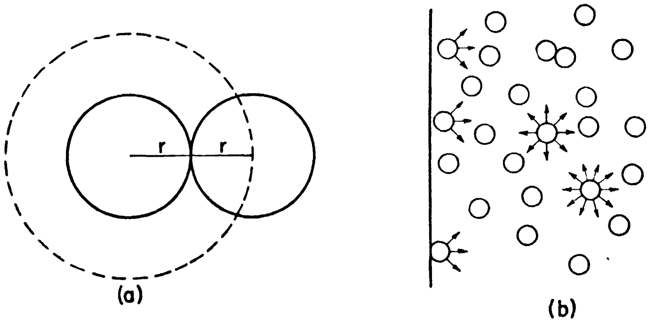


Fig. 7.3. Corrections to perfect gas law. (a) Excluded volume. (b) Intermolecular forces.

The consideration of the finite molecular volumes leads therefore to a gas equation of the form: $P(V - b) = RT$. A second correction to the perfect gas formula comes from consideration of the forces of cohesion between the molecules. We recall that the thermodynamic definition of the ideal gas includes the requirement that $(\partial E/\partial V)_T = 0$. If this condition is not fulfilled, when the gas is expanded work must be done against the cohesive forces between the molecules. The way in which these attractive forces enter into the gas equation may be seen by considering Fig. 7.3. (b). The molecules completely surrounded by other gas molecules are in a uniform field of force, whereas the molecules near to or colliding with the container walls experience a net inward pull towards the body of the gas. This tends to decrease the pressure compared to that which would be exerted by molecules in the absence of such attractive forces.

The total inward pull is proportional to the number of surface-layer molecules being pulled, and to the number of molecules in the inner layer of the gas that are doing the pulling. Both factors are proportional to the density of the gas, giving a pull proportional to ρ^2, or equal to $c\rho^2$, where c is a constant. Since the density is inversely proportional to the volume at any given pressure and temperature, the pull may also be written a/V^2. This amount must therefore be added to the pressure to make up for the effect of the attractive forces. Then,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{7.13}$$

This is the famous equation of state first given by van der Waals in 1873. It provides a good representation of the behavior of gases at moderate densities, but deviations become very appreciable at higher densities. The values of the constants a and b are obtained from the experimental PVT data at moderate densities, or more usually from the critical constants of the gas. Some of these values were collected in Table 1.1 on p. 14.

Equation (7.13) may also be written in the form

$$PV = RT + bP - \frac{a}{V} + \frac{ab}{V^2} \tag{7.14}$$

The way in which this equation serves to interpret PV vs. P data may be seen from an examination of the compressibility factor curves at different temperatures, shown in Fig. 1.5 (p. 15). At sufficiently high temperatures the intermolecular potential energy, which is not temperature dependent, becomes negligible compared to the kinetic energy of the molecules, which increases with temperature. Then the equation reduces to $PV = RT + bP$. At lower temperatures, the effect of intermolecular forces becomes more appreciable. Then, at moderate pressures the $-a/V$ term becomes important, and there are corresponding declines in the PV vs. P curves. At still higher pressures, however, the term $+ab/V^2$ predominates, and the curves eventually rise again.

10. Collisions between molecules. Now that the oversimplification that the molecules of a gas occupy no volume themselves has been abandoned, it is possible to consider further the phenomena that depend on collisions between the molecules. Let us suppose that all the molecules have a diameter d, and consider as in Fig. 7.4 the approach of a molecule A toward another molecule B.

A "collision" occurs whenever the distance between their centers becomes as small as d. Let us imagine the center of A to be surrounded by a sphere of *radius d.* A collision occurs whenever the *center* of another molecule comes within this sphere. If A is traveling with the average speed $\bar{c}$, its "sphere of influence" sweeps out in unit time a volume $\pi d^2\bar{c}$. Since this volume contains n molecules per cc, there are $\pi n d^2 \bar{c}$ collisions experienced by A per second.

A more exact calculation takes into consideration that only the speed of a molecule *relative* to other moving molecules determines the number of collisions Z_1 that it experiences. This fact leads to the expression

$$Z_1 = \sqrt{2}\pi n d^2 \bar{c} \tag{7.15}$$

The origin of the $\sqrt{2}$ factor may be seen by considering, in Fig. 7.5, the relative velocities of two molecules just before or just after a collision. The limiting cases are the head-on collision and the grazing collision. The average case appears to be the 90° collision, after which the magnitude of the relative velocity is $\sqrt{2}\bar{c}$.

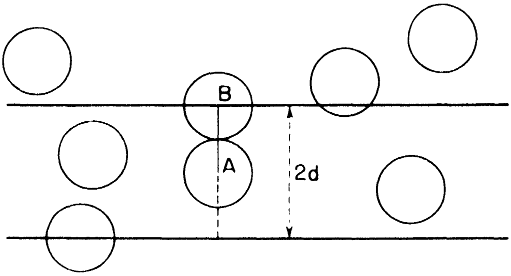


Fig. 7.4. Molecular collisions.

If we now examine the similar motions of all the molecules, the total number of collisions per second of all the n molecules contained in one cc of gas is found, from eq. (7.15), to be

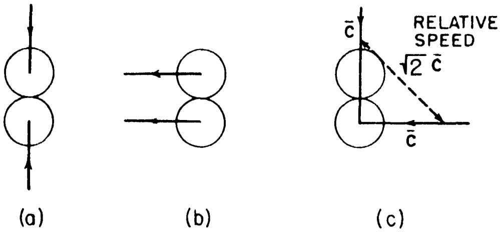


Fig. 7.5. Relative speeds. (a) Head-on collision. (b) Grazing collision. (c) Right-angle collision.

$$Z_{11} = \tfrac{1}{2}\sqrt{2}\pi n^2 d^2 \bar{c} \tag{7.16}$$

The factor $\frac{1}{2}$ is introduced so that each collision is not counted twice (once as A hits B, and once as B hits A).

11. Mean free paths. An important quantity in kinetic theory is the average distance a molecule travels between collisions. This is called the *mean free path.* The average number of collisions experienced by one molecule in one second is, from eq. (7.15), $Z_1 = \sqrt{2}\pi n d^2 \bar{c}$. In this time the molecule has traveled a distance $\bar{c}$. The mean free path λ is therefore $\bar{c}/Z_1$, or

$$\lambda = \frac{1}{\sqrt{2}\pi n d^2} \tag{7.17}$$

In order to calculate the mean free path, we must know the molecular diameter d. This might be obtained, for example, from the van der Waals b ($= 4V_m$) if the value of Avogadro's Number N were known. So far, our development of kinetic theory has provided no method for obtaining this number. The theory of gas viscosity as developed by James Clerk Maxwell presents a key to this problem, besides affording one of the most striking demonstrations of the powers of the kinetic theory of gases.

12. The viscosity of a gas. The concept of viscosity is first met in problems of fluid flow, treated by hydrodynamics and aerodynamics, as a measure of the frictional resistance that a fluid in motion offers to an applied shearing force. The nature of this resistance may be seen from Fig. 7.6 (a). If a fluid is flowing past a stationary plane surface, the layer of fluid adjacent to the plane boundary is stagnant; successive layers have increasingly higher velocities. The frictional force f, resisting the relative motion of any two adjacent layers, is proportional to S, the area of the interface between them, and to dv/dr, the velocity gradient between them. This is Newton's Law of Viscous Flow,

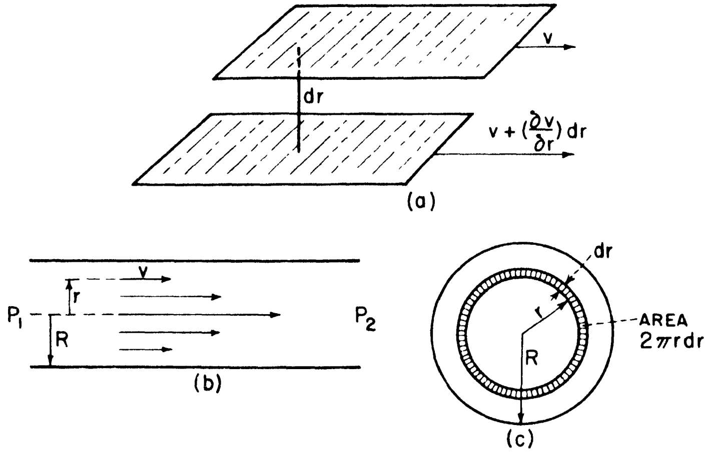


Fig. 7.6. Viscosity of fluids.

$$f = \eta S \frac{dv}{dr} \tag{7.18}$$

The proportionality constant η is called the *coefficient of viscosity*. It is evident that the dimensions of η are $ml^{-1}t^{-1}$. In the CGS system, the unit is g per cm sec, called the *poise*.

The kind of flow governed by this relationship is called *laminar* or *streamline* flow. It is evidently quite different in character from the effusive (or diffusive) flow previously discussed, since it is a massive flow of fluid, in which there is superimposed on all the random molecular velocities a component of velocity in the direction of flow.

An especially important case of viscous flow is the flow through pipes or tubes when the diameter of the tube is large compared with the mean free path in the fluid. The study of flow through tubes has been the basis for many of the experimental determinations of the viscosity coefficient. The theory of the process was first worked out by J. L. Poiseuille, in 1844.

Consider an incompressible fluid flowing through a tube of circular cross section with radius R and length L. The fluid at the walls of the tube is assumed to be stagnant, and the rate of flow increases to a maximum at the center of the tube [see Fig. 7.6 (b)]. Let v be the linear velocity at any distance r from the axis of the tube. A cylinder of fluid of radius r experiences a viscous drag given by eq. (7.18) as

$$\overleftarrow{f_r} = -\eta \frac{dv}{dr} \cdot 2\pi r L$$

For steady flow, this force must be exactly balanced by the force driving the fluid in this cylinder through the tube. Since pressure is the force per unit area, the driving force is

$$\overrightarrow{f_r} = \pi r^2 (P_1 - P_2)$$

where P_1 is the fore pressure and P_2 the back pressure.

Thus, for steady flow,
$$\overrightarrow{f_r} = \overleftarrow{f_r}$$

$$-\eta \frac{dv}{dr} \cdot 2\pi r L = \pi r^2 (P_1 - P_2)$$

$$dv = -\frac{r}{2\eta L}(P_1 - P_2)\, dr$$

On integration,
$$v = -\frac{(P_1 - P_2)}{4\eta L} r^2 + \text{const}$$

According to our hypothesis, $v = 0$ when $r = R$; this boundary condition enables us to determine the integration constant, so that we obtain finally

$$v = \frac{P_1 - P_2}{4L\eta}(R^2 - r^2)$$

The total volume of fluid flowing through the tube per second is calculated by integrating over each element of cross-sectional area, given by $2\pi r\, dr$ [see Fig. 7.6 (c)]. Thus

$$\frac{dV}{dt} = \int_0^R 2\pi r v\, dr = \frac{\pi(P_1 - P_2)R^4}{8L\eta} \tag{7.19}$$

This is Poiseuille's equation. It was derived for an incompressible fluid and therefore may be satisfactorily applied to liquids but not to gases. For gases, the volume is a strong function of the pressure. The average pressure along the tube is $(P_1 + P_2)/2$. If P_0 is the pressure at which the volume is measured, the equation becomes

$$\frac{dV}{dt} = \frac{\pi(P_1 - P_2)R^4}{8L\eta} \cdot \frac{P_1 + P_2}{2P_0} = \frac{\pi(P_1^2 - P_2^2)R^4}{16L\eta P_0} \tag{7.20}$$

By measuring the volume rate of flow through a tube of known dimensions, the viscosity η of the gas can be determined. Some results of such measurements are collected in Table 7.4.

TABLE 7.4

TRANSPORT PHENOMENA IN GASES

(At 0°C and 1 atm)

Gas	Mean Free Path λ, Å	Viscosity η, Poise $\times 10^{-6}$	Thermal Conductivity κ, cal/g sec °C $\times 10^{-6}$	Specific Heat, c_v cal/g	$\eta c_v/\kappa$
Ammonia	441	97.6	51.3	0.399	0.76
Argon	635	213	38.8	0.0750	0.41
Carbon dioxide	397	138	34.3	0.153	0.62
Carbon monoxide	584	168	56.3	0.177	0.53
Chlorine	287	123	18.3	0.0818	0.55
Ethylene	345	93.3	40.7	0.286	0.66
Helium	1798	190	336	0.743	0.42
Hydrogen	1123	84.2	406	2.40	0.50
Nitrogen	600	167	58.0	0.176	0.51
Oxygen	647	192	58.9	0.155	0.51

13. Kinetic theory of gas viscosity. The kinetic picture of gas viscosity has been represented by the following analogy: Two railroad trains are moving in the same direction, but at different speeds, on parallel tracks. The passengers on these trains amuse themselves by jumping back and forth from one to the other. When a passenger jumps from the more rapidly moving train to the slower one he transports momentum of amount *mv*, where *m* is his mass and *v* the velocity of his train. He tends to speed up the more slowly moving train when he lands upon it. A passenger who jumps from the slower to the faster train, on the other hand, tends to slow it down. The net result of the jumping game is thus a tendency to equalize the velocities of the two trains. An observer from afar who could not see the jumpers might simply note this result as a frictional drag between the trains.

The mechanism by which one layer of flowing gas exerts a viscous drag on an adjacent layer is exactly similar, the gas molecules taking the role of the playful passengers. Consider in Fig. 7.7 a gas in a state of laminar flow parallel to the Y axis. Its velocity increases from zero at the plane $x = 0$ to larger and larger values of v with increasing x. If a molecule at P crosses to Q, in one of its free paths between collisions, it will bring to Q, on the average, an amount of momentum which is less than that common to the position Q by virtue of its distance along the X axis. Conversely, if a molecule travels from Q to P it will transport to the lower, more slowly moving layer, an amount of momentum in excess of that belonging to that layer. The net result of the random thermal motions of the molecules is to decrease the average velocities of the molecules in the layer at Q and to increase those in the layer at P. This transport of momentum tends to counteract the velocity gradient set up by the shear forces acting on the gas.

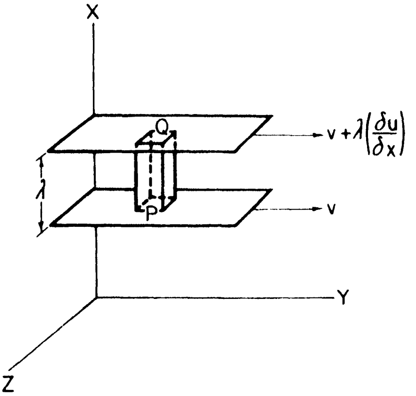


Fig. 7.7. Kinetic theory of gas viscosity.

The length of the mean free path λ may be taken as the average distance over which momentum is transferred.[8] If the velocity gradient is du/dx, the difference in velocity between the two ends of the free path is $\lambda\, du/dx$. A molecule of mass m, passing from the upper to the lower layer, thus transports momentum equal to $m\lambda\, du/dx$. On the average, one-third of the molecules are moving up and down; if n is the number of molecules per cc and $\bar{c}$ their average speed, the number traveling up and down per second per square cm is $\frac{1}{3}\, n\bar{c}$. The momentum transport per second is then $\frac{1}{3}n\bar{c} \cdot m\lambda(du/dx)$.[9]

This momentum change with time is equivalent to the frictional force of eq. (7.18) which was $f = \eta(du/dx)$ per unit area. Hence

$$\eta \frac{du}{dx} = \tfrac{1}{3}nm\bar{c}\lambda \frac{du}{dx}$$

$$\eta = \tfrac{1}{3}nm\bar{c}\lambda = \tfrac{1}{3}\rho\bar{c}\lambda \tag{7.21}$$

The measurement of the viscosity thus allows us to calculate the value of the mean free path λ. Some values obtained in this way are included in Table 7.4, in Ångstrom units (1 Å = 10^{-8} cm).

---

[8] This is not strictly true, and proper averaging indicates $\frac{2}{3} \cdot \lambda$ should be used.

[9] The factor $\frac{1}{3}$ obtained here results from the cancellation of two errors in the derivation. From eq. (7.9) one should take $\frac{1}{2}n\bar{c}$ as the molecules moving across unit area but proper averaging gives the distance between planes as $\frac{2}{3}\lambda$ instead of λ.

By eliminating λ between eqs. (7.17) and (7.21), one obtains

$$\eta = \frac{m\bar{c}}{3\sqrt{2}\pi d^2} \tag{7.22}$$

This equation indicates that the viscosity of a gas is independent of its density. This seemingly improbable result was predicted by Maxwell on purely theoretical grounds, and its subsequent experimental verification was one of the great triumphs of the kinetic theory. The physical reason for the result is clear from the preceding derivation: At lower densities, fewer molecules jump from layer to layer in the flowing gas, but, because of the longer free paths, each jump carries proportionately greater momentum. For imperfect gases, the equation fails and the viscosity increases with density.

The second important conclusion from eq. (7.22) is that the viscosity of a gas increases with increasing temperature, linearly with the $\sqrt{T}$. This conclusion has been well confirmed by the experimental results, although the viscosity increases somewhat more rapidly than predicted by the $\sqrt{T}$ law.

14. Thermal conductivity and diffusion. Gas viscosity depends on the transport of momentum across a momentum (velocity) gradient. It is a typical *transport phenomenon.* An exactly similar theoretical treatment is applicable to thermal conductivity and to diffusion. The thermal conductivity of gases is a consequence of the transport of kinetic energy across a temperature (*i.e.*, kinetic energy) gradient. Diffusion of gases is the transport of mass across a concentration gradient.

The thermal conductivity coefficient κ is defined as the heat flow per unit time $\dot{q}$, per unit temperature gradient across unit cross-sectional area, *i.e.*, by

$$\dot{q} = \kappa \cdot S \cdot \frac{dT}{dx}$$

By comparison with eq. (7.21),

$$\kappa \frac{dT}{dx} = \frac{1}{3} n\bar{c}\lambda \frac{d\varepsilon}{dx}$$

where $d\varepsilon/dx$ is the gradient of ε, the average kinetic energy per molecule. Now

$$\frac{d\varepsilon}{dx} = \frac{dT}{dx} \cdot \frac{d\varepsilon}{dT} \quad \text{and} \quad \frac{d\varepsilon}{dT} = mc_v,$$

where m is the molecular mass and c_v is the specific heat (heat capacity per gram). It follows that

$$\kappa = \tfrac{1}{3} nmc_v\bar{c}\lambda = \tfrac{1}{3}\rho c_v\bar{c}\lambda = \eta c_v \tag{7.23}$$

Some thermal conductivity coefficients are included in Table 7.4. It should be emphasized that, even for an ideal gas, the simple theory is approximate, since it assumes that all the molecules are moving with the same speed, $\bar{c}$, and that energy is exchanged completely at each collision.

The treatment of diffusion is again similar. Generally one deals with the diffusion in a mixture of two different gases. The diffusion coefficient D is the number of molecules per second crossing unit area under unit concentration gradient. It is found to be[10]

$$D = \tfrac{1}{3}\lambda_1\bar{c}_1X_2 + \tfrac{1}{3}\lambda_2\bar{c}_2X_1$$

where X_1 and X_2 are the mole fractions of the two gases in the mixture. If the two kinds of molecules are essentially the same, for example radioactive chlorine in normal chlorine, the *self-diffusion coefficient* is obtained as

$$D = \tfrac{1}{3}\lambda\bar{c} \tag{7.24}$$

The results of the simple mean-free-path treatments of the transport processes may be summarized as follows:

Process	Transport of	Simple Theoretical Expression	CGS Units of Coefficient
Viscosity . . .	Momentum mv	$\eta = \frac{1}{3}\rho\bar{c}\lambda$	g/cm sec
Thermal conductivity .	Kinetic energy $\frac{1}{2}mv^2$	$\kappa = \frac{1}{3}\rho\bar{c}\lambda c_v$	ergs/cm sec degree
Diffusion . . .	Mass m	$D = \frac{1}{3}\lambda\bar{c}$	cm²/sec

15. Avogadro's number and molecular dimensions. Equation (7.22) may be written, from eq. (7.8),

$$\eta = \frac{M\bar{c}}{3\sqrt{2}N\pi d^2} = \frac{2\sqrt{RTM}}{3\pi^{3/2}Nd^2}$$

Now van der Waals' b is given by

$$b = 4Nv_M = 4N \cdot \pi\frac{d^3}{6} = \frac{2}{3}\pi Nd^3 \tag{7.25}$$

Multiplying these two equations, and solving for d,

$$d = \frac{9}{4}\sqrt{\frac{\pi}{RTM}}\,\eta b \tag{7.26}$$

Let us substitute the appropriate values for the hydrogen molecule, H_2, all in CGS units.

$$M = 2.016 \qquad b = 26.6$$
$$\eta = 0.93 \times 10^{-4} \qquad T = 298°\text{K}$$
$$R = 8.314 \times 10^7$$

Solving for d, we find $d = 2.2 \times 10^{-8}$ cm.

---

[10] For example, see E. H. Kennard, *Kinetic Theory of Gases* (New York: McGraw-Hill, 1938), p. 188.

This value may be substituted back into eq. (7.25) to obtain a value for Avogadro's Number N equal to about 10^{24}.

Because of the known approximations involved in the van der Waals formula, this value of N is only approximate. It is nevertheless of the correct order of magnitude, and it is interesting that the value can be obtained purely from kinetic-theory calculations. Later methods, which will be discussed in a subsequent chapter, give the value $N = 6.02 \times 10^{23}$.

We may use this figure to obtain more accurate values for molecular diameters from viscosity or thermal conductivity measurements. Some of these values are shown in Table 7.5, together with values obtained from van der Waals' b, and by the following somewhat different method.

TABLE 7.5

MOLECULAR DIAMETERS

(Ångstrom Units)

Molecule	From Gas Viscosity	From van der Waals' b	From Molecular Refraction*	From Closest Packing
A	2.86	2.86	2.96	3.83
CO	3.80	3.16	—	4.30
CO_2	4.60	3.24	2.86	—
Cl_2	3.70	3.30	3.30	4.65
He	2.00	2.48	1.48	—
H_2	2.18	2.76	1.86	—
Kr	3.18	3.14	3.34	4.02
Hg	3.60	2.38	—	—
Ne	2.34	2.66	—	3.20
N_2	3.16	3.14	2.40	4.00
O_2	2.96	2.90	2.34	3.75
H_2O	2.72	2.88	2.26	—

* The theory of this method is discussed in Section 11-18.

In the solid state the molecules are closely packed together. If we assume that these molecules are spherical in shape, the closest possible packing of spheres leaves a void space of 26 per cent of the total volume. The volume occupied by a mole of molecules is M/ρ, where M is the molecular weight and ρ the density of the solid. For spherical molecules we may therefore write $(\pi/6)Nd^3 = 0.74(M/\rho)$. Values of d obtained from this equation may be expected to be good approximations for the monatomic gases (He, Ne, A, Kr) and for spherical molecules like CH_4, CCl_4. The equation is only roughly applicable to diatomic molecules like N_2 or O_2.

The rather diverse values often obtained for molecular diameters calculated by different methods are indications of the inadequacy of a rigid-sphere model, even for very simple molecules.

The extreme minuteness of the molecules and the tremendous size of the

Avogadro Number N are strikingly shown by two popular illustrations given by Sir James Jeans. If the molecules in a glass of water were turned into grains of sand, there would be enough sand produced to cover the whole United States to a depth of about 100 feet. A man breathes out about 400 cc at each breath, or about 10^{22} molecules. The earth's atmosphere contains about 10^{44} molecules. Thus, one molecule is the same fraction of a breath of air as the breath is of the entire atmosphere. If the last breath of Julius Caesar has become scattered throughout the entire atmosphere, the chances are that we inhale one molecule from it in each breath we take.

16. The softening of the atom. We noted before that the viscosity of a gas increases more rapidly with temperature than is predicted by the $\sqrt{T}$ law. This is because the molecules are not actually hard spheres, but must be regarded as being somewhat soft, or surrounded by fields of force. This is true even for the atom-molecules of the inert gases. The higher the temperature, the faster the molecules are moving, and hence the further one molecule can penetrate into the field of force of another, before it is repelled or bounced away. The molecular diameter thus appears to be smaller at higher temperatures. This correction has been embodied in a formula due to Sutherland (1893)

$$d^2 = d_\infty^2\left(1 + \frac{C}{T}\right) \tag{7.27}$$

Here d_∞ and C are constants, d_∞ being interpreted as the value of d as T approaches infinity.

More recent work has sought to express the temperature coefficient of the viscosity in terms of the laws of force between the molecules. Thus here, just as in the discussion of the equation of state, the qualitative picture of rigid molecules must be modified to consider the fields of force between molecules.

We recall from Chapter 1 that forces may be represented as derivatives of a potential-energy function, $f = -(\partial U/\partial r)$, and a representation of this function serves to illustrate the nature of the forces. In Fig. 7.8 we have drawn the mutual potential energy of pairs of molecules of several different gases. We may imagine the motion of one molecule as it approaches rapidly toward another to be represented by that of a billiard ball rolled with considerable force along a track having the shape of the potential curve. As the molecule approaches another it is accelerated at first, but then slowed down as it reaches the steep ascending portion of the curve. Finally it is brought to a halt when its kinetic energy is completely used up, and it rolls back down and out the curve again. Since the kinetic energy is almost always greater than the depth of the potential-energy trough, there is little chance of a molecule's becoming trapped therein. (If it did, another collision would soon knock it out again.)

This softening of the original kinetic-theory picture of the atom as a hard rigid sphere was of the greatest significance. It immediately suggested that the atoms could not be the ultimate building units in the construction of matter, and that man must seek still further for an indestructible reality to explain the behavior of material things.

So far in this chapter we have dealt with average properties of large collections of molecules: average velocities, mean free paths, viscosity, and so on. In what follows, the contributions of the individual molecules to these averages will be considered in some detail.

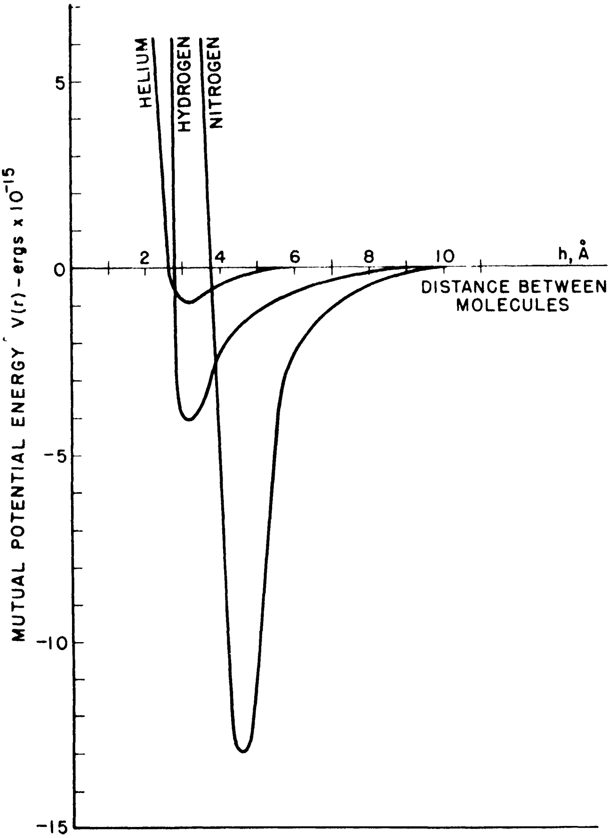


Fig. 7.8. Mutual potential energy of pairs of molecules.

17. The distribution of molecular velocities. The molecules of a gas in their constant motion collide many times with one another, and these collisions provide the mechanism through which the velocities of individual molecules are continually changing. As a result, there exists a distribution of velocities among the molecules; most have velocities with magnitudes close to the average, and relatively few have velocities much above or much below the average.

A molecule may acquire an exceptionally high speed as the result of a series of especially favorable collisions. The theory of probability shows that the chance of a molecule's experiencing a series of n lucky hits is proportional to a factor of the form e^{-an}, where a is a constant.[11] Thus the probability of the molecule's having the energy E above the average energy is likewise proportional to e^{-bE}. The exact derivation of this factor may be carried out in several ways, and the problems involved in the distribution of velocities, and hence of kinetic energies, among the molecules, form one of the most important parts of the kinetic theory.

18. The barometric formula. It is common knowledge that the density of the earth's atmosphere decreases with increasing altitude. If one makes the simplifying assumption that a column of gas extending upward into the atmosphere is at constant temperature, a formula may be derived for this variation of gas pressure in the gravitational field. The situation is pictured in Fig. 7.9.

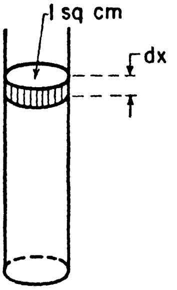


Fig. 7.9. Barometric formula.

The weight of a thin layer of gas of thickness dx and one cm^2 cross section is its mass times the acceleration due to gravity, or $\rho g\ dx$, where ρ is the gas density. The difference in pressure between the upper and lower boundaries of the layer is $(-dP/dx)\,dx$, equal to the weight of the layer of unit cross section. Thus

$$-dP = \rho g\,dx$$

For an ideal gas,

$$\rho = \frac{PM}{RT}$$

Therefore

$$-\frac{dP}{P} = \frac{Mg}{RT}\,dx$$

Integrating between the limits $P = P_0$ at $x = 0$, and $P = P$ at $x = x$,

$$\ln\frac{P}{P_0} = -\frac{Mgx}{RT}$$

$$P = P_0\,e^{-Mgx/RT} \tag{7.28}$$

Now, Mgx is simply the gravitational potential energy at the point x, which may be written as E_p per mole. Then

$$P = P_0\,e^{-E_p/RT} \tag{7.29}$$

If, instead of the molar energy, we consider that of the individual molecule, ε_p, eq. (7.29) becomes

$$P = P_0\,e^{-\varepsilon_p/kT} \tag{7.30}$$

---

[11] If the chance of one lucky hit is $1/c$, the chance P for n in a row is $P = (1/c)^n$. Then

The constant k is called the *Boltzmann constant*. It is the gas constant per molecule.

$$k = \frac{R}{N} = \frac{8.315 \times 10^7 \text{ erg/°C mole}}{6.02 \times 10^{23} \text{ mole}^{-1}} = 1.381 \times 10^{-16} \text{ erg/°C}$$

Equation (7.30) is but one special case of a very general expression derived by L. Boltzmann in 1886. This states that if n_0 is the number of molecules in any given state, the number n in a state whose potential energy is ε above that of the given state is

$$n = n_0 e^{-\varepsilon/kT} \tag{7.31}$$

19. The distribution of kinetic energies.[12] To analyze more closely the kinetic picture underlying the barometric formula, let us consider the individual gas molecules moving with their diverse velocities in the earth's gravitational field. The velocity components parallel to the earth's surface (in the y and z directions along which no field exists) are not now of interest and only the vertical or x component u need be considered.

The motion of a molecule with an upward velocity u is just like that of a ball thrown vertically into the air. If its initial velocity is u_0, it will rise with continuously decreasing speed, as its kinetic energy is transformed into potential energy according to the equation

$$mgx = \tfrac{1}{2}mu_0^2 - \tfrac{1}{2}mu^2$$

At the height, $x = u_0^2/2g$, it will stop, and then fall back to earth.

The gravitational field acts as a device that breaks up the mixture of various molecular velocities into a "spectrum" of velocities. The slowest molecules can rise only a short distance; the faster ones can rise proportionately higher. By determining the number of molecules that can reach any given height, we can likewise determine how many had a given initial velocity component.

As is to be expected from the physical picture of the process, the distribution of kinetic energies ε_K among the molecules must follow an exponential law just as the potential energy distribution does. Representing the fraction of molecules having a velocity between u and $u + du$ by dn/n_0, this law may be written from eq. (7.31) as

$$\frac{dn}{n_0} = Ae^{-\varepsilon_K/kT}\, du \tag{7.32}$$

Here A is a constant whose value is yet to be determined.

20. Consequences of the distribution law. This distribution law is completely unaffected by collisions between molecules, since a collision results only in an interchange of velocity components between two molecules. Expressions exactly similar to eq. (7.32) must also hold for the velocity

---

[12] The method suggested here is given in detail by K. F. Herzfeld in H. S. Taylor's *Treatise on Physical Chemistry*, 2nd ed. (New York: Van Nostrand, 1931), p. 93.

distributions in the y and z directions, since it is necessary only to imagine some sort of potential field in these directions in order to analyze the velocities into their spectrum.

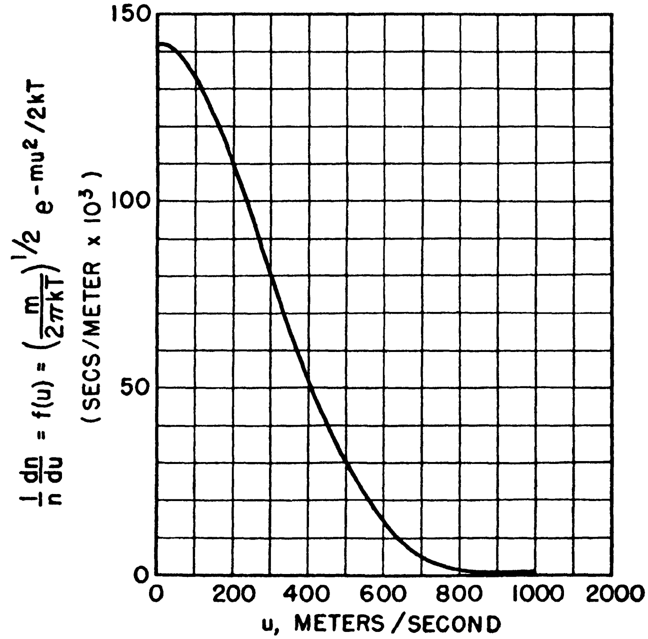


Fig. 7.10. One-dimensional velocity distribution (nitrogen at 0°C).

The constant A, in eq. (7.32), may be evaluated from the fact that the sum of all the *fractions* of molecules in all the velocity ranges must be unity. Thus, integrating over all possible velocities from $-\infty$ to $+\infty$, we have

$$A\int_{-\infty}^{+\infty} e^{-mu^2/2kT}\,du = 1$$

Letting

$$\frac{mu^2}{2kT} = x^2$$

$$A\left(\frac{2kT}{m}\right)^{1/2}\int_{-\infty}^{+\infty} e^{-x^2}\,dx = 1$$

Since

$$\int_{-\infty}^{+\infty} e^{-x^2}\,dx = \pi^{1/2}, \qquad A = \left(\frac{m}{2\pi kT}\right)^{1/2}$$

Therefore, eq. (7.32) becomes

$$\frac{dn}{n_0} = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mu^2/2kT}\,du \tag{7.33}$$

This function is shown plotted in Fig. 7.10. It will be noted that the fraction of the molecules with a velocity component in a given range declines at first slowly and then rapidly as the velocity is increased. From the curve and from a consideration of eq. (7.33), it is evident that as long as $\frac{1}{2}mu^2 < kT$ the fraction of molecules having a velocity u falls off slowly with increasing u. When $\frac{1}{2}mu^2 = 10kT$, the fraction has decreased to e^{-10}, or 5×10^{-5} times its value at $\frac{1}{2}mu^2 = kT$. Thus only a very small proportion of any lot of molecules can have kinetic energies much greater than kT per degree of freedom.

If, instead of a one-dimensional gas (one degree of freedom of translation), a two-dimensional gas is considered, it can be proved[13] that the probability of a molecule having a given x velocity component u in no way depends on the value of its y component v. The fraction of the molecules having simultaneously velocity components between u and $u + du$, and v and $v + dv$, is then simply the product of the two individual probabilities.

$$\frac{dn}{n_0} = \left(\frac{m}{2\pi kT}\right) e^{-\frac{1}{2}m(u^2+v^2)/kT}\, du\, dv \tag{7.34}$$

This sort of distribution may be graphically represented as in Fig. 7.11, where a coordinate system with u and v axes has been drawn. Any point in the (u, v) plane represents a simultaneous value of u and v; the plane is a two-dimensional velocity space similar to that used on p. 168. The dots have been drawn so as to represent schematically the density of points in this space, *i.e.*, the relative frequency of occurrence of sets of simultaneous values of u and v.

The graph bears a striking resemblance to a target that has been peppered with shots by a marksman aiming at the bull's-eye. In the molecular case, each individual molecular-velocity component, u or v, aims at the value zero. The resulting distribution represents the statistical summary of the results. The more skilful the marksman, the more closely will his results cluster around the center of the target. For the molecules, the skill of the marksman has its analogue in the temperature of the gas. The lower the temperature, the better the chance a molecular-velocity component has of coming close to zero.

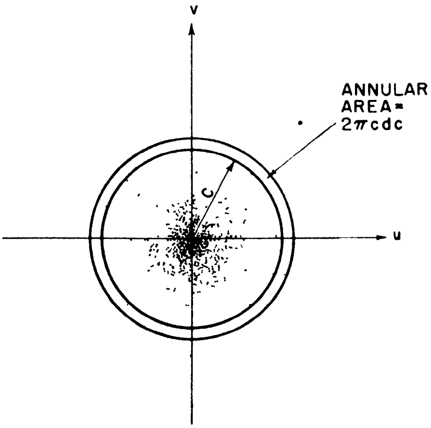


Fig. 7.11. Distribution of points in two-dimensional velocity space: $v_x = u;\ v_y = v$.

If, instead of the individual components u and v, the resultant speed c is considered, where $c^2 = u^2 + v^2$, it is evident that its most probable value is not zero. This is because the number of ways in which c can be made up

---

[13] For a discussion of this theorem see, for example, J. Jeans, *Introduction to the Kinetic Theory of Gases* (London: Cambridge, 1940), p. 105.

from u and v increases in direct proportion with c, whereas at first the probability of any value of u or v declines rather slowly with increasing velocity.

From Fig. 7.11, it appears that the distribution of c, regardless of direction, is obtainable by integrating over the annular area between c and $c + dc$, which is $2\pi c\, dc$. The required fraction is then

$$\frac{dn}{n_0} = \frac{m}{kT} e^{-mc^2/2kT} c\, dc \tag{7.35}$$

21. Distribution law in three dimensions. The three-dimensional distribution law may now be obtained by a simple extension of this treatment. The fraction of molecules having simultaneously a velocity component between u and $u + du$, v and $v + dv$, and w and $w + dw$, is

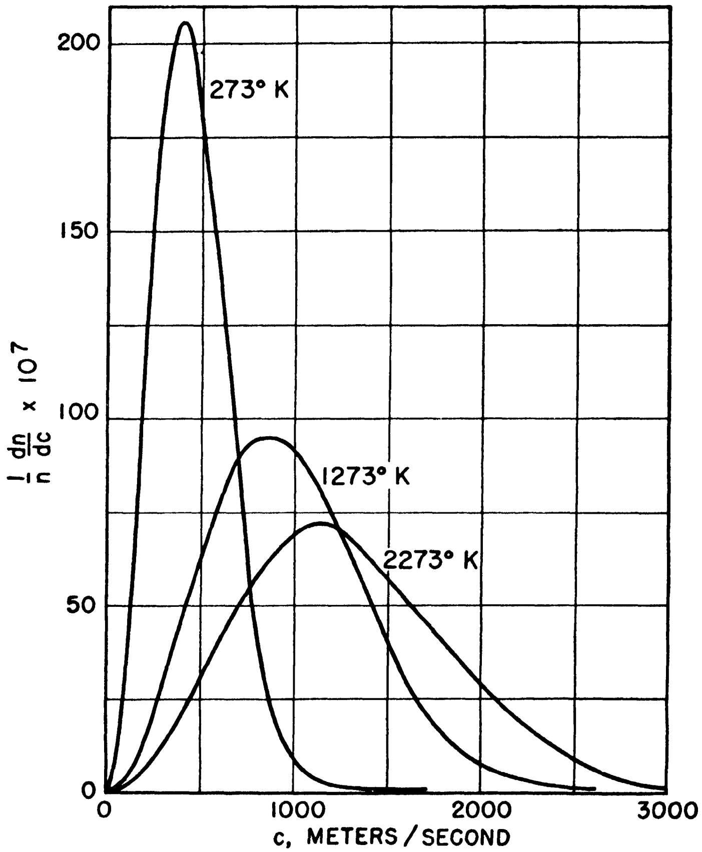


Fig. 7.12. Distribution of molecular speeds (nitrogen).

$$\frac{dn}{n_0} = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-m(u^2+v^2+w^2)/2kT}\, du\, dv\, dw \tag{7.36}$$

We wish an expression for the number with a speed between c and $c + dc$, regardless of direction, where $c^2 = u^2 + v^2 + w^2$.

These are the molecules whose velocity points lie within a spherical shell of thickness dc at a distance c from the origin. The volume of this shell is $4\pi c^2 dc$, and therefore the desired distribution function is

$$\frac{dn}{n_0} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} e^{\quad mc^2/2kT} c^2 \, dc \tag{7.37}$$

This is the usual expression of the distribution equation derived by James Clerk Maxwell in 1860.

The equation is plotted in Fig. 7.12 at several different temperatures, showing how the curve becomes broader and less peaked at the higher temperatures, as relatively more molecules acquire kinetic energies greater than the average of $\frac{3}{2}kT$.

22. The average speed. The average value $\bar{r}$ of any property r of the molecules is obtained by multiplying each value of r, r_i, by the number of molecules n_i having this value, adding these products, and then dividing by the total number of molecules. Thus

$$\bar{r} = \frac{\sum n_i r_i}{\sum n_i} = \frac{1}{n_0} \sum n_i r_i \tag{7.38}$$

where $\sum n_i = n_0$ is the total number of molecules.

In case n is known as a continuously varying function of r, $n(r)$, instead of the summations of eq. (7.38) we have the integrations

$$\bar{r} = \frac{\int_0^\infty r \, dn(r)}{\int_0^\infty dn(r)} = \frac{1}{n_0} \int_0^\infty r \, dn(r) \tag{7.39}$$

This formula may be illustrated by the calculation of the average molecular speed $\bar{c}$. Using eq. (7.37), we have

$$\bar{c} = \frac{1}{n_0} \int_0^\infty c \, dn = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty e^{-mc^2/2kT} c^3 \, dc$$

The evaluation of this integral can be obtained[14] from

$$\int_0^\infty e^{-ax^2} x^3 \, dx = \frac{1}{2a^2}$$

Making the appropriate substitutions, we find

$$\bar{c} = \left(\frac{8kT}{\pi m}\right)^{1/2} \tag{7.40}$$

[14] Letting $x^2 = z$,

$$\int_0^\infty e^{-ax^2} x \, dx = \frac{1}{2} \int_0^\infty e^{\quad az} \, dz = \frac{1}{2} \left(\frac{e^{-az}}{-a}\right)_0^\infty = \frac{1}{2a}$$

Then,

$$\int_0^\infty e^{-ax^2} x^3 \, dx = -\frac{d}{da} \int_0^\infty e^{-ax^2} x \, dx = \frac{1}{2a^2}$$

Similarly, the average kinetic energy can readily be evaluated as

$$\tfrac{1}{2}m\overline{c^2} = \frac{m}{2n_0}\int_0^\infty c^2\,dn$$

This yields

$$\tfrac{1}{2}(\overline{mc^2}) = \tfrac{3}{2}kT \tag{7.41}$$

23. The equipartition of energy. Equation (7.41) gives the average translational kinetic energy of a molecule in a gas. It will be noted that the average energy is independent of the mass of the molecule. Per mole of gas,

$$E_{K\,(\text{trans})} = \tfrac{3}{2}NkT = \tfrac{3}{2}RT \tag{7.42}$$

For a monatomic gas, like helium, argon, or mercury vapor, this translational kinetic energy is the total kinetic energy of the gas. For diatomic gases, like N_2 or Cl_2, and polyatomic gases, like CH_4 or N_2O, there may also be energy associated with rotational and vibrational motions.

A useful model for a molecule is obtained by supposing that the masses of the constituent atoms are concentrated at points. As will be seen in Chapter 9, almost all the atomic mass is in fact concentrated in a tiny nucleus, the radius of which is about 10^{-13} cm. Since the over-all dimensions of molecules are of the order of 10^{-8} cm, a model based on point masses is physically most reasonable. Consider a molecule composed of n atoms. In order to represent the instantaneous locations in space of n mass points, we should require $3n$ coordinates. The number of coordinates required to locate all the mass points (atoms) in a molecule is called the number of its *degrees of freedom*. Thus a molecule of n atoms has $3n$ degrees of freedom.

The atoms within each molecule move through space as a connected entity, and we can represent the translational motion of the molecule as a whole by the motion of the *center of mass* of its constituent atoms. Three coordinates (degrees of freedom) are required to represent the instantaneous position of the center of mass. The remaining $(3n - 3)$ coordinates represent the so-called *internal degrees of freedom*.

The internal degrees of freedom may be further subdivided into *rotations* and *vibrations*. Since the molecule has moments of inertia I about suitably chosen axes, it can be set into rotation about these axes. If its angular velocity about an axis is ω, the rotational kinetic energy is $\frac{1}{2}I\omega^2$. The vibratory motion, in which one atom in a molecule oscillates about an equilibrium separation from another, is associated with both kinetic and potential energies, being in this respect exactly like the vibration of an ordinary spring. The vibrational kinetic energy is also represented by a quadratic expression, $\frac{1}{2}mv^2$. The vibrational potential energy can in some cases be represented also by a quadratic expression, but in the coordinates q rather than in the velocities, for example, $\frac{1}{2}\kappa q^2$. Each vibrational degree of freedom would then contribute two quadratic terms to the total energy of the molecule.

By an extension of the derivation leading to eq. (7.41), it can be shown that each of these quadratic terms that comprise the total energy of the molecule has an average value of $\frac{1}{2}kT$. This conclusion, a direct consequence of the Maxwell-Boltzmann distribution law, is the most general expression of the Principle of Equipartition of Energy.

24. Rotation and vibration of diatomic molecules. The rotation of a diatomic molecule may be visualized by reference to the so-called dumbbell model in Fig. 7.13, which might represent a molecule such as H_2, N_2, HCl,

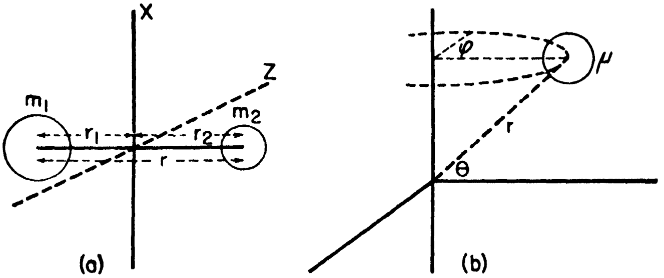


Fig. 7.13. Dumbbell rotator.

or CO. The masses of the atoms, m_1 and m_2, are concentrated at points, distant r_1 and r_2, respectively, from the center of mass. The molecule therefore has moments of inertia about the X and Z axes, but not about the Y axis on which the mass points lie.

The energy of rotation of a rigid body is given by

$$E_{\text{rot}} = \tfrac{1}{2}I\omega^2 \tag{7.43}$$

where ω is the angular velocity of rotation, and I is the moment of inertia. For the dumbbell model, $I = m_1r_1^2 + m_2r_2^2$.

The distances r_1 and r_2 from the center of mass are

$$r_1 = \frac{m_2}{m_1 + m_2}\,r, \qquad r_2 = \frac{m_1}{m_1 + m_2}\,r$$

Thus

$$I = \frac{m_1m_2}{m_1 + m_2}\,r^2 = \mu r^2 \tag{7.44}$$

The quantity

$$\mu = \frac{m_1m_2}{m_1 + m_2} \tag{7.45}$$

is called the *reduced mass* of the molecule. The rotational motion is equivalent to that of a mass μ at a distance r from the intersection of the axes.

Only two coordinates are required to describe such a rotation completely; for example, two angles θ and ϕ suffice to fix the orientation of the rotator in space. There are thus two degrees of freedom for the rotation of a dumbbell-like structure. According to the principle of the equipartition of energy, the average rotational energy should therefore be $\bar{E}_{\text{rot}} = 2N(\frac{1}{2}kT) = RT$.

The simplest model for a vibrating diatomic molecule (Fig. 7.14) is the harmonic oscillator. From mechanics we know that simple harmonic motion occurs when a particle is acted on by a restoring force directly proportional to its distance from the equilibrium position. Thus

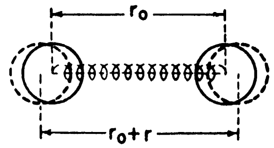


Fig. 7.14. Harmonic oscillator.

$$f = -\kappa r = m\frac{d^2r}{dt^2} \tag{7.46}$$

The constant κ is called the *force constant.* The motion of a particle under the influence of such a restoring force may be represented by a potential energy function $U(r)$.

$$f = -\left(\frac{\partial U}{\partial r}\right) = -\kappa r$$

$$U(r) = \tfrac{1}{2}\kappa r^2 \tag{7.47}$$

This is the equation of a parabola and the potential-energy curve is drawn in Fig. 7.15. The motion of the particle, as has been pointed out in previous cases, is analogous to that of a ball moving on such a surface. Starting from rest at any position r, it has only potential energy, $U = \frac{1}{2}\kappa r^2$. As it rolls down the surface, it gains kinetic energy up to a maximum at position $r = 0$, the equilibrium interatomic distance. The kinetic energy is then reconverted to potential energy as the ball rolls up the other side of the incline. The total energy at any time is always a constant,

$$E_{\text{vib}} = \tfrac{1}{2}m\left(\frac{dr}{dt}\right)^2 + \tfrac{1}{2}\kappa r^2$$

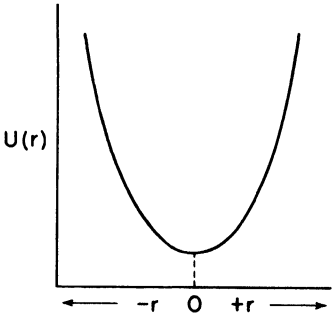


Fig. 7.15. Potential curve of harmonic oscillator.

It is apparent, therefore, that vibrating molecules when heated can take up energy as both potential and kinetic energy of vibration. The equipartition principle states that the average energy for each vibrational degree of freedom is therefore kT, $\frac{1}{2}kT$ for the kinetic energy plus $\frac{1}{2}kT$ for the potential energy.

For a diatomic molecule the total average energy per mole therefore becomes

$$E = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} = \tfrac{3}{2}RT + RT + RT = \tfrac{7}{2}RT$$

25. Motions of polyatomic molecules. The motions of polyatomic molecules can also be represented by the simple mechanical models of the rigid rotator and the harmonic oscillator. If the molecule contains n atoms, there are $(3n - 3)$ internal degrees of freedom. In the case of the diatomic molecule, $3n - 3 = 3$. Two of the three internal coordinates are required to represent the rotation, leaving one vibrational coordinate.

In the case of a triatomic molecule, $3n - 3 = 6$. In order to divide these six internal degrees of freedom into rotations and vibrations, we must first consider whether the molecule is linear or bent. If it is linear, all the atomic mass points lie on one axis, and there is therefore no moment of inertia about this axis. A linear molecule behaves like a diatomic molecule in regard to rotation, and there are only two rotational degrees of freedom. For a linear triatomic molecule, there are thus $3n - 3 - 2 = 4$ vibrational degrees of freedom. The average energy of the molecules according to the Equipartition Principle would therefore be

$$\begin{aligned} E &= E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} \\ &= 3(\tfrac{1}{2}RT) + 2(\tfrac{1}{2}RT) + 4(RT) = 6\tfrac{1}{2}RT \text{ per mole} \end{aligned}$$

A nonlinear (bent) triatomic molecule has three principal moments of inertia, and therefore three rotational degrees of freedom. Any nonlinear polatomic molecule has $3n - 6$ vibrational degrees of freedom. For the triatomic case, there are therefore three vibrational degrees of freedom. The average energy according to the Equipartition Principle would be

$$\begin{aligned} E &= 3(\tfrac{1}{2}RT) + 3(\tfrac{1}{2}RT) + 3(RT) \\ &= 6RT \text{ per mole} \end{aligned}$$

Examples of linear triatomic molecules are HCN, CO_2, and CS_2. Bent triatomic molecules include H_2O and SO_2.

The vibratory motion of a collection of mass points bound together by linear restoring forces [*i.e.*, a polyatomic molecule in which the individual atomic displacements obey eq. (7.46)] may be quite complicated. It is always possible, however, to represent the complex vibratory motion by means of a number of simple motions, the so-called *normal modes of vibration*. In a normal mode of vibration, each atom in the molecule is oscillating with the same frequency. Examples of the normal modes for linear and bent triatomic molecules are shown in Fig. 7.16. The bent molecule has three distinct normal modes, each with a characteristic frequency. The frequencies of course have different numerical values in different compounds. In the case of the linear molecule, there are four normal modes; two correspond to stretching of the molecule (ν_1, ν_3) and two correspond to bending (ν_{2a}, ν_{2b}). The two bending vibrations differ only in that one is in the plane of the paper and one normal to the plane (denoted by $+$ and $-$). These vibrations have the same frequency, and are called *degenerate vibrations*.

When we described the translational motions of molecules and their consequences for the kinetic theory of gases, it was desirable at first to employ a very simplified model. The same procedure has been followed in this discussion of the internal molecular motions. Thus diatomic molecules do not really behave as rigid rotators, since, at rapid rotation speeds, centrifugal force tends to separate the atoms by stretching the bond between them.

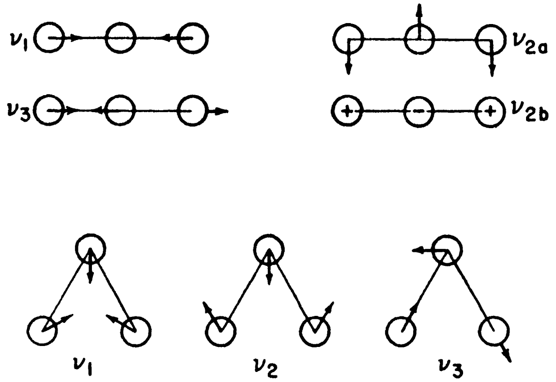


Fig. 7.16. Normal modes of vibration of triatomic molecules.

Likewise, a more detailed theory shows that the vibrations of the atoms are not strictly harmonic.

26. The equipartition principle and the heat capacity of gases. According to the equipartition principle, a gas on warming should take up energy in all its degrees of freedom, $\frac{1}{2}RT$ per mole for each translational or rotational coordinate, and RT per mole for each vibration. The heat capacity at constant volume, $C_V = (\partial E/\partial T)_V$, could then be readily calculated from the average energy.

From eq. (7.42) the translational contribution to C_V is $(\frac{3}{2})R$. Since $R = 1.986$ cal per degree C, the molar heat capacity is 2.98 cal per degree C. When this figure is compared with the experimental values in Table 7.6, it is found to be confirmed for the monatomic gases, He, Ne, A, Hg, which

TABLE 7.6

MOLAR HEAT CAPACITY C_V OF GASES

Gas	Temperature (°C)				
	−100	0	100	400	600
He, Ne, A, Hg .	2.98	2.98	2.98	2.98	2.98
H_2 . . .	4.18	4.92	4.97	4.99	5.00
N_2 . . .	4.95	4.95	4.96	5.30	5.42
O_2 . . .	4.98	5.00	5.15	5.85	6.19
Cl_2 . . .	—	5.85	5.88	6.24	6.40
H_2O . .	—	—	6.37	6.82	7.60
CO_2 . . .	—	6.75	7.68	9.86	10.90

have no internal degrees of freedom. The observed heat capacities of the diatomic and polyatomic gases are always higher, and increase with temperature, so that it may be surmised that rotational and vibrational contributions are occurring.

For a diatomic gas, the equipartition principle predicts an average energy of $(\frac{7}{2})RT$, or $C_V = (\frac{7}{2})R = 6.93$. This value seems to be approached at high temperatures for H_2, N_2, O_2, and Cl_2, but at lower temperatures the experimental C_V values fall much below the theoretical ones. For polyatomic gases, the discrepancy with the simple theory is even more marked. The equipartition principle cannot explain why the observed C_V is less than predicted, why C_V increases with temperature, nor why the C_V values differ for the different diatomic gases. The theory is thus satisfactory for translational motion, but most unsatisfactory when applied to rotation and vibration.

Since the equipartition principle is a direct consequence of the kinetic theory, and in particular of the Maxwell-Boltzmann distribution law, it is evident that an entirely new basic theory will be required to cope with the heat capacity problem. Such a development is found in the quantum theory introduced in Chapter 10.

27. Brownian motion. In 1827, shortly after the invention of the achromatic lens, the botanist Robert Brown[15] studied pollen grains under his microscope and watched a curious behavior.

> While examining the form of these particles immersed in water, I observed many of them very evidently in motion; their motion consisting not only of a change of place in the fluid, manifested by alterations of their relative positions, but also not infrequently of a change in form of the particle itself; a contraction or curvature taking place repeatedly about the middle of one side, accompanied by a corresponding swelling or convexity on the opposite side of the particle. In a few instances the particle was seen to turn on its longer axis. These motions were such as to satisfy me, after frequently repeated observations, that they arose neither from currents in the fluid, nor from its gradual evaporation, but belonged to the particle itself.

In 1888, G. Gouy proposed that the particles were propelled by collisions with the rapidly moving molecules of the suspension liquid. Jean Perrin recognized that the microscopic particles provide a visible illustration of many aspects of the kinetic theory. The dancing granules should be governed by the same laws as the molecules in a gas.

One striking confirmation of this hypothesis was discovered in Perrin's work on the distribution of colloidal particles in a gravitational field, the sedimentation equilibrium. By careful fractional centrifuging, he was able to prepare suspensions of gamboge[16] particles that were spherical in shape and very uniform in size. It was possible to measure the radius of the particles either microscopically or by weighing a counted number. If these granules

---

[15] Brown, *Phil. Mag.*, *4*, 161 (1828); *6*, 161 (1829); *8*, 41 (1830).

[16] Gamboge is a gummy material from the desiccation of the latex secreted by *garcinia morella* (Indo-China). It is used as a bright yellow water color.

behave in a gravitational field like gas molecules, their equilibrium distribution throughout a suspension should obey the Boltzmann equation

$$n = n_0 e^{-mgh/kT} \tag{7.48}$$

Instead of m we may write $\frac{4}{3}\pi r^3(\rho - \rho_l)$ where r is the radius of the particle, and ρ and ρ_l are the densities of the gamboge and of the suspending liquid. Then eq. (7.48) becomes

$$\ln \frac{n_0}{n} = \frac{\frac{4}{3}\pi r^3 gh(\rho - \rho_l)}{RT} \cdot N \tag{7.49}$$

By determining the difference in the numbers of particles at heights separated by h, it is possible to calculate a value for Avogadro's Number N.

A drawing of the results of Perrin's microscopic examination of the equilibrium distribution with granules of gamboge 0.6μ in diameter[17] is shown in Fig. 7.17. The relative change in density observed in 10μ of this suspension is equivalent to that occurring in 6 km of air, a magnification of six hundred million.

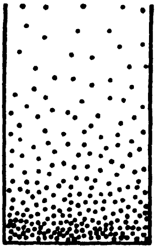


Fig. 7.17. Sedimentation equilibrium.

The calculation from eq. (7.49) resulted in a value of $N = 6.5 \times 10^{23}$. This value is in good agreement with other determinations, and is evidence that the visible microscopic particles are behaving as giant molecules in accordance with the kinetic theory. These studies were welcomed at the time as a proof of molecular reality.

28. Thermodynamics and Brownian motion. A striking feature of the Brownian motion of microscopic particles is that it never stops, but goes on continuously without any diminution of its activity. This perpetual motion is not in contradiction with the First Law, for the source of the energy that moves the particles is the kinetic energy of the molecules of the suspending liquid. We may assume that in any region where the colloid particles gain kinetic energy, there is a corresponding loss in kinetic energy by the molecules of the fluid, which undergoes a localized cooling. This amounts to perpetual motion of the second kind, for the transformation of heat into mechanical energy is prohibited by the Second Law, unless there is an accompanying transfer of heat from a hot to a cold reservoir.

The study of Brownian motion thus reveals an important limitation of the scope of the Second Law, which also allows us to appreciate its true nature. The increase in potential energy in small regions of a colloidal suspension is equivalent to a spontaneous decrease in the entropy of the region. On the average, of course, over long periods of time the entropy of the entire

---

[17] 1 micron (μ) = 10^{-3} mm = 10^{-6} m.

system does not change. In any microscopic region, however, the entropy fluctuates, sometimes increasing and sometimes decreasing.

On the macroscopic scale such fluctuations are never observed, and the Second Law is completely valid. No one observing a book lying on a desk would expect to see it spontaneously fly up to the ceiling as it experienced a sudden chill. Yet it is not *impossible* to imagine a situation in which all the molecules in the book moved spontaneously in a given direction. Such a situation is only extremely *improbable*, since there are so many molecules in any macroscopic portion of matter.

29. Entropy and probability. The law of the increase of entropy is thus a probability law. When the number of molecules in a system becomes sufficiently small, the probability of observing a spontaneous decrease in entropy becomes appreciable.

The relation between entropy and probability may be clarified by considering (Fig. 7.18) two different gases, *A* and *B*, in separate containers. When the partition is removed the gases diffuse into each other, the process continuing until they are perfectly mixed. If they were originally mixed, we should never expect them to become spontaneously unmixed by diffusion, since this condition would require the simultaneous adjustment of some 10^{24} different velocity components per mole of gas.

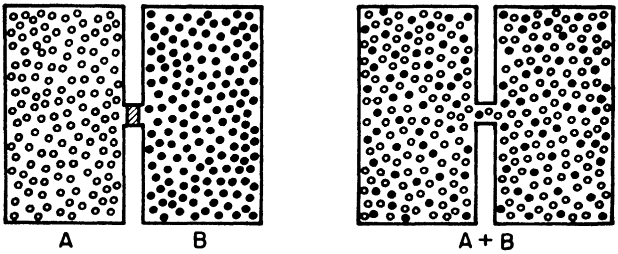


Fig. 7.18. Increase in randomness and entropy on mixing.

The mixed condition is the condition of greater randomness, of greater disorder; it is the condition of greater entropy since it arises spontaneously from unmixed conditions. [The entropy of mixing was given in eq. (3.42).] Hence entropy is sometimes considered a measure of the degree of disorder or of randomness in a system. The system of greatest randomness is also the system of highest statistical probability, for there are many arrangements of molecules that can comprise a disordered system, and much fewer for an ordered system. When one considers how seldom thirteen spades are dealt in a bridge hand,[18] one can realize how much more probable is the mixed condition in a system containing 10^{24} molecules.

Mathematically, the probabilities of independent individual events are multiplied together to obtain the probability of the combined event. The

[18] Once in 653,013,559,600 deals, if the decks are well-shuffled and the dealers virtuous.

probability of drawing a spade from a pack of cards is 1/4; the probability of drawing two spades in a row is (1/4)(12/51); the probability of drawing the ace of spades is (1/4)(1/13) = 1/52. Thus $W_{12} = W_1W_2$. Entropy, on the other hand, is an additive function, $S_{12} = S_1 + S_2$. This difference enables us to state that the relation between entropy S and probability W must be a logarithmic one. Thus,

$$S = a \ln W + b \tag{7.50}$$

The value of the constant a may be derived by analyzing from the viewpoint of probability a simple change for which the ΔS is known from thermodynamics. Consider the expansion of one mole of an ideal gas, originally at pressure P_1 in a container of volume V_1, into an evacuated container of volume V_2. The final pressure is P_2 and the final volume, $V_1 + V_2$. For this change,

$$\Delta S = S_2 - S_1 = R \ln \left(\frac{V_1 + V_2}{V_1}\right) = k \ln \left(\frac{V_1}{V_1 + V_2}\right)^{-N} \tag{7.51}$$

When the containers are connected, the probability w_1 of finding one given molecule in the first container is simply the ratio of the volume V_1 to the total volume $V_1 + V_2$ or $w_1 = V_1/(V_1 + V_2)$. Since probabilities are multiplicative, the chance of finding all N molecules in the first container, *i.e.*, the probability W_1 of the original state of the system, is

$$W_1 = \left(\frac{V_1}{V_1 + V_2}\right)^N$$

Since in the final state all the molecules must be in one or the other of the containers, the probability $W_2 = 1^N = 1$.

Therefore from eq. (7.50),

$$\Delta S = S_2 - S_1 = a \ln \frac{W_2}{W_1} = a \ln \left[\frac{1}{V_1/(V_1 + V_2)}\right]^N = a \ln \left(\frac{V_1}{V_1 + V_2}\right)^{-N}$$

Comparison with eq. (7.51) shows that a is equal to k, the Boltzmann constant. Thus

$$S = k \ln W + b$$

$$\Delta S = S_2 - S_1 = k \ln \frac{W_2}{W_1} \tag{7.52}$$

This relation was first given by Boltzmann in 1896.

For physicochemical applications, we are concerned always with entropy changes, and may conveniently set the constant b equal to zero.[19]

The application of eq. (7.52) cannot successfully be made until we have more detailed information about the energy states of atoms and molecules.

---

[19] A further discussion of this point is to be found in Chapter 12.

This information will allow us to calculate W and hence the entropy and other thermodynamic functions.

The relative probability of observing a decrease in entropy of ΔS below the equilibrium value may be obtained by inverting eq. (7.52):

$$\frac{W}{W_{\mathrm{eq}}} = e^{-\Delta S/k} \tag{7.53}$$

For one mole of helium, S/k at $273° = 4 \times 10^{25}$. The chance of observing an entropy decrease one-millionth of this amount is about $e^{-10^{19}}$. It is evident, therefore, that anyone observing a book flying spontaneously into the air is dealing with a poltergeist and not an entropy fluctuation (probably!). Only when the system is very small is there an appreciable chance of observing a large *relative* decrease in entropy.

A further analysis may be made of the driving force of a chemical reaction or other change, $-\Delta F = -\Delta H + T\Delta S$. It is made up of two terms, the heat of the reaction and the increase in randomness times the temperature. The higher the temperature, the greater is the driving force due to the increase in disorder. This may be physically clearer in the converse statement: The lower the temperature, the more likely it is that ordered states can persist. The drive toward equilibrium is a drive toward minimum potential energy and toward maximum randomness. In general, both cannot be achieved in the same system under any given set of conditions. The free-energy minimum represents (at constant T and P) the most satisfactory compromise that can be attained.

PROBLEMS

1. At what speeds would molecules of hydrogen and oxygen have to leave the surface of (a) the earth, (b) the moon, in order to escape into space? At what temperatures would the average speeds of these molecules equal these "speeds of escape"? The mass of the moon can be taken as $\frac{1}{80}$ that of the earth.

2. Calculate the number of (a) ergs per molecule, (b) kcal per mole corresponding to one electron volt per molecule. The electron volt is the energy acquired by an electron in falling through a potential difference of one volt. What is the mean kinetic energy of a molecule at 25°C in ev? What is k in ev per °C?

3. The density of nitrogen at 0°C and 3000 atm is 0.835 g per cc. Calculate the average distance apart of the centers of the molecules. How does this compare with the molecular diameter calculated from van der Waals' $b = 39.1$ cc per mole?

4. In the method of Knudsen [Ann. Physik, *29*, 179 (1909)], the vapor pressure is determined by the rate at which the substance, under its equilibrium pressure, diffuses through an orifice. In one experiment, beryllium powder was placed inside a molybdenum bucket having an effusion hole 0.318 cm in diameter. At 1537°K, it was found that 0.00888 g of Be effused in 15.2 min. Calculate the vapor pressure of Be at 1537°K.

5. Two concentric cylinders are 10 cm long, and 2.00 and 2.20 cm in diameter. The space between them is filled with nitrogen at 10^{-2} mm pressure. Estimate the heat flow by conduction between the two cylinders when they differ in temperature by 10°C.

6. At 25°C what fraction of the molecules in hydrogen gas have a kinetic energy within $kT \pm 10$ per cent? What fraction at 500°C? What fraction of molecules in mercury vapor?

7. Derive an expression for the fraction of molecules in a gas that have an energy greater than a given value E in two degrees of freedom.

8. Show that the *most probable speed* of a molecule in a gas equals $\sqrt{2kT/m}$.

9. Derive the expression $(\frac{1}{2}\overline{mc^2}) = \frac{3}{2}kT$ from the Maxwell distribution law.

10. In a cc of oxygen at 1 atm and 300°K, how many molecules have translational kinetic energies greater than 2 electron volts? At 1000°K?

11. What is the mean free path of argon at 25°C and a pressure of 1 atm? Of 10^{-5} atm?

12. A pinhole 0.2 micron in diameter is punctured in a liter vessel containing chlorine gas at 300°K and 1 mm pressure. If the gas effuses into a vacuum, how long will it take for the pressure to fall to 0.5 mm?

13. Perrin studied the distribution of uniform spherical (0.212 μ radius) grains of gamboge ($\rho = 1.206$) suspended in water at 15°C by taking counts on four equidistant horizontal planes across a cell 100 μ deep. The relative concentrations of grains at the four levels were

level:	5 μ	35 μ	65 μ	95 μ
concentration:	100	47	22.6	12

Estimate Avogadro's Number from these data.

14. Show that the number of collisions per second between unlike molecules, A and B, in one cc of gas is

$$Z_{12} = \pi n_A n_B \left(\frac{d_A + d_B}{2}\right)^2 \sqrt{\frac{8kT}{\pi\mu}}$$

where the reduced mass, $\mu = (m_A m_B)/(m_A + m_B)$. In an equimolar mixture of H_2 and I_2 at 500°K and 1 atm calculate the number of collisions per sec per cc between H_2 and H_2, H_2 and I_2, I_2 and I_2. For H_2 take $d = 2.18$Å, for I_2, $d = 3.76$ Å.

15. The force constant of O_2 is 11.8×10^5 dynes per cm and $r_0 = 1.21$ Å. Estimate the potential energy per mole at $r = 0.8r_0$.

16. Calculate the moments of inertia of the following molecules: (a) NaCl, $r_0 = 2.51$ Å; (b) H_2O, $r_{OH} = 0.957$ Å, $\angle$ HOH $= 105° 3'$.

17. In Fig. 7.18, assume that there are 10 white balls and 10 black balls distributed at random between the two containers of equal volume. What is the ΔS between the random configuration and one in which there are 8 white balls and 2 black balls in the left-hand container, and 2 whites and 8 blacks in the right. Calculate the answer by eq. (7.52) and also by eq. (3.42). What is the explanation of the different answers?

18. In a carefully designed high vacuum system it is possible to reach a pressure as low as 10^{-10} mm. Calculate the mean free path of helium at this pressure and 25°C.

19. The permeability constant at 20°C of pyrex glass to helium is given as 6.4×10^{-12} cc sec^{-1} per cm^2 area per mm thickness per cm of Hg pressure difference. The helium content of the atmosphere at sea level is about 5×10^{-4} mole per cent. Suppose a 100 cc round pyrex flask with walls 2 mm thick was evacuated to 10^{-10} mm and sealed. What would be the pressure at the end of one year due to inward diffusion of helium?

REFERENCES

BOOKS

1. Herzfeld, K. F. and H. M. Smallwood, "Kinetic Theory of Ideal Gases," in *Treatise on Physical Chemistry*, vol. II, edited by H. S. Taylor and S. Glasstone (New York: Van Nostrand, 1951).
2. Jeans, J. H., *Introduction to the Kinetic Theory of Gases* (London: Cambridge, 1940).
3. Kennard, E. H., *Kinetic Theory of Gases* (New York: McGraw-Hill, 1938).
4. Knudsen, M., *The Kinetic Theory of Gases* (London: Methuen, 1950).
5. Loeb, L. B., *Kinetic Theory of Gases* (New York: McGraw-Hill, 1927).

ARTICLES

1. Furry, W. H., *Am. J. Phys.*, *16*, 63–78 (1948), "Diffusion Phenomena in Gases."
2. Pease, R. N., *J. Chem. Ed.*, *16*, 242–47, 366–73 (1939), "The Kinetic Theory of Gases."
3. Rabi, I. I., *Science in Progress*, vol. IV (New Haven: Yale Univ. Press. 1945), 195–204, "Streams of Atoms."
4. Rodebush, W. H., *J. Chem. Ed.*, *27*, 39–43 (1950), "The Dynamics of Gas Flow."
5. Wheeler, T. S., *Endeavour*, *11*, 47–52 (1952), "William Higgins, Chemist."

CHAPTER 8

The Structure of the Atom

1. Electricity. The word "electric" was coined in 1600 by Queen Elizabeth's physician, William Gilbert, from the Greek, ηλεκτρον, "amber." It was applied to bodies that when rubbed with fur acquired the property of attracting to themselves small bits of paper or pith. Gilbert was unwilling to admit the possibiliy of "action at a distance," and in his treatise *De Magnete* he advanced an ingenious theory for the electrical attraction.

> An effluvium is exhaled by the amber and is sent forth by friction. Pearls carnelian, agate, jasper, chalcedony, coral, metals, and the like, when rubbed are inactive; but is there nought emitted from them also by heat and friction? There is indeed, but what is emitted from the dense bodies is thick and vaporous [and thus not mobile enough to cause attractions].
>
> A breath, then . . . reaches the body that is to be attracted and as soon as it is reached it is united to the attracting electric. For as no action can be performed by matter save by contact, these electric bodies do not appear to touch, but of necessity something is given out from the one to the other to come into close contact therewith, and to be a cause of incitation to it.

Further investigation revealed that materials such as glass, after rubbing with silk, exerted forces opposed to those observed with amber. Two varieties of electricity were thus distinguished, the vitreous and the resinous. Two varieties of effluvia, emanating from the pores of the electrics, were invoked in explanation. Electricity was supposed to be an imponderable fluid similar in many ways to "caloric." Frictional machines for generating high electrostatic potentials were devised, and used to charge condensers in the form of Leiden jars.

Benjamin Franklin (1747) considerably simplified matters by proposing a one-fluid theory. According to this theory, when bodies are rubbed together they acquire a surplus or deficit of the electric fluid, depending on their relative attraction for it. The resultant difference in charge is responsible for the observed forces. Franklin established the convention that the vitreous type of electricity is positive (fluid in excess), and the resinous type is negative (fluid in defect).

In 1791, Luigi Galvani accidentally brought the bare nerve of a partially dissected frog's leg into contact with a discharging electrical machine. The sharp convulsion of the leg muscles led to the discovery of galvanic electricity, for it was soon found that the electric machine was unnecessary and that the twitching could be produced simply by bringing the nerve ending and the end of the leg into contact through a metal strip. The action was enhanced when two dissimilar metals completed the circuit. Galvani, a physician, named the new phenomenon "animal electricity" and believed that it was characteristic only of living tissues.

Alessandro Volta, a physicist, Professor of Natural Philosophy at Pavia, soon discovered that the electricity was of inanimate origin; and using dissimilar metals in contact with moist paper, he was able to charge an electroscope. In 1800 he constructed his famous "pile," consisting of many consecutive plates of silver, zinc, and cloth soaked in salt solution. From the terminals of the pile the thitherto static-electrical manifestations of shock and sparks were obtained.

The news of Volta's pile was received with an enthusiasm and amazement akin to that occasioned by the uranium pile in 1945. In May of 1800, Nicholson and Carlyle decomposed water into hydrogen and oxygen by means of the electric current, the oxygen appearing at one pole of the pile and the hydrogen at the other. Solutions of various salts were soon decomposed, and in 1806–1807, Humphry Davy used a pile to isolate sodium and potassium from their hydroxides. The theory that the atoms in a compound were held together by the attraction between unlike charges immediately gained a wide acceptance.

2. Faraday's Laws and electrochemical equivalents. In 1813 Michael Faraday, then 22 years old and a bookbinder's apprentice, went to the Royal Institution as Davy's laboratory assistant. In the following years, he carried out the series of researches that were the foundations of electrochemistry and electromagnetism.

Faraday studied intensively the decomposition of solutions of salts, acids, and bases by the electric current. With the assistance of the Rev. William Whewell, he devised the nomenclature universally used in these studies: electrode, electrolysis, electrolyte, ion, anion, cation. The positive electrode is called the *anode* (*οδος*, "path"); the negative ion (*ιον*, "going"), which moves toward the anode, is called the *anion*. The positive ion, or *cation*, moves toward the negative electrode, or *cathode*.

Faraday proceeded to study quantitatively the relation between the amount of electrolysis, or chemical action produced by the current, and the quantity of electricity. The unit of electric quantity is now the coulomb or ampere second. The results were summarized as follows:[1]

> The chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes. . . . The substances into which these [electrolytes] divide, under the influence of the electric current, form an exceedingly important general class. They are combining bodies, are directly associated with the fundamental parts of the doctrine of chemical affinity; and have each a definite proportion, in which they are always evolved during electrolytic action. I have proposed to call . . . the numbers representing the proportions in which they are evolved *electrochemical equivalents*. Thus hydrogen, oxygen, chlorine, iodine, lead,

---

[1] *Phil. Trans. Roy. Soc.*, *124*, 77 (1834).

> tin, are *ions*; the three former are *anions*, the two metals are *cations*, and 1, 8, 36, 125, 104, 58 are their *electrochemical equivalents* nearly.
>
> Electrochemical equivalents coincide, and are the same, with ordinary chemical equivalents. I think I cannot deceive myself in considering the doctrine of definite electrochemical action as of the utmost importance. It touches by its facts more directly and closely than any former fact, or set of facts, have done, upon the beautiful idea that ordinary chemical affinity is a mere consequence of the electrical attractions of different kinds of matter. . . .
>
> A very valuable use of electrochemical equivalents will be to decide, in cases of doubt, what is the true chemical equivalent, or definite proportional, or atomic number [weight] of a body. . . . I can have no doubt that, assuming hydrogen as 1, and dismissing small fractions for the simplicity of expression, the equivalent number or atomic weight of oxygen is 8, of chlorine 36, of bromine 78.4, of lead 103.5, of tin 59, etc , notwithstanding that a very high authority doubles several of these numbers.

The "high authority" cited was undoubtedly Jöns Jakob Berzelius, who was then using atomic weights based on combining volumes and gas-density measurements. Faraday believed that when a substance was decomposed, it always yielded one positive and one negative ion. Since the current liberates from water eight grams of oxygen for each gram of hydrogen, he concluded that the formula was HO and that the atomic weight of oxygen was equal to 8. It will be recalled that the work of Avogadro, which held the key to this problem, was lying forgotten during these years.

3. The development of valence theory. Much new knowledge about the combinations of atoms was being gained by the organic chemists. Especially noteworthy was the work of Alexander Williamson. In 1850 he treated potassium alcoholate with ethyl iodide and obtained ordinary ethyl ether.

At that time, most chemists, using $O = 8$, $C = 6$, were writing alcohol as $C_4H_5O{\cdot}OH$, and ether C_4H_5O. If $O = 16$, $C = 12$ were used, the formulas would be

$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O \quad \text{and} \quad \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$$

Williamson realized that his reaction could be readily explained on this basis as

$$\left.\begin{matrix}C_2H_5\\K\end{matrix}\right\}O + C_2H_5I = KI + \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$$

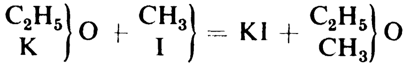
The older system could still be maintained, however, if a two-step reaction was postulated:

$$C_4H_5O \cdot OK = KO + C_4H_5O$$
$$C_4H_5I + KO = KI + C_4H_5O$$

Williamson settled the question by treating potassium *ethylate* with *methyl* iodide. If the reaction proceeded in two steps, he should obtain equal amounts of diethyl and dimethyl ethers:

$$C_4H_5O \cdot OK = KO + C_4H_5O$$
$$C_2H_3I + KO = KI + C_2H_3O$$

On the other hand, if the oxygen atom held *two* radicals, a new compound, methyl ethyl ether, should be the product:



$$\left.\begin{matrix}C_2H_5\\K\end{matrix}\right\}O+\left.\begin{matrix}CH_3\\I\end{matrix}\right\}=KI+\left.\begin{matrix}C_2H_5\\CH_3\end{matrix}\right\}O$$

The new compound was indeed obtained. This was the first unequivocal chemical demonstration that the formulas based on $C = 12$, $O = 16$, must be correct. The concept of valence was gradually developed as a result of such organic-chemical researches.

It should be mentioned that as early as 1819 two other important criteria for establishing atomic weights were proposed. Pierre Dulong and Alexis Petit pointed out that, for most solid elements, especially the metals, the product of the specific heat and the atomic weight appeared to be a constant, with a value of around 6 calories per °C. If this relation is accepted as a general principle, it provides a guide by which the proper atomic weight can be selected from a number of multiples.

In the same year, Eilhard Mitscherlich published his work on isomorphism of crystals, based on an examination of such series as the alums and the vitriols. He found that one element could often be substituted for an analogous one in such a series without changing the crystalline form, and concluded that the substitute elements must enter into the compound in the same atomic proportions. Thus if alum is written $KAl(SO_4)_2 \cdot 12\,H_2O$, ferric alum must be $KFe(SO_4)_2 \cdot 12\,H_2O$, and chrome alum must be $KCr(SO_4)_2 \cdot 12\,H_2O$. The analyst is thus enabled to deduce a consistent set of atomic weights for the analogous elements in the crystals.

Avogadro's Hypothesis, when resurrected at the 1860 conference, resolved all remaining doubts, and the old problem of how to determine the atomic weights was finally solved.

We now recognize that ions in solution may bear more than one elementary charge, and that the electrochemical equivalent weight is the atomic weight M divided by the number of charges on the ion z. The amount of electricity required to set free one equivalent is called the *faraday*, and is equal to 96,519 coulombs.

The fact that a definite quantity of electric charge, or a small integral multiple thereof, was always associated with each charged atom in solution strongly suggested that electricity was itself atomic in nature. Hence, in 1874, G. Johnstone Stoney addressed the British Association as follows:

> Nature presents us with a single definite quantity of electricity which is independent of the particular bodies acted on. To make this clear, I shall express Faraday's Law in the following terms. . . . For each chemical bond which is ruptured within an electrolyte a certain quantity of electricity traverses the electrolyte which is the same in all cases.

In 1891, Stoney proposed that this natural unit of electricity should be given a special name, the *electron*. Its magnitude could be calculated by dividing the faraday by Avogadro's Number.

$$e = \frac{\mathscr{F}}{N} \tag{8.1}$$

4. The Periodic Law. The idea that matter was constituted of some ninety different kinds of fundamental building blocks was not one that could appeal for long to the mind of man. We have seen how during the nineteenth century evidence was being accumulated from various sources, especially the kinetic theory of gases, that the atom was not merely a minute billiard ball, a more detailed structure being required to explain the interactions between atoms.

In 1815, William Prout proposed that all atoms were composed of atoms of hydrogen. In evidence for this hypothesis, he noted that all the atomic weights then known were nearly whole numbers. Prout's hypothesis won many converts, but their enthusiasm was lessened by the careful atomic weight determinations of Jean Stas, who found, for example, that chlorine had a weight of 35.46.

Attempts to correlate the chemical properties of the elements with their atomic weights continued, but without striking success till after 1860, when unequivocal weights became available. In 1865, John Newlands tabulated the elements in the order of their atomic weights, and noted that every eighth element formed part of a set with very similar chemical properties. This regularity he unfortunately called "The Law of Octaves." The suggested similarity to a musical scale aroused a good deal of scientific sarcasm, and the importance of Newland's observations was drowned in the general merriment.

From 1868 to 1870, a series of important papers by Julius Lothar Meyer and Dmitri Mendeleev clearly established the fundamental principles of the Periodic Law. Meyer emphasized the periodic nature of the physical properties of the elements. This periodicity is illustrated by the well-known graph of atomic volume vs. atomic weight. Mendeleev arranged the elements in his famous Periodic Table. This Table immediately systematized inorganic chemistry, made it possible to predict the properties of undiscovered elements, and pointed strongly to the existence of an underlying regularity in atomic architecture.

Closer examination revealed certain defects in the arrangement of elements according to their atomic weights. Thus the most careful determinations showed that tellurium had a higher atomic weight than iodine, despite the positions in the Table obviously required by their properties. After Sir William Ramsay's discovery of the rare gases (1894–1897), it was found that argon had an atomic weight of 39.88, which was greater than that of potassium, 39.10. Such exceptions to the arrangement by weights suggested that the whole truth behind the Periodic Law was not yet realized.

5. The discharge of electricity through gases. The answer to this and many other questions about atomic structure was to be found in a quite unexpected quarter—the study of the discharge of electricity through gases.

William Watson,[2] who proposed a one-fluid theory of electricity at the same time as Franklin, was the first to describe the continuous discharge of an electric machine through a rarefied gas (1748).

> It was a most delightful spectacle, when the room was darkened, to see the electricity in its passage: to be able to observe not, as in the open air, its brushes or pencils of rays an inch or two in length, but here the corruscations were of the whole length of the tube between the plates, that is to say, thirty-two inches.

Progress in the study of the discharge was retarded by the lack of suitable air pumps. In 1855, Geissler invented a mercury pump that permitted the attainment of higher degrees of vacuum. In 1858, Julius Plücker observed the deflection of the negative glow in a magnetic field and in 1869 his student, Hittorf, found that a shadow was cast by an opaque body placed between the cathode and the fluorescent walls of the tube, suggesting that rays from the cathode were causing the fluorescence. In 1876, Eugen Goldstein called these rays *cathode rays* and confirmed the observation that they traveled in straight lines and cast shadows. Sir William Crookes (1879) regarded the rays as a torrent of negatively ionized gas molecules repelled from the cathode. The charged particle theory was contested by many who believed the rays were electromagnetic in origin, and thus similar to light waves. This group was led by Heinrich Hertz, who showed that the cathode radiation could pass through thin metal foils, which would be impossible if it were composed of massive particles.

Hermann von Helmholtz, however, strongly championed the particle theory; in a lecture before the Chemical Society of London in 1881 he declared:

> If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions which behave like atoms of electricity.

6. The electron. In 1895, Wilhelm Roentgen discovered that a very penetrating radiation was emitted from solid bodies placed in the path of cathode rays. An experimental arrangement for the production of these "X rays" is shown in Fig. 8.1.

J. J. Thomson in his *Recollections and Reflections*[3] has described his first work in this field:

> It was a most fortunate coincidence that the advent of research students at the Cavendish Laboratory came at the same time as the announcement by Roentgen of his discovery of the X rays. I had a copy of his apparatus made and set up at the Laboratory, and the first thing I did with it was to see what effect the passage of

---

[2] *Phil. Trans. Roy. Soc.*, *40*, 93 (1748); *44*, 362 (1752).

[3] G. Bell and Sons, London, 1933.

these rays through a gas would produce on its electrical properties. To my great delight I found that this made it a conductor of electricity, even though the electric force applied to the gas was exceedingly small, whereas the gas when it was not exposed to the rays did not conduct electricity unless the electric force were increased many thousandfold. . . The X rays seemed to turn the gas into a gaseous electrolyte.

I started at once, in the late autumn of 1895, on working at the electric properties of gases exposed to Roentgen rays, and soon found some interesting and suggestive results. . . . There is an interval when the gas conducts though the rays have ceased to go through it. We studied the properties of the gas in this state, and found that the conductivity was destroyed when the gas passed through a filter of glass wool.

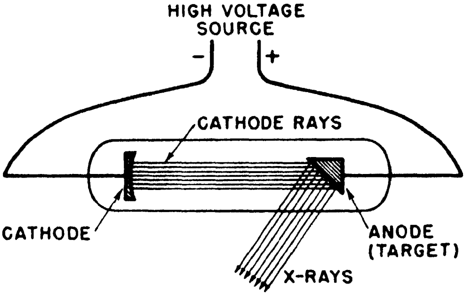


Fig. 8.1. Production of X-rays.

A still more interesting discovery was that the conductivity could be filtered out without using any mechanical filter by exposing the conducting gas to electric forces. The first experiments show that the conductivity is due to particles present in the gas, and the second shows that these particles are charged with electricity. The conductivity due to the Roentgen rays is caused by these rays producing in the gas a number of charged particles.

7. The ratio of charge to mass of the cathode particles. J. J. Thomson next turned his attention to the behavior of cathode rays in electric and magnetic fields,[4] using the apparatus shown in Fig. 8.2.

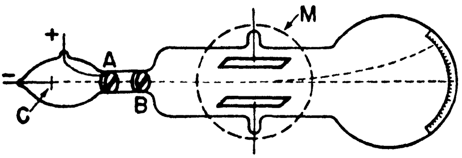


Fig. 8.2. Thomson's apparatus for determining e/m of cathode particles.

The rays from the cathode C pass through a slit in the anode A, which is a metal plug fitting tightly into the tube and connected with the earth; after passing through a second slit in another earth-connected metal plug B, they travel between two parallel aluminium plates about 5 cm apart; they then fall on the end of the tube

[4] *Phil. Mag.*, *44*, 293 (1897).

> and produce a narrow well-defined phosphorescent patch. A scale pasted on the outside of the tube serves to measure the deflection of this patch.
>
> At high exhaustions the rays were deflected when the two aluminium plates were connected with the terminal of a battery of small storage cells; the rays were depressed when the upper plate was connected with the negative pole of the battery, the lower with the positive, and raised when the upper plate was connected with the positive, the lower with the negative pole.

In an electric field of strength E, a particle with charge e will be subject to a force of magnitude Ee. The trajectory of an electron in an electric field of strength E perpendicular to its direction of motion may be illustrated by

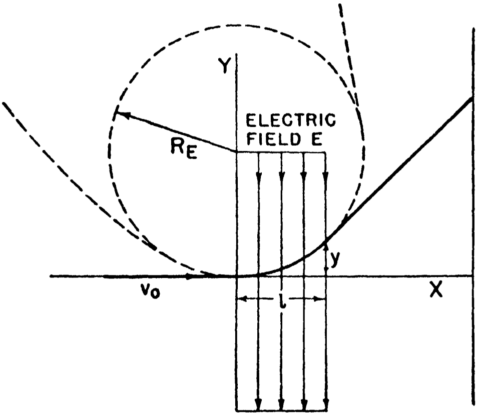


Fig. 8.3. Deflection of electron in an electric field.

the diagram in Fig. 8.3. If m is the mass of the electron, the equations of motion may be written:

$$m\frac{d^2x}{dt^2} = 0, \qquad m\frac{d^2y}{dt^2} = Ee \tag{8.2}$$

With $t = 0$ as the instant the particle enters the electric field, its velocity in the y direction is zero at $t = 0$. This velocity increases while the electron is in the field, while its initial velocity in the x direction, v_0, remains constant. Integrating eqs. (8.2) we obtain

$$x = v_0t, \qquad y = \frac{eE}{2m}t^2 \tag{8.3}$$

Equations (8.3) define a parabolic path, as is evident when t is eliminated from the equations, giving

$$y = \frac{eE}{2mv_0^2}x^2 \tag{8.4}$$

After the electron leaves the field, it travels along a straight line tangent to this parabolic path. In many experimental arrangements, its total path is considerably longer than the length of the electric field, so that the deflection in the y direction experienced while in the field is comparatively small compared to the total observed deflection. To a good approximation, therefore, the parabolic path can be considered as a circular arc of radius R_E, with the force exerted by the field equal to the centrifugal force on the electron in this circular path,

$$eE = \frac{mv^2}{R_E} \tag{8.5}$$

The time required to traverse the field of length l is simply l/v_0 so that the deflection in eq. (8.3) becomes

$$y = \frac{eE}{2m}\frac{l^2}{v_0^2}$$

Thus

$$\frac{e}{m} = \frac{2yv_0^2}{l^2E} \tag{8.6}$$

The ratio of charge to mass may be calculated from the deflection in the electric field, provided the velocity of the particles is known. This may be obtained by balancing the deflection in the electric field by an opposite deflection in a magnetic field. This magnetic field is applied by the pole pieces of a magnet M mounted outside the apparatus in Fig. 8.2, so that the field is at right angles to both the electric field and to the direction of motion of the cathode rays.

A moving charged particle is equivalent to a current of electricity, the strength of the current being the product of the charge on the particle and its velocity. From Ampère's Law, therefore, the magnitude of the force on the moving charge is given by

$$f = evB \sin \theta \tag{8.7}$$

where θ is the angle between the velocity vector $\boldsymbol{v}$ and the magnetic induction vector $\boldsymbol{B}$. When the magnetic field is perpendicular to the direction of motion, this equation becomes

$$f = evB \tag{8.8}$$

Figure 8.4 illustrates the directional factors involved.

The force on the electron due to the magnetic field is always perpendicular to its direction of motion, and thus a magnetic field can never change the speed of a moving charge, but simply changes its direction. As in eq. (8.5), the force may be equated to the centrifugal force on the electron, which in this case moves in a truly circular path. Thus

$$Bev = \frac{mv^2}{R_B} \tag{8.9}$$

If now the force due to the magnetic field exactly balances that due to the electric field, the phosphorescent patch in Thomson's apparatus will be brought back to its initial position. When this occurs, $evB = Ee$ and $v = E/B$. When this value is substituted in eq. (8.6) one obtains

$$\frac{e}{m} = \frac{2vE}{l^2B^2} \tag{8.10}$$

The units in this equation may be taken to be those of the absolute practical (MKS) system. The charge e is in coulombs; the electric field E in volts per meter; the magnetic induction B in webers per square meter (1 weber per meter^2 = 10^4 gausses); and lengths and masses are in meters and kilograms, respectively.

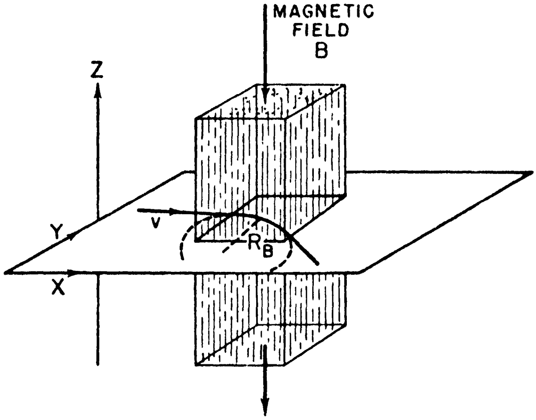


Fig. 8.4. Deflection of moving electron in magnetic field.

Thomson found the experimental ratio of charge to mass to be of the order of 10^{11} coulombs per kilogram. The most recent value of e/m for the electron is $e/m = 1.7589 \times 10^{11}$ coulomb per kilogram $= 5.273 \times 10^{17}$ esu per gram.

The value found for the hydrogen ion, H^+, in electrolysis was 1836 times less than this. The most reasonable explanation seemed to be that the mass of the cathode particle was only $\frac{1}{1836}$ that of the hydrogen ion; this presumption was soon confirmed by measurements of e, the charge borne by the particle.

8. The charge of the electron. In 1898, Thomson succeeded in measuring the charge of the cathode particles. Two years before, C. T. R. Wilson had shown that gases rendered ionizing by X rays caused the condensation of clouds of water droplets from an atmosphere supersaturated with water vapor. The ions formed acted as nuclei for the condensation of the water droplets. This principle was later used in the Wilson Cloud Chamber to render visible the trajectories of individual charged corpuscles, and thus made possible much of the experimental development of modern nuclear physics.

Thomson and Townsend observed the rate of fall of a cloud in air and from this calculated an average size for the water droplets. The number of droplets in the cloud could then be estimated from the weight of water precipitated. The total charge of the cloud was measured by collecting the charged droplets on an electrometer. The conditions of cloud formation were such that condensations occurred only on negatively charged particles. Making the assumption that each droplet bore only one charge, it was now possible to estimate that the value of the elementary negative charge was $e = 6.5 \times 10^{-10}$ esu. This was of the same order of magnitude as the charge on the hydrogen ion, and thus further evidence was provided that the cathode particles themselves were "atoms" of negative electricity, with a mass $\frac{1}{1836}$ that of the hydrogen atom.

The exact proof of this hypothesis of the atomic nature of electricity and a careful measurement of the elementary electronic charge were obtained in 1909 by Robert A. Millikan in his beautiful oil-drop experiments. Millikan was able to isolate individual droplets of oil bearing an electric charge, and to observe their rate of fall under the combined influences of gravity and an electric field.

A body falls in a viscous medium with an increasing velocity until the gravitational force is just balanced by the frictional resistance, after which it falls at a constant "terminal velocity," v. The frictional resistance to a spherical body is given by Stoke's equation of hydrodynamics as

$$f = 6\pi\eta r v \tag{8.11}$$

where η is the coefficient of viscosity of the medium and r the radius of the sphere. The gravitational force (weight) is equal to this at terminal velocity, so that, if ρ is the density of the body, and ρ_0 that of the fluid medium,

$$\tfrac{4}{3}\pi r^3 g(\rho - \rho_0) = 6\pi\eta r v \tag{8.12}$$

If a charged oil droplet falls in an electric field, it can be brought to rest when the upward electric force is adjusted to equal the downward gravitational force,

$$eE = \tfrac{4}{3}\pi r^3 g(\rho - \rho_0) \tag{8.13}$$

Since r may be calculated from the terminal velocity in eq. (8.12), only the charge e remains unknown in eq. (8.13). Actually, somewhat better results were obtained in experiments in which the droplet was observed falling freely and then moving in an electric field. In all cases, the charge on the oil droplets was found to be an exact multiple of a fundamental unit charge. This is the charge on the electron, whose presently accepted value is[5]

$$\begin{aligned} e &= (4.8022 \pm 0.0001) \times 10^{-10} \text{ esu} \\ &= (1.6018 \pm 0.00004) \times 10^{-19} \text{ coulomb} \end{aligned}$$

---

[5] Millikan's result of 4.774×10^{-10} esu was low, owing to his use of an erroneous value for the viscosity of air. J. D. Stranathan, *The Particles of Modern Physics* (Philadelphia: Blakiston, 1954), Chap. 2, gives a most interesting account of the measurements of *e*.

9. Radioactivity. The penetrating nature of the X rays emitted when cathode rays impinged upon solid substances was a matter of great wonder and interest for the early workers in the field, and many ingenious theories were advanced to explain the genesis of the radiation. It was thought at one time that it might be connected with the fluorescence observed from the irradiated walls of the tubes. Henri Becquerel therefore began to investigate a variety of fluorescent substances to find out whether they emitted penetrating rays. All trials with various minerals, metal sulfides, and other compounds known to fluoresce or phosphoresce on exposure to visible light gave negative results, until he recalled the striking fluorescence of a sample of potassium uranyl sulfate that he had prepared 15 years previously. After exposure to an intense light, the uranium salt was placed in the dark-room under a photographic plate wrapped in "two sheets of thick black paper." The plate was darkened after several hours' exposure.

Becquerel soon found that this amazing behavior had nothing to do with the fluorescence of the uranyl salt, since an equally intense darkening could be obtained from a sample of salt that had been kept for days in absolute darkness, or from other salts of uranium that were not fluorescent. The penetrating radiation had its source in the uranium itself, and Becquerel proposed to call this new phenomenon *radioactivity*.[6]

It was discovered that radioactive materials, like X rays, could render gases conducting so that charged bodies would be discharged, and the discharge rate of electroscopes could therefore be used as a measure of the intensity of the radiation. Marie Curie examined a number of uranium compounds and ores in this way, and found that the activity of crude pitchblende was considerably greater than would be expected from its uranium content. In 1898, Pierre and Marie Curie announced the separation from pitchblende of two extremely active new elements, polonium and radium.

Three different types of rays have been recognized and described in the radiation from radioactive materials. The β rays are high-velocity electrons, as evidenced by their deviation in electric and magnetic fields, and ratio of charge to mass. Their velocities range from 0.3 to 0.99 that of light. The α rays are made up of particles of mass 4 ($O = 16$ scale) bearing a positive charge of 2 ($e = -1$ scale). They are much less penetrating than β rays, by a factor of about 100. Their velocity is around 0.05 that of light. The γ rays are an extremely penetrating (about 100 times β rays) electromagnetic radiation, undeflected by either magnetic or electric fields. They are similar to X rays, but have a much shorter wave length.

Owing to their large mass, the α particles travel through gases in essentially straight lines, producing a large amount of ionization along their paths. The paths of β particles are longer than those of α's, but are much more irregular on account of the easy deflection of the lighter β particle.

The phenomena of radioactivity as well as the observations on the

---

[6] *Compt. rend.*, *127*, 501, March 2, 1896.

electrical discharge in gases provided evidence that electrons and positive ions were component parts of the structure of atoms.

10. The nuclear atom. The problem of the number of electrons contained in an atom attracted the attention of Thomson and of C. G. Barkla. From measurements of the scattering of light, X rays, and beams of electrons, it was possible to estimate that this number was of the same order as the atomic weight. To preserve the electrical neutrality of the atom, an equal number of positive charges would then be necessary. Thomson proposed an atom model that consisted of discrete electrons embedded in a uniform sphere of positive charge.

Lord Rutherford[7] has told the story of the next great development in the problem, at the University of Manchester in 1910.

> In the early days I had observed the scattering of α particles, and Dr. Geiger in my laboratory had examined it in detail. He found in thin pieces of heavy metal that the scattering was usually small, of the order of one degree. One day Geiger came to me and said, "Don't you think that young Marsden, whom I am training in radioactive methods, ought to begin a small research?" Now I had thought that too, so I said, "Why not let him see if any α particles can be scattered through a large angle?" I may tell you in confidence that I did not believe they would be, since we knew that the α particle was a very fast massive particle, with a great deal of energy, and you could show that if the scattering was due to the accumulated effect of a number of small scatterings, the chance of an α particle's being scattered backwards was very small. Then I remember two or three days later Geiger coming to me in great excitement and saying, "We have been able to get some of the α particles coming backwards. . . ." It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you.
>
> On consideration I realized that this scattering backwards must be the result of a single collision and when I made calculations I saw it was impossible to get anything of that order of magnitude unless you took a system in which the greater part of the mass of the atom was concentrated in a minute nucleus. . . .

In the experimental arrangement used by Marsden and Geiger, a pencil of α particles was passed through a thin metal foil and its deflection observed on a zinc sulfide screen, which scintillated whenever struck by a particle.

Rutherford enunciated the nuclear model of the atom in a paper published[8] in 1911. The positive charge is concentrated in the massive center of the atom, with the electrons revolving in orbits around it, like planets around the sun. Further scattering experiments indicated that the number of elementary positive charges in the nucleus of an atom is equal within the experimental uncertainty to one-half its atomic weight. Thus carbon, nitrogen, and oxygen would have 6, 7, and 8 electrons, respectively, revolving around a like positive charge. It follows that the charge on the nucleus or the number of orbital electrons may be set equal to the *atomic number* of the element, the ordinal number of the position that it occupies in the periodic table.

---

[7] Ernest Rutherford, Lecture at Cambridge, 1936, in *Background to Modern Science*, ed. by J. Needham and W. Pagel (London: Cambridge, 1938).

[8] *Phil. Mag.*, *21*, 669 (1911).

According to the nuclear hypothesis, the α particle is therefore the nucleus of the helium atom. It was, in fact, known that α particles became helium gas when they lost their energy.

11. X rays and atomic number. The significance of atomic number was strikingly confirmed by the work of H. G. J. Moseley.[9] Barkla had discovered that in addition to the *general* or *white* X radiation emitted by all the elements, there were several series of *characteristic* X-ray lines peculiar to each element. Moseley found that the frequency ν of a given line in the characteristic X radiation of an element depended on its atomic number Z in such a way that

$$\sqrt{\nu} = a(Z - b) \tag{8.14}$$

where, for each series, a and b are constant for all the elements. The method by which the wave length of X rays is measured by using the regular interatomic spacings in a crystal as a diffraction grating will be discussed in Chapter 13.

When the Moseley relationship was plotted for the K_α X-ray lines of the elements, discontinuities in the plot appeared corresponding to missing elements in the periodic table. These vacant spaces have since been filled. This work provided further convincing evidence that the atomic number and not the atomic weight governs the periodicity of the properties of the chemical elements.

12. The radioactive disintegration series. Rutherford in 1898, soon after the discovery of radioactivity, observed that the activity from thorium would diffuse through paper but not through a thin sheet of mica. The radioactivity could also be drawn into an ionization chamber by means of a current of air. It was therefore evident that radioactive thorium was continuously producing an "emanation" that was itself radioactive. Furthermore, this emanation left a deposit on the walls of containers, which was likewise active. Each of these activities could be quantitatively distinguished from the others by its time of decay. As a result of a large amount of careful research by Rutherford, Soddy, and others, it was gradually established that a whole series of different elements was formed by consecutive processes of radioactive change.

The number of radioactive atoms that decomposes per second is directly proportional to the number of atoms present. Thus

$$-\frac{dN}{dt} = \lambda N$$

$$\frac{N}{N_0} = e^{-\lambda t} \tag{8.15}$$

if N_0 is the number of radioactive atoms present at $t = 0$. The constant λ is

---

[9] *Phil. Mag.*, *26*, 1024 (1913); *27*, 703 (1914).

called the *radioactive-decay constant*; the larger the value of λ, the more rapid the decay of the radioactivity.

The exponential decay law of eq. (8.15) is plotted in curve *A*, Fig. 8.5, the experimental points being those obtained from uranium X_1, the first product in the uranium series. A sample of uranium or of any of its salts is found to emit both α and β particles. If an iron salt is added to a solution of a uranium salt, and the iron then precipitated as the hydroxide, it is found that the β activity is removed from the uranium and coprecipitated with the ferric hydroxide. This β activity then gradually decays according to the exponential curve *A* of Fig. 8.5. The original uranium sample gradually regains β activity, according to curve *B*. It is apparent that the sum of the activities given by curves *A* and *B* is always a constant. The amount of UX_1 (the β emitter) decomposing per second is just equal to the amount being formed from the parent uranium.

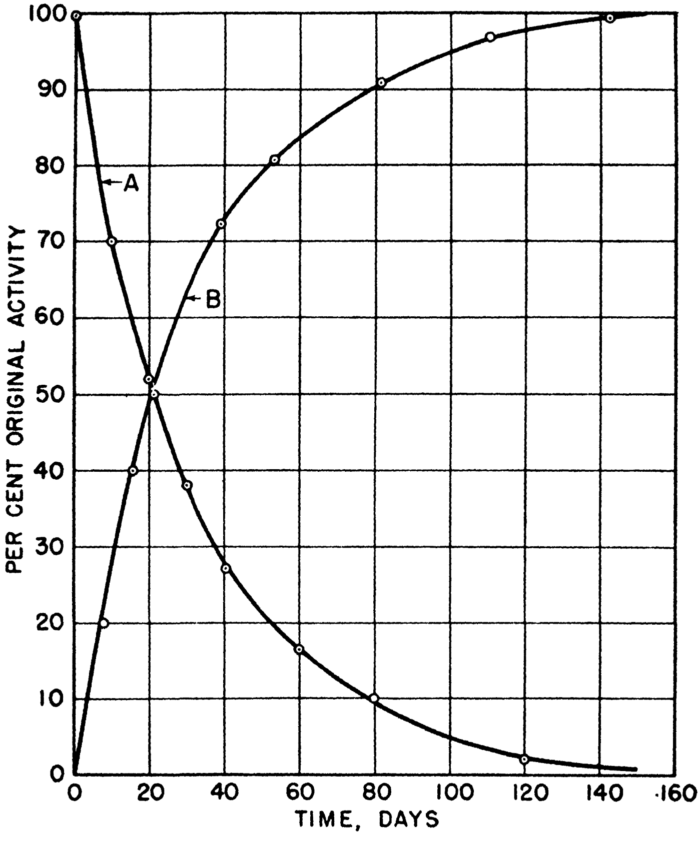


Fig. 8.5. Radioactive decay and regeneration of UX_1.

element is the *half-life period* τ, the time required for the activity to be reduced to one-half its initial value. From eq. (8.15), therefore,

$$\tfrac{1}{2} = e^{-\lambda\tau}$$

$$\tau = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda} \tag{8.16}$$

The half life of uranium is 4.4×10^9 years, whereas that of UX_1 is 24.5 days. Because of the long life of uranium compared to UX_1, the number of uranium atoms present in a sample is effectively constant over measurable experimental periods, and the recovery curve of Fig. 8.5 reaches effectively the same initial activity after repeated separations of daughter UX_1 from the parent uranium.

Many careful researches of this sort by Rutherford, Soddy, A. S. Russell, K. Fajans, R. Hahn, and others, are summarized in the complete *radioactive series*, such as that for the uranium family shown in Table 8.1. Examination of the properties of the elements in this table established two important general principles. When an atom emits an α particle, its position is shifted two places to the left in the periodic table; *i.e.*, its atomic number is decreased by two. The emission of a β particle shifts the position one place to the right, increasing the atomic number by one. It is evident, therefore, that the source of the β particles is in the nucleus of the atom, and not in the orbital electrons. No marked change in atomic weight is associated with the β emission, whereas α emission decreases the atomic weight by four units.

TABLE 8.1

RADIOACTIVE SERIES—URANIUM FAMILY

Name	Symbol of Element	At. No. Z	Mass No. A	Particle Emitted	Half Life
Uranium I	U	92	238	α	4.56×10^9 y
Uranium X_1	Th	90	234	β	24.1 d
Uranium X_2	Pa	91	234	β, γ	1.14 m
Uranium II	U	92	234	α	2.7×10^5 y
Ionium	Th	90	230	α	8.3×10^4 y
Radium	Ra	88	226	α	1590 y
Radon	Rn	86	222	α	3.825 d
Radium A	Po	84	218	α	3.05 m
Radium B	Pb	82	214	β, γ	26.8 m
Radium C	Bi	83	214	α, β, γ	19.7 m
Radium C′ (99.96%)	Po	84	214	α	1.5×10^{-4} s
Radium C″ (0.04%)	Tl	81	210	β	1.32 m
Radium D	Pb	82	210	β, γ	22 y
Radium E	Bi	83	210	β, γ	5.0 d
Radium F	Po	84	210	α	140 d
Radium G	Pb	82	206		

13. Isotopes. An important consequence of the study of the radioactive series was the demonstration of the existence of elements having the same atomic number but different atomic weights. These elements were called *isotopes* by Soddy, from the Greek *ισος τοπος*, "the same place" (*i.e.*, in the periodic table).

It was soon found that the existence of isotopes was not confined to the radioactive elements. The end product of the uranium series is lead, which, from the number of intermediate α particle emissions, should have an atomic weight of 206, compared to 207.21 for ordinary lead. Lead from the mineral curite (containing 21.3 per cent lead oxide and 74.2 per cent uranium trioxide), which occurs at Katanga, Belgian Congo, was shown to have an atomic weight of 206.03. This fact provided confirmation of the existence of nonradioactive isotopes and indicated that substantially all the lead in curite had arisen from the radioactive decay of uranium. The time at which the uranium was originally deposited can therefore be calculated from the amount of lead that has been formed. The geologic age of the earth obtained in this way is of the order of 5×10^9 years. This is the time elapsed since the minerals crystallized from the magma.

The existence of isotopes provided the solution to the discrepancies in the periodic table and to the problem of nonintegral atomic weights. The measured atomic weights are weighted averages of those of a number of isotopes, each having a weight that is nearly a whole number. The generality of this solution was soon shown by the work of Thomson on positive rays.

14. Positive-ray analysis. In 1886, Eugen Goldstein, using a discharge tube with a perforated cathode, discovered a new type of radiation streaming into the space behind the cathode, to which he gave the name *Kanalstrahlen*. Eleven years later the nature of these rays was elucidated by W. Wien, who showed that they were composed of positively charged particles with ratios e/m of the same magnitude as those occurring in electrolysis. It was reasonable to conclude that they were free positive ions.

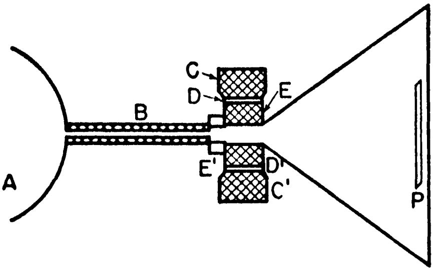


Fig. 8.6. Thomson's apparatus for positive-ray analysis.

In 1912, Thomson took up the problem of the behavior of positive rays in electric and magnetic fields, using the apparatus shown in Fig. 8.6. The positive rays, generated by ionization of the gas in a discharge tube A, were drawn out as a thin pencil through the elongated hole in the cathode B. They were then subjected in the region EE' simultaneously to a magnetic and to an electric field.

This was accomplished by inserting strips of mica insulation (D, D') in the soft iron pole pieces of the magnet. Then by connecting E and E' to a bank of batteries, it was possible to supply an electric field that would act parallel to the magnetic field of the magnet. The trace of the deflected positive rays was recorded on the photographic plate P.

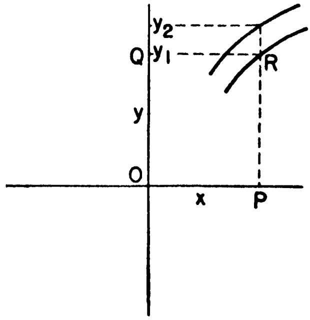


Fig. 8.7. Thomson's parabola method.

The effect of the superimposed fields may be seen from Fig. 8.7. Consider a positive ion with charge e' to be moving perpendicular to the plane of the paper so that, if undeflected, it would strike the origin O. If it is subjected somewhere along its path to the action of an electric field directed along the positive X direction, it will be deflected from O to P, the deflection being inversely proportional to the radius of curvature of the approximately circular path traveled in the electric field between the plates at EE' in Thomson's apparatus. The actual magnitude of the deflection depends on the dimensions of the apparatus. From eq. (8.5) and Fig. 8.3, the deflection may therefore be written, taking k_1 as a proportionality constant,

$$x = \frac{k_1}{R_E} = \frac{k_1 e' E}{mv^2} \tag{8.17}$$

If instead of the electric field a magnetic field in the same direction acts on the moving ion, it will be deflected upwards from O to Q, the deflection being given from eq. (8.9) by

$$y = \frac{k_1}{R_B} = \frac{k_1 e' B}{mv} \tag{8.18}$$

The constants k_1 are the same in eqs. (8.17) and (8.18) if the electric and magnetic fields act over the same length of the ion's path, as is the case in Thomson's apparatus.

If the electric and magnetic fields act simultaneously, the ion will be deflected to a point R dependent on its velocity v, and its ratio of charge to mass. In general, the individual positive ions in a beam are traveling with different velocities, and the pattern they form on a viewing screen may be calculated by eliminating v between eqs. (8.17) and (8.18). Thus

$$y^2 = k_1 \frac{B^2}{E} \cdot \frac{e'}{m} x \tag{8.19}$$

This is the equation of a parabola. The important conclusion is thereby established that all ions of given ratio of charge to mass will strike the screen along a certain parabolic curve. Since the charge e' must be an integral multiple of the fundamental electronic charge e, the position of the parabola will effectively be determined only by the mass of the positive ion.

The first evidence that isotopes existed among the stable elements was found in Thomson's investigation of neon in 1912. He observed a weak parabola accompanying that of Neon 20, which could be ascribed only to a Neon 22.

As a result of the work of A. J. Dempster, F. W. Aston, and others, positive-ray analysis has been developed into one of the most precise methods for measuring atomic masses. The existence of isotopes has been shown to be the rule rather than the exception among the chemical elements. Apparatus for measuring the masses of positive ions are known as mass spectrographs when a photographic record is obtained, and otherwise as mass spectrometers.

15. Mass spectra—The Dempster method. The disadvantage of the parabola method is that the ions of any given e/m are spread out along a curve so that the density of the pictures obtained is low at reasonable times of exposure. It was most desirable to make use of some method that would bring all ions of the same e/m to a sharp focus.

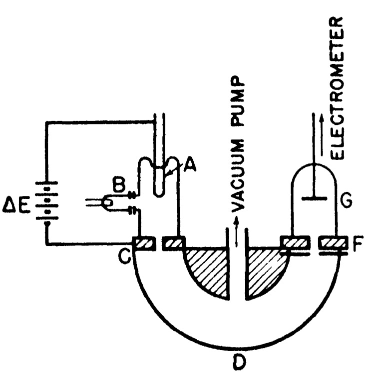


Fig. 8.8. Dempster's mass spectrometer (direction focusing).

One way of doing this, devised by A. J. Dempster in 1918, is shown in Fig. 8.8. The positive ions are obtained by vaporizing atoms from a heated filament A, and then ionizing them by means of a beam of electrons from an "electron gun"[10] at B. Alternatively, ions can be formed by passing the electron beam through samples of gas. A potential difference V between A and the slit C accelerates the ions uniformly, so that they issue from the slit with approximately the same kinetic energies,

$$\tfrac{1}{2}mv^2 = V \cdot e' \tag{8.20}$$

The region D is a channel between two semicircular pieces of iron, through which is passed the field from a powerful electromagnet. The field direction is perpendicular to the plane of the paper. The ions emerge from the slit C in various directions, but since they all have about the same velocity, they

---

[10] An electron gun is an arrangement by which electrons emitted from a filament are accelerated by an electric field and focused into a beam with an appropriate slit system.

are bent into circular paths of about the same radius, given by eq. (8.9) as $R = mv/Be$. Therefore, from eq. (8.20),

$$\frac{m}{e'} = \frac{B^2R^2}{2V} \tag{8.21}$$

It is apparent that for any fixed value of the magnetic field B, the accelerating potential can be adjusted to bring the ions of the same m/e' to a focus at the second slit F, through which they pass to the electrometer G. The electrometer measures the charge collected or the current carried through the tube by the ions. This was the method used by Dempster in operating the apparatus; it is called "direction focusing." A typical curve of ion current vs. the mass number calculated from eq. (8.21) is shown in Fig. 8.9, the heights of the peaks corresponding to the relative abundances of the isotopes.

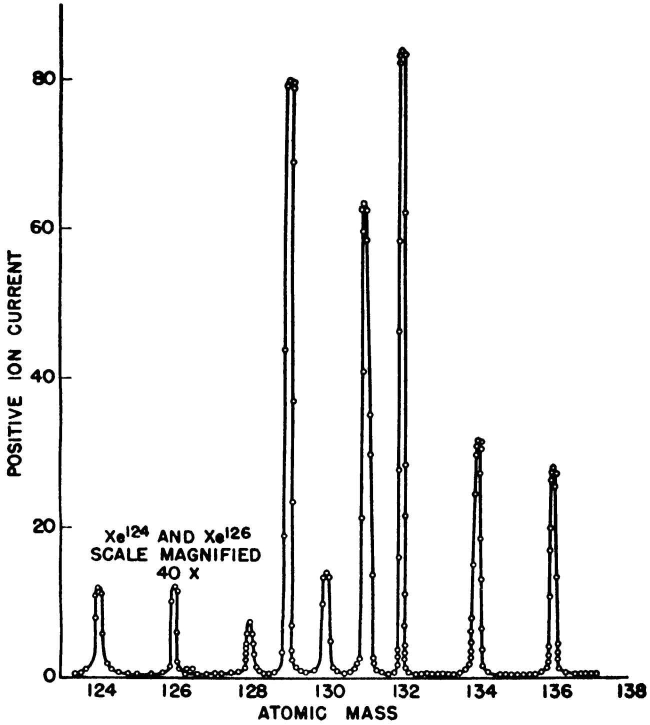


Fig. 8.9. Isotopes of xenon.

16. Mass spectra—Aston's mass spectrograph. A different method of focusing was devised by F. W. Aston in 1919, and used by him in the first extensive investigations of the occurrence of stable isotopes. The principle of this method may be seen from Fig. 8.10.

Positive ions are generated in a gas discharge tube (not shown) and drawn off through the very narrow parallel slits S_1 and S_2. Thus, in contrast with

Dempster's system, a thin ribbon of rays of closely defined direction is taken for analysis; the velocities of the individual ions may vary considerably, since they have been accelerated through different potentials in the discharge tube.

The thin beam of positive rays first passes through the electric field between parallel plates P_1 and P_2. The slower ions experience a greater deflection, since they take longer to traverse the field; the beam is accordingly spread out, as well as being deflected as shown.

A group of these rays, selected by the diaphragm D, next passes between the parallel pole pieces of the magnet M. The slower ions again experience the greater deflection. If the magnetic deflection ϕ is more than twice the electric deflection θ, all the ions, regardless of velocity, will be brought to a sharp focus at some point on the photographic plate P. Aston's method is therefore called "velocity focusing."

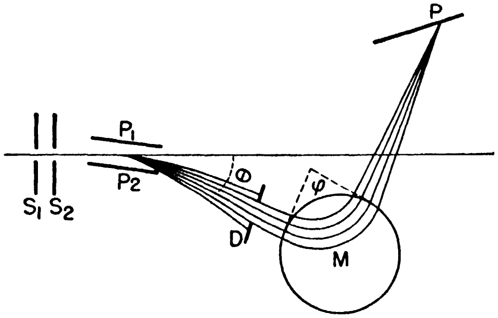


Fig. 8.10. Aston's mass spectrograph (velocity focusing).

More recent developments in mass spectrometry have combined velocity and direction focusing in a single instrument. The design has been refined to such an extent that it is possible to determine atomic masses to an accuracy of one part in 100,000. The precise determination of atomic weights with the mass spectrometer is accomplished by carefully comparing sets of closely spaced peaks. Thus one may resolve doublets such as H_2^+ and He^{++}, $^{16}O^+$ and CH_4^+, C^{++} and D_3^+.[11] By working with such doublets, instrumental errors are minimized.

Mass spectrometers are finding increasing application in the routine analysis of complex mixtures of compounds, especially of hydrocarbons. For example, a few tenths of a milliliter of a liquid mixture of isomeric hexanes and pentanes can be quantitatively analyzed with a modern mass spectrometer, a task of insuperable difficulty by any other method. Hydrocarbon isomers do not differ in mass, but each isomer ionizes and decomposes in a different way as a result of electron impact. Therefore each isomer yields a characteristic pattern of mass peaks in the spectrometer. Most commercial mass spectrometers follow the Dempster-type design.

---

[11] The symbol D stands for deuterium or heavy hydrogen, H^2, which will be discussed in following sections.

It may be noted that mass-spectrometer chemistry often seems to have little respect for our preconceived notions of allowable ionic species. Thus H_3^+ and D_3^+ are observed, and benzene vapor yields some C_6^+, a benzene ring completely stripped of its hydrogens. Such ions have, of course, a less than ephemeral lifetime, since they take only about a microsecond (10^{-6} sec) to traverse the spectrometer tube.

17. Atomic weights and isotopes. A partial list of naturally occurring stable isotopes and their relative abundance is given in Table 8.2. Not all of these isotopes were first discovered by positive-ray analysis, one notable exception being heavy hydrogen or deuterium, whose existence was originally demonstrated from the optical spectrum of hydrogen.

The isotopic weights in Table 8.2 are not exactly integral. Thus the old

TABLE 8.2

Atomic Number Z	Element	Symbol	Mass Number A	Isotopic Physical Atomic Weight (O^{16} = 16)M	Relative Abundance (per cent)
1	Hydrogen	H	1	1.008131	99.985
		D	2	2.01473	0.015
2	Helium	He	3	3.01711	10^{-5}
			4	4.00389	100
3	Lithium	Li	6	6.01686	7.8
			7	7.01818	92.1
4	Beryllium	Be	9	9.01504	100
5	Boron	B	10	10.01631	20
			11	11.01292	80
6	Carbon	C	12	12.00398	98.9
			13	13.00761	1.1
7	Nitrogen	N	14	14.00750	99.62
			15	15.00489	0.38
8	Oxygen	O	16	16.000000	99.76
			17	17.00450	0.04
			18	18.00369	0.20
9	Fluorine	F	19	19.00452	100
10	Neon	Ne	20	19.99881	90.00
			21	21.00018	0.27
			22	21.99864	9.73
15	Phosphorus	P	31	30.98457	100
16	Sulfur	S	32	31.98306	95.1
			33	32.98260	0.74
			34	33.97974	4.2
			36		0.016
17	Chlorine	Cl	35	34.98107	75.4
			37	36.97829	24.6
82	Lead	Pb	204		1.5
			206		23.6
			207		22.6
			208	208.060	52.3
92	Uranium	U	234		0.006
			235		0.720
			238		99.274

hypothesis of Prout is nearly but not exactly confirmed. The nearest whole number to the atomic weight is called the *mass number* of an atomic species. A particular isotope is conventionally designated by writing the mass number

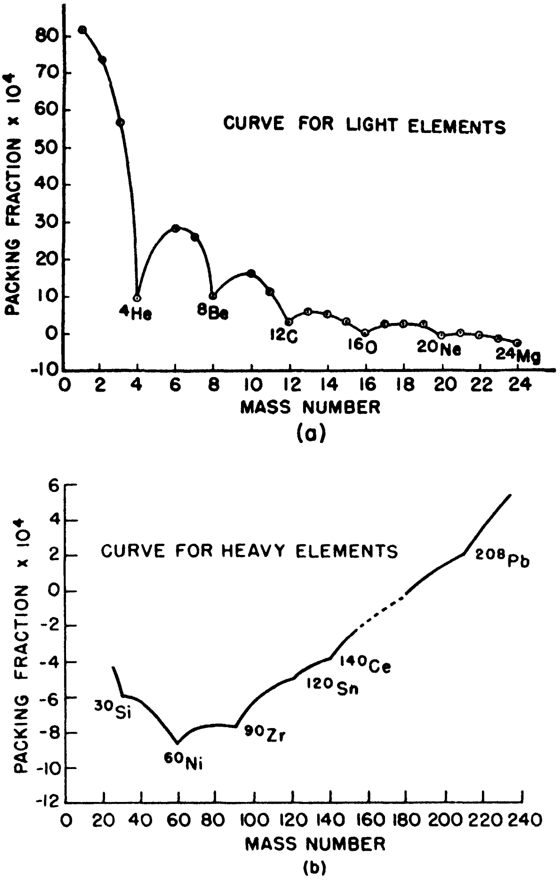


Fig. 8.11. Packing fraction curves. (a) Curve for light elements. (b) Curve for heavy elements.

as a left- or right-hand superscript to the symbol of the element; *e.g.*, ^{2}H, U^{235}, and so on.

The *packing fraction* of an isotope is defined by

$$\text{packing fraction} = \frac{\text{atomic weight} - \text{mass number}}{\text{mass number}}$$

The curves in Fig. 8.11 show how the packing fraction varies with mass number, according to the latest atomic-weight data. The further discussion of these curves, whose explanation requires an enquiry into the structure of the atomic nucleus, will be postponed till the following chapter.

It will be noted that oxygen, the basic reference element for the calculation of atomic weights, is itself composed of three isotopes, 16, 17, and 18. Chemists have been unable to abandon the convention by which the mixture of isotopes constituting ordinary oxygen is assigned the atomic weight $O = 16$. Weights calculated on this basis are called *chemical atomic weights*. The physicists prefer to call $O^{16} = 16$, whence ordinary oxygen becomes $O = 16.0043$. This leads to a set of *physical atomic weights*.

18. Separation of isotopes. For a detailed discussion of separation methods, reference may be made to standard sources.[12] Several of the more important procedures will be briefly discussed.

1. *Gaseous diffusion.* This was the method used to separate $^{235}UF_6$ from $^{238}UF_6$ in the plant at Oak Ridge, Tennessee. The fundamental principle involved has been discussed in connection with Section 7-8 on the effusion of gases.

The *separation factor* f of a process of isotope separation is defined as the ratio of the relative concentration of a given species after processing to its relative concentration before processing. Thus $f = (n_1'/n_2')/(n_1/n_2)$, where (n_1, n_1') and (n_2, n_2') are the concentrations of species 1 and 2 before and after processing. Uranium 235 occurs in natural uranium to the extent of one part in 140 $(n_1/n_2 = 1/140)$. If it is desired to separate 90 per cent pure U^{235} from U^{238}, therefore, the over-all separation factor must be $f = (9/1)/(1/140) = 1260$.

For a single stage of diffusion the separation factor cannot exceed the ideal value α, given from Graham's Law, as $\alpha = \sqrt{M_2/M_1}$, where M_2 and M_1 are the molecular weights of the heavy and light components, respectively. For the uranium hexafluorides, $\alpha = \sqrt{352/349} = 1.0043$.

Actually, the value of f for a single stage will be less than this, owing to diffusion in the reverse direction, nonideal mixing at the barrier surface, and partially nondiffusive flow through the barrier. It is therefore necessary to use several thousand stages in a cascade arrangement to effect a considerable concentration of $^{235}UF_6$. The theory of a cascade is very similar to that of a fractionating column with a large number of theoretical plates. The light fraction that passes through the barrier becomes the feed for the next stage, while the heavier fraction is sent back to an earlier stage.

It may be noted that UF_6 has at least one advantage for use in a process for separating uranium isotopes, in that there are no isotopes of fluorine except ^{19}F.

2. *Thermal diffusion.* This method was first successfully employed by H. Clusius and G. Dickel,[13] and the experimental arrangement is often

---

[12] H. S. Taylor and S. Glasstone, *Treatise on Physical Chemistry*, 3rd ed. (New York: Van Nostrand, 1941); H. D. Smyth, *Atomic Energy for Military Purposes* (Princeton Univ. Press, 1945); F. W. Aston, *Mass Spectra and Isotopes*, 4th ed. (New York: Longmans, 1942).

[13] *Naturwissenschaften*, *26*, 546 (1938). For the theory of the thermal diffusion separation see K. Schäfer, *Angew. Chem.*, *59*, 83 (1947). The separation depends not only on mass but also on difference in intermolecular forces. With isotopic molecules the mass effect predominates and the lighter molecules accumulate in the warmer regions.

called a *Clusius column.* It consists of a long vertical cylindrical pipe with an electrically heated wire running down its axis. When a temperature gradient is maintained between the hot inner wire and the cold outer walls, the lighter isotope diffuses preferentially from the cold to the warmer regions. The separation is tremendously enhanced by the convection currents in the tube, which carry the molecules arriving near the warm inner wire upwards to the top of the column. The molecules at the cold outer wall are carried downwards by convection.

With columns about 30 meters high and a temperature difference of about 600°C, Clusius was able to effect a virtually complete separation of the isotopes of chlorine, Cl^{35} and Cl^{37}.

The cascade principle can also be applied to batteries of thermal diffusion columns, but for mass production of isotopes this operation is in general less economical than pressure-diffusion methods.

3. *Electromagnetic separators.* This method employs large mass spectrometers with split collectors, so that heavy and light ions are collected separately. Its usefulness is greatest in applications in which the throughput of material is comparatively small.

4. *Separation by exchange reactions.* Different isotopic species of the same element differ significantly in chemical reactivity. These differences are evident in the equilibrium constants of the so-called *isotopic exchange reactions.* If isotopes did not differ in reactivity, the equilibrium constants of these reactions would all be equal to unity. Some actual examples follow:

$$\begin{array}{cl}
\tfrac{1}{2}\,S^{16}O_2 + H_2{}^{18}O = \tfrac{1}{2}\,S^{18}O_2 + H_2{}^{16}O & K = 1.028 \text{ at } 25^\circ\text{C} \\
{}^{13}CO + {}^{12}CO_2 = {}^{12}CO + {}^{13}CO_2 & K = 1.086 \text{ at } 25^\circ\text{C} \\
{}^{15}NH_3(g) + {}^{14}NH_4^+(aq.) = {}^{14}NH_3(g) + {}^{15}NH_4^+(aq.) & K = 1.023 \text{ at } 25^\circ\text{C}
\end{array}$$

Such differences in affinity are most marked for the lighter elements, for which the *relative* differences in isotopic masses are greater.

Exchange reactions can be applied to the separation of isotopes. The possible separation factors in a single-stage process are necessarily very small, but the cascade principle is again applicable. H. C. Urey and H. G. Thode concentrated ^{15}N through the exchange between ammonium nitrate and ammonia. Gaseous ammonia was caused to flow countercurrently to a solution of NH_4^+ ions, which trickled down columns packed with glass helices or saddles. After equilibrium was attained in the exchange columns, 8.8 grams of 70.67 per cent ^{15}N could be removed from the system, as nitrate, every twelve hours.

As a result of exchange reactions, the isotopic compositions of naturally occurring elements show small but significant variations depending on their sources. If we know the equilibrium constant of an exchange reaction over a range of temperatures, it should be possible to calculate the temperature at which a product was formed, from a measurement of the isotopic ratio in the product. Urey has applied this method, based on $O^{18} : O^{16}$ ratios, to the determination of the temperature of formation of calcium carbonate deposits. The exchange equilibrium is that between the oxygen in water and in bicarbonate ions. The temperature of the seas in remote geologic eras can be estimated to within 1°C from the $O^{18} : O^{16}$ ratio in deposits of the shells of prehistoric molluscs.

19. Heavy hydrogen. The discovery of the hydrogen isotope of mass 2, which is called *deuterium*, and the investigation of its properties comprise one of the most interesting chapters in physical chemistry.

In 1931, Urey, Brickwedde, and Murphy proved the existence of the hydrogen isotope of mass 2 by a careful examination of the spectrum of a sample of hydrogen obtained as the residue from the evaporation of several hundred liters of liquid hydrogen. Deuterium is contained in hydrogen to the extent of one part in 4500.

In 1932, Washburn and Urey discovered that an extraordinary concentration of *heavy water*, D_2O, occurred in the residue from electrolysis of water.[14] The production of 99 per cent pure D_2O in quantities of tons per day is now a feasible operation. Some of the properties of pure D_2O as compared with ordinary H_2O are collected in Table 8.3.

TABLE 8.3

PROPERTIES OF HEAVY WATER AND ORDINARY WATER

Property	Units	Ordinary Water	Heavy Water
Density at 25°C	g/cc	0.997044	1.104625
Temperature of maximum density . .	°C	4.0	11.6
Melting point	°C	0.000	3.802
Boiling point	°C	100.00	101.42
Heat of fusion	cal/mole	1436	1510
Heat of vaporization at 25° . . .	cal/mole	10,484	10,743
Dielectric constant	—	81.5	80.7
Refractive index at 20° (Na D line) .	—	1.33300	1.32828
Surface tension (20°C)	dynes/cm	72.75	72.8
Viscosity (10°C)	millipoise	13.10	16.85

PROBLEMS

1. An Na^+ ion is moving through an evacuated vessel in the positive x direction at a speed of 10^7 cm per sec. At $x = 0$, $y = 0$, it enters an electric field of 500 volts per cm in the positive y direction. Calculate its position (x, y) after 10^{-6} sec.

2. Make calculations as in Problem 1 except that the field is a magnetic field of 1000 gauss in the positive z direction.

---

[14] The mechanism of the separation of H^1 from H^2 during electrolysis is still obscure. For discussions see Eyring, *et al.*, *J. Chem. Phys.*, *7*, 1053 (1939); Urey and Teal, *Rev. Mod. Phys.*, *7*, 34 (1935).

3. Calculate the final position of the Na^+ ion in the above problems if the electric and magnetic fields act simultaneously.

4. Consider a Dempster mass spectrometer, as shown in Fig. 8.8, with a magnetic field of 3000 gauss and a path radius of 5.00 cm. At what accelerating voltage will (a) H^+ ions, (b) Na^+ ions be brought to focus at the ion collector?

5. Radium-226 decays by α particle emission with a half life of 1590 years, the product being radon-222. Calculate the volume of radon evolved from 1 g of radium over a period of 50 years.

6. The half life of radon is 3.825 days. How long would it take for 90 per cent of a sample of radon to disintegrate? How many disintegrations per second are produced in a microgram (10^{-6} g) of radium?

7. Derive an expression for the average life of a radioactive atom in terms of the half life τ.

8. The half life of thorium-C is 60.5 minutes. How many disintegrations would occur in 15 minutes from a sample containing initially 1 mg of Th-C (at wt. 212)?

9. Radioactivity is frequently measured in terms of the *curie* (c) defined as the quantity of radioactive material producing 3.7×10^{10} disintegrations per sec. The millicurie is 10^{-3} c, the microcurie, 10^{-6} c. How many grams of (a) radium, (b) radon are there in one curie?

10. It is found that in 10 days 1.07×10^{-3} cc of helium is formed from the α particles emitted by one gram of radium. Calculate a value for the half life of radium from this result.

11. The half life of U-238 is 4.56×10^9 years. The final decay product is Pb-206, the intermediate steps being fast compared with the uranium disintegration. In Lower Pre-Cambrian minerals, lead and uranium are found associated in the ratio of approximately 1 g Pb to 3.5 g U. Assuming that all the Pb has come from the U, estimate the age of the mineral deposit.

12. A β particle moving through a cloud chamber under a magnetic field of 10 oersteds traverses a circular path of 18 cm radius. What is the energy of the particle in ev?

REFERENCES

BOOKS

1. Born, M., *Atomic Physics* (London: Blackie, 1951).
2. Feather, N., *Lord Rutherford* (London: Blackie, 1940).
3. Finkelnburg, W., *Atomic Physics* (New York: McGraw-Hill, 1950).
4. Rayleigh, Lord, *Life of J. J. Thomson* (Cambridge University Press, 1942).
5. Richtmeyer, F. K., and E. A. Kennard, *Introduction to Modern Physics* (New York: McGraw-Hill, 1947).
6. Semat, H., *Introduction to Atomic Physics* (New York: Rinehart, 1946).

7. Stranathan, J. D., *The Particles of Modern Physics* (Philadelphia: Blakiston, 1954).
8. Tolansky, S., *Introduction to Atomic Physics* (London: Longmans, 1949).
9. Van Name, F., *Modern Physics* (New York: Prentice-Hall, 1952).

ARTICLES

1. Birge, R. T., *Am. J. Phys.*, *13*, 63–73 (1945), "Values of Atomic Constants."
2. Glasstone, S., *J. Chem. Ed.*, *24*, 478–81 (1947), "William Prout."
3. Hooykaas, R., *Chymia*, *2*, 65–80 (1949), "Atomic and Molecular Theory before Boyle."
4. Jauncey, G. E., *Am. J. Phys.*, *14*, 226–41 (1946), "The Early Years of Radioactivity."
5. Lemay, P., and R. E. Oesper, *Chymia*, *1*, 171–190 (1948), "Pierre Louis Dulong."
6. Mayne, K. I., *Rep. Prog. Phys.*, *15*, 24–48 (1952), "Mass Spectrometry."
7. Rayleigh, Lord, *J. Chem. Soc.*, 467–75 (1942), "Sir Joseph J. Thomson."
8. Urey, H. C., *Science in Progress*, vol. I (New Haven: Yale University Press, 1939), 35–77, "Separation of Isotopes."
9. Winderlich, R., *J. Chem. Ed.*, *26*, 358–62 (1949), "Eilard Mitscherlich."

CHAPTER 9

Nuclear Chemistry and Physics

1. Mass and energy. During the nineteenth century, two important principles became firmly established in physics: the conservation of mass and the conservation of energy. Mass was the measure of matter, the substance out of which the physical world was constructed. Energy seemed to be an independent entity that moved matter from place to place and changed it from one form to another.

In a sense, matter contained energy, for heat was simply the kinetic energy of the smallest particles of matter, and potential energy was associated with the relative positions of material bodies. Yet there seemed to be one instance, at least, in which energy existed independently of matter, namely in the form of radiation. The electromagnetic theory of Clerk Maxwell required an energy in the electromagnetic field and the field traversed empty space. Yet no experiments can be performed in empty space, so that actually this radiant energy was detected only when it impinged on matter. Now a very curious fact was observed when this immaterial entity, light energy, struck a material body.

The observation was first made in 1628 by Johannes Kepler, who noted that the tails of comets always curved away from the sun. He correctly assigned the cause of this curvature to a pressure exerted by the sun's rays. In 1901 this radiation pressure was experimentally demonstrated in the laboratory, by means of delicate torsion balances. Thus the supposedly immaterial light exerts a pressure. The pressure implies a momentum associated with the light ray, and a momentum implies a mass. If we return to Newton's picture of a light ray as made up of tiny particles, simple calculations show that the energy of the particles E is related to their mass by the equation

$$E = c^2 m \tag{9.1}$$

where c is the speed of light.

As a result of Albert Einstein's special theory of relativity (1905) it appeared that the relation $E = c^2 m$ was applicable to masses and energies of any origin. He showed first of all that no particle could have a speed greater than that of light. Thus the inertial resistance that a body offers to acceleration by an applied force must increase with the speed of the body. As the speed approaches that of light, the mass must approach infinity. The relation between mass and speed v is found to be

$$m = m_0 \left(1 - \frac{v^2}{c^2}\right)^{-1/2} \tag{9.2}$$

When $v = 0$ the body has a *rest mass*, m_0. Only at speeds comparable with that of light does the variation of mass with speed become detectable. Equation (9.2) has been confirmed experimentally by measurements of e/m for electrons accelerated through large potential differences.

If a rapidly moving particle has a larger mass than the same particle would have at rest, it follows that the larger the kinetic energy, the larger the mass, and once again it turns out that the increase in mass Δm and the increase in kinetic energy ΔE are related by $\Delta E = c^2 \Delta m$. As we shall see in the next section, the Einstein equation $E = c^2 m$ has been conclusively checked by experiments on nuclear reactions.

The situation today is therefore that mass and energy are not two distinct entities. They are simply *two different names for the same thing*, which for want of a better term is called *mass-energy*. We can measure mass-energy in mass units or in energy units. In the CGS system, the relation between the two is: 1 gram $= c^2$ ergs $= 9 \times 10^{20}$ ergs. One gram of energy is sufficient to convert 30,000 tons of water into steam.

2. Artificial disintegration of atomic nuclei. In 1919, Rutherford found that when α particles from Radium C were passed through nitrogen, protons were ejected from the nitrogen nuclei. This was the first example of the disintegration of a normally stable nucleus. It was soon followed by the demonstration of proton emission from other light elements bombarded with α particles.

In 1923, P. M. S. Blackett obtained cloud-chamber photographs showing that these reactions occurred by capture of the α particle, a proton and a new nucleus then being formed. For example,

$$_7\mathrm{N}^{14} + {}_2\mathrm{He}^4 \rightarrow ({}_9\mathrm{F}^{18}) \rightarrow {}_1\mathrm{H}^1 + {}_8\mathrm{O}^{17}$$

This type of reaction does not occur with heavy elements because of the large electrostatic repulsion between the doubly charged alpha and the high positive charges of the heavier nuclei.

It was realized that the singly charged proton, ${}_1\mathrm{H}^1$, would be a much more effective nuclear projectile, but it was not available in the form of high-velocity particles from radioactive materials. J. D. Cockroft and E. T. S. Walton[1] therefore devised an electrostatic accelerator. This apparatus was the forerunner of many and ever more elaborate machines for producing high-velocity particles. The protons produced by ionization of hydrogen in an electric discharge were admitted through slits to the accelerating tube, accelerated across a high potential difference, and finally allowed to impinge on the target.

The energy unit usually used in atomic and nuclear physics, the electron volt, is the energy acquired by an electron in falling through a potential difference of one volt. Thus 1 ev $= eV = 1.602 \times 10^{-19}$ volt coulomb

---

[1] *Proc. Roy. Soc.*, *A 129*, 477 (1930); *136*, 619 (1932).

(joule) $= 1.602 \times 10^{-12}$ erg. The usual chemical unit is the kilocalorie per *mole.*

$$1 \text{ ev} = \frac{1.602 \times 10^{-19} \times 6.02 \times 10^{23}}{4.183 \times 10^{3}} = 23.05 \text{ kcal per mole}$$

One of the first reactions to be studied by Cockroft and Walton was

$${}_1H^1 + {}_3Li^7 \rightarrow 2\,{}_2He^4$$

The bombarding protons had energies of 0.3 million electron volt (mev.) From the range of the emergent α particles in the cloud chamber, 8.3 cm, their energy was calculated to be 8.6 mev each, or more than 17 mev for the pair. It is evident that the bombarding proton is merely the trigger that sets off a tremendously exothermic nuclear explosion.

The energies involved in these nuclear reactions are several million times those in the most exothermic chemical changes. Thus an opportunity is provided for the quantitative experimental testing of the $E = c^2m$ relation. The mass-spectrographic values for the rest masses of the reacting nuclei are found to be

$$\begin{array}{c} H + Li = 2\ He \\ 1.00812 + 7.01822 \quad 2 \times 4.00391 \end{array}$$

Thus the reaction occurs with a decrease in rest mass $-\Delta m$ of 0.01852 g per mole. This is equivalent to an energy of

$$0.01852 \times 9 \times 10^{20} = 1.664 \times 10^{19} \text{ erg per mole}$$

or

$$\frac{1.664 \times 10^{19}}{6.02 \times 10^{23}} = 2.763 \times 10^{-5} \text{ erg per lithium nucleus}$$

or

$$2.763 \times 10^{-5} \times 6.242 \times 10^{11} = 17.25 \times 10^{6} = 17.25 \text{ mev}$$

This figure is in excellent agreement with the energy observed from the cloud-chamber experiments. Nor is this an isolated example, for hundreds of these nuclear reactions have been studied and completely convincing evidence for the validity of the equation $E = c^2m$ has been obtained.

It has become rather common to say that a nuclear reaction like this illustrates the conversion of mass to energy, or even the annihilation of matter. This cannot be true in view of the fact that mass and energy are the same. It is better to explain what happens as follows: Rest mass is a particularly concentrated variety of energy; Jeans once called it bottled energy. When the reaction ${}_1H^1 + {}_3Li^7 \rightarrow 2\,{}_2He^4$ takes place, a small amount of this bottled energy is released; it appears as kinetic energy of the particles reacting, which is gradually degraded into the random kinetic energy or heat of the environment. As the molecules of the environment gain kinetic energy, they gain mass. The hotter a substance, the greater is its mass. Thus, in the nuclear explosion, the concentrated rest mass (energy) is degraded into the heat mass (energy) of the environment. There has been no over-all change in mass and no over-all change in energy; mass-energy is conserved.

The measurement of the large amounts of energy released in nuclear reactions now provides the most accurate known means of determining small mass differences. The reverse process of calculating atomic masses from the observed energies of nuclear reactions is therefore widely applied in the determination of precise atomic weights. A few of the values so obtained are collected in Table 9.1 and compared with mass-spectrometer data. The agreement between the two methods is exact, within the probable error of the experiments. It would be hard to imagine a more convincing proof of the equivalence of mass and energy. The starred isotopes are radioactive, and the only available mass values are those from the $E = c^2m$ relation.

TABLE 9.1

ATOMIC WEIGHTS (O^{16} = 16.0000)

Atom	*Mass Spectrometer Value*	*Mass-Energy Value*
H^1	1.008141	1.008142
H^2	2.014732	2.014735
*H^3	—	3.01700
He^3	—	3.01698
He^4	4.00386	4.00387
*He^6	—	6.02047
Li^6	6.0145	6.01686
Li^7	7.01818	7.01822
C^{12}	12.00381	12.00380

3. Methods for obtaining nuclear projectiles. It was at about this point in its development that nuclear physics began to outgrow the limitations of small-scale laboratory equipment. The construction of machines for the production of enormously accelerated ions, capable of overcoming the repulsive forces of nuclei with large atomic numbers, demanded all the resources of large-scale engineering.

One of the most generally useful of these atom-smashing machines has been the cyclotron, shown in the schematic drawing of Fig. 9.1, which was invented by E. O. Lawrence of the University of California. The charged particle is fed into the center of the "dees" where it is accelerated by a strong electric field. The magnetic field, however, constrains it to move in a circular path. The time required to traverse a semicircle is $t = \pi R_B/v = (\pi/B) \cdot (m/e)$ from eq. (8.9); this is a constant for all particles having the same ratio e/m. The electric field is an alternating one, chosen so that its polarity changes with a frequency twice that of the circular motion of the charged particle. On each passage across the dees, therefore, the particle receives a new forward impulse, and describes a trajectory of ever increasing radius until it is drawn from the accelerating chamber of the cyclotron. The 184-in. machine at Berkeley, California, will produce a beam of 100 mev deuterons (nuclei of deuterium atoms) having a range in air of 140 feet.

A limit to the energy of ions accelerated in the original type of cyclotron is the relativistic increase of mass with velocity; this eventually destroys the synchronization in phase between the revolving ions and the accelerating field across the dees. This problem has been overcome in the *synchrocyclotron*, in which frequency modulation, applied to the alternating accelerating potential, compensates for the relativistic defocusing. This modification of the original design of the Berkeley instrument has more than doubled the maximum ion energies obtained.

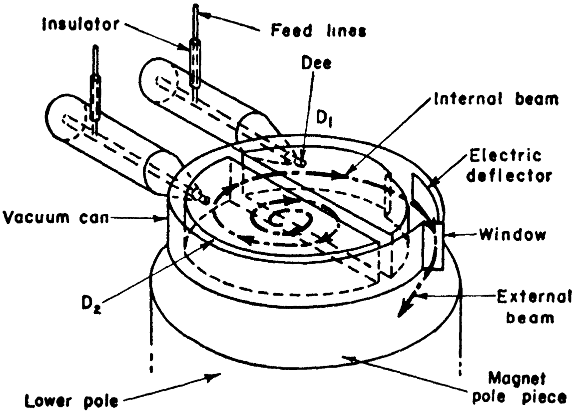


Fig. 9.1. Schematic diagram of the cyclotron. (From Lapp and Andrews, *Nuclear Radiation Physics*, 2nd Ed. Prentice-Hall, 1954.)

The *synchrotron* employs modulation of both the electric accelerating field and the magnetic focusing field. With this principle, it is possible to achieve the billion-volt range for protons. The *cosmotron*, a synchrotron completed in 1952 at Brookhaven National Laboratory, accelerates protons in a toroidal vacuum chamber with orbits 60 ft in diameter. The C-shaped magnets are placed around the vacuum chamber. Pulses of about 10^{11} protons at 3.6 mev are fired into the chamber. After about 3×10^6 revolutions, the pulse of protons has reached 3 bev (3000 mev), and is brought to the target. A similar machine at Berkeley is designed to produce 10 bev protons. These particles are thus well within the energy range of cosmic rays.

4. The photon. The essential duality in the nature of radiation has already been remarked: sometimes it is appropriate to treat it as an electromagnetic wave, while at other times a corpuscular behavior is displayed. The particle of radiation is called the *photon*.

A more detailed discussion of the relation between waves and particles will be given in the next chapter. One important result may be stated here. A homogeneous radiation of wave length λ or frequency $\nu = c/\lambda$ may be considered to be composed of photons whose energy is given by the relation,

$$\varepsilon = h\nu \tag{9.3}$$

Here h is a universal constant, called *Planck's constant*, with the value 6.624×10^{-27} erg sec. A photon has no rest mass, but since $\varepsilon = mc^2$, its mass is $m = h\nu/c^2$.

The corpuscular nature of light was first clearly indicated by the photoelectric effect, discovered by Hertz in 1887, and theoretically elucidated by Einstein in 1905. Many substances, but notably the metals, emit electrons when illuminated with light of appropriate wave lengths. A simple linear relation is observed between the maximum kinetic energy of the photoelectrons emitted and the frequency of the incident radiation. The slope of the straight line is found to be Planck's constant h. Thus,

$$\tfrac{1}{2}mv^2 = h\nu - \phi_0 \tag{9.4}$$

Such an equation can be interpreted only in terms of light quanta, or photons, which in some way transmit their energy $h\nu$ to electrons in the metal, driving them beyond the field of attraction of the metal ions. The term ϕ_0 represents the energy necessary to overcome the attractive force tending to hold the electron within the metal.

If a photon (*e.g.*, from X or γ rays) strikes an electron, an interchange of energy may take place during the collision. The scattered photon will have a higher frequency if it gains energy, a lower frequency if it loses energy. This is called the *Compton effect*.

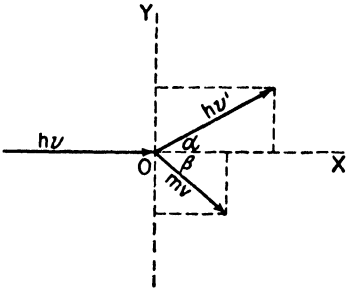


Fig. 9.2. The Compton effect.

Consider in Fig. 9.2 a photon, with initial energy $h\nu$, hitting an electron at rest at O. Let $h\nu'$ be the energy of the scattered photon and let the scattered electron acquire a speed v. Then if m is the mass of the electron, its momentum will be mv and its kinetic energy $\frac{1}{2}mv^2$. The scattering angles are α and β. The laws of conservation of energy and of momentum both apply to the collision. From the first,

$$h\nu = h\nu' + \tfrac{1}{2}mv^2$$

From the second, for the x and y components of the momentum,

$$\frac{h\nu}{c} = \frac{h\nu'}{c}\cos\alpha + mv\cos\beta$$

$$0 = \frac{h\nu'}{c}\sin\alpha - mv\sin\beta$$

Eliminating β from the momentum equations by setting $\sin^2\beta + \cos^2\beta = 1$, and assuming that $\nu' - \nu \ll \nu$, we find for the momentum imparted to the electron,

$$mv = \frac{2h\nu}{c}\sin\frac{\alpha}{2} \tag{9.5}$$

Then from the energy equation, by eliminating v, the change in frequency of the photon is

$$\Delta\nu = \nu - \nu' = \frac{h\nu^2}{mc^2}(1 - \cos\alpha)$$

The predicted angular dependence of the change in frequency has been confirmed experimentally in studies of the Compton scattering of X rays by electrons in crystals. The Compton effect has also been observed in cloud-chamber photographs.

5. The neutron. In 1930, W. Bothe and H. Becker discovered that a very penetrating secondary radiation was produced when α particles from polonium impinged on light elements such as beryllium, boron, or lithium. They believed this radiation to consist of γ rays of very short wavelength, since no track was made in a cloud chamber, and therefore charged particles were not being formed.

In 1932, Frederic and Irene Curie-Joliot found that this new radiation had much greater ionizing power after it had passed through paraffin, or some other substance having a high hydrogen content, and during its passage protons were emitted from these hydrogen-rich materials.

James Chadwick[2] solved the problem of the new "radiation." He realized that it was made up of particles of a new kind, having a mass comparable with that of the proton, but bearing no electric charge. These particles were called *neutrons*. Because of its electrical neutrality, forces between the neutron and other particles become appreciable only at very close distances of approach. The neutron, therefore, loses energy only slowly as it passes through matter; in other words, it has a great penetrating power. The hydrogen nucleus is most effective in slowing a neutron, since it is of comparable mass, and energy exchange is a maximum between particles of like mass, during actual collisions or close approaches.

The reaction producing the neutron can now be written

$${}_2\mathrm{He}^4 + {}_4\mathrm{Be}^9 \rightarrow {}_6\mathrm{C}^{12} + {}_0n^1$$

Neutrons can be produced by similar reactions of other light elements with high energy α particles, protons, deuterons, or even γ rays, for example:

$${}_1\mathrm{H}^2 + h\nu \rightarrow {}_1\mathrm{H}^1 + {}_0n^1$$

$${}_1\mathrm{H}^1 + {}_3\mathrm{Li}^7 \rightarrow {}_4\mathrm{Be}^7 + {}_0n^1$$

Beams of neutrons can be formed by means of long pinholes or slits in thick blocks of paraffin, and methods are available for producing beams of uniform energy.[3]

Because it can approach close to an atomic nucleus without being electrostatically repelled, the neutron is an extraordinarily potent reactant in nuclear processes.

---

[2] *Proc. Roy. Soc.*, *A 136*, 692 (1932).

[3] E. Fermi, J. Marshall, and L. Marshall, *Phys. Rev.*, *72*, 193 (1947); W. Zinn, *ibid.*, *71*, 757 (1947).

6. Positron, meson, neutrino. The year 1932 was a successful one for nuclear physics, because two new fundamental particles were discovered, the neutron and the positron. The latter was detected by Carl D. Anderson in certain cloud-chamber tracks from cosmic rays. The positron is the positive electron e^+. It had previously been predicted by the theoretical work of Dirac. In 1933 Frederic and Irene Curie-Joliot found that a shower of positrons was emitted when α rays from polonium impinged on a beryllium target. When targets of boron, magnesium, or aluminum were used, the emission of positrons was observed to continue for some time after the particle bombardment was stopped. This was the first demonstration of *artificial radioactivity*.[4] A typical reaction sequence is the following:

$$_5B^{10} + {}_2He^4 \rightarrow {}_0n^1 + {}_7N^{13}; \qquad {}_7N^{13} \rightarrow {}_6C^{13} + e^+$$

More than a thousand artificially radioactive isotopes are now known, produced in a variety of nuclear reactions.[5]

The positron escaped detection for so long because it can exist only until it happens to meet an electron. Then a reaction occurs that annihilates both of them, producing a γ-ray photon:

$$e^+ + e^- \rightarrow h\nu$$

The energy equivalent to the rest mass of an electron is:

$$\varepsilon = mc^2 = 9.11 \times 10^{-28} \times (3.00 \times 10^{10})^2 = 8.20 \times 10^{-7}\ \text{erg}$$

If this is converted into a single γ-ray photon, the wavelength would be

$$\lambda = \frac{h}{mc} = \frac{6.62 \times 10^{-27}}{9.11 \times 10^{-28} \times 3.00 \times 10^{10}} = 2.42 \times 10^{-10}\ \text{cm} = 0.0242\ \text{Å}$$

The γ radiation obtained in the annihilation of electron-positron pairs has either this wavelength or one-half of it. The latter case corresponds to the conversion of the masses of both e^+ and e^- into a single γ-ray photon. The reverse process, the production of an electron-positron pair from an energetic photon, has also been observed.

In 1935, H. Yukawa proposed for the structure of the nucleus a theory that postulated the existence of a hitherto unknown kind of particle, which would be unstable and have a mass of about 150 (electron = 1). From 1936 to 1938 Anderson's work at Pasadena revealed the existence of particles, produced by cosmic rays, which seemed to have many of the properties predicted by Yukawa. These particles are the *μ-mesons*, which may be charged plus or minus, have a mass of 209 ± 2, and a half life of 2.2×10^{-6} sec. The particles required by the theory, however, resemble more closely the *π-mesons*, discovered in 1947 by the Bristol cosmic-ray group headed by C. F. Powell. These have a mass of 275, and decay to μ-mesons, with a half life of 2.0×10^{-8} sec. Several other particles, with masses of 800 to

---

[4] *C. R. Acad. Sci. Paris*, *198*, 254, 559 (1934).

[5] G. Seaborg and I. Perlman, *Rev. Mod. Phys.*, *20*, 585 (1948).

1300, have also been discovered. The theoretical interpretation of the variety of particles now known will require some new great advance in fundamental theory.

In order to satisfy the law of conservation of mass-energy in radioactive decays, decay of mesons, and similar processes, it is necessary to postulate the existence of neutral particles with rest masses smaller than that of the electron. These *neutrinos* have not yet been detected by physical methods, since their effects are necessarily small.

7. The structure of the nucleus. The discovery of the neutron led to an important revision in the previously accepted picture of nuclear structure. Instead of protons and electrons, it is now evident that protons and neutrons are the true building units. These are therefore called *nucleons*.

Each nucleus contains a number of protons equal to its atomic number Z, plus a number of neutrons n, sufficient to make up the observed mass number A. Thus, $A = n + Z$.

The *binding energy* E of the nucleus is the sum of the masses of the nucleons minus the actual nuclear mass M. Thus,

$$E = Zm_H + (A - Z)m_n - M \tag{9.6}$$

The proton mass $m_H = 1.00815$, the neutron mass $m_n = 1.00893$ in atomic mass units. To convert this energy from grams per mole to mev per nucleon, it must be multiplied by

$$\frac{c^2}{N \times 10^6 \times 1.602 \times 10^{-12}} = 934$$

One of the convincing arguments against the existence of electrons as separate entities in the nucleus is based on the magnitude of the observed binding energies. For example, if the deuteron $_1H^2$ were supposed to be made up of two protons and an electron, the binding energy would be 0.00153 gram per mole. Yet the electron's mass is only 0.00055 gram per mole. For the electron to preserve its identity in the nucleus while creating a binding energy about three times its own mass would seem to be physically most unreasonable.

We do not yet know the nature of the forces between nucleons. The nuclear diameter is given approximately by $d = 1.4 \times 10^{-13} A^{1/3}$ cm, A being the mass number. The forces therefore must be extremely short-range, unlike electrostatic or gravitational forces. The density of nuclear material is around 10^{14} g per cc. A drop big enough to see would weigh 10^7 tons. There is an electrostatic repulsion between two protons, but this longer-range (inverse square) force is outweighed by the short-range attraction, so that at separations around 10^{-13} cm the attraction between two protons is about the same as that between two neutrons or a neutron and a proton. According to Yukawa's theory, the attractive forces between nucleons are due to a new type of radiation field, in which the mesons play a role like that of the photons in an ordinary electromagnetic field.

A further insight into nuclear forces can be obtained by examining the composition of the stable (nonradioactive) nuclei. In Fig. 9.3 the number of neutrons in the nucleus is plotted against the number of protons. The line has an initial slope of unity, corresponding to a one-to-one ratio, but it curves upward at higher atomic numbers. The reason for this fact is that the electrostatic repulsion of the protons increases as the nucleus becomes larger, since it is a longer range force than the attraction between protons. To compensate for this repulsion more neutrons are necessary. Yet there is a limit to the number of extra neutrons that can be accommodated and still produce added stability, so that the heavier nuclei become less stable.

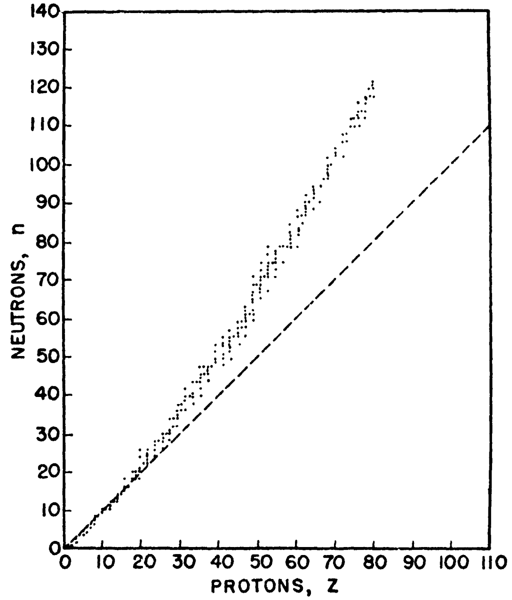


Fig. 9.3. Number of neutrons vs. number of protons in stable nuclei.

This effect is illustrated clearly in Fig. 9.4, which shows the binding energy per nucleon as a function of the mass number. Only the stable isotopes lie on this reasonably smooth curve. Natural or artificial radioactive elements fall below the curve by an amount that is a measure of their instability relative to a stable isotope of the same mass number.

The successive maxima in the early part of the curve occur at the following nuclei: He^4, Be^8, C^{12}, O^{16}, Ne^{20}. These are all nuclei containing an equal number of protons and neutrons, and in fact they are all polymers of He^4. It is possible to say, therefore, that the forces between nucleons become saturated, like the valence bonds between atoms. The unit He^4, two protons and two neutrons, appears to be one of exceptional stability. The nuclear shell structure is also clearly indicated in the packing-fraction vs. mass number curves of Fig. 8.11. The lower the packing fraction, the greater is the binding energy per nucleon.

Another viewpoint is to consider that there are certain allowed energy levels in the nucleus. Each level can hold either two neutrons or two protons.[6] The upper proton levels become raised in energy owing to the coulombic repulsion. Of all the stable nuclei, 152 have both n and Z even; 52 have Z odd, n even; 55, Z even, n odd; and only 4 have both n and Z odd. The four odd-odd nuclei are H^2, Li^6, B^{10}, N^{14}. Not only are the even-even nuclei the most frequent, they also usually have the greatest relative abundance. It can be concluded that filled nuclear energy levels confer exceptional stability.

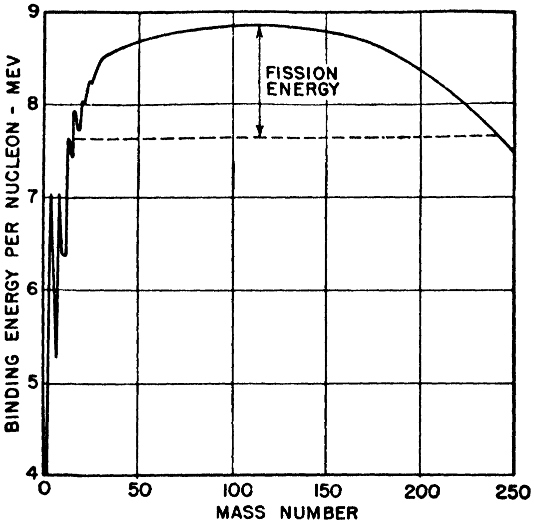


Fig. 9.4. Binding energy per nucleon as a function of atomic mass number.

8. Neutrons and nuclei. Since the neutron is an uncharged particle, it is not repelled as it approaches a nucleus, even if its energy is very low. We often distinguish fast neutrons, with a kinetic energy of > 100 ev, and slow neutrons, with energies from 0.01 to 10 ev. If the energies have the same magnitude as those of ordinary gas molecules (kT), the neutrons are called *thermal neutrons.* At 300°K, $kT = 0.026$ ev.

The interaction of a neutron and a nucleus can be represented by the intermediate formation of a *compound nucleus* which may then react in several ways. If the neutron is released again, with the reformation of the original nucleus, the process is called *scattering.* If the neutron is retained for some time, although there may be a subsequent decomposition of the compound nucleus into new products, the process is called *capture* or *absorption*.

---

[6] See Section 10-25 and discussion of nuclear spin on p. 247.

A quantitative description of the interaction between a nucleus and a neutron is given in terms of the *effective nuclear cross section*, σ. Consider a beam of neutrons in which the neutron flux is n per cm^2 per sec. If the beam passes through matter in which there are c nuclei of a given kind per cc, the number of neutrons intercepted per sec in a thickness dx is given by

$$-dn = n\sigma c\, dx \tag{9.7}$$

An initial flux of n_0 is therefore reduced after a distance x to $n_x = n_0 e^{-c\sigma x}$. The scattering cross section σ_s is distinguished from the absorption cross section σ_a, and $\sigma = \sigma_s + \sigma_a$. Nuclear cross sections are generally of the order 10^{-24} cm^2, and the whimsical physicists have called this unit the *barn*.

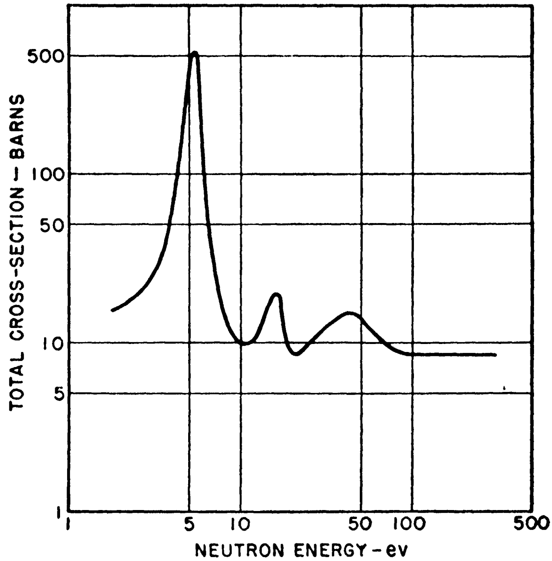


Fig. 9.5. Nuclear cross section of silver. [From Rainwater, Havens, Wu, and Dunning, *Phys. Rev. 71, 65 (1947)*.]

The cross sections depend on the kinetic energy of the neutrons and may be quite different in the low- and high-velocity ranges. The dependence of σ on energy yields important information about energy levels in the nucleus, for when the neutron energy is very close to a nuclear energy level, a "resonance" occurs that greatly facilitates capture of the neutron, and hence greatly increases the value of σ_a. For example, for thermal neutrons, $\sigma_a({}_1H^1) = 0.31$ barn, $\sigma_a({}_1H^2) = 0.00065$ barn. Both ${}_1H^1$ and ${}_1H^2$ have high scattering cross sections, and are therefore effective in slowing fast neutrons, but many of the thermal neutrons produced would be lost by capture to ${}_1H^1$ (${}_1H^1 + {}_0n^1 \rightarrow {}_1H^2$). It is for this reason that heavy water is a much more efficient neutron *moderator* than light water. In H_2O a thermal neutron would have, on the average, 150 collisions before capture; in D_2O, 10^4; in pure graphite, 10^3.

A particularly important scattering cross section is that of cadmium. The cadmium nucleus has a resonance level in the thermal neutron region, leading to the tremendously high $\sigma = 7500$ at 0.17 ev. Thus a few millimeters of cadmium sheet is practically opaque to thermal neutrons.

The cross section for silver is shown in Fig. 9.5 as a function of neutron energy. The peaks in the curve correspond to definite neutron energy levels in the nucleus. The task of the nuclear physicist is to explain these levels, as the extranuclear energy levels of the electrons have been explained by the Bohr theory and quantum mechanics. (See Chapter 10.)

9. Nuclear reactions. The different types of nuclear reactions are conveniently designated by an abbreviated notation that shows the reactant particle and the particle emitted. Thus an (n, p) reaction is one in which a neutron reacts with a nucleus to yield a new nucleus and a proton, *e.g.*, ${}_7N^{14} + {}_0n^1 \rightarrow {}_6C^{14} + {}_1H^1$ would be written ${}_7N^{14}(n,p){}_6C^{14}$.

In Table 9.2 the various nuclear reaction types are summarized. The

TABLE 9.2

TYPES OF NUCLEAR REACTIONS

Reaction Type	Normal Mass Change	Dependence on Energy of Projectile	Yield	Type of Radio-activity Usually Produced	Example
n capture	+	Resonance	100 per cent	β^-	$Ag^{107} + n^1 = Ag^{108}$
np	Slightly +	Smooth	High for light elements	β^-	$N^{14} + n^1 = C^{14} + H^1$
$n\alpha$	sl + light elem. sl − heavy	Smooth	High for light elements	β^-	$Mg^{26} + n^1 = Ne^{23} + He^4$
$n, 2n$	Very −	Smooth	Low	β^+	$P^{31} + n^1 = P^{30} + 2n$
p capture	+	Resonance	High	β^+	$C^{12} + H^1 = N^{13}$
pn	−	Threshold then smooth	High	β^+	$Cu^{63} + H^1 = Zn^{63} + n^1$
$p\alpha$	sl + light elem. − heavy	Smooth	High	Stable	$F^{19} + H^1 = O^{16} + He^4$
pd	Very −	Smooth	Low	—	$Be^9 + H^1 = Be^8 + H^2$
αn	sl − light elem. + heavy	Smooth	High for light elements	β^+	$C^{12} + He^4 = O^{15} + n^1$
αp	sl + except for light elem.	Smooth	High for light elements	Stable	$N^{14} + He^4 = O^{17} + H^1$
dp	Always +	Smooth	High for light elements	β^-	$Co^{59} + H^2 = Co^{60} + H^1$
dn	Always +	Smooth	High for light elements	β^+	$C^{12} + H^2 = N^{13} + H^1$
$d\alpha$	Always +	Smooth	High for light elements	Stable	$O^{16} + H^2 = N^{14} + He^4$
γn	Always −	Sharp threshold	Low	β^+	$Be^9 + \gamma = Be^8 + n^1$
γp	Always −	Sharp threshold	Low	—	$H^2 + \gamma = H^1 + n^1$

second column gives the normal rest-mass change for the reaction. A positive mass change is equivalent to an endothermic reaction, a negative mass change to an exothermic reaction. The next column indicates how the yield depends on the energy of the bombarding particle. In most cases there is a smooth increase in yield with increasing energy, but for capture processes there is a marked resonance effect.

10. Nuclear fission. Perusal of the binding energy curve in Fig. 9.4 reveals that a large number of highly exothermic nuclear reactions are possible, since the heavy nuclei toward the end of the periodic table are all unstable relative to the nuclei lying around the maximum of the curve.

In the January 1939 number of *Naturwissenschaften*, Otto Hahn and S. Strassman reported that when the uranium nucleus is bombarded with neutrons it may split into fragments, one of which they identified as an isotope of barium. About 200 mev of energy is released at each fission.

It was immediately realized that secondary neutrons would very possibly be emitted as a result of uranium fission, making a chain reaction possible. The likelihood of this may be seen as follows: Consider the fission of a ${}_{92}U^{235}$ nucleus to yield, typically, a ${}_{56}Ba^{139}$ as one of the observed disintegration products. If balance is to be achieved between the numbers of protons and neutrons before and after fission, the other product would have to be ${}_{36}Kr^{96}$. This product would be far heavier than any previously known krypton isotope, the heaviest of which was ${}_{36}Kr^{87}$, a β^- emitter of 4 hours half-life. Now the hypothetical ${}_{36}Kr^{96}$ can get back to the proton-neutron curve of Fig. 9.3 by a series of β^- emissions, and in fact a large number of new β^- emitters have been identified among the fission products. The same result can be achieved, however, if a number of neutrons are set free in the fission process. Actually, both processes occur.

The fission process usually consists, therefore, of a disintegration of uranium into two lighter nuclei, one of mass number from 82 to 100, and the other from 128 to 150, plus a number, perhaps about three, of rapidly moving neutrons. In only about one case in a thousand does symmetrical fission into two nuclei of approximately equal mass occur.

To determine which isotope of uranium is principally responsible for fission, A. O. Nier and his coworkers separated small samples of U^{235} (0.7 per cent abundance) and U^{238} (99.3 per cent) with a mass spectrometer. It was found that U^{235} undergoes fission even when it captures a slow thermal neutron, but U^{238} is split only by fast neutrons with energies greater than 1 mev. As usual, the capture cross section for slow neutrons is much greater than that for fast neutrons, so that U^{235} fission is a much more likely process than that of U^{238}. The process of fission can be visualized by considering the nucleus as a drop of liquid. When a neutron hits it, oscillations are set up. The positive charges of the protons acquire an unsymmetrical distribution, and the resulting repulsion can lead to splitting of the nuclear drop. Since U^{235} contains an odd number of neutrons, when it gains a neutron considerable energy is set free. This kinetic energy starts the disturbance within the nucleus that leads to fission. The isotope U^{238} already contains an even number of neutrons, and the capture process is not so markedly exothermic. Therefore the neutron must be a fast one, bringing considerable kinetic energy into the nucleus, in order to initiate fission. Fission of other heavy elements, such as lead, has been produced by bombardment with 200 mev deuterons produced by the Berkeley cyclotron. Fission can also be induced by γ rays with energies greater than about 5 mev (*photofission*).

In Fig. 9.6 are shown the mass distributions of the fission products in three different cases that have been carefully studied. When fission is produced

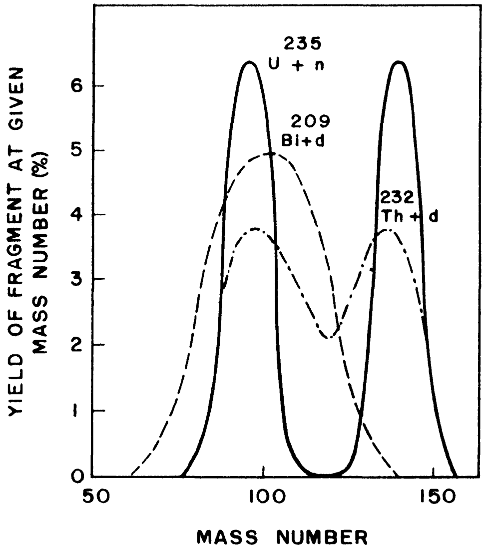


Fig. 9.6. Mass distribution of products in three different fission reactions. The energies of the particles initiating the fission are: *n*, thermal; α, 38 mev; *d*, 200 mev. Note how the distribution becomes more symmetrical as the energy of the incident particle increases. (From P. Morrison, "A Survey of Nuclear Reactions" in *Experimental Nuclear Physics*, ed. E. Segré, Wiley, 1953.)

by highly energetic particles, the distribution of masses is quite symmetrical, and the most probable split is one that yields two nuclei of equal mass. This is the result that would be expected from the liquid-drop model. The unsymmetrical splitting that follows capture of slower particles has not yet received a satisfactory theoretical explanation, but it is undoubtedly related to the detailed shell structure inside the nucleus.

A nuclear reaction of great interest is *spontaneous fission*, discovered in 1940 by Flerov and Petrzhak in the U.S.S.R. It cannot be attributed to cosmic radiation or to any other known external cause, and it must be considered to be a new type of natural radioactivity. For example, when about 6 g of Th^{232} were observed for 1000 hr, 178 spontaneous fissions were detected. Spontaneous fission is usually a very rare reaction, but it becomes much more frequent in some of the transuranium elements.

11. The transuranium elements. In 1940, E. McMillan and P. H. Abelson[7] found that when U^{238} is irradiated with neutrons, a resonance capture can occur that leads eventually to the formation of two new transuranium elements.

$$_{92}U^{238} + {_0n^1} \rightarrow {_{92}U^{239}}$$

$$_{92}U^{239} \xrightarrow{23\text{ min}} {_{93}Np^{239}} + \beta$$

$$_{93}Np^{239} \xrightarrow{2.3\text{ days}} {_{94}Pu^{239}} + \beta$$

The $_{94}Pu^{239}$ is a weakly radioactive α emitter ($\tau = 2.4 \times 10^4$ years). Its most important property is that, like U^{235}, it undergoes fission by slow neutrons.

It was shown by G. T. Seaborg[8] and his coworkers that bombardment of U^{238} with α particles leads by an (α, n) reaction to Pu^{241}. This is a β emitter and decays to give $_{95}Am^{241}$, an isotope of americium which is α-radioactive with 500 years half-life. By 1954, the last of the transuranium elements to have been prepared were curium (96), berkelium (97), californium (98), and elements (99) and (100). Curium can be made by an (α, n) reaction on Pu^{239}:

$$_{94}Pu^{239} + {_2He^4} \rightarrow {_0n^1} + {_{96}Cm^{242}}$$

The preparation of new examples of the transuranium elements has been facilitated by the technique of using heavy ions accelerated in the cyclotron. Thus high energy beams of carbon ions, $({_6C^{12}})^{6+}$, can increase the atomic number of a target nucleus by six units in one step. For example, isotopes of californium have been synthesized as follows:[9]

$$_{92}U^{238} + {_6C^{12}} \rightarrow {_{98}Cf^{246}} + 4n$$

$$_{92}U^{238} + {_6C^{12}} \rightarrow {_{98}Cf^{244}} + 6n$$

Element (99) was prepared by:

$$_{92}U^{238} + {_7N^{14}} \rightarrow {_{99}X^{247}} + 5n$$

12. Nuclear chain reactions. Since absorption of one neutron can initiate fission, and more than one neutron is produced at each fission, a branching chain can occur in a mass of fissionable material. The rate of escape of neutrons from a mass of U^{235}, for example, depends on the area of the mass, whereas the rate of production of neutrons depends on the volume. As the volume of the mass is increased, therefore, a critical point is finally reached at which neutrons are being produced more rapidly than they are being lost.

---

[7] *Phys. Rev.*, *57*, 1185 (1940).

[8] *Science*, *104*, 379 (1946); *Chem. Eng. News*, *25*, 358 (1947).

[9] A. Ghiorso, S. G. Thompson, K. Street, and G. T. Seaborg, *Phys. Rev. 81*, 1954 (1951).

If two masses of U^{235} of subcritical mass are suddenly brought together a nuclear explosion can take place.

For the continuous production of power, a *nuclear pile* is used. The fissionable material is mixed with a moderator such as graphite or heavy water, to slow down the neutrons. Control of the rate of fission is effected by introducing rods of a material such as cadmium, which absorbs the thermal neutrons. The depth to which the cadmium rods are pushed into the pile controls the rate of fission.

The pile also serves as a source of intense beams of neutrons for research purposes. As shown in Fig. 9.7, a diagram of the Brookhaven pile, these beams can be either fast neutrons from the center of the pile, or thermal neutrons drawn out through a layer of moderator.

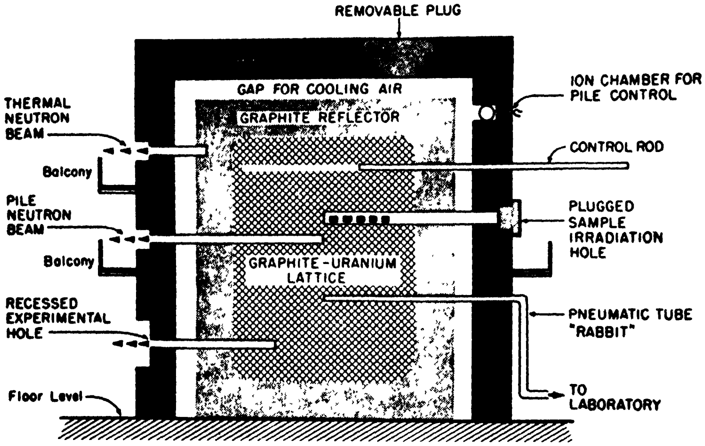


Fig. 9.7. Diagrammatic sketch of the Brookhaven pile showing the features of importance for pile neutron research. (From D. J. Hughes, *Pile Neutron Research*, Addison-Wesley, 1953.)

13. Energy production by the stars. The realization of the immense quantities of energy that are released in exothermic nuclear reactions has also provided an answer to one of the great problems of astrophysics—the source of the energy of the stars. At the enormous temperatures prevailing in stellar interiors (*e.g.*, around 10 million degrees in the case of our sun) the nuclei have been stripped of electrons and are moving with large kinetic-theory velocities. Thus the mean thermal kinetic energy of an α particle at room temperature is of the order of $\frac{1}{40}$ ev, but at the temperature of the sun it has become 10^4 ev. In other words, at stellar temperatures many of the nuclei have attained energies comparable with those of the high-velocity particles produced on earth by means of the cyclotron and similar devices.

Nuclei with these high energies will be able to overcome the strong electrostatic repulsion between their positive charges and approach one another sufficiently closely to initiate various nuclear reactions. It is these so-called *thermonuclear reactions* that account for the energy production of the stars.

In 1938, Carl von Weizsäcker and Hans Bethe independently proposed a most ingenious mechanism for stellar-energy production. This is a cycle proceeding as follows:

$$\begin{aligned} C^{12} + H^1 &\rightarrow N^{13} + h\nu \\ N^{13} &\rightarrow C^{13} + e^+ \\ C^{13} + H^1 &\rightarrow N^{14} + h\nu \\ N^{14} + H^1 &\rightarrow O^{15} + h\nu \\ O^{15} &\rightarrow N^{15} + e^+ \\ N^{15} + H^1 &\rightarrow C^{12} + He^4 \end{aligned}$$

The net result is the conversion of four H nuclei into one He nucleus through the mediation of C^{12} and N^{14} as "catalysts" for the nuclear reaction; 30 mev are liberated in each cycle. This *carbon cycle* appears to be the principal source of energy in very hot stars ($T > 5 \times 10^8$ °K).

The energy of somewhat cooler stars, like our sun ($T \sim 10^7$ °K), appears to be generated by the proton-proton cycle:

$$\begin{aligned} {}_1H^1 + {}_1H^1 &\rightarrow {}_1H^2 + e^+ + 0.42 \text{ mev} \\ {}_1H^1 + {}_1H^2 &\rightarrow {}_2He^3 + \gamma + 5.5 \text{ mev} \\ {}_2He^3 + {}_2He^3 &\rightarrow {}_2He^4 + 2\,{}_1H^1 + 12.8 \text{ mev} \end{aligned}$$

The net result is the conversion of 4 protons to one helium nucleus, with the liberation of 24.6 mev plus the annihilation energy of the positron.

Gamow has estimated[10] that reactions between hydrogen nuclei (${}_1H^1 + {}_1H^2 \rightarrow {}_2He^3 + \gamma$; $2\,{}_1H^2 \rightarrow {}_2He^4 + \gamma$) would have an appreciable rate at temperatures below 10^6 degrees; reactions of protons with lithium nuclei (${}_1H^1 + {}_3Li^6 \rightarrow {}_2He^4 + {}_2He^3$; ${}_1H^1 + {}_3Li^7 \rightarrow 2\,{}_2He^4$) require about 6×10^6 degrees; reactions such as ${}_1H^1 + {}_5B^{10} \rightarrow {}_6C^{11} + \gamma$ require about 10^7 degrees.

The temperatures attainable by means of uranium or plutonium fission are high enough to initiate thermonuclear reactions of the lighter elements. The fission reaction acts as a "match" to start the fusion reactions. Easiest of all to "ignite" should be mixtures containing tritium, the hydrogen isotope of mass 3.

$$\begin{aligned} {}_1H^3 + {}_1H^2 &= {}_2He^4 + {}_0n^1 + 17.6 \text{ mev } (\gamma) \\ {}_1H^3 + {}_1H^1 &= {}_2He^4 + 19.6 \text{ mev } (\gamma) \end{aligned}$$

The tritium can be prepared by pile reactions such as ${}_3Li^6 + {}_0n^1 \rightarrow {}_2He^4 + {}_1H^3$. The isotope Li^6 has an abundance of 7.52 atom per cent.

14. Tracers. The variety of radioactive isotopes now available has made possible many applications in *tracer experiments*, in which a given type of atom can often be followed through a sequence of chemical or physical

---

[10] George Gamow, *The Birth and Death of the Sun* (New York: Penguin, 1945), p. 128.

changes. Stable isotopes can also be used as tracers, but they are not so easily followed and are available for relatively few elements. Radioactive isotopes can be obtained from four principal sources: (1) natural radioactivity; (2) irradiation of stable elements with beams of ions or electrons obtained from accelerators such as cyclotrons, betatrons, etc.; (3) pile irradiation with neutrons; (4) fission products. In Table 9.3 are listed a few of the many available isotopes.

TABLE 9.3

ARTIFICIAL RADIOACTIVE ELEMENTS

Nucleus	*Activity*	*Half Life*
C^{11}	β^+, γ	21 min
C^{14}	β^-	5700 yr
N^{13}	β^+, γ	9.9 min
O^{15}	β^+	125 sec
Na^{22}	β^+, γ	3.0 yr
Na^{24}	β^-, γ	14.8 hr
P^{32}	β^-	14.3 days
S^{35}	β^-	87.1 days
Ca^{45}	β^-	152 days
Fe^{59}	β^-, γ	46 days
Co^{60}	β^-, γ	5.3 yr
Cu^{64}	β^+, β^-	12.8 hr

One of the earliest studies with radioactive tracers used radioactive lead to follow the diffusion of lead ions in solid metals and salts. For example, a thin coating of radiolead can be plated onto the surface of a sample of metallic lead. After this is maintained at constant temperature for a definite time, thin slices are cut off and their radioactivity measured with a Geiger counter. The self-diffusion constant of Pb in the metal can readily be calculated from the observed distribution of activity. Many such diffusion studies have now been made in metals and in solid compounds. The results obtained are of fundamental importance in theories of the nature and properties of the solid state. Diffusion in liquids, as well as the permeability of natural and synthetic membranes, can also be conveniently followed by radioactive tracer methods.

The solubility of water in pure hydrocarbons is so low that it is scarcely measurable by ordinary methods. If water containing radioactive hydrogen, or tritium, ${}_1H^3$, a β^- emitter of 12 years half life, is used, even minute amounts dissolved in the hydrocarbons are easily measured.[11]

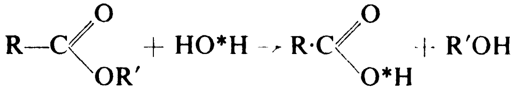
A useful tracer method is *isotopic dilution analysis*. An example is the determination of amino acids in the products of protein hydrolysis. The conventional method would require the complete isolation of each amino acid in pure form. Suppose, however, a known amount of an amino acid

---

[11] C. Black, G. G. Joris, and H. S. Taylor, *J. Chem. Phys.*, *16*, 537 (1948).

labeled with deuterium or carbon-14 is added to the hydrolysate. After thorough mixing, a small amount of the given acid is isolated and its activity measured. From the decrease in activity, the total concentration of the acid in the hydrolysate can be calculated.

Tracers are used to elucidate reaction mechanisms. One interesting problem was the mechanism of ester hydrolysis. Oxygen does not have a radioactive isotope of long enough half life to be a useful tracer, but the stable O^{18} can be used. By using water enriched with heavy oxygen (O^*) the reaction was shown to proceed as follows:



$$\mathrm{R{-}C(=O)OR' + HO^{*}H \rightarrow R{\cdot}C(=O)O^{*}H + R'OH}$$

The tagged oxygen appeared only in the acid, showing that the OR group is substituted by $-O^*H$ in the hydrolysis.[12]

Radioactive isotopes of C, Na, S, P, etc., are of great use in investigations of metabolism. They supplement the stable isotopes of H, N, and O. For example it has been found that labeled phosphorus tends to accumulate preferentially in rapidly metabolizing tissues. This has led to its trial in cancer therapy. The results in this case have not been particularly encouraging, but it may be possible to find metabolites or dyes that are specifically concentrated in tumor tissues, and then to render these compounds radioactive by inclusion of appropriate isotopic atoms.[13]

15. Nuclear spin. In addition to its other properties, the nucleus may have an intrinsic angular momentum or *spin*. All elementary particles (*i.e.*, neutrons, protons, and electrons) have a spin of one-half in units of $h/2\pi$. The spin of the electron will be considered in some detail in the next chapter. The spin of the elementary particles can be either plus or minus. If an axis is imagined passing through the particle, the sign corresponds to a clockwise or counterclockwise spin, although this picture is a very crude one. The spin of a nucleus is the algebraic sum of the spins of the protons and neutrons that it contains.

The hydrogen nucleus, or proton, has a spin of one-half. If two hydrogen atoms are brought together to form H_2, the nuclear spins can be either parallel (↑↑) or antiparallel (↑↓). Thus there are two *nuclear spin isomers* of H_2. The molecule with parallel spins is called "orthohydrogen," the one with antiparallel spins is called "parahydrogen." Since spins almost never change their orientation spontaneously, these two isomers are quite stable. They have different heat capacities and different molecular spectra. Other molecules composed of two identical nuclei having nonzero spin behave similarly, but only in the cases of H_2 and D_2 are there marked differences in physical properties.

---

[12] M. Polanyi and A. L. Szabo, *Trans. Farad. Soc.*, *30*, 508 (1934).

[13] M. D. Kamen, *Radioactive Tracers in Biology* (New York: Academic, 1947).

PROBLEMS

1. What is the Δm in g per mole for the reaction $H_2 + \frac{1}{2} O_2 = H_2O$ for which $\Delta H = -57.8$ kcal per mole?

2. From the atomic weights in Table 9.1, calculate the ΔE in kcal per mole for the following reactions:

$$_1H^1 + {_0n^1} = {_1H^2}, \quad {_1H^2} + {_0n^1} = {_1H^3}, \quad {_1H^1} + e = {_0n^1}, \quad 2\,{_1H^2} = {_2He^4}$$

3. Calculate the energies in (a) ev (b) kcal per mole of photons having wavelengths of 2.0 Å, 1000 Å, 6000 Å, 1 mm, 1 m.

4. To a hydrolysate from 10 g of protein is added 100 mg of pure CD_3CHNH_2COOH (deuterium-substituted alanine). After thorough mixing, 100 mg of crystalline alanine is isolated which has a deuterium content of 1.03 per cent by weight. Calculate the per cent alanine in the protein.

5. A 10-g sample of iodobenzene is shaken with 100 ml of a 1 M KI solution containing 2500 counts per min radio-iodine. The activity of the iodobenzene layer at the end of 2 hours is 250 cpm. What per cent of the iodine atoms in the iodobenzene have exchanged with the iodide ions in solution?

6. Calculate the mass of an electron accelerated through a potential of 2×10^8 volts. What would the mass be if the relativity effect is ignored?

7. Naturally occurring oxygen consists of 99.76 per cent O^{16}, 0.04 per cent O^{17}, and 0.20 per cent O^{18}. Calculate the ratio of atomic weights on the physical scale to those on the chemical scale.

8. The work function of a cesium surface is 1.81 volts. What is the longest wavelength of incident light that can eject a photoelectron from Cs?

9. The π-meson has a mass about 285 times that of the electron; the μ-meson has a mass about 215 times that of the electron. The π-meson decays into a μ-meson plus a neutrino. Estimate ΔE for the reaction in ev.

10. Calculate the energy necessary to produce a pair of light mesons. This pair production has been accomplished with the 200-in. California cyclotron.

11. The scattering cross section, σ, of lead is 5 barns for fast neutrons. How great a thickness of lead is required to reduce the intensity of a neutron beam to 5 per cent of its initial value? How great a thickness of magnesium with $\sigma = 2$ barns?

12. According to W. F. Libby [*Science*, *109*, 227 (1949)] it is probable that radioactive carbon-14 ($\tau = 5720$ years) is produced in the upper atmosphere by the action of cosmic-ray neutrons on N^{14}, being thereby maintained at an approximately constant concentration of 12.5 cpm per g of carbon. A sample of wood from an ancient Egyptian tomb gave an activity of 7.04 cpm per g C. Estimate the age of the wood.

13. A normal male subject weighing 70.8 kg was injected with 5.09 ml of water containing tritium (9×10^9 cpm). Equilibrium with body water was reached after 3 hr when a 1-ml sample of plasma water from the subject had an activity of 1.8×10^5 cpm. Estimate the weight per cent of water in the human body.

14. When $_{38}Sr^{88}$ is bombarded with deuterons, $_{38}Sr^{89}$ is formed. The cross section for the reaction is 0.1 barn. A $SrSO_4$ target 1.0 mm thick is exposed to a deuteron beam current of 100 microamperes. If scattering of deuterons is neglected, compute the number of Sr atoms transmuted in 1.0 hr. The Sr^{88} is 82.6 per cent of Sr, and Sr^{89} is a β-emitter of 53-day half life. Compute the curies of Sr^{89} produced.

15. When $_{79}Au^{197}$ (capture cross section $\sigma_c = 10^{-22}$ cm^2) is irradiated with slow neutrons it is converted into $_{79}Au^{198}$ ($\tau = 2.8$ days). Show that in general the number of unstable nuclei present after irradiation for a time t is

$$n = \frac{\sigma n_0 \phi}{\lambda}(1 - e^{-\lambda t})$$

Here n_0 is the number of target atoms and ϕ is the slow neutron flux. For the case in question, calculate the activity in microcuries of a 100-mg gold sample exposed to a neutron flux of 200/cm^2 sec for 2 days.

16. The conventional unit of quantity of X radiation is the roentgen, *r*. It is the quantity of radiation that produces 1 esu of ions in 1 cc of air at STP (1 esu $= 3.3 \times 10^{-10}$ coulomb). If 32.5 ev are required to produce a single ion pair in air, calculate the energy absorbed in 1 liter of air per roentgen.

17. Potassium-40 constitutes 0.012 per cent of natural K, and K is 0.35 per cent of the weight of the body. K^{40} emits β and γ rays and has $\tau = 4.5 \times 10^8$ yr. Estimate the number of disintegrations per day of the K^{40} in each gram of body tissue.

18. The isotope $_{89}Ac^{225}$ has $\tau = 10$ days and emits an α with energy of 5.80 mev. Calculate the power generation in watts per 100 mg of the isotope.

REFERENCES

BOOKS

1. Baitsell, G. A. (editor), *Science in Progress*, vol. VI (New Haven: Yale Univ. Press, 1949). Articles by H. D. Smyth on Fission; J. A. Wheeler on Elementary Particles; E. O. Lawrence on High Energy Physics; G. T. Seaborg on Transuranium Elements.
2. Bethe, H., *Elementary Nuclear Theory* (New York: Wiley, 1947).
3. Friedlander, G., and J. W. Kennedy, *Introduction to Radiochemistry* (New York: Wiley, 1949).
4. Gamow, G., and C. L. Critchfield, *Theory of Atomic Nucleus and Nuclear Energy Sources* (New York: Oxford, 1949).
5. Goodman, C. (editor), *The Science and Engineering of Nuclear Power* (2 vols) (Boston: Addison-Wesley, 1947, 1949).

6. Halliday, D., *Introductory Nuclear Physics* (New York: Wiley, 1950).
7. Hughes, D. J., *Pile Neutron Research* (Boston: Addison-Wesley, 1953).
8. Lapp, R. E., and H. L. Andrews, *Nuclear Radiation Physics*, 2nd ed. (New York: Prentice-Hall, 1954).
9. Libby, W. F., *Radiocarbon Dating* (Chicago: Univ. of Chicago Press, 1952).

ARTICLES

1. Anderson, C. D., *Science in Progress*, *7*, 236–249 (1951), "The Elementary Particles of Physics."
2. Curtan, S. C., *Quart. Rev.*, *7*, 1–18 (1953), "Geological Age by Means of Radioactivity."
3. Dunning, J. R., *Science in Progress*, *7*, 291–355 (1951), "Atomic Structure and Energy."
4. Hevesy, G. C., *J. Chem. Soc.*, 1618–1639 (1951), "Radioactive Indicators in Biochemistry."
5. Pryce, M. H. L., *Rep. Prog. Phys.*, *17*, 1–35 (1954), "Nuclear Shell Structure."
6. Wilkinson, M. K., *Am. J. Phys.*, *22*, 263–76 (1954), "Neutron Diffraction."

CHAPTER 10

Particles and Waves

1. The dual nature of light. It has already been noted that in the history of light two different theories were alternately in fashion, one based on the particle model and the other on the wave model. At the present time both must be regarded with equal respect. In some experiments light displays notably corpuscular properties: the photoelectric and Compton effects can be explained only by means of light particles, or photons, having an energy $\varepsilon = h\nu$. In other experiments, which appear to be just as convincing, the wave nature of light is manifest: polarization and interference phenomena require an undulatory theory.

This unwillingness of light to fit neatly into a single picture frame has been one of the most perplexing problems of natural philosophy. The situation recalls the impasse created by the "null result" of the Michelson-Morley experiment. This result led Einstein to examine anew one of the most basic of physical concepts, the idea of the simultaneity of events in space and time. The consequence of his searching analysis was the scientific revolution expressed in the relativity theories.

An equally fundamental enquiry has been necessitated by the developments arising from the dual nature of light. These have finally required a re-examination of the meaning and limitations of physical measurement when applied to systems of atomic dimensions or smaller. The results of this analysis are as revolutionary as the relativity theory; they are embodied in what is called *quantum theory* or *wave mechanics*. Before discussing the significant experiments that led inexorably to the new theories, we shall review briefly the nature of vibratory and wave motions.

2. Periodic and wave motion. The vibration of a simple harmonic oscillator, discussed on page 190, is a good example of a motion that is periodic in time. The equation of motion ($f = ma$) is $m\,d^2x/dt^2 = -\kappa x$. This is a simple linear differential equation.[1] It can be solved by first making the substitution $p = dx/dt$. Then $d^2x/dt^2 = dp/dt = (dp/dx)(dx/dt) = p(dp/dx)$, and the equation becomes $p(dp/dx) + (\kappa/m)x = 0$. Integrating, $p^2 + (\kappa/m)x^2 = \text{const.}$

The integration constant can be evaluated from the fact that when the oscillator is at the extreme limit of its vibration, $x = A$, the kinetic energy is zero, and hence $p = 0$. Thus the constant $= (\kappa/m)A^2$. Then

$$p^2 = \left(\frac{dx}{dt}\right)^2 = \frac{\kappa}{m}(A^2 - x^2)$$

---

[1] See, for example, Granville *et al.*, *Calculus*, p. 383.

$$\frac{dx}{dt} = \sqrt{\frac{\kappa}{m}(A^2 - x^2)}$$

$$\frac{dx}{\sqrt{A^2 - x^2}} = \sqrt{\frac{\kappa}{m}}\, dt$$

$$\sin^{-1}\frac{x}{A} = \sqrt{\frac{\kappa}{m}}\, t + \text{const}$$

This integration constant can be evaluated from the initial condition that at $t = 0$, $x = 0$; therefore constant $= 0$.

The solution of the equation of motion of the simple harmonic oscillator is accordingly:

$$x = A \sin \sqrt{\frac{\kappa}{m}}\, t \qquad (10.1)$$

If we set $\sqrt{\kappa/m} = 2\pi\nu$, this becomes

$$x = A \sin 2\pi\nu t \qquad (10.2)$$

The simple harmonic vibration can be represented graphically by this sine function, as shown in Fig. 10.1. A cosine function would do just as well. The constant ν is called the *frequency* of the motion; it is the number of vibrations in unit time. The reciprocal of the frequency, $\tau = 1/\nu$, is called the *period* of the motion, the time required for a single vibration. Whenever $t = n(\tau/2)$, where n is an integer, the displacement x passes through zero.

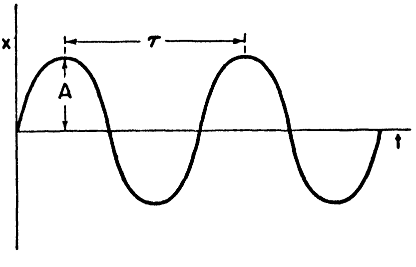


Fig. 10.1. Simple harmonic vibration.

The quantity A, the maximum value of the displacement, is called the *amplitude* of the vibration. At the position $x = A$, the oscillator reverses its direction of motion. At this point, therefore, the kinetic energy is zero, and all the energy is potential energy E_p. At position $x = 0$, all the energy is kinetic energy E_k. Since the total energy, $E = E_p + E_k$, is always a constant, it must equal the potential energy at $x = A$. On page 190 the potential energy of the oscillator was shown to be equal to $\frac{1}{2}\kappa x^2$, so that the total energy is

$$E = \tfrac{1}{2}\kappa A^2 \qquad (10.3)$$

The total energy is proportional to the square of the amplitude. This important relation holds true for all periodic motions.

The motion of a harmonic oscillator illustrates a displacement periodic with time, temporally periodic. If such an oscillator were immersed in a fluid medium it would set up a disturbance which would travel through the medium. Such a disturbance would be not only temporally periodic but also spatially periodic. It would constitute what is called a *wave*. For example, a tuning fork vibrating in air sets up sound waves. An oscillating electric dipole sets up electromagnetic waves in space.

Let us consider a simple harmonic wave moving in one dimension, x. If one takes an instantaneous "snapshot" of the wave, it will have the form of a sine or cosine function. This snapshot is the *profile* of the wave. If at a point $x = 0$ the magnitude of the disturbance ϕ equals 0, then at some further point $x = \lambda$, the magnitude will again be zero, and so on at 2λ, 3λ . . . $n\lambda$. This quantity λ is called the *wavelength*. It is the measure of the wave's periodicity in space, just as the period τ is the measure of its periodicity in time. The profile of the simple sine wave has the form:

$$\phi = A \sin 2\pi \frac{x}{\lambda} \tag{10.4}$$

Now consider the expression for the wave at some later time t. The idea of the velocity of the wave must then be introduced. If the disturbance is moving through the medium with a velocity c in the positive x direction, in a time t it will have moved a distance ct. The wave profile will have exactly the same form as before if the origin is shifted from $x = 0$ to a new origin at $x = ct$. Referred to this moving origin, the wave profile always maintains the form of eq. (10.4). To refer the disturbance back to the stationary origin, it is necessary only to subtract the distance moved in time t from the value of x. Then the equation for the moving wave becomes

$$\phi = A \sin \frac{2\pi}{\lambda} (x - ct) \tag{10.5}$$

Note that the nature of the disturbance ϕ need not be specified: in the case of a water wave it is the height of the undulation; in the case of an electromagnetic wave it is the strength of an electric or magnetic field.

Now it is evident that c/λ is simply the frequency: $\nu = c/\lambda$. The number of wavelengths in unit distance is called the *wave number*, $k = 1/\lambda$, so that eq. (10.5) can be written in the more convenient form:

$$\phi = A \sin 2\pi(kx - \nu t) \tag{10.6}$$

3. Stationary waves. In Fig. 10.2, two waves, ϕ_1 and ϕ_2, are shown that have the same amplitude, wavelength, and frequency. They differ only in that ϕ_2 has been displaced along the X axis relative to ϕ_1 by a distance $\delta/2\pi k$. Thus they may be written

$$\phi_1 = A \sin 2\pi(kx - \nu t)$$

$$\phi_2 = A \sin [2\pi(kx - \nu t) + \delta]$$

The quantity δ is called the *phase* of ϕ_2 *relative to* ϕ_1.

When the displacement is exactly an integral number of wavelengths, the two waves are said to be *in phase*; this occurs when $\delta = 2\pi$, 4π, or any even multiple of π. When $\delta = \pi$, 3π, or any odd multiple of π, the two waves are exactly *out of phase*. Interference phenomena are readily explained in terms of these phase relationships, for when two superimposed waves of equal amplitude are out of phase, the resultant disturbance is reduced to zero.

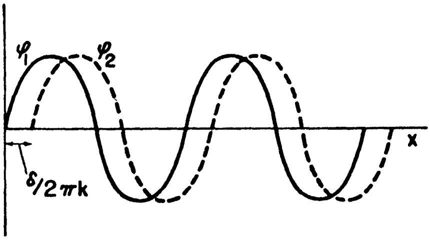


Fig. 10.2. Waves differing in phase.

The expression (10.6) is one solution of the general partial differential equation of wave motion, which governs all types of waves, from tidal waves to radio waves. In one dimension this equation is

$$\frac{\partial^2\phi}{\partial x^2} = \frac{1}{c^2}\cdot\frac{\partial^2\phi}{\partial t^2} \tag{10.7}$$

In three dimensions the equation becomes

$$\nabla^2\phi \equiv \frac{\partial^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial y^2} + \frac{\partial^2\phi}{\partial z^2} = \frac{1}{c^2}\cdot\frac{\partial^2\phi}{\partial t^2} \tag{10.8}$$

The operator ∇^2 (del squared) is called the *Laplacian*.

One important property of the wave equation is apparent upon inspection. The disturbance ϕ and all its partial derivatives appear only in terms of the first degree and there are no other terms. This is therefore a *linear homogeneous* differential equation.[2] It can be verified by substitution that if ϕ_1 and ϕ_2 are any two solutions of such an equation, then a new solution can be written having the form

$$\phi = a_1\phi_1 + a_2\phi_2 \tag{10.9}$$

where a_1 and a_2 are arbitrary constants. This is an illustration of the *principle of superposition*. Any number of solutions can be added together in this way to obtain new solutions. This is essentially what is done when a complicated vibratory motion is broken down into its *normal modes* (page 191), or when a periodic function is represented by a Fourier series.

An important application of the superposition principle is found in the addition of two waves of the form of eq. (10.6) that are exactly the same

[2] Granville, *loc. cit.*, pp. 372, 377.

except that they are going in opposite directions. Then the new solution will be

$$\phi = A \sin 2\pi(kx - \nu t) + A \sin 2\pi(kx + \nu t)$$

or $$\phi = 2A \sin 2\pi kx \cos 2\pi\nu t \tag{10.10}$$

since $$\sin x + \sin y = 2 \sin \frac{x + y}{2} \cos \frac{x - y}{2}$$

This new wave, which does not move either forward or backward, is a *stationary wave*. The waves of the original type [eq. (10.6)] are called *progressive waves*. It will be noted that in the stationary wave represented by eq. (10.10), the disturbance ϕ always vanishes, irrespective of the value of t, for points at which $\sin 2\pi kx = 0$ or $x = 0, \frac{1}{2}k, \frac{2}{2}k, \frac{3}{2}k \ldots (n/2)k$. These points are called *nodes*. The distance between successive nodes is $\frac{1}{2}k$ or $\lambda/2$, one-half a wavelength. Midway between the nodes are the positions of maximum amplitude, or *antinodes*.

Solutions of the one-dimensional type, which have just been discussed, will apply to the problem of a vibrating string in the idealized case in which there is no damping of the vibrations. In a string of infinite length one can picture the occurrence of progressive waves. Consider, however, as in Fig. 10.2, a string having a certain finite length L. This limitation imposes certain *boundary conditions* on the permissible solutions of the wave equation. If the ends of the string are held fixed: at $x = 0$ and at $x = L$, the displacement ϕ must $= 0$. Thus there must be an integral number of nodes between 0 and L, so that the allowed wavelengths are restricted to those that obey the equation

$$n\frac{\lambda}{2} = L \tag{10.11}$$

where n is an integer. This occurrence of whole numbers is very typical of solutions of the wave equation under definite boundary conditions. In order to prevent destruction of the wave by interference, there must be an integral number of half wavelengths fitted within the boundary. This principle will be seen to have important consequences in quantum theory.

4. Interference and diffraction. The interference of light waves can be visualized with the aid of the familiar construction of Huygens. Consider, for example, in (a) Fig. 10.3, an effectively plane wave front from a single source, incident upon a set of slits. The latter is the prototype of the well known diffraction grating. Each slit can now be regarded as a new light source from which there spreads a semicircular wave (or hemispherical in the three-dimensional case). If the wavelength of the radiation is λ, a series of concentric semicircles of radii λ, 2λ, 3λ . . . may be drawn with these sources as centers. Points on these circles represent the consecutive maxima in amplitude of the new wavelets. Now, following Huygens, the new resultant wave fronts are the curves or surfaces that are simultaneously tangent to the secondary wavelets. These are called the "envelopes" of the wavelet curves and are shown in the illustration.

The important result of this construction is that there are a number of possible envelopes. The one that moves straight ahead in the same direction as the original incident light is called the zero-order beam. On either side of this are first-, second-, third-, etc., order diffracted beams. The angles by which the diffracted beams deviate from the original direction evidently depend on the wavelength of the incident radiation. The longer the wavelength, the greater is the diffraction. This is, of course, the basis for the use of the diffraction grating in the measurement of the wavelength of radiation.

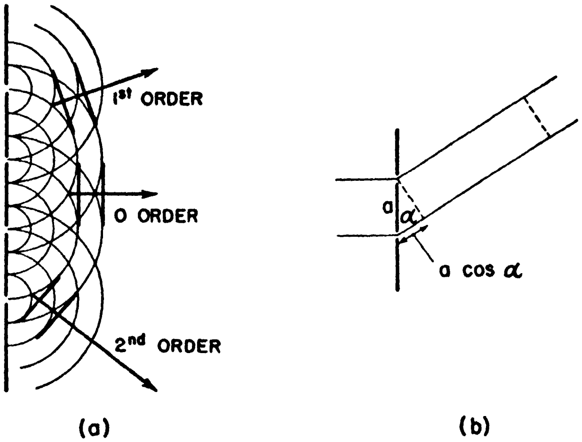


Fig. 10.3. Diffraction: (a) Huygens' construction; (b) path difference.

The condition for formation of a diffracted beam can be derived from a consideration of (b) Fig. 10.3, where attention is focused on two adjacent slits. If the two diffracted rays are to reinforce each other they must be in phase, otherwise the resultant amplitude will be cut down by interference. The condition for reinforcement is therefore that the difference in path for the two rays must be an integral number of wavelengths. If α is the angle of diffraction and a the separation of the slits, this path difference is $a \cos \alpha$ and the condition becomes

$$a \cos \alpha = h\lambda \tag{10.12}$$

where h is an integer.

This equation applies to a linear set of slits. For a two-dimensional plane grating, there are two similar equations to be satisfied. For the case of light incident normal to the grating,

$$a \cos \alpha = h\lambda$$
$$b \cos \beta = k\lambda$$

It will be noted that the diffraction is appreciable only when the spacings of the grating are not very much larger than the wavelength of the incident light. In order to obtain diffraction effects with X rays, for example, the spacings should be of the order of a few Ångstrom units.[3]

Max von Laue, in 1912, realized that the interatomic spacings in crystals were probably of the crder of magnitude of the wavelengths of X rays. Crystal structures should therefore serve as three-dimensional diffraction gratings for X rays. This prediction was immediately verified in the critical experiment of Friedrich, Knipping, and Laue. A typical X-ray diffraction picture is shown in Fig. 13.7 on page 375. The far-reaching consequences of Laue's discovery will be considered in some detail in a later chapter. It is mentioned here as a demonstration of the wave properties of X rays.

5. Black-body radiation. The first definite failure of the old wave theory of light was not found in the photoelectric effect, a particularly clear-cut case, but in the study of *black-body radiation.* All objects are continually absorbing and emitting radiation. Their properties as absorbers or emitters may be extremely diverse. Thus a pane of window glass will not absorb much of the radiation of visible light but will absorb most of the ultraviolet. A sheet of metal will absorb both the visible and the ultraviolet but may be reasonably transparent to X rays.

In order for a body to be in equilibrium with its environment, the radiation it is emitting must be equivalent (in wavelength and amount) to the radiation it is absorbing. It is possible to conceive of objects that are perfect absorbers of radiation, the so-called *ideal black bodies.* Actually, no substances approach very closely to this ideal over an extended range of wavelengths. The best laboratory approximation to an ideal black body is not a substance at all, but a cavity.

This cavity, or *hohlraum*, is constructed with excellently insulating walls, in one of which a small orifice is made. When the cavity is heated, the radiation from the orifice will be a good sample of the equilibrium radiation within the heated enclosure, which is practically ideal black-body radiation.

There is a definite analogy between the behavior of the radiation within such a *hohlraum* and that of gas molecules in a box. Both the molecules and the radiation are characterized by a density and both exert pressure on the confining walls. One difference is that the gas density is a function of the volume and the temperature, whereas the radiation density is a function of temperature alone. Analogous to the various velocities distributed among the gas molecules are the various frequencies distributed among the oscillations that comprise the radiation.

At any given temperature there is a characteristic distribution of the gas velocities given by Maxwell's equation. The corresponding problem of the spectral distribution of black-body radiation, that is, the fraction of the

---

[3] It is also possible to use larger spacings and work with extremely small angles of incidence. The complete equation, corresponding to eq. (10.12), for incidence at an angle α_0, is $a(\cos \alpha - \cos \alpha_0) = h\lambda$.

total energy radiated that is within each range of wavelength, was first explored experimentally (1877–1900) by O. Lummer and E. Pringsheim. Some of their results are shown in Fig. 10.4. These curves indeed have a marked resemblance to those of the Maxwell distribution law. At high temperatures the position of the maximum is shifted to shorter wavelengths—an iron rod glows first dull red, then orange, then white as its temperature is raised and higher frequencies become appreciable in the radiation.

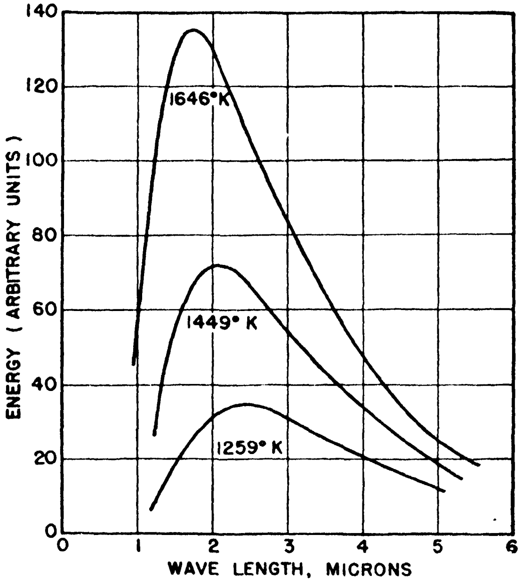


Fig. 10.4. Data of Lummer and Pringsheim on spectral distribution of radiation from a black body at three different temperatures.

When these data of Lummer and Pringsheim appeared, attempts were made to explain them theoretically by arguments based on the wave theory of light and the principle of equipartition of energy. Without going into the details of these efforts, which were uniformly unsuccessful, it is possible to see why they were foredoomed to failure.

According to the principle of the equipartition of energy, an oscillator in thermal equilibrium with its environment should have an average energy equal to kT, $\frac{1}{2}kT$ for its kinetic energy and $\frac{1}{2}kT$ for its potential energy, where k is the Boltzmann constant. This classical theory states that the average energy depends in no way on the *frequency* of the oscillator. In a system containing 100 oscillators, 20 with a frequency ν_1 of 10^{10} cycles per sec and 80 with $\nu_2 = 10^{14}$ cycles per sec, the equipartition principle predicts that 20 per cent of the energy shall be in the low-frequency oscillators and 80 per cent in the high-frequency oscillators.

The radiation within a *hohlraum* can be considered to be made up of standing waves of various frequencies. The problem of the energy distribution over the various frequencies (intensity I vs. ν) apparently reduces to the determination of the number of allowed vibrations in any range of frequencies.

The possible high-frequency vibrations greatly outnumber the low-frequency ones. The one-dimensional case of the vibrating string can be used to illustrate this fact. We have seen in eq. (10.11) that in a string of length L, standing waves can occur only for certain values of the wavelength given by $\lambda = 2L/n$. It follows that the number of allowed wavelengths from any given value λ to the maximum $2L$ is equal to $n = 2L/\lambda$. We wish to find the additional number of allowed wavelengths that arise if the limiting wavelength value is decreased from λ to $\lambda - d\lambda$. The result is obtained by differentiation[4] as

$$dn = \frac{2L}{\lambda^2}\,d\lambda \tag{10.13}$$

This indicates that the number of allowed vibrations in a region from λ to $\lambda - d\lambda$ increases rapidly as the wavelength decreases (or the frequency increases). There are many more high-frequency than low-frequency vibrations. The calculation in three dimensions is more involved[5] but it yields essentially the same answer. For the distribution of standing waves in an enclosure of volume V, the proper formula is $dn = (8\pi V/\lambda^4)d\lambda$, or

$$dn = 8\pi \frac{V}{c^3}\,\nu^2\,d\nu \tag{10.14}$$

Since there are many more permissible high frequencies than low frequencies, and since by the equipartition principle all frequencies have the same average energy, it follows that the intensity I of black-body radiation should rise continuously with increasing frequency. This conclusion follows inescapably from classical Newtonian mechanics, yet it is in complete disagreement with the experimental data of Lummer and Pringsheim, which show that the intensity of the radiation rises to a maximum and then falls off sharply with increasing frequency. This abject failure of classical mechanical principles when applied to radiation was viewed with unconcealed dismay by the physicists of the time. They called it the "ultraviolet catastrophe."

6. Planck's distribution law. The man who first dared to discard classical mechanics and the equipartition of energy was Max Planck. Taking this step in 1900, he was able to derive a new distribution law, which explained the experimental data on black-body radiation.

Newtonian mechanics (and relativity mechanics too) was founded upon the ancient maxim that *natura non facit saltum* ("nature does not make a jump"). Thus an oscillator could be presumed to take up energy *continuously*

---

[4] It is assumed that in a region of large L and small λ, n is so large that it can be considered to be a continuous function of λ.

[5] R. H. Fowler, *Statistical Mechanics* (London: Cambridge, 1936), p. 112.

in arbitrarily small increments. Although matter was believed to be atomic in its constitution, energy was assumed to be strictly continuous.

Planck discarded this precept and suggested that an oscillator, for example, could acquire energy only in discrete units, called *quanta*. The quantum theory began therefore as an atomic theory of energy. The magnitude of the quantum or atom of energy was not fixed, however, but depended on the oscillator frequency according to

$$\varepsilon = h\nu \tag{10.15}$$

Planck's constant h has the dimensions of energy times time (*e.g.*, 6.62×10^{-27} erg sec), a quantity known as *action.*

According to this hypothesis it is easy to see qualitatively why the intensity of black-body radiation always falls off at high frequencies. At frequencies such that $h\nu \gg kT$, the size of the quantum becomes much larger than the mean kinetic energy of the atoms comprising the radiator. The larger the quantum, the smaller is the chance of an oscillator having the necessary energy, since this chance depends on an $e^{-h\nu/kT}$ Boltzmann factor. Thus oscillators of high frequency have a mean energy considerably less than the kT of the classical case.

Consider a collection of N oscillators having a fundamental vibration frequency ν. If these can take up energy only in increments of $h\nu$, the allowed energies are 0, $h\nu$, $2h\nu$, $3h\nu$, etc. Now according to the Boltzmann formula, eq. (7.31), if N_0 is the number of systems in the lowest energy state, the number N_i having an energy ε_i above this ground state is given by

$$N_i = N_0 e^{-\varepsilon_i/kT} \tag{10.16}$$

In the collection of oscillators, for example,

$$N_1 = N_0 e^{-h\nu/kT}$$
$$N_2 = N_0 e^{-2h\nu/kT}$$
$$N_3 = N_0 e^{-3h\nu/kT}$$

The total number of oscillators in all energy states is therefore

$$\begin{aligned} N &= N_0 + N_0 e^{-h\nu/kT} + N_0 e^{-2h\nu/kT} + \dots \\ &= N_0 \sum_{i=0}^{\infty} e^{-ih\nu/kT} \end{aligned}$$

The total energy of all the oscillators equals the energy of each level times the number in that level.

$$\begin{aligned} E &= 0 \cdot N_0 + h\nu N_0 e^{-h\nu/kT} + 2h\nu N_0 e^{-2h\nu/kT} + \dots \\ &= N_0 \sum_{i=0}^{\infty} ih\nu\, e^{-ih\nu/kT} \end{aligned}$$

The average energy of an oscillator is therefore

$$\bar{\varepsilon} = \frac{E}{N} = \frac{h\nu \Sigma i e^{-ih\nu/kT}}{\Sigma\, e^{-ih\nu/kT}}.$$

Or, if $x = h\nu/kT$,

$$\bar{\varepsilon} = h\nu \frac{\Sigma i e^{-ix}}{\Sigma e^{-ix}} = \frac{h\nu}{e^x - 1} = \frac{h\nu}{e^{h\nu/kT} - 1}. \qquad (10.17)^6$$

According to this expression, the mean energy of an oscillator whose fundamental frequency is ν approaches the classical value of kT when $h\nu$ becomes much less than kT.[7] Using this equation in place of the classical equipartition of energy, Planck derived an energy-distribution formula in excellent agreement with the experimental data for black-body radiation. The energy density $E(\nu)\,d\nu$ is simply the number of oscillations per unit volume between ν and $\nu + d\nu$ [eq. (10.14)] times the average energy of an oscillation [eq. (10.17)]. Hence Planck's Law is

$$E(\nu)\,d\nu = \frac{8\pi h\nu^3}{c^3} \cdot \frac{d\nu}{e^{h\nu/kT} - 1} \qquad (10.18)$$

7. Atomic spectra. Planck's quantum theory of energy appeared in 1901. Strong confirmation was provided by the theory of the photoelectric effect proposed by Einstein in 1905. Another most important application of the theory was soon made, in the study of atomic spectra.

An incandescent gas emits a spectrum composed of lines at definite wavelengths. Similarly if white light is transmitted through a gas, certain wavelengths are absorbed, causing a pattern of dark lines on a bright background when the emergent light is analyzed with a spectrograph. These emission and absorption spectra must be characteristic of certain preferred frequencies in the gaseous atoms and molecules. A sharply defined *line spectrum* is typical of atoms. Molecules give rise to spectra made up of *bands*, which can often be analyzed further into closely packed lines. For example, the spectra of atomic hydrogen (H) and of molecular nitrogen (N_2) are shown in Fig. 10.5a and b.

In 1885, J. J. Balmer discovered a regular relationship between the frequencies of the atomic hydrogen lines in the visible region of the spectrum. The wave numbers ν' are given by

$$\nu' = \mathscr{R}\left(\frac{1}{2^2} - \frac{1}{n_1^{\,2}}\right)$$

with $n_1 = 3, 4, 5 \ldots$ etc. The constant $\mathscr{R}$ is called the *Rydberg constant*, and has the value 109,677.581 cm^{-1}. It is one of the most accurately known physical constants.

---

[6] In eq. (10.17) let $e^{-x} = y$, then the denominator $\Sigma y^i = 1 + y + y^2 + \ldots = 1/(1 - y)$, $(y < 1)$. The numerator, $\Sigma i y^i = y(1 + 2y + 3y^2 + \ldots) = y/(1 - y)^2$, $(y < 1)$ so that eq. (10.17) becomes $h\nu y/(1 - y) = h\nu/(e^{h\nu/kT} - 1)$.

[7] When $h\nu \ll kT$, $e^{h\nu/kT} \approx 1 + (h\nu/kT)$.

Other hydrogen series were discovered later, which obeyed the more general formula,

$$\nu' = \mathcal{R}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{10.19}$$

Lyman found the series with $n_2 = 1$ in the far ultraviolet, and others were found in the infrared by Paschen ($n_2 = 3$), Brackett ($n_2 = 4$), and Pfund ($n_2 = 5$). A great number of similar series have been observed in the atomic spectra of other elements.

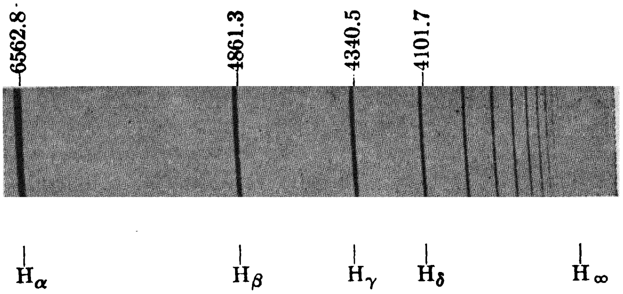


Fig. 10.5a. Spectra of atomic hydrogen. (From Herzberg, *Atomic Spectra and Atomic Structure*, Dover, 1944.)

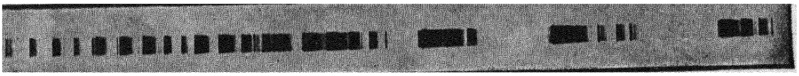


Fig. 10.5b. Spectra of molecular nitrogen. (From Harrison, Lord, and Loofbourow, *Practical Spectroscopy*, Prentice-Hall, 1948.)

8. The Bohr theory. These characteristic atomic line spectra could not be explained on the basis of the Rutherford atom. According to this model, electrons are revolving around a positively charged nucleus, the coulombic attraction balancing the force due to the centripetal acceleration. The classical theory of electromagnetic radiation demands that an accelerated electric charge must continuously emit radiation. If this continuous emission of energy actually occurred, the electrons would rapidly execute a descending spiral and fall into the nucleus. The Rutherford atom is therefore inherently unstable according to classical mechanics, but the predicted continuous radiation does not in fact occur. The fact that the electrons in atoms do not follow classical mechanics is also clearly shown by the heat-capacity values of gases. The C_V for monatomic gases equals $\frac{3}{2}R$, which is simply the amount expected for the translation of the atom as a whole. It is evident that the electrons in the atoms do not take up energy as the gas is heated.

Niels Bohr, in 1913, suggested that the electrons can revolve around the nucleus only in certain definite orbits, corresponding to certain allowed energy states. Radiation is emitted in discrete quanta whenever an electron falls from an orbit of high to one of lower energy, and is absorbed whenever an electron is raised from a low to a higher energy orbit. If E_{n_1} and E_{n_2} are the energies of two allowed states of the electron, the frequency of the spectral line arising from a transition is

$$\nu = \frac{\Delta E}{h} = \frac{1}{h}(E_{n_1} - E_{n_2}) \qquad (10.20)$$

A separate and arbitrary hypothesis is needed to specify which orbits are allowed. The simplest orbits of one electron moving in the field of force of a positively charged nucleus are the circular ones. For these orbits, Bohr postulated the following frequency condition:[8] only those orbits occur for which the angular momentum mvr is an integral multiple of $h/2\pi$.

$$mvr = n\frac{h}{2\pi}, \qquad n = 1, 2, 3 \ldots \qquad (10.21)$$

The integer n is called a *quantum number*.

The mechanics of motion of the electron in its circular orbit of radius r can be analyzed starting with Newton's equation, $f = ma$. The force is the coulombic attraction between nucleus, with charge Ze, and electron, *i.e.*, Ze^2/r^2. The acceleration is the centripetal acceleration, v^2/r. Therefore $Ze^2/r^2 = mv^2/r$, and

$$r = \frac{Ze^2}{mv^2} \qquad (10.22)$$

Then, from eq. (10.21)

$$r = n^2 \frac{h^2}{4\pi^2 me^2 Z} \qquad (10.23)$$

In the case of a hydrogen atom $Z = 1$, and the smallest orbit, $n = 1$, would have a radius,

$$a_0 = \frac{h^2}{4\pi^2 me^2} = 0.529 \text{ Å} \qquad (10.24)$$

This radius is of the same order of magnitude as that obtained from the kinetic theory of gases.

It may be noted that the radii of the circular Bohr orbits depend on the square of the quantum number. It can now be demonstrated that the Balmer series arises from transitions between the orbit with $n = 2$ and outer orbits; in the Lyman series, the lower term is the orbit with $n = 1$; the other series are explained similarly. These results are obtained by calculating the energies corresponding to the different orbits and applying eq. (10.20). The *energy level diagram* for the hydrogen atom is shown in Fig. 10.6.

---

[8] It will be seen a little later that this condition is simply another form of Planck's hypothesis that h is the quantum of action.

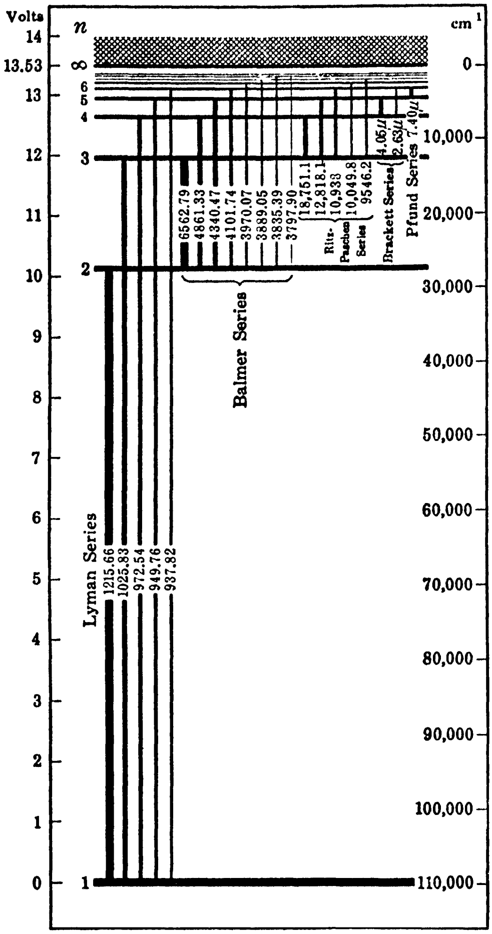


Fig. 10.6. Energy levels of the H atom. (After G. Herzberg, *Atomic Spectra*, Dover, 1944.)

The total energy E of any state is the sum of the kinetic and potential energies:

$$E = E_k + E_p = \tfrac{1}{2}mv^2 - \frac{Ze^2}{r}$$

From eq. (10.22),
$$E = -\frac{Ze^2}{r} + \frac{Ze^2}{2r} = -\frac{Ze^2}{2r}$$

Therefore from eq. (10.23),
$$E = -\frac{2\pi^2 me^4}{h^2} \cdot \frac{Z^2}{n^2} \tag{10.25}$$

The frequency of a spectral line is then

$$\nu = \frac{1}{h}(E_{n_2} - E_{n_1}) = \frac{2\pi^2 me^4}{h^3} Z^2 \left(\frac{1}{n_2^{\,2}} - \frac{1}{n_1^{\,2}}\right) \tag{10.26}$$

Comparison with the experimental eq. (10.19) yields a theoretical value of the Rydberg constant for atomic hydrogen of

$$\mathscr{R} = \frac{2\pi^2 me^4}{ch^3} = 109{,}737 \text{ cm}^{-1}$$

This is in excellent agreement with the experimental value.

This pleasing state of affairs represented a great triumph for the Bohr theory and lent some solid support to the admittedly *ad hoc* hypothesis on which it is based.

Several improvements in the original Bohr theory were made by Arnold Sommerfeld. He considered the possible elliptical orbits of an electron around the nucleus as one focus. Such orbits are known to be stable configurations in dynamical systems such as the planets revolving around the sun.

For a circular orbit, the radius r is constant so that only angular momentum, associated with the variable θ, need be considered. For elliptical orbits two quantum numbers are needed, for the two variables r and θ. The *azimuthal quantum number* k was introduced to give the angular momentum in units of $h/2\pi$. The *principal quantum number* n was defined[9] so that the ratio of the major axis to the minor axis of the elliptical orbit was n/k. Then k can take any value from 1 to n, the case $n = k$ corresponding to a circular orbit.

9. Spectra of the alkali metals. An electron moving about a positively charged nucleus is moving in a spherically symmetrical coulombic field of force. Besides the hydrogen atom, a series of *hydrogenlike ions* satisfy this condition. These ions include He^+, Li^{++}, and Be^{+++}, each of which has a single electron. Their spectra are observable when electric sparks discharge through the vapour of the element (spark spectra). They are very similar in structure to the hydrogen spectrum, but the different series are displaced to shorter wavelengths, as a consequence of the dependence of frequency on the square of the nuclear charge, given by eq. (10.26).

If an electron is moving in a spherically symmetrical field, the energy level is the same for all elliptical orbits of major axis a as it is for the circular orbit of radius a. In other words, the energy is a function only of the principal quantum number n. All energy levels with the same n are the same, irrespective of the value of k, the azimuthal quantum number. For example, if $n = 3$, there are three superimposed levels or terms of identical energy, having $k = 1$, 2, or 3. Such an energy level is said to have a threefold *degeneracy*. Actually, even in hydrogen, a very slight splitting of these degenerate levels is found in the *fine structure* of the spectra, revealed by spectrographs of high resolving power.

---

[9] Derivations and detailed discussions of these aspects of the old quantum theory may be found in S. Dushman's article in Taylor's *Treatise on Physical Chemistry*, 2nd ed., p. 1170.

For most of the atoms and ions that may give rise to spectra the electrons concerned in the transitions are not moving in spherically symmetric fields. Consider, for example, the case of the lithium atom, which is typical of the alkali metals. The electron whose transitions are responsible for the observed spectrum is the outer, *valence*, or *optical* electron. This electron does not move in a spherical field, since its position at any instant is influenced by the positions of the two inner electrons. If the outer electron is on one side of the nucleus, it is less likely that the other two will be there also, because of the electrostatic repulsions. Thus the field is no longer spherical, and the elliptical orbits can no longer have the same energy as a circular orbit of the same n value. The elliptical orbits will have different energy levels depending on their ellipticity, which is governed by the allowed values of the azimuthal quantum number k. For each n, there will be n different energy levels characterized by different k's.

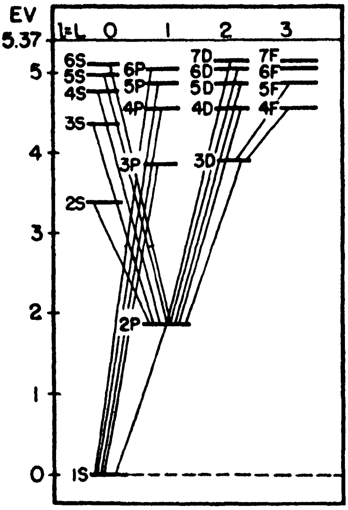


Fig. 10.7. Energy levels and spectral transitions in the lithium atom.

The lowest or *ground state* is that for which $n = 1$ and $k = 1$. States with $k = 1$ are called s states. This is therefore a $1s$ state. When $n = 2$, k can be either 1 or 2. States with $k = 2$ are called p states. We therefore have a $2s$ state and a $2p$ state. Similarly, when $n = 3$, we have $3s$, $3p$, and $3d$ ($k = 3$) states; when $n = 4$, we have $4s$, $4p$, $4d$, and $4f$ ($k = 4$) states.

In this discussion there has been a tacit assumption that the energy levels of the atom are determined solely by the quantum states of the valence electrons. This is actually not true, and all the electrons and even the nucleus should be considered in discussing the allowed energy states. Then, instead of the quantum number k, which gives the angular momentum of the single electron, a new quantum number L must be used that gives the resultant angular momentum of all the electrons. According as $L = 0, 1, 2, 3 \ldots$ etc., we refer to the *atomic states* as $S, P, D, F \ldots$ etc. In the case of atoms like the alkali metals, which have only one valence electron, it turns out that the resultant angular momenta of the inner electrons add vectorially to zero. Therefore in this case only the single electron need be considered after all.[10] Nevertheless we shall use the more proper notation, S, P, D, F, to refer to the energy levels.

The energy-level diagram for lithium is shown in Fig. 10.7. The observed

---

[10] The situation becomes more complicated when there are two or more optical electrons. An excellent discussion is given by G. H. Herzberg, *Atomic Spectra and Atomic Structure* (New York: Dover Publications, 1944).

spectral series arise from the combinations of these terms, as shown in the diagram. It will be noted that only certain transitions are *allowed*; others are *forbidden*. Certain selection rules must be obeyed, as for example in this case the rule that ΔL must be $+1$ or -1.

Experimentally four distinct series have been observed in the atomic spectra of the alkalis. The *principal* series is the only one found in absorption spectra and arises from transitions between the ground state $1S$ and the various P states. It may be written symbolically:

$$\nu = 1S - mP$$

Absorption spectra almost always arise from transitions from the ground state only, since at ordinary temperatures the proportion of atoms in excited states is usually vanishingly small, being governed by the exponential Boltzmann factor $e^{-\Delta E/kT}$. At the much higher temperatures required to excite emission spectra, some of the higher states are sufficiently populated by atoms to give rise to a greater variety of lines.

Thus in the emission spectra of the alkali metals, in addition to the principal series, three other series appear. These may be written symbolically as

$\nu = 2P - mS$	the *sharp* series
$\nu = 2P - mD$	the *diffuse* series
$\nu = 3D - mF$	the *fundamental* series

The names are not notably descriptive, although the lines in the sharp series are indeed somewhat narrower than the others.

10. Space quantization. So far in the discussion of allowed Bohr orbits, we have not considered the question of how the orbits can be oriented in space. This is because in the absence of an external electric or magnetic field there is no way of distinguishing between different orientations, since there is no physically established axis of reference. If an atom is placed in a magnetic field, however, one can ask how the orbits will be oriented relative to the field direction.

The answer given by the Bohr theory is that only certain orientations are allowed. These are determined by the condition that the *component* of angular momentum in the direction of the magnetic field, *e.g.*, in the Z direction, must be an integral multiple of $h/2\pi$. Thus

$$p_z = \frac{mh}{2\pi} \tag{10.27}$$

where m is the *magnetic quantum number.* This behavior is called *space quantization.*

The allowed values of m are ± 1, ± 2, ± 3, etc., up to $\pm k$, k being the azimuthal quantum number, which gives the magnitude of the total angular momentum in units of $h/2\pi$. An example of space quantization for the case $k = 3$ is illustrated in Fig. 10.8.

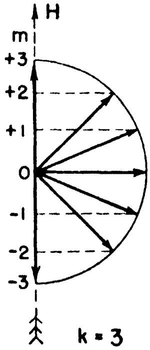


Fig. 10.8. Spatial quantization of angular momentum in a magnetic field *H*.

For any value of k, there are $2k$ allowed orientations corresponding to the different values of m. In the absence of an external field, the corresponding energy level will be $2k$-fold degenerate. In the presence of an electric or magnetic field this energy level will be split into its individual components. This splitting gives rise to a splitting of the corresponding spectral lines. In a magnetic field this is called the *Zeeman effect*; in an electric field, the *Stark effect*. This observed splitting of the spectral lines is the experimental basis for the introduction into the Bohr theory of space quantization and the quantum number m.

11. Dissociation as series limit. It will be noted in the term diagram for lithium that the energy levels become more closely packed as the height above the ground state increases. They finally converge to a common limit whose height above the ground level corresponds to the energy necessary to remove the electron completely from the field of the nucleus. In the observed spectrum, the lines become more and more densely packed and finally merge into a continuum at the onset of dissociation. The reason for the continuous absorption or emission is that the free electron no longer has quantized energy states but can take up kinetic energy of translation continuously.

The energy difference between the series limit and the ground level represents the *ionization potential* I of the atom or ion. Thus the *first ionization potential* of Li is the energy of the reaction $\text{Li}^+ + e \rightarrow \text{Li}$. The *second ionization potential* is the energy of $\text{Li}^{++} + e \rightarrow \text{Li}^+$.

Examples of ionization potentials are given in Table 10.1. The way in which the values of I vary with position in the periodic table should be noted. This periodicity is very closely related to the periodic character of the chemical properties of the elements, for it is the outer electrons of an atom that enter into its chemical reactions. Thus the alkali metals have low ionization potentials; the inert gases, high ionization potentials.

12. The origin of X-ray spectra. The origin of the characteristic X-ray line series studied by Moseley (see Chapter 8) is readily understood in terms of the Bohr theory. The optical spectra are caused by transitions of outer or valence electrons, but the X-ray spectra are caused by transitions of the inner electrons. X rays are generated when high-velocity particles such as electrons impinge upon a suitable target. As the result of such a collision, an electron may be driven completely from its orbit, leaving a "hole" in the

TABLE 10.1

IONIZATION POTENTIALS OF CHEMICAL ELEMENTS (IN ELECTRON VOLTS)

Element	*First Ionization Potential*	*Second Ionization Potential*
H	13.60	
He	24.58	54.41
Li	5.39	75.62
Be	9.32	18.21
B	8.30	25.12
C	11.27	24.38
N	14.55	29.61
O	13.62	35.08
F	17.42	34.98
Ne	21.56	40.96
Na	5.14	47.29
Mg	7.65	15.03
Al	5.99	18.82
Si	8.15	16.34
P	10.98	19.65
S	10.36	23.41
Cl	12.96	23.80
A	15.76	27.62
K	4.34	31.81
Ca	6.11	11.87

target atom. When electrons in outer shells, having larger values of the principal quantum number n, drop into this hole, a quantum of X radiation is emitted.

13. Particles and waves. One might go on from here to describe the further application of the Bohr theory to more complex problems in atomic structure and spectra. Many other quite successful results were obtained, but there were also a number of troublesome failures. Attempts to treat cases in which more than one outer electron is excited, as in the helium spectrum, were in general rather discouraging.

The Bohr method is essentially nothing more than the application of a diminutive celestial mechanics, with coulombic rather than gravitational forces, to tiny solar-system models of the atom. Certain quantum conditions have been arbitrarily superimposed on this classical foundation. The rather capricious way in which the quantum numbers were introduced and adjusted always detracted seriously from the completeness of the theory.

Now there is one branch of physics in which, as we have seen, integral numbers occur very naturally, namely in the stationary-state solutions of the equation for wave motion. This fact suggested the next great advance in physical theory: the idea that electrons, and in fact all material particles, must possess wavelike properties. It was already known that radiation exhibited both corpuscular and undulatory aspects. Now it was to be shown, first theoretically and soon afterwards experimentally, that the same must be true of matter.

This new way of thinking was first proposed in 1923 by Duc Louis de Broglie. In his Nobel Prize Address he has described his approach as follows.[11]

> . . . When I began to consider these difficulties [of contemporary physics] I was chiefly struck by two facts. On the one hand the quantum theory of light cannot be considered satisfactory, since it defines the energy of a light corpuscle by the equation $E = h\nu$, containing the frequency ν. Now a purely corpuscular theory contains nothing that enables us to define a frequency; for this reason alone, therefore, we are compelled, in the case of light, to introduce the idea of a corpuscle and that of periodicity simultaneously.
>
> On the other hand, determination of the stable motion of electrons in the atom introduces integers; and up to this point the only phenomena involving integers in Physics were those of interference and of normal modes of vibration. This fact suggested to me the idea that electrons too could not be regarded simply as corpuscles, but that periodicity must be assigned to them also.

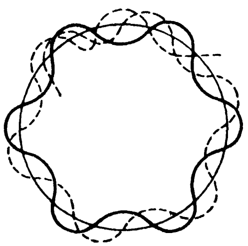


Fig. 10.9. Schematic drawing of an electron wave constrained to move around nucleus. The solid line represents a possible stationary wave. The dashed line shows how a wave of somewhat different wavelength would be destroyed by interference.

A simple two-dimensional illustration of this viewpoint may be seen in Fig. 10.9. There are shown two possible electron waves of different wavelengths for the case of an electron revolving around an atomic nucleus. In one case, the circumference of the electron orbit is an integral multiple of the wavelength of the electron wave. In the other case, this condition is not fulfilled and as a result the wave is destroyed by interference, and the supposed state is nonexistent. The introduction of integers associated with the permissible states of electronic motion therefore occurs quite naturally once the electron is given wave properties. The situation is exactly analogous with the occurrence of stationary waves on a vibrating string. The necessary condition for a stable orbit of radius r_e is that

$$2\pi r_e = n\lambda \tag{10.28}$$

A free electron is associated with a progressive wave so that any energy is allowable. A bound electron is represented by a standing wave, which can have only certain definite frequencies.

In the case of a photon there are two fundamental equations to be obeyed: $\varepsilon = h\nu$, and $\varepsilon = mc^2$. When these are combined, one obtains $h\nu = mc^2$ or $\lambda = c/\nu = h/mc = h/p$, where p is the momentum of the photon. Broglie considered that a similar equation governed the wavelength of the electron wave. Thus,

$$\lambda = \frac{h}{mv} = \frac{h}{p} \tag{10.29}$$

---

[11] L. de Broglie, *Matter and Light* (New York: Dover Publications [1st ed., W. W. Norton Co.], 1946).

The original Bohr condition for a stable orbit was given by eq. (10.21) as $2\pi mvr_e = nh$. By combination with eq. (10.28), one again obtains eq. (10.29) so that the Broglie formulation gives the Bohr condition directly.

The Broglie relation, eq. (10.29), is the fundamental one between the momentum of the electron considered as a particle and the wavelength of its associated wave. Consider, for example, an electron that has been accelerated through a potential difference V of 10 kilovolts. Then $Ve = \frac{1}{2}mv^2$, and its velocity would be 5.9×10^9 cm per sec, about one-fifth that of light. The wavelength of such an electron would be

$$\lambda = \frac{h}{mv} = \frac{6.62 \times 10^{-27}}{(9.11 \times 10^{-28})(5.9 \times 10^9)} = 0.12 \text{ Å}$$

This is about the same wavelength as that of rather hard X rays.

TABLE 10.2

WAVELENGTHS OF VARIOUS PARTICLES

Particle	Mass (g)	Velocity (cm/sec)	Wavelength (Å)
1-volt electron	9.1×10^{-28}	5.9×10^7	12.0
100-volt electron	9.1×10^{-28}	5.9×10^8	1.2
10,000-volt electron	9.1×10^{-28}	5.9×10^9	0.12
100-volt proton	1.67×10^{-24}	1.38×10^7	0.029
100-volt α particle	6.6×10^{-24}	6.9×10^6	0.015
H_2 molecule at 200°C	3.3×10^{-24}	2.4×10^5	0.82
α particle from radium	6.6×10^{-24}	1.51×10^9	6.6×10^{-5}
22-rifle bullet	1.9	3.2×10^4	1.1×10^{-23}
Golf ball	45	3×10^3	4.9×10^{-24}
Baseball	140	2.5×10^3	1.9×10^{-24}

Table 10.2 lists the theoretical wavelengths associated with various particles.[12] The wavelengths of macroscopic bodies are exceedingly short, so that any wave properties will escape our observation. Only in the atomic world does the wave nature of matter become manifest.

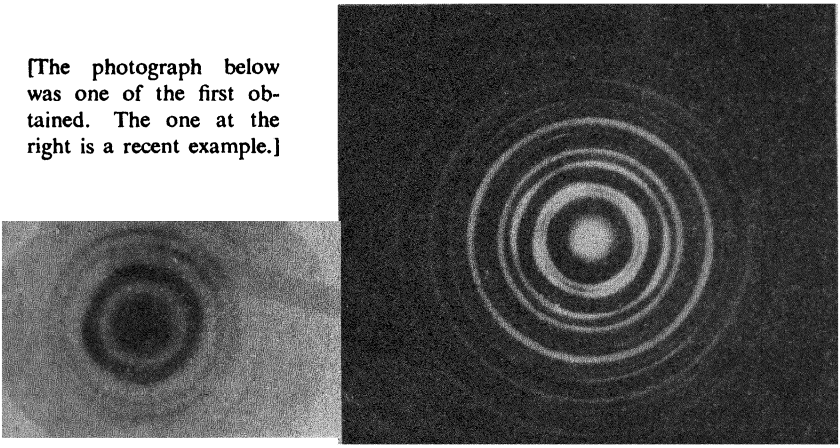
14. Electron diffraction. If any physical reality is to be attached to the idea that electrons have wave properties, a 1.0 Å electron wave should be diffracted by a crystal lattice in very much the same way as an X-ray wave. Experiments along this line were first carried out by two groups of workers, who shared a Nobel prize for their efforts. C. Davisson and L. H. Germer worked at the Bell Telephone Laboratories in New York, and G. P. Thomson, the son of J. J. Thomson, and A. Reid were at the University of Aberdeen. Diffraction diagrams obtained by Thomson by passing beams of

---

[12] After J. D. Stranathan, *The Particles of Modern Physics* (Philadelphia: Blakiston, 1942), p. 540.

electrons through thin gold foils are shown in Fig. 10.10. The wave nature of the electron was unequivocally demonstrated by these researches. More recently, excellent diffraction patterns have been obtained from crystals placed in beams of neutrons.

Electron beams, owing to their negative charge, have one advantage not possessed by X rays as a means of investigating the fine structure of matter. Appropriate arrangements of electric and magnetic fields can be designed to act as "lenses" for electrons. These arrangements have been applied in the development of electron microscopes capable of resolving images as small as 20 Å in diameter. We could wish for no clearer illustrations of the wave properties of electrons than the beautiful electron micrographs of viruses, fibers, and colloidal particles that have been obtained with these instruments.



[The photograph below was one of the first obtained. The one at the right is a recent example.]

Fig. 10.10. Diffraction diagrams obtained by passing beams of electrons through thin gold foils. (Courtesy Professor Sir George Thomson.)

15. The uncertainty principle. In the development of atomic physics we have noted the repeated tendency toward the construction of models of the atom and its constituents from building blocks that possess all the normal properties of the sticks and stones of everyday life. One fundamental axiom of the classical mechanics developed for commonplace occurrences was the possibility of simultaneously measuring different events at different places. Such measurement appears at first to be perfectly possible because to a first approximation the speed of light is infinitely large, and it takes practically no time to signal from place to place. More refined measurements must consider the fact that this speed is really not infinite, but only 3×10^{10} cm per sec. This speed is indeed large compared with that of a rocket, but not compared with that of an accelerated electron. As a result, attempts to apply the old mechanics to moving electrons were a failure, and the new relativisitic mechanics of Einstein was needed to correct the situation.

In a similar way, in our ordinary macroscopic world, the value of the Planck constant h may be considered to be effectively zero. The Broglie wavelengths of ordinary objects are vanishingly small, and a batter need not consider diffraction phenomena when he swings at an inside curve. If we enter into the subatomic world, h is no longer so small as to be negligible. The Broglie wavelengths of electrons are of such a magnitude that diffraction effects occur in crystal structures.

One of the fundamental tenets of classical mechanics is that it is possible to specify simultaneously the position and momentum of any body. The strict determinism of mechanics rested upon this basic assumption. Knowing the position and velocity of a particle at any instant, Victorian mechanics would venture to predict its position and velocity at any other time, past or future. Systems were completely reversible in time, past configurations being obtained simply by substituting $-t$ for t in the dynamical equations. But, is it really possible to measure simultaneously the position and momentum of any particle? The possible methods of measurement must be analyzed in detail before an answer can be given.

To measure with precision the position of a very small object, a microscope of high resolving power is required. With visible light one cannot expect to locate objects much smaller than a tenth of a micron. The size of the smallest body that can be observed is limited by diffraction effects, which begin to create a fuzziness in the image when the object is of the same order of magnitude as the wavelength of the incident light. The limit of resolution is given according to the well known formula of Abbé as $R = \lambda/2A$, and the maximum value of the numerical aperture A is unity.

In order to determine the position of an *electron* to within a few per cent uncertainty, radiation of wavelength around 10^{-10} cm or 10^{-2} Å would have to be used. We shall conveniently evade the technical problems involved in the design and manufacture of a microscope using these γ rays. With such very short rays, there will be a very large Compton effect, and the γ ray will impart considerable momentum to the electron under observation. This momentum is given by eq. (9.5) as $mv = 2(h\nu/c) \sin \alpha/2$. Since the range in scattering angle is from 0 to $\pi/2$, corresponding to the aperture of the microscope ($A = 1$), the momentum is determined only to within an uncertainty of $\Delta p = mv \approx h/\lambda$. On account of diffraction, the error Δq in the determination of position is of the order of the wavelength λ.

The product of the uncertainty in momentum times the uncertainty in position is therefore of the order of h,

$$\Delta p \cdot \Delta q \sim h \tag{10.30}$$

This is the famous *uncertainty principle* of Werner Heisenberg (1926). It is impossible to specify simultaneously the exact position and momentum of a particle because our measuring instruments necessarily disturb the object being measured. This disturbance is negligible with man-sized objects, but the disturbance of atom-sized particles cannot be neglected. Herein is the essential meaning of the failure of classical mechanics and the success of wave mechanics.[13]

16. Waves and the uncertainty principle. Some kind of uncertainty principle is always associated with a wave motion. This fact can be seen very clearly in the case of sound waves. Consider the case of an organ pipe, set into vibration by depressing a key, whose vibration is stopped as soon as the key is released. The vibrating pipe sets up a train of sound waves in the air, which we hear as a note of definite frequency. Now suppose the time between the depression and the release of the key is gradually shortened. As a result, the length of the train of waves is shortened also. Finally the time will come when the period during which the key is depressed is actually less than the period τ of the sound wave, the time required for one complete vibration. Once this happens, the frequency of the wave is no longer precisely determined, for at least one complete vibration must take place to define the frequency. It appears, therefore, that the time and the frequency cannot both be fixed at any arbitrary value. If a very small time is chosen, the frequency becomes indeterminate.

When waves are associated with particles, a similar uncertainty principle is a necessary consequence. If the wavelength or frequency of an electron wave, for example, is to be a definitely fixed quantity, the wave must be infinite in extent. Any attempt to confine a wave within boundaries requires destructive interference at these boundaries in order to reduce the resultant amplitudes there to zero. This interference can be secured only by superimposing waves of different frequencies. It follows that an electron wave of perfectly definite frequency, or momentum, must be infinitely extended and therefore must have a completely indeterminate position. In order to fix the position, superimposed waves of different frequency are required, and as the position becomes more closely defined the momentum becomes fuzzier.

The uncertainty relation eq. (10.30) can be expressed not only in terms of position and momentum but also for energy and time. Thus,

$$\Delta p \cdot \Delta q = \Delta E \cdot \Delta t \approx h \tag{10.31}$$

This equation is used to estimate the sharpness of spectral lines. In general, lines arising from transitions from the ground state of an atom are sharp. This is because the optical electron spends a long time in the ground state and thus ΔE, the uncertainty in the energy level, is very small. On the other hand, the lifetime of excited states may sometimes be very short, and transitions between such excited energy levels may give rise to diffuse or broadened lines as a result of the uncertainty ΔE in the energy levels, which is

---

[13] Many natural philosophers would not agree with this statement. See H. Margenau, *Physics Today*, 7, 6 (1954).

reflected in an uncertainty, $\Delta\nu = \Delta E/h$, in the frequency of the observed line.[14]

17. Zero-point energy. According to the old quantum theory, the energy levels of a harmonic oscillator were given by $E_n = nh\nu$. If this were true the lowest energy level would be that with $n = 0$, and would therefore have zero energy. This would be a state of complete rest, represented by the minimum in the potential energy curve in Fig. 7.15.

The uncertainty principle does not allow such a state of completely defined position and completely defined (in this case, zero) momentum. As a result, the wave treatment shows that the energy levels of the oscillators are given by

$$E_n = (n + \tfrac{1}{2})h\nu \tag{10.32}$$

Now, even when $n = 0$, the ground state, there is a residual *zero-point energy* amounting to

$$E_0 = \tfrac{1}{2}h\nu \tag{10.33}$$

This must be added to the Planck expression for the mean energy of an oscillator, which was derived in eq. (10.17).

18. Wave mechanics—the Schrödinger equation. In 1926, Erwin Schrödinger and W. Heisenberg independently laid the foundations for a distinctly new sort of mechanics which was expressive of the wave-particle duality of matter. This is called *wave* or *quantum mechanics.*

The starting point for most quantum mechanical discussions is the Schrödinger wave equation. We may recall that the general differential equation of wave motion in one dimension is given by eq. (10.7) as

$$\frac{\partial^2\phi}{\partial x^2} = \frac{1}{v^2}\cdot\frac{\partial^2\phi}{\partial t^2}$$

where ϕ is the displacement and v the velocity. In order to separate the variables, let $\phi = \psi(x)\cdot\sin 2\pi\nu t$. On substitution in the original equation, this yields

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2\nu^2}{v^2}\psi = 0 \tag{10.34}$$

This is the wave equation with the time dependence removed. In order to apply this equation to a "matter wave," the Broglie relation is introduced, as follows: The total energy E is the sum of the potential energy U and the kinetic energy $p^2/2m$. $E = p^2/2m + U$. Thus, $p = [2m(E - U)]^{1/2}$, or $\lambda = h/p = h[2m(E - U)]^{-1/2}$. Substituting this in eq. (10.34), one obtains:

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - U)\psi = 0 \tag{10.35}$$

---

[14] This is not the only cause of broadening of spectral lines. There is in addition a *pressure broadening* due to interaction with the electric fields of neighboring atoms or molecules, and a *Doppler broadening,* due to motion of the radiating atom or molecule with respect to the observer.

This is the famous Schrödinger equation in one dimension. For three dimensions it takes the form

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - U)\psi = 0 \tag{10.36}$$

Although the equation has been obtained in this way from the ordinary wave equation and Broglie's relation, it is actually so fundamental that it is now more usual simply to postulate the equation as the starting point of quantum mechanics, just as Newton's $f = ma$ is postulated as the starting point of ordinary mechanics.

As is usual with differential equations, the solutions of eq. (10.36) for any particular set of physical conditions are determined by the particular boundary conditions imposed upon the system. Just as the simple wave equation for a vibrating string yields a discrete set of stationary-state solutions when the ends of the string are held fixed, so in general solutions are obtained for the Schrödinger equation only for certain energy values E. In many cases the allowed energy values are discrete and separated, but in certain other cases they form a continuous spectrum of values. The allowed energy values are called the *characteristic*, *proper*, or *eigen- values* for the system. The corresponding wave functions ψ are called the *characteristic functions* or *eigenfunctions*.

19. Interpretation of the ψ functions. The eigenfunction ψ is by nature a sort of amplitude function. In the case of a light wave, the intensity of the light or energy of the electromagnetic field at any point is proportional to the square of the amplitude of the wave at that point. From the point of view of the photon picture, the more intense the light at any place, the more photons are falling on that place. This fact can be expressed in another way by saying that the greater the value of ψ, the amplitude of a light wave in any region, the greater is the *probability* of a photon being within that region.

It is this interpretation that is most useful when applied to the eigenfunctions of Schrödinger's equation. They are therefore sometimes called *probability amplitude functions.* If $\psi(x)$ is a solution of the wave equation for an electron, then the probability of finding the electron within the range from x to $x + dx$ is given[15] by $\psi^2(x)dx$.

The physical interpretation of the eigenfunction as a probability amplitude function is reflected in certain mathematical conditions that it must obey. It is required that $\psi(x)$ be single-valued, finite, and continuous for all physically possible values of x. It must be single-valued, since the probability of finding the electron at any point x must have one and only one value. It cannot be infinite at any point, for then the electron would be fixed at exactly that point, which would be inconsistent with the wave properties. The requirement of continuity is helpful in the selection of physically reasonable solutions for the wave equation.

---

[15] Since the function ψ may be a complex quantity, the probability is written more generally as $\bar{\psi}\psi$, where $\bar{\psi}$ is the complex conjugate of ψ. Thus, *e.g.*, if $\psi = e^{-ix}$, $\bar{\psi} = e^{ix}$.

20. Solution of wave equation—the particle in a box. The problem of finding the solution of the wave equation in any particular case may be an extremely difficult one. Sometimes a solution can be devised in principle that in practice would involve several decades of calculations. The recent development of high-speed calculating machines has greatly extended the range of problems for which numerical solutions can be obtained.

The simplest case to which the wave equation can be applied is that of a free particle; *i.e.*, one moving in the absence of any potential field. In this case we may set $U = 0$ and the one-dimensional equation becomes

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} E\psi = 0 \tag{10.37}$$

A solution of this equation is readily found[16] to be

$$\psi = A \sin\left(\frac{2\pi}{h}\sqrt{2mE}\cdot x\right) \tag{10.38}$$

where A is an arbitrary constant. This is a perfectly allowable solution as long as E is positive, since the sine of a real quantity is everywhere single-valued, finite, and continuous. Thus *all* positive values of E are allowable and the free particle has a continuous spectrum of energy states. This conclusion is in accord with the picture previously given of the onset of the *continuum* in atomic spectra as the result of dissociation of an electron from the atom.

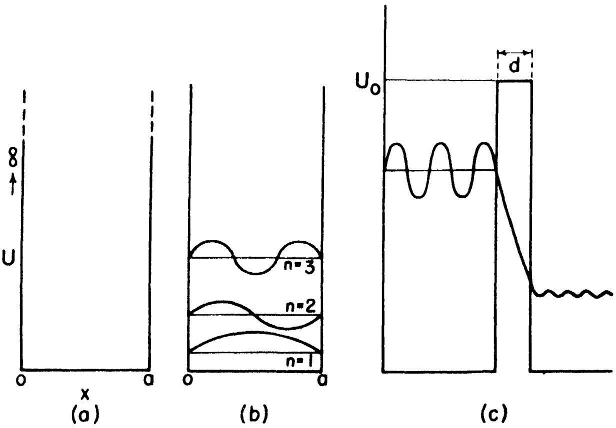


Fig. 10.11. Electron in a one-dimensional box. (a) the potential function. (b) allowed electron waves. (c) tunnel effect.

What is the effect of imposing a constraint upon the free particle by requiring that its motion be confined within fixed boundaries? In three

---

[16] See, for example, Granville *et al.*, *op. cit.*, p. 390. The solution can be verified by substitution into the equation.

dimensions this is the problem of a particle enclosed in a box. The one-dimensional problem is that of a particle required to move between set points on a straight line. The potential function that corresponds to such a condition is shown in (a), Fig. 10.11. For values of x between 0 and a the particle is completely free, and $U = 0$. At the boundaries, however, the particle is constrained by an infinite potential wall over which there is no escape; thus $U = \infty$ when $x = 0$, $x = a$.

The situation now is similar to that of the vibrating string considered at the beginning of the chapter. Restricting the electron wave within fixed boundaries corresponds to seizing hold of the ends of the string. In order to obtain stable standing waves, it is again necessary to restrict the allowed wavelengths so that there is an integral number of half wavelengths between 0 and a; *i.e.*, $n(\lambda/2) = a$. Some of the allowed electron waves are shown in (b), Fig. 10.11, superimposed upon the potential-energy diagram.

The permissible values of the kinetic energy E_n of the electron in a box can be obtained from the Broglie relation $\lambda = h/mv$.

$$E_n = \tfrac{1}{2}mv^2 = \tfrac{1}{2}m\left(\frac{h}{m\lambda}\right)^2 = \tfrac{1}{2}m\left(\frac{h \cdot n}{m \cdot 2a}\right)^2$$

$$E_n = \frac{n^2h^2}{8ma^2} \qquad (10.39)$$

From this equation, two important consequences can be deduced which will hold true for the energy of electrons, not only in this special case, but quite generally. First of all, it is apparent that as the value of a increases, the energy decreases. Other factors being the same, the more room the electron has to move about in, the lower will be its energy. *The more localized is its motion, the higher will be its energy.* Remember that the lower the energy, the greater the stability of a system.

Secondly, the integer n is a typical *quantum number*, which now appears quite naturally and without any *ad hoc* hypotheses. It determines the *number of nodes* in the electron wave. When $n = 1$ there are no nodes. When $n = 2$ there is a node in the center of the box; when $n = 3$ there are two nodes, and so on. The value of the energy depends directly on n^2, and therefore rises rapidly as the number of nodes increases.

The extension of the one-dimensional result to a three-dimensional box of sides a, b, and c is very simple. The allowed energy levels for the three-dimensional case depend on a set of three integers (n_1, n_2, n_3): since there are three dimensions, there are three quantum numbers.

$$E = \frac{h^2}{8m}\left(\frac{n_1{}^2}{a^2} + \frac{n_2{}^2}{b^2} + \frac{n_3{}^2}{c^2}\right) \qquad (10.40)$$

This result shows that according to wave mechanics even the translational motion of a particle in a box is quantized. Because of the extremely small value of h^2 these levels lie very closely packed together except in cases where the dimensions of the box are vanishingly small.

If electron waves in one dimension are comparable with vibrations of a violin string, those in two dimensions are like the pulsations of a drumhead, whereas those in three dimensions are like the vibrations of a block of steel. The waves can then have nodes along three directions, and the three quantum numbers determine the number of nodes.

21. The tunnel effect. Let us take a baseball, place it in a well constructed box, and nail the lid down tightly. Now any proper Newtonian will assure us that the ball is in the box and is going to stay there until someone takes it out. There is no probability that the ball will be found on Monday inside the box and on Tuesday rolling along outside it. Yet if we transfer our attention from a baseball in a box to an electron in a box, quantum mechanics predicts exactly this unlikely behavior.

To be more precise, consider in (c), Fig. 10.11, a particle moving in a "one-dimensional box" with a kinetic energy E_k. It is confined by a potential-energy wall of thickness d and height U_0. Classical mechanics indicates that the particle can simply move back and forth in its potential energy well; since the potential-energy barrier is higher than the available kinetic energy, the possibility of escape is absolutely nil.

Quantum mechanics tells a different story. The wave equation (10.35) for the region of constant potential energy U_0 is

$$(d^2\psi/dx^2) + (8\pi^2 m/h^2)(E - U_0)\psi = 0$$

This equation has the general solution

$$\psi = Ae^{(2\pi i/h)\sqrt{2m(E-U_0)}x}$$

In the region within the box $E > U_0$ and this solution is simply the familiar sine or cosine wave of eq. (10.38) written in the complex exponential form.[17] In the region within the potential-energy barrier, however, $U_0 > E$, so that the expression under the square root sign is negative. One can therefore multiply out a $\sqrt{-1}$ term, obtaining the following result:

$$\psi = Ae^{-(2\pi/h)\sqrt{2m(U_0-E)}\cdot x} \qquad (10.41)$$

This exponential function describes the behavior of the wave function within the barrier. It is evident that according to wave mechanics the probability of finding an electron in the region of negative energy is not zero, but is a certain finite number that falls off exponentially with the distance of penetration within the barrier. The behavior of the wave function is shown in (c), Fig. 10.11. So long as the barrier is not infinitely high nor infinitely wide there is always a certain probability that electrons (or particles in general) will leak through. This is called the *tunnel effect*.

---

[17] See, for example, Courant and Robbins, *What Is Mathematics* (New York: Oxford, 1941), p. 92, for a description of this notation: $e^{i\theta} = \cos\theta + i\sin\theta$.

The phenomenon is not observed with baseballs in boxes or with cars in garages,[18] being rendered extremely improbable by the various parameters in the exponential. In the world of atoms, however, the effect is a common one. One of the best examples is the emission of an α particle in a radioactive disintegration. The random nature of this emission is a reflection of the fact that the position of the particle is subject to probability laws.

22. The hydrogen atom. If the translational motion of the atom as a whole and the motion of the atomic nucleus are neglected, the problem of the hydrogen atom can be reduced to that of a single electron in a coulombic field. This is in a sense a modification of the problem of a particle in a three-dimensional box, except that now the box is spherical. Also, instead of steep walls and zero potential energy within, there is now a gradual rise in potential with distance from the nucleus: at $r = \infty$, $U = 0$; at $r = 0$, $U = -\infty$.

The potential energy of the electron in the field of the nucleus is given by $U = -e^2/r$. The Schrödinger equation therefore becomes

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}\left(E + \frac{e^2}{r}\right)\psi = 0$$

In view of the spherical symmetry of the potential field, it is convenient to transform this expression into spherical coordinates,

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin^2\theta}\cdot\frac{\partial^2\psi}{\partial\phi^2} + \frac{1}{r^2\sin\theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{8\pi^2 m}{h^2}\left(E + \frac{e^2}{r}\right)\psi = 0$$

The polar coordinates r, θ, and ϕ have their usual significance (Fig. 7.2, page 168). The coordinate r measures the radial distance from the origin; θ is a "latitude"; and ϕ a "longitude." Since the electron is moving in three dimensions, three coordinates obviously suffice to describe its position at any time.

In this equation, the variables can be separated, since the potential is a function of r alone. Let us substitute

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

That is, the wave function is a product of three functions, one of which depends only on r, one only on θ, and the last only on ϕ. We shall skip the intervening steps in the solution and the application of the boundary conditions that permit only certain allowed eigenfunctions to be physically meaningful.[19] From our previous experience, however, we shall not be surprised to find that the final solutions represent a set of discrete stationary

---

[18] This extreme example is described by G. Gamow in *Mr. Tompkins in Wonderland* (New York: Macmillan, 1940), which is recommended as an introduction to this chapter in *Physical Chemistry*.

[19] For the steps in the solution see, for example, L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (New York: McGraw-Hill, 1935), Chap. V.

energy states for the hydrogen atom, characterized by certain quantum numbers, n, l, and m. Nor is it surprising that exactly three quantum numbers are required for this three-dimensional motion, just as one sufficed for the waves on a string, whereas three were needed for the particle in a box.

The allowed eigenfunctions are certain polynomials whose properties had been extensively studied by mathematicians well before the advent of quantum mechanics. In order to give them a measure of concreteness, some examples of these hydrogen wave functions are tabulated in Table 10.3 for the lower values of the quantum numbers n, l, and m.

TABLE 10.3

THE HYDROGENLIKE WAVE FUNCTIONS

K Shell

$n = 1, l = 0, m = 0$:

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

L Shell

$n = 2, l = 0, m = 0$:

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

$n = 2, l = 1, m = 0$:

$$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos\theta$$

$n = 2, l = 1, m = \pm 1$:

$$\psi_{2p_x} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin\theta \cos\phi$$

$$\psi_{2p_y} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin\theta \sin\phi$$

These quantum numbers can be assigned a significance purely in terms of the wave-mechanical picture, but they are also the logical successors to the numbers of the old quantum theory.

Thus n is still called the *principal quantum number*. It determines the total number of nodes in the wave function, which is equal to $n - 1$. These nodes may be either in the radial function $R(r)$, or in the azimuthal function $\Theta(\theta)$. When the quantum number l is zero, there are no nodes in the Θ function. In this case the number of nodes in $R(r)$ equals $n - 1$.

The *azimuthal* quantum number l replaces the $k(= l + 1)$ of old quantum theory. The angular momentum is given by $\sqrt{l(l+1)}\, h/2\pi$. Now l can take any value from 0 to $n - 1$; then l is the number of nodal surfaces passing through the origin.

The ***magnetic quantum number*** ***m*** still gives the value of the components of angular momentum along the z axis, since $p_{\theta,z} = mh/2\pi$, exactly as in eq. (10.27). The allowed values of m now run from $-l$ to $+l$, including zero.

The great advantage of the new theory is that these numbers all arise quite naturally from Schrödinger's equation.

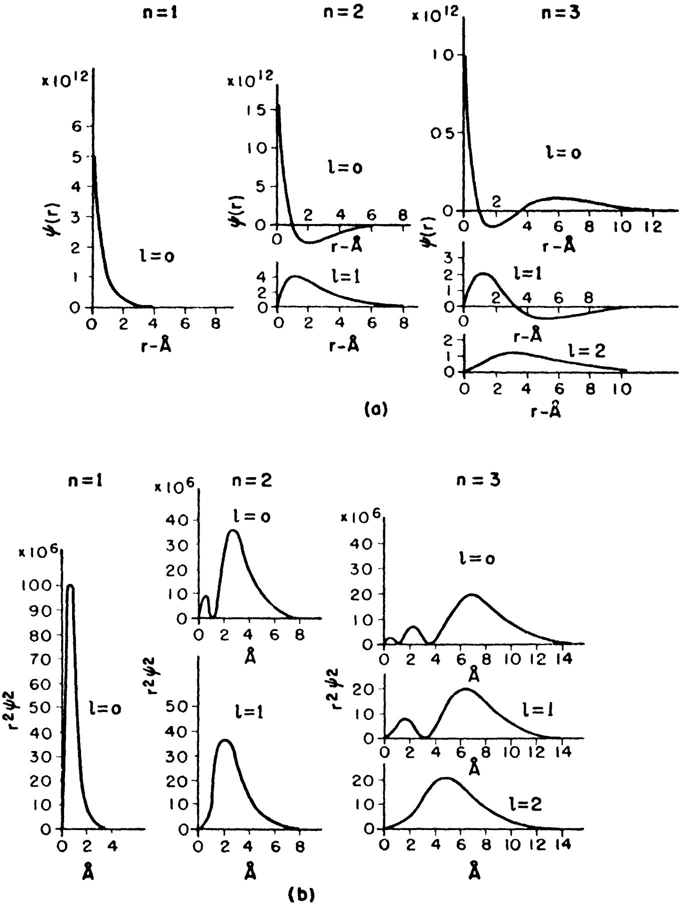
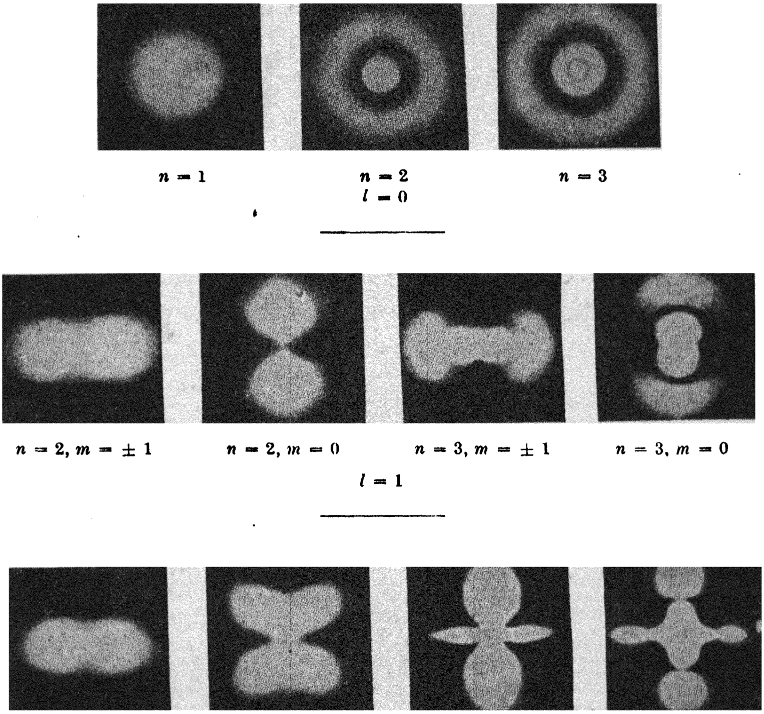


Fig. 10.12. (a) Radial part of wave functions for hydrogen atom. (b) Radial distribution functions—giving probability of finding electrons at a given distance from nucleus. (After G. Herzberg, *Atomic Spectra*, Dover, 1944.)

23. The radial wave functions. In (a), Fig. 10.12, the radial wave functions have been plotted for various choices of n and l. In case $l = 0$, all the nodes appear in the radial function.

The value of $\psi^2(r)$ is proportional to the probability of finding the electron at any particular distance r in some definite direction from the nucleus. More important physically is the *radial distribution function*, $4\pi r^2\psi^2(r)$, which gives the probability of finding the electron within a spherical shell of thickness dr

at a distance r from the nucleus, irrespective of direction. (Compare the problem of gas-velocity distribution on page 187.) The radial distribution functions are shown in (b), Fig. 10.12. In place of the sharply defined electron orbits of the Bohr theory, there is a more diffuse distribution of electric charge. The maxima in these distribution curves, however, correspond closely with the radii of the old Bohr orbits. Yet there is always a definite probability



$n = 1$ $n = 2$ $n = 3$

$l = 0$

$n = 2, m = \pm 1$ $n = 2, m = 0$ $n = 3, m = \pm 1$ $n = 3, m = 0$

$l = 1$

$n = 3, m = \pm 2$ $n = 3, m = \pm 1$ $n = 3, m = 0$ $n = 4, m = 0$

$l = 2$

Fig. 10.13. Electron clouds of the H atom. (From Herzberg, *Atomic Spectra and Atomic Structure*, Dover, 1944.)

of finding the electrons much closer to or much farther from the nucleus. The strict determinism of position in the classical description has been replaced by the probability language of wave mechanics.

A particularly clear illustration of the wave mechanical representation of the hydrogen atom can be obtained from the illustrations in Fig. 10.13. Here the intensity of the shading is proportional to the value of ψ^2, the probability distribution function. There is a greater probability of an electron being in a light-colored region. It should be clearly understood that quantum mechanics does not say that the electron itself is smeared out into a cloud.

It is still to be regarded as a point charge. Its position and momentum cannot be simultaneously fixed, and all that the theory can predict that has physical meaning is the probability that the electron is in any given region.

A wave function for an electron is sometimes called an *orbital*. When $l = 0$ we have an *s* orbital, which is always spherically symmetrical. When $l = 1$ we have a *p* orbital. The *p* orbitals can have various orientations in space corresponding to the allowed values of m, which may be $-1, 0$, or $+1$. In Fig. 10.14, the angular parts of the wave functions are represented for *s*

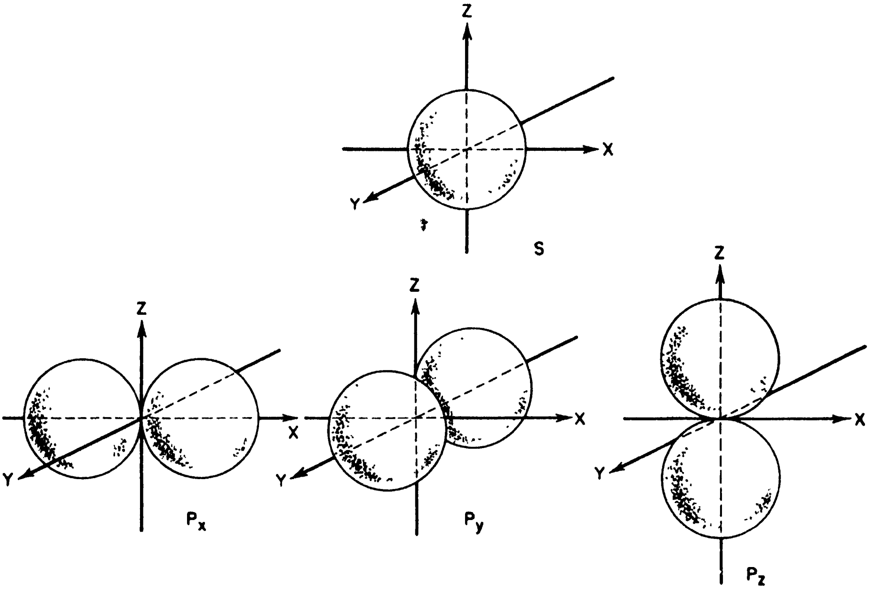


Fig. 10.14. Polar representation of absolute values of angular part of wave function for the H atom. The *s*-type function ($l = 0$) is spherically symmetrical. There are three possible *p*-type functions, directed along mutually perpendicular axes (x, y, z).

and *p* orbitals, and the directional character of the *p* orbitals is very evident. It will be shown later that the directional character of certain chemical bonds is closely related to the directed orientations of these orbitals.

24. The spinning electron. There is one aspect of atomic spectra that cannot be explained on the basis of either the old quantum theory or the newer wave mechanics. This is the multiplicity or multiplet structure of spectral lines. Typical of this multiplicity are the doublets occurring in the spectra of the alkali metals: for example, in the principal series each line is in reality a closely spaced double line. This splitting is revealed immediately with a spectroscope of good resolving power. The occurrence of double lines indicates that each term or energy level for the optical electron must also be split into two.

A satisfactory explanation for the occurrence of multiple energy levels was first proposed in 1925 by G. E. Uhlenbeck and S. Goudsmit. They postulated that an electron itself may be considered to be spinning on its axis.[20] As a result of spin the electron has an inherent angular momentum. Along any prescribed axis in space, for example, the direction of a magnetic field, the components of the spin angular momentum are restricted to values given by $sh/2\pi$, where s can have only a value of $+\frac{1}{2}$ or $-\frac{1}{2}$.

In effect, the electron spin adds a new quantum number s to those required to describe completely the state of an electron. We now have, therefore, the following quantum numbers:

n—the principal quantum number; allowed values 1, 2, 3, . . .
l—the azimuthal quantum number, which gives the orbital angular momentum of the electron; allowed values 0, 1, 2, . . ., $n - 1$.
m—the magnetic quantum number, which gives the allowed orientation of the "orbits" in an external field; allowed values $-l$, $-l + 1$, $-l + 2$, . . ., $+ l$.
s—the spin quantum number; allowed values $+\frac{1}{2}$ or $-\frac{1}{2}$.

25. The Pauli Exclusion Principle. An exact solution of the wave equation for an atom has been obtained only in the case of hydrogen; *i.e.*, for the motion of a single electron in a spherically symmetric coulombic field. Nevertheless, in more complex atoms the energy levels can still be specified in terms of the four quantum numbers n, l, m, s, although in many cases the physical picture of the significance of the numbers will be lost. This is especially true of electrons in inner shells, for which a spherically symmetric field would be a very poor approximation. On the other hand, the behavior of an outer or valence electron is sometimes strikingly similar to that of the electron in the hydrogen atom. In any case, the important fact is that the four quantum numbers still suffice to specify completely the state of an electron even in a complex atom.

There is a most important principle that determines the allowable quantum numbers for an electron in an atom and consequently has the most profound consequences for chemistry. It is the *Exclusion Principle*, first enunciated by Wolfgang Pauli. *In a single atom no two electrons can have the same set of four quantum numbers, n, l, m, s.* At present this principle cannot be derived from fundamental concepts, but it may have its ultimate origin in relativity theory. It is suggestive that relativity theory introduces a "fourth dimension," so that a fourth quantum number becomes necessary.

26. Structure of the periodic table. The general structure of the periodic table is immediately clarified by the Exclusion Principle. We recall that even in a complex atom the energy levels of the electrons can be specified by

---

[20] No attempt will be made to reconcile this statement with the idea that an electron is a point charge. It is merely a convenient pictorial way of speaking of one of the fundamental properties of electrons, about which the complete story is not yet written.

means of four quantum numbers: n, l, m, s. The Exclusion Principle requires that no two electrons in an atom can have the same values for all four quantum numbers. The most stable state, or ground state, of an atom will be that in which the electrons are in the lowest possible energy levels that are consistent with the Exclusion Principle. The structure of the periodic table is a direct consequence of this requirement.

The lowest atomic energy state is that for which the principal quantum number n is 1, and the azimuthal quantum number l is 0. This is a $1s$ state. The hydrogen atom has one electron and this goes therefore into the $1s$ level. The helium atom has two electrons, which may both be accommodated in the $1s$ state if they have opposing spins. With two electrons in the $1s$ state, there is an inert gas configuration since the shell $n = 1$ or K shell is completed. The completed shell cannot add electrons and a large energy would be needed to remove an electron.

Continuing to feed electrons into the lowest lying energy levels, we come to lithium with 3 electrons. The first two go into the $1s$ levels, and the third electron must occupy a $2s$ level. The $2s$ electron is much less tightly bound than the $1s$ electrons. The first ionization potential of Li is 5.39 ev, the second 75.62 ev. This is true because the $2s$ electron is usually much farther from the nucleus than the $1s$, and besides it is partially shielded from the $+3$ nuclear charge by the two $1s$ electrons. A $1s$ electron, on the other hand, is held by the almost unshielded $+3$ nuclear charge.

The L shell, with $n = 2$, can hold 8 electrons—two $2s$ and six $2p$ electrons, the quantum numbers being as follows:

n	l	m	s
2	0	0	$\pm\frac{1}{2}$
	1	-1	$\pm\frac{1}{2}$
		0	$\pm\frac{1}{2}$
		$+1$	$\pm\frac{1}{2}$

When the L shell is filled, the next electron must enter the higher-lying M shell of principal quantum number $n = 3$.

A qualitative picture of the stability of the complete octet is obtained by considering the elements on either side of neon.

	Z	$1s$	$2s$	$2p$	$3s$
O . .	8	2	2	4	
F . .	9	2	2	5	
Ne . .	10	2	2	6	
Na . .	11	2	2	6	1
Mg . .	12	2	2	6	2

The attraction of an electron by the positively charged nucleus is governed by Coulomb's Law, but for electrons outside the innermost shell the shielding effect of the other electrons must be taken into consideration. For a given electron, the shielding effect of other electrons is pronounced only if they lie in a shell between the given electron and the nucleus. Electrons in the same shell as the given electron have little shielding effect.

Thus in fluorine, the nuclear charge is +9; each of the five 2*p* electrons is attracted by this +9 charge minus the shielding of the 1*s* and 2*s* electrons, four in all, resulting in an effective nuclear charge of about +5. The 2*p* electrons in fluorine are therefore tightly held, the first ionization potential being about 18 volts. If an extra electron is added to the 2*p* level in fluorine, forming the fluoride ion F^-, the added electron is also tightly held by the effective +5 nuclear charge. The electron affinity of F is 4.12 ev; that is, $F + e \rightarrow F^- + 4.12$ ev.

Now suppose one attempted to add another electron to F^- to form $F^{=}$. This electron would have to go into the 3*s* state. In this case, all ten of the inner electrons would be effective in shielding the +9 nucleus, and indeed the hypothetical eleventh electron would be repelled rather than attracted. Thus the fluoride ion is by far the most stable configuration and the −1 valence of fluorine is explained. If the tendency of one atom to add an electron (electron affinity) is of the same magnitude as the tendency of another atom to lose an electron (ionization potential) a stable electrovalent bond is possible.

Considering now the sodium atom, we can see that its eleventh electron, $3s^1$, is held loosely ($I = 5.11$ ev). It is shielded from the +11 nucleus by 10 inner electrons.

If we continue to feed electrons into the allowed levels, we find that the 3*p* level is complete at argon ($1s^2 2s^2 2p^6 3s^2 3p^6$), which has the stable s^2p^6 octet associated with inert gas properties.

27. Atomic energy levels. In Table 10.4 the assignment of electrons to levels is shown for all the elements, in accordance with our best present knowledge as derived from chemical and spectroscopic data.

In the element following argon, potassium with $Z = 19$, the last electron enters the 4*s* orbital. This is required by its properties as an alkali metal, and the fact that its spectral ground state is ^1S as in Li and Na. We may well ask, however, why the 4*s* orbitals are lower than the 3*d* orbitals, which provide 10 vacant places. The answer to this question should help to clarify the structure of the remainder of the periodic table and the properties of the elements in the transition series. It may be noted that in this section we are speaking of orbitals, or quantum mechanical wave functions ψ for the electrons. The Bohr picture was useful in dealing with the lighter elements (up to A) but it gives an inadequate picture of the remainder of the periodic table.

The reason why the 4*s* orbital for potassium has a lower energy than a 3*d* orbital arises from the fundamental difference in form of *s*, *p*, and *d* orbitals. The electron distributions in the 3*s*, 3*p*, and 3*d* orbitals for the hydrogen atom were shown in (b), Fig. 10.12. The ordinates of the curves are proportional to the radial distribution functions, and therefore to the

TABLE 10.4
ELECTRON CONFIGURATIONS OF THE ELEMENTS

Shell:	*K*	*L*		*M*			*N*			
Element	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*
1. H	1									
2. He	2									
3. Li	2	1								
4. Be	2	2								
5. B	2	2	1							
6. C	2	2	2							
7. N	2	2	3							
8. O	2	2	4							
9. F	2	2	5							
10. Ne	2	2	6							
11. Na	2	2	6	1						
12. Mg	2	2	6	2						
13. Al	2	2	6	2	1					
14. Si	2	2	6	2	2					
15. P	2	2	6	2	3					
16. S	2	2	6	2	4					
17. Cl	2	2	6	2	5					
18. A	2	2	6	2	6					
19. K	2	2	6	2	6		1			
20. Ca	2	2	6	2	6		2			
21. Sc	2	2	6	2	6	1	2			
22. Ti	2	2	6	2	6	2	2			
23. V	2	2	6	2	6	3	2			
24. Cr	2	2	6	2	6	5	1			
25. Mn	2	2	6	2	6	5	2			
26. Fe	2	2	6	2	6	6	2			
27. Co	2	2	6	2	6	7	2			
28. Ni	2	2	6	2	6	8	2			
29. Cu	2	2	6	2	6	10	1			
30. Zn	2	2	6	2	6	10	2			
31. Ga	2	2	6	2	6	10	2	1		
32. Ge	2	2	6	2	6	10	2	2		
33. As	2	2	6	2	6	10	2	3		
34. Se	2	2	6	2	6	10	2	4		
35. Br	2	2	6	2	6	10	2	5		
36. Kr	2	2	6	2	6	10	2	6		

Shell:	*K*	*L*	*M*	*N*				*O*					*P*			*Q*
Element				4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	5*g*	6*s*	6*p*	6*d*	7*s*
37. Rb	2	8	18	2	6			1								
38. Sr	2	8	18	2	6			2	6				2			
39. Y	2	8	18	2	6	1		2								
40. Zr	2	8	18	2	6	2		2								
41. Nb	2	8	18	2	6	4		1								
42. Mo	2	8	18	2	6	5		1								
43. Tc	2	8	18	2	6	(5)		(2)								
44. Ru	2	8	18	2	6	7		1								
45. Rh	2	8	18	2	6	8		1								
46. Pd	2	8	18	2	6	10										

TABLE 10.4 (*Cont.*)

Shell:	*K*	*L*	*M*	*N*				*O*					*P*			*Q*
Element				4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	5*g*	6*s*	6*p*	6*d*	7*s*
47. Ag	2	8	18	2	6	10		1								
48. Cd	2	8	18	2	6	10		2								
49. In	2	8	18	2	6	10		2	1							
50. Sn	2	8	18	2	6	10		2	2							
51. Sb	2	8	18	2	6	10		2	3							
52. Te	2	8	18	2	6	10		2	4							
53. I	2	8	18	2	6	10		2	5							
54. Xe	2	8	18	2	6	10		2	6							
55. Cs	2	8	18	2	6	10		2	6				1			
56. Ba	2	8	18	2	6	10		2	6				2			
57. La	2	8	18	2	6	10		2	6	1			2			
58. Ce	2	8	18	2	6	10	2	2	6				2			
59. Pr	2	8	18	2	6	10	3	2	6				2			
60. Nd	2	8	18	2	6	10	4	2	6				2			
61. Pm	2	8	18	2	6	10	5	2	6				2			
62. Sm	2	8	18	2	6	10	6	2	6				2			
63. Eu	2	8	18	2	6	10	7	2	6				2			
64. Gd	2	8	18	2	6	10	7	2	6	1			2			
65. Tb	2	8	18	2	6	10	8	2	6	1			2			
66. Dy	2	8	18	2	6	10	9	2	6	1			2			
67. Ho	2	8	18	2	6	10	10	2	6	1			2			
68. Er	2	8	18	2	6	10	11	2	6	1			2			
69. Tu	2	8	18	2	6	10	13	2	6				2			
70. Yb	2	8	18	2	6	10	14	2	6				2			
71. Lu	2	8	18	2	6	10	14	2	6	1			2			
72. Hf	2	8	18	2	6	10	14	2	6	2			2			
73. Ta	2	8	18	2	6	10	14	2	6	3			2			
74. W	2	8	18	2	6	10	14	2	6	4			2			
75. Re	2	8	18	2	6	10	14	2	6	5			2			
76. Os	2	8	18	2	6	10	14	2	6	6			2			
77. Ir	2	8	18	2	6	10	14	2	6	7			2			
78. Pt	2	8	18	2	6	10	14	2	6	9			1			
79. Au	2	8	18	2	6	10	14	2	6	10			1			
80. Hg	2	8	18	2	6	10	14	2	6	10			2			
81. Tl	2	8	18	2	6	10	14	2	6	10			2	1		
82. Pb	2	8	18	2	6	10	14	2	6	10			2	2		
83. Bi	2	8	18	2	6	10	14	2	6	10			2	3		
84. Po	2	8	18	2	6	10	14	2	6	10			2	4		
85. At	2	8	18	2	6	10	14	2	6	10			2	5		
86. Rn	2	8	18	2	6	10	14	2	6	10			2	6		
87. Fr	2	8	18	2	6	10	14	2	6	10			2	6		1
88. Ra	2	8	18	2	6	10	14	2	6	10			2	6		2
89. Ac	2	8	18	2	6	10	14	2	6	10			2	6	1	2
90. Th	2	8	18	2	6	10	14	2	6	10			2	6	2	2
91. Pa	2	8	18	2	6	10	14	2	6	10	2		2	6	1	2
92. U	2	8	18	2	6	10	14	2	6	10	3		2	6	1	2
93. Np	2	8	18	2	6	10	14	2	6	10	5		2	6		2
94. Pu	2	8	18	2	6	10	14	2	6	10	6		2	6		2
95. Am	2	8	18	2	6	10	14	2	6	10	7		2	6		2
96. Cm	2	8	18	2	6	10	14	2	6	10	7		2	6	1	2
97. Bk	2	8	18	2	6	10	14	2	6	10	8		2	6	1	2
98. Cf	2	8	18	2	6	10	14	2	6	10	9		2	6	1	2

probability of finding an electron within a given region. Now, of course, these hydrogen wave functions are not a completely accurate picture of the orbitals in a more complex atom with many electrons. The approximation is satisfactory, however, for valence electrons, which move in the hydrogen-like field of a nucleus shielded by inner electrons.

The 4*s* and 3*p* orbitals predict a considerable concentration of the charge cloud closely around the nucleus,[21] whereas the 3*d* orbital predicts an extremely low probability of finding the electron close to the nucleus. As a result of this *penetration* of the 4*s* orbital inward towards the nucleus, a 4*s* electron will be more tightly bound by the positive nuclear charge, and will therefore be in a lower energy state than a 3*d* electron, whose orbital does not penetrate, and which is therefore more shielded from the nucleus by the inner shells. It is true that the most probable position for a 4*s* electron is farther from the nucleus than that for a 3*d* electron; the penetration effect more than makes up for this, since the coulombic attraction decreases as the square of r, the distance of the electron from the nucleus. Since 4*s* lies lower than 3*d*, the nineteenth electron in potassium enters the 4*s* rather than the 3*d* level, and potassium is a typical alkali metal.

In Fig. 10.15 the relative energies of the orbitals are plotted as functions of the atomic number (nuclear charge). This graph is not quantitatively exact, but is designed to show roughly how the relative energy levels of the various orbitals change with increasing nuclear charge. The energies are obtained from atomic spectra.

Although the effect is not shown in the figure, it should be noted that the energy levels of the *s* and *p* orbitals fall steadily with increasing atomic number, since the increasing nuclear charge draws the penetrating *s* and *p* orbitals closer and closer to the nucleus. At low atomic numbers, up to $Z = 20$ (Ca), the 3*d* levels are not lowered, since there are not yet sufficient electrons present for the *d*'s to penetrate the electron cloud that surrounds and shields the nucleus. As more electrons are added, however, the 3*d* orbitals eventually penetrate the shielding electrons and begin to fall with increasing Z. This phenomenon is repeated later with the 4*d* and 4*f* orbitals. At high Z, therefore, orbitals with the same principal quantum number tend to lie together; at low Z they may be widely separated because of different penetration effects.

Following calcium, the 3*d* orbitals begin to be filled rather than the 4*p*. One obtains the first transition series of metals, Sc, Ti, V, Cr, Mn, Fe, Co, Ni. These are characterized by variable valence and strongly colored compounds. Both these properties are associated with the closeness of the 4*s* and 3*d* levels,

---

[21] The distinct difference between this quantum-mechanical picture and the classical Bohr orbits should be carefully noted. There are four successive maxima in the ψ function for the 4*s* orbital, at different distances from the nucleus. The quantum mechanical picture of an atom is a nucleus surrounded by a cloud of negative charge. There are differences in density of the cloud at different distances from the nucleus. The cloud is the superposition of the ψ functions for all the orbitals occupied by electrons.

which provide a variable number of electrons for bond formation, and possible excited levels at separations corresponding with the energy available in visible light ($\sim$ 2 ev).

The filling of the 3*d* shell is completed with copper, which has the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$. Copper is not an alkali metal despite the outer 4*s* electron, since the 3*d* level is only slightly below the 4*s* and Cu^{++} ions are readily formed.

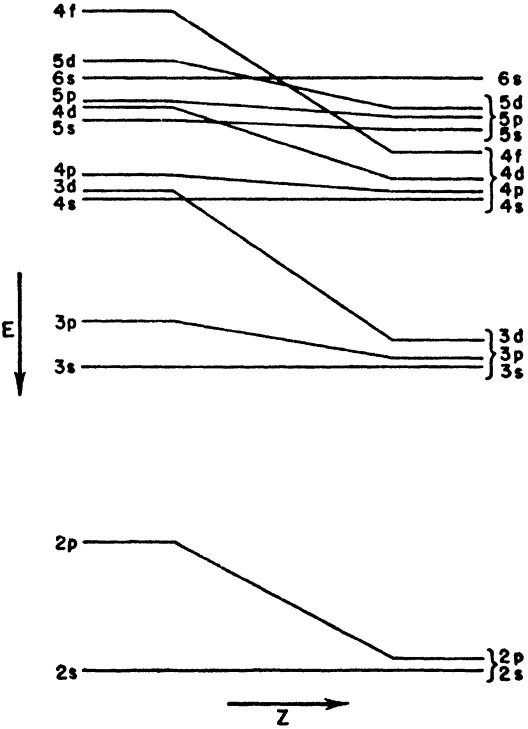


Fig. 10.15. Dependence of energies of orbitals on the nuclear charge *Z*.

The next electrons gradually fill the 4*s* and 4*p* levels, the process being completed with krypton. The next element, rubidium, is a typical alkali with one 5*s* electron outside the $4s^2 4p^6$ octet. Strontium, with two 5*s* electrons, is a typical alkaline earth of the Mg, Ca, Sr, Ba series.

Now, however, the 4*d* levels become lowered sufficiently to be filled before the 5*p*. This causes the second transition series, which is completed with palladium. Silver follows with the copper type structure, and the filling of the 5*s* and 5*p* levels is completed with xenon. A typical alkali (Cs) and alkaline earth (Ba) follow with one and two 6*s* electrons.

The next electron, in lanthanum, enters the 5*d* level, and one might suspect that a new transition series is underway. Meanwhile, however, with increasing nuclear charge, the $4f$ orbitals have been drastically lowered. The $4f$ levels can hold exactly 14 electrons.[22] As these levels are filled, we obtain the 14 rare earths with their remarkably similar chemical properties, determined by the common $5s^25p^6$ outer configuration of their ions. This process is complete with lutecium.

The next element is hafnium, with $5d^26s^2$. Its properties are very similar to those of zirconium with $4d^25s^2$. This similarity in electronic structures was predicted before the discovery of hafnium, and led Coster and Hevesy to look for the missing element in zirconium minerals, where they found it in 1923.

Following Hf the $5d$ shell is filled, and then the filling of the $6p$ levels is completed, the next s^2p^6 octet being attained with radon. The long missing halogen (85) and alkali (87) below and above radon have been found as artificial products from nuclear reactions.[23] They are called "astatine" and "francium."

Radium is a typical alkaline earth metal with two $7s$ electrons. In the next element, actinium, the extra electron enters the $6d$ level, so that the outer configuration is $6d^17s^2$; this is to be compared with lanthanum with $5d^16s^2$. It was formerly thought that the filling of the $6d$ levels continued in the elements following actinium. As a result of studies of the properties of the new transuranium elements it now appears more likely that actinium marks the beginning of a new rare-earth group, successive electrons entering the $5f$ shell. Thus the trivalent state becomes more stable compared to the quadrivalent state as one proceeds through Ac, Th, Pa, U, Np, Pu, Am, Cm, just as it does in the series La, Ce, Pr, Nd, Pm, Sm, Eu, etc. This is true because successive electrons added to the f shell are more tightly bound as the nuclear charge increases. The *actinide* "rare earths" therefore resemble the *lanthanide* rare earths rather than the elements immediately above themselves in the periodic table.

PROBLEMS

1. What is the average energy, $\bar{\varepsilon}$, of a harmonic oscillator of frequency 10^{13} sec^{-1} at 0°, 200°, 1000°C? What is the ratio $\bar{\varepsilon}/kT$ at each temperature?

2. The K_α X-ray line of iron has a wavelength of 1.932 Å. A photon of this wavelength is emitted when an electron falls from the L shell into a vacancy in the K shell. Write down the electronic configuration of the ions before and after emission of this line. What is the energy difference in kcal per mole between these two configurations?

---

[22] As follows:

n — 4
l — 3
m — $-3, -2, -1, 0, +1, +2, +3$
s — $\pm\frac{1}{2}, \pm\frac{1}{2}, \pm\frac{1}{2}, \pm\frac{1}{2}, \pm\frac{1}{2}, \pm\frac{1}{2}, \pm\frac{1}{2}$

[23] For an excellent account, see Glenn T. Seaborg, "The Eight New Synthetic Elements," *American Scientist*, *36*, 361 (1948).

3. The fundamental vibration frequency of N_2 corresponds to a wave number of 2360 cm^{-1}. What fraction of N_2 molecules possess no vibrational energy (except their zero-point energy) at 25°C?

4. The first line in the Lyman series lies at 1216 Å, in the Balmer series, at 6563 Å. In the *absorption* spectra of a certain star, the Balmer line appears to have one-fourth the intensity of the Lyman line. Estimate the temperature of the star.

5. Calculate the ionization potential of hydrogen as the energy required to remove the electron from $r = r_0 = 0.53$Å to infinity against the coulombic attraction of the proton.

6. An excited energy level has a lifetime of 10^{-10} sec. What is the minimum width of the spectral line arising in a transition from the ground state to this level?

7. Calculate the wavelength of a proton accelerated through a potential difference of 1 mev.

8. For a particle of mass 9×10^{-28} g confined to a one-dimensional box 100 Å long, calculate the number of energy levels lying between 9 and 10 ev.

9. Consider an electron moving in a circular path around the lines of force in a magnetic field. Apply the Bohr quantum condition eq. (10.21) to this rotation. What is the radius of the orbit of quantum number $n = 1$ in a magnetic field of 10^5 gauss?

10. The $K_{\alpha 1}$ X-ray line is emitted when an electron falls from an L level to a hole in the K level. Assume that the Rydberg formula holds for the energy levels in a complex atom, with an effective nuclear charge Z' equal to the atomic number minus the number of electrons in shells between the given electron and the nucleus. On this basis, estimate the wavelength of the $K_{\alpha 1}$ X-ray line in chromium. The experimental value is 2.285 Å.

11. The wave function for the electron in the ground state of the hydrogen atom is $\psi_{1s} = (\pi a_0^3)^{-1/2} e^{-r/a_0}$, where a_0 is the radius of the Bohr orbit. Calculate the probability that an electron will be found somewhere between 0.9 and 1.1 a_0. What is the probability that the electron will be beyond 2 a_0?

12. Write an account of the probable inorganic chemistry of Np, Pu, Am, Cm, in view of their probable electron configurations. Compare the chemistry of astatine and iodine, francium and cesium.

REFERENCES

BOOKS

1. de Broglie, L., *Matter and Light* (New York: Dover, 1946).
2. Heitler, W., *Elementary Wave Mechanics* (New York: Oxford, 1945).
3. Herzberg, G., *Atomic Spectra and Atomic Structure* (New York: Dover Publications, 1944).

4. Mott, N. F., *Elements of Wave Mechanics* (Cambridge: Cambridge Univ. Press, 1952).
5. Pauling, L., and E. B. Wilson, *Introduction to Quantum Mechanics* (New York: McGraw-Hill, 1935).
6. Pitzer, K. S., *Quantum Chemistry* (New York: Prentice-Hall, 1953).
7. Slater, J. C., *Quantum Theory of Matter* (New York: McGraw-Hill, 1951).
8. Whittaker, E. T., *From Euclid to Eddington, A Study of Conceptions of the External World* (London: Cambridge, 1949).

ARTICLES

1. Compton, A. H., *Am. J. Phys.*, *14*, 80–84 (1946), "Scattering of X-Ray Photons."
2. de Vault, D., *J. Chem. Ed.*, *21*, 526–34, 575–81 (1944), "The Electronic Structure of the Atom."
3. Glockler, G., *J. Chem. Ed.*, *18*, 418–23 (1941), "Teaching the Introduction to Wave Mechanics."
4. Margenau, H., *Am. J. Phys.*, *13*, 73–95 (1945); *12*, 119–30, 247–68 (1944), "Atomic and Molecular Theory Since Bohr."
5. Meggers, W. F., *J. Opt. Soc. Am.*, *41*, 143–8 (1951), "Fundamental Research in Atomic Spectra."
6. Zworykin, V. K., *Science in Progress*, vol. III (New Haven: Yale Univ. Press, 1942), pp. 69–107, "Image Formation by Electrons."

CHAPTER 11

The Structure of Molecules

1. The development of valence theory. The electrical discoveries at the beginning of the nineteenth century strongly influenced the concept of the chemical bond. Indeed, Berzelius proposed in 1812 that all chemical combination was caused by electrostatic attraction. As it turned out 115 years later, this theory happened to be true, though not in the sense supposed by its originator. It did much to postpone the acceptance of diatomic structures for the common gaseous elements, such as H_2, N_2, and O_2. It was admitted that most organic compounds fitted very poorly into the electrostatic scheme, but until 1828 it was widely believed that these compounds were held together by "vital forces," arising by virtue of their formation from living things. In that year, Wöhler's synthesis of urea from ammonium cyanate destroyed this distinction between organic and inorganic compounds, and the vital forces gradually retreated to their present refuge in living cells.

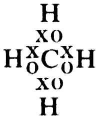
Two general classes of compounds came to be distinguished, with an assortment of uncomfortably intermediate specimens. The *polar* compounds, of which NaCl was a prime example, could be adequately explained as being composed of positive and negative ions held together by coulombic attraction. The nature of the chemical bond in the *nonpolar* compounds, such as CH_4, was completely obscure. Nevertheless, the relations of valence with the periodic table, which were demonstrated by Mendeleev, emphasized the remarkable fact that the valence of an element in a definitely polar compound was usually the same as that in a definitely nonpolar compound, *e.g.*, O in K_2O and $(C_2H_5)_2O$.

In 1904 Abegg pointed out the *rule of eight*: To many elements in the periodic table there could be assigned a *negative valence* and a *positive valence* the sum of which was eight, for example, Cl in LiCl and Cl_2O_7, N in NH_3 and N_2O_5. Drude suggested that the positive valence was the number of loosely bound electrons that an atom could give away, and the negative valence was the number of electrons that an atom could accept.

Once the concept of atomic number was clearly established by Moseley (1913), further progress was possible, for then the number of electrons in an atom became known. The special stability of a complete outer octet of electrons was soon noticed. For example: He, 2 electrons; Ne, 2 + 8 electrons; A, 2 + 8 + 8 electrons. In 1916, W. Kossel made an important contribution to the theory of the electrovalent bond, and in the same year G. N. Lewis proposed a theory for the nonpolar bond.

Kossel explained the formation of stable ions by a tendency of the atoms to gain or lose electrons until they achieve an inert-gas configuration. Thus argon has a completed octet of electrons. Potassium has 2 + 8 + 8 + 1, and it tends to lose the outer electron, becoming the positively charged K^+ ion having the argon configuration. Chlorine has 2 + 8 + 7 electrons and tends to gain an electron, becoming Cl^- with the argon configuration. If an atom of Cl approaches one of K, the K donates an electron to Cl, and the resulting ions combine as K^+Cl^-, the atoms displaying their valences of one. The extension to other ionic compounds is familiar.

G. N. Lewis proposed that the links in nonpolar compounds resulted from the *sharing of pairs* of electrons between atoms in such a way as to form stable octets to the greatest possible extent. Thus carbon has an atomic number of 6; *i.e.*, 6 outer electrons, or 4 less than the stable neon configuration. It can share electrons with hydrogen as follows:



$$\begin{array}{c} \mathrm{H} \\ \mathrm{xo} \\ \mathrm{H}{}^{\mathrm{x}}_{\mathrm{o}}\mathrm{C}{}^{\mathrm{x}}_{\mathrm{o}}\mathrm{H} \\ \mathrm{xo} \\ \mathrm{H} \end{array}$$

Each pair of shared electrons constitutes a single *covalent bond.* The Lewis theory explained why the covalence and electrovalence of an atom are usually identical, for an atom usually accepts one electron for each covalent bond that it forms.

The development of the Bohr theory led to the idea that the electrons were contained in shells or energy levels at various distances from the nucleus. These shells were specified by the quantum numbers. By about 1925, a systematic picture of electron shells was available that represented very well the structure of the periodic table and the valence properties of the elements. The reason why the electrons are arranged in this way was unknown. The reason why a shared electron pair constitutes a stable chemical bond was also unknown.

An answer to both these fundamental chemical problems was provided by the Pauli Exclusion Principle. Its application to the problem of the periodic table was shown in the previous chapter. Its success in explaining the nature of the chemical bond has been equally remarkable.

2. The ionic bond. The simplest type of molecular structure to understand is that formed from two atoms, one of which is strongly electropositive (low ionization potential) and the other, strongly electronegative (high electron affinity). Such, for example, would be sodium and chlorine. In crystalline sodium chloride, one cannot speak of an NaCl molecule since the stable arrangement is a three-dimensional crystal structure of Na^+ and Cl^- ions. In the vapor, however, a true NaCl molecule exists, in which the binding is almost entirely ionic.

The attractive force between two ions with charges q_1 and q_2 can be represented at moderate distances of separation r by the coulombic force

$q_1 q_2/r^2$ or by a potential $U = -q_1 q_2/r$. If the ions are brought so close together that their electron clouds begin to overlap, a mutual repulsion between the positively charged nuclei becomes evident. Born and Mayer have suggested a repulsive potential having the form $U = be^{-r/a}$, where a and b are constants.

The net potential for two ions is therefore

$$U = \frac{-q_1 q_2}{r} + be^{-r/a} \tag{11.1}$$

This potential-energy function is plotted in Fig. 11.1 for NaCl, the minimum in the curve representing the stable internuclear separation for a Na^+Cl^-

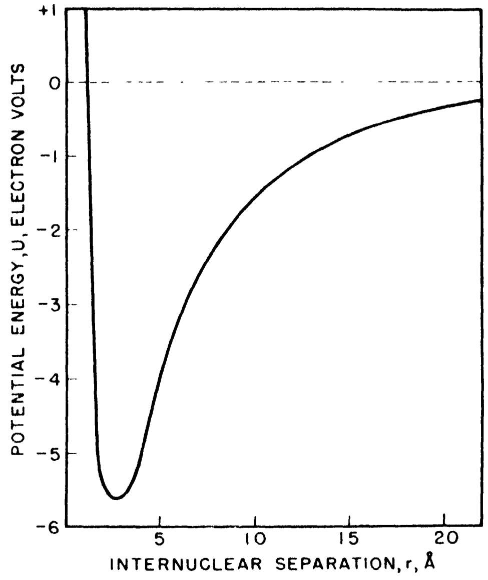


Fig. 11.1. Potential energy of $Na^+ + Cl^-$. (The internuclear distance in the stable molecule is 2.51 Å. Note the long range of the coulombic attraction.)

molecule. Spectra of this molecule are observed in the vapor of sodium chloride.

3. The covalent bond. One of the most important of all the applications of quantum mechanics to chemistry has been the explanation of the nature of the covalent bond. The simplest example of such a bond is found in the H_2 molecule. Although Lewis, in 1918, declared that this bond consists of a shared pair of electrons, it was in 1927 that a real understanding of the nature of the binding was provided by the work of W. Heitler and F. London.

If two H atoms are brought together there results a moderately complicated system consisting of two +1 charged nuclei and two electrons. If the atoms are very far apart their mutual interaction is effectively nil. In other words, the potential energy of interaction $U = 0$ when the internuclear distance $r \to \infty$. At the other extreme, if the two atoms are forced very closely together, there is a large repulsive force between the two positively charged nuclei, so that as $r \to 0$, $U \to \infty$. Experimentally we know that two hydrogen atoms can unite to form a stable hydrogen molecule, whose dissociation energy is 4.48 ev, or 103.2 kcal per mole. The internuclear separation in the molecule is 0.74 Å.

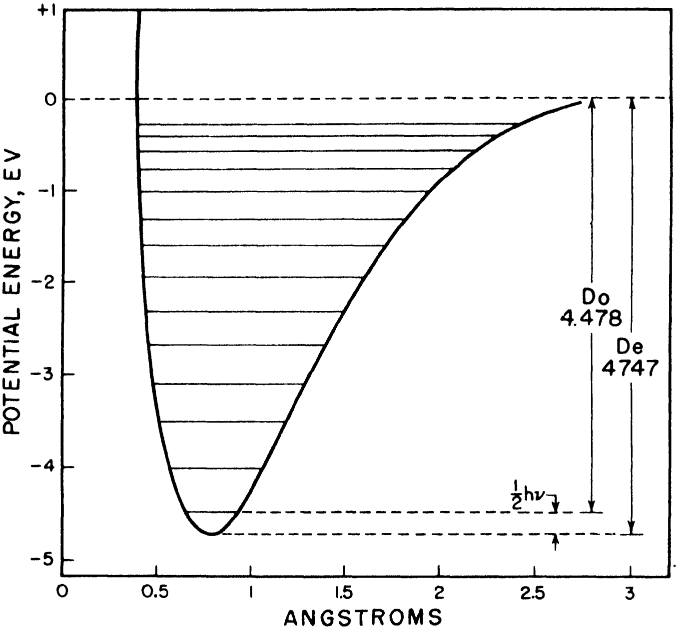


Fig. 11.2. Potential energy curve for hydrogen molecule. (Note the shorter range of the valence forces in H_2, as compared with the ionic molecule NaCl shown in Fig. 11.1.)

These facts about the interaction of two H atoms are summarized in the potential-energy curve of Fig. 11.2. The problem before us is to explain the minimum in the curve. This is simply another way of asking why a stable molecule is formed, or what is the essential nature of the covalent bond in H_2.

The quantum-mechanical problem is to solve the Schrödinger equation for the system of two electrons and two protons. Consider the situation in Fig. 11.3, where the outer electron orbits overlap somewhat. According to quantum mechanics, of course, these orbits are not sharp. There are eigenfunctions $\psi(1)$ for electron (1) and $\psi(2)$ for electron (2), which determine the probability of finding the electrons at any point in space. As long as the atoms are far apart, the eigenfunction for electron (1) on nucleus (a) will be simply that found on page 281 for the ground state of a hydrogen atom—namely, $\psi_{1s}(1) = (\pi a_0^3)^{-1/2} e^{-r/a_0}$.

For the two electrons, a wave function is required that expresses the probability of simultaneously finding electron (1) on nucleus (*a*) and electron (2) on nucleus (*b*). Since the combined probability is the product of the two individual probabilities, such a function would be $a(1)b(2)$. Here $a(1)$ and $b(2)$ represent eigenfunctions for electron (1) on nucleus (*a*) and electron (2) on nucleus (*b*).

A very important principle must now be considered. There are no physical differences and no way of distinguishing between a system with (1) on (*a*) and (2) on (*b*) and a system with (2) on (*a*) and (1) on (*b*). *The electrons cannot be labeled.* The proper wave function for the system must contain in itself an expression of this fundamental truth.

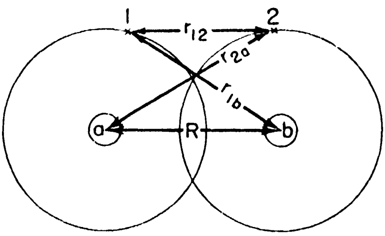


Fig. 11.3. Interaction of two hydrogen atoms.

To help solve this problem we need only recall from page 254 that if ψ_1 and ψ_2 are two solutions of the wave equation, then any linear combination of these solutions is also a solution, *e.g.*, $c_1\psi_1 + c_2\psi_2$. There are two particular linear combinations that inherently express the principle that the electrons are indistinguishable. These are

$$\psi_+ = a(1)b(2) + a(2)b(1)$$
$$\psi_- = a(1)b(2) - a(2)b(1)$$

If the electrons are interchanged in these functions, ψ_+ is not changed at all; it is called a *symmetric function.* ψ_- is changed to $-\psi_-$, but this in itself does not change the electron distribution since it is ψ^2 which gives the probability of finding an electron in a given region, and $(-\psi)^2 = \psi^2$. The function ψ_- is called *antisymmetric.*

So far the spin properties of the electrons have not been included, and this must be done in order to obtain a correct wave function. The electron-spin quantum number s, with allowed values of either $+\frac{1}{2}$ or $-\frac{1}{2}$, determines the magnitude and orientation of the spin. We introduce two spin functions α and β corresponding to $s = +\frac{1}{2}$ and $s = -\frac{1}{2}$. For the two-electron system there are then four possible complete spin functions:

Spin Function	*Electron 1*	*Electron 2*
$\alpha(1)\alpha(2)$	$+\frac{1}{2}$	$+\frac{1}{2}$
$\alpha(1)\beta(2)$	$+\frac{1}{2}$	$-\frac{1}{2}$
$\beta(1)\alpha(2)$	$-\frac{1}{2}$	$+\frac{1}{2}$
$\beta(1)\beta(2)$	$-\frac{1}{2}$	$-\frac{1}{2}$

When the spins have the same direction they are said to be *parallel*; when they have opposite directions, *antiparallel.*

Once again, however, the fact that the electrons are indistinguishable forces us to choose linear combinations for the two-electron system which are either symmetric or antisymmetric. There are three possible symmetric spin functions:

$$\left.\begin{array}{c}\alpha(1)\alpha(2)\\ \beta(1)\beta(2)\\ \alpha(1)\beta(2)+\alpha(2)\beta(1)\end{array}\right\}\ \text{sym}$$

There is one antisymmetric spin function:

$$\alpha(1)\beta(2)-\alpha(2)\beta(1)\quad\text{antisym}$$

The possible complete wave functions for the H-H system are obtained by combining these four possible spin functions with the two possible orbital wave functions. This leads to eight functions in all.

At this point in the argument the Pauli Principle enters in an important way. The Principle is stated in a more general form than was used before: "Every allowable eigenfunction for a system of two or more electrons must be antisymmetric for the interchange of the coordinates of any pair of electrons." It will be shown a little later that the prohibition against four identical quantum numbers is a special case of this statement.

As a consequence of the exclusion principle, the only allowable eigenfunctions are those made up either of symmetric orbitals and antisymmetric spins or of antisymmetric orbitals and symmetric spins. There are four such combinations for the H-H system:

Orbital	Spin	Total Spin	Term
$a(1)b(2)+a(2)b(1)$	$\alpha(1)\beta(2)-\alpha(2)\beta(1)$	0 (singlet)	$^1\Sigma$
$a(1)b(2)-a(2)b(1)$	$\alpha(1)\alpha(2)$ $\beta(1)\beta(2)$ $\alpha(1)\beta(2)+\alpha(2)\beta(1)$	1 (triplet)	$^3\Sigma$

The term symbol Σ expresses the fact that the molecular state has a total angular momentum of zero, since it is made up of two atomic S terms. The multiplicity of the term, or number of eigenfunctions corresponding with it, is added as a left-hand superscript. This multiplicity is always $2\mathscr{S}+1$ where $\mathscr{S}$ is the total spin.

The way in which the general statement of the exclusion principle reduces to that in terms of quantum numbers can readily be seen in a typical example. Multiplying out the $^1\Sigma$ function gives $\psi = a\alpha(1)b\beta(2) - a\alpha(2)b\beta(1)$. If the quantum numbers n, l, m are the same for both electrons, their orbital functions are identical, $a = b$, so that $\psi = a\alpha(1)a\beta(2) - a\alpha(2)a\beta(1)$. If the fourth quantum number s is also the same for both, either $\frac{1}{2}$ or $-\frac{1}{2}$, the spin functions must be either both α or both β. Then $\psi = 0$, that is, the probability of such a system is zero. In other words, eigenfunctions that assign identical values of n, l, m, and s to two electrons are outlawed. This result was shown in a special case, but it is in fact a completely general consequence of the requirement of antisymmetry.

4. Calculation of the energy in H-H molecule. The next step is to calculate the energy for the interaction of two hydrogen atoms using the allowed wave functions. The different electrostatic interactions are shown in Fig. 11.3:

i. electron (1) with electron (2), potential, $U_1 = -e^2/r_{12}$
ii. electron (1) with nucleus (b), $U_2 = e^2/r_{1b}$
iii. electron (2) with nucleus (a), $U_3 = e^2/r_{2a}$
iv. nucleus (a) with nucleus (b), $U_4 = -e^2/r_{ab}$

Note that the interactions of electron (1) with its own nucleus (a) and of electron (2) with nucleus (b) are already taken into account by the fact that we are starting with two hydrogen *atoms*.

The potential for the interaction of two electrons a distance r_{12} apart is $U_1 = -e^2/r_{12}$. In order to find the energy of interaction, we must multiply this by the probability of finding an electron in a given element of volume dv, and then integrate over all of space. Since the required probability is $\psi^2 dv$, this gives $E = \int U_1 \psi^2 dv$. Since the total potential is $U = U_1 + U_2 + U_3 + U_4$, the total energy of interaction of the two hydrogen atoms becomes

$$E = \int U \psi^2 dv \tag{11.2}$$

This energy must now be calculated for both the symmetric and the antisymmetric orbital wave functions. Squaring these functions, one obtains

$$\psi^2 = a^2(1)b^2(2) + a^2(2)b^2(1) \pm 2a(1)b(2)a(2)b(1)$$

The + sign is for the $^1\Sigma$ function, the − sign for the $^3\Sigma$ function.

The integral in eq. (11.2) can therefore be written

$$E = 2C \pm 2A \tag{11.3}$$

where

$$\begin{aligned} C &= \int U a^2(1) b^2(2) dv \\ A &= \int U a(1) b(1) a(2) b(2) dv \end{aligned} \tag{11.4}$$

C is called the *coulombic energy*, and A is called the *exchange energy*.

The coulombic energy is the result of the ordinary electrostatic interaction between the charges of the electrons and the nuclei. The behavior of this coulombic energy as the two hydrogen atoms approach each other can be estimated qualitatively as follows, although the actual integration is not too difficult if we use the simple $1s$ orbitals for a and b. At large internuclear distances, C is zero. At very small distances C approaches infinity owing to the strong repulsions between the nuclei. At intermediate distances where the electron clouds overlap there is a net attractive potential since portions of the diffuse electron clouds are close to the nuclei and the resulting attraction more than compensates for the repulsions between different parts of the diffuse clouds and between the still relatively distant nuclei. The resulting dependence of the coulombic energy on the internuclear distance r is shown as curve C in Fig. 11.4.

The depth of the minimum in the coulombic potential energy curve is only about 0.6 ev compared to the observed 4.75 ev for the H-H bond. The classical electrostatic interaction between two hydrogen atoms is thus completely inadequate to explain the strong covalent bond. The solution to the problem must be in the specifically quantum mechanical phenomenon of the exchange energy A.

The exchange energy arises from the fact that the electrons are indistinguishable, and besides considering the interaction of electron 1 on nucleus a, we have to consider interactions occurring as if electron 1 were on nucleus b. Since quantum mechanics is expressed in the language of ψ functions, we even have to consider interactions arising between charge densities that represent electron 1 on both a and b simultaneously. Even to try to express the phenomenon in terms of artificially labeled electrons involves us in difficulties, but it is clear qualitatively that "exchange" may increase the density of electronic charge around the positive nuclei and so increase the binding energy.

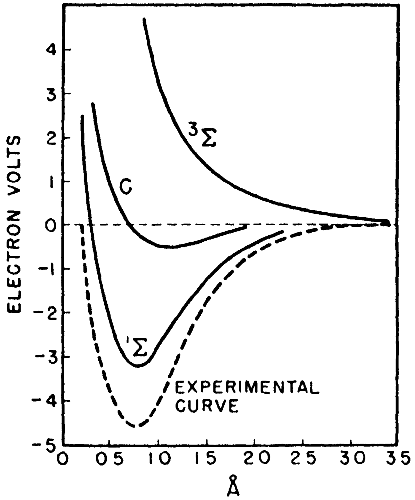


Fig. 11.4. Heitler-London treatment of the H_2 molecule.

Like the coulombic energy, the exchange energy is zero when there is no overlap. At a position of large overlap it may lead to a large attractive force and large negative potential energy. The exact demonstration of this fact would require the evaluation of the integral. When this is done we obtain a curve for the variation of A with r.

The total energy of interaction $2C \pm 2A$ can now be plotted. It is clear that $2C + 2A$ leads to a deep minimum in the potential energy curve. This is the solution for the symmetric orbital wave function; *i.e.*, the antisymmetric spin function. It is the case, therefore, in which the electron spins are antiparallel. The spin of one electron is $+\frac{1}{2}$, and that of the other is $-\frac{1}{2}$. The other curve, $2C-2A$, corresponds to the antisymmetric orbital wave function, which requires symmetric spin functions, or parallel spins. The two curves are drawn as $^1\Sigma$ and $^3\Sigma$ in Fig. 11.4. The deep minimum in the $^1\Sigma$ curve indicates that the Heitler-London theory has successfully explained the covalent chemical bond in the hydrogen molecule. The binding energy is about 10 per cent coulombic, and 90 per cent exchange energy.

Since the covalent bond is formed between atoms that share a pair of electrons with opposite spins, covalence is often called *spin valence.* Only when the spins are opposed is there an attractive interaction due to the exchange phenomenon. If the spins are parallel, there is a net repulsion between two approaching hydrogen atoms. It is interesting to note that if two H atoms are brought together, there is only one chance in four that they will attract each other, since the stable state is a singlet and the repulsive state is a triplet.

The Heitler-London theory is an example of the *valence-bond* (V.B.) approach to molecular structure.

5. Molecular orbitals. An alternative to the Heitler-London method of applying quantum mechanics to molecular problems is the *method of molecular orbitals,* developed by Hund, Mulliken, and Lennard-Jones. Instead of starting with definite atoms, it assumes the *nuclei* in a molecule to be held fixed at their equilibrium separations, and considers the effect of gradually feeding the electrons into the resulting field of force. Just as the electrons in an atom have definite orbitals characterized by quantum numbers, n, l, m, and occupy the lowest levels consistent with the Pauli Principle, so the electrons in a molecule have definite molecular orbitals and quantum numbers, and only two electrons having opposite spins can occupy any particular molecular orbital. In our description of the molecular orbital (M.O.) method we shall follow an excellent review by C. A. Coulson.[1]

For diatomic molecules, the molecular quantum numbers include a principal quantum number n, and a quantum number λ, which gives the components of angular momentum in the direction of the internuclear axis. This λ takes the place of the atomic quantum number l. We may have states designated $\sigma, \pi, \delta \ldots$ as $\lambda = 0, 1, 2 \ldots.$

6. Homonuclear diatomic molecules. Homonuclear diatomic molecules are those that are formed from two identical atoms, like H_2, N_2, and O_2. Such molecules provide the simplest cases for application of the M.O. method.

If a hydrogen molecule, H_2, is pulled apart, it gradually separates into two hydrogen atoms, H_a and H_b, each with a single $1s$ atomic orbital. If the process is reversed and the hydrogen atoms are squeezed together, these atomic orbitals coalesce into the molecular orbital occupied by the electrons in H_2. We therefore adopt the principle that the molecular orbital can be constructed from a linear combination of atomic orbitals (L.C.A.O.). Thus

$$\psi = \psi(A : 1s) + \gamma\psi(B : 1s)$$

Since the molecules are completely symmetrical, γ must be ± 1. Then there are two possible molecular orbitals:

$$\psi_g = \psi(A : 1s) + \psi(B : 1s)$$
$$\psi_u = \psi(A : 1s) - \psi(B : 1s)$$

---

[1] *Quarterly Reviews,* *1,* 144 (1947).

These molecular orbitals are given a pictorial representation in (a), Fig. 11.5. The 1*s* A.O.'s are spherically symmetrical (see page 283). If two of these are brought together until they overlap, the M.O. resulting can be represented as shown. The additive one, ψ_g, leads to a building up of charge

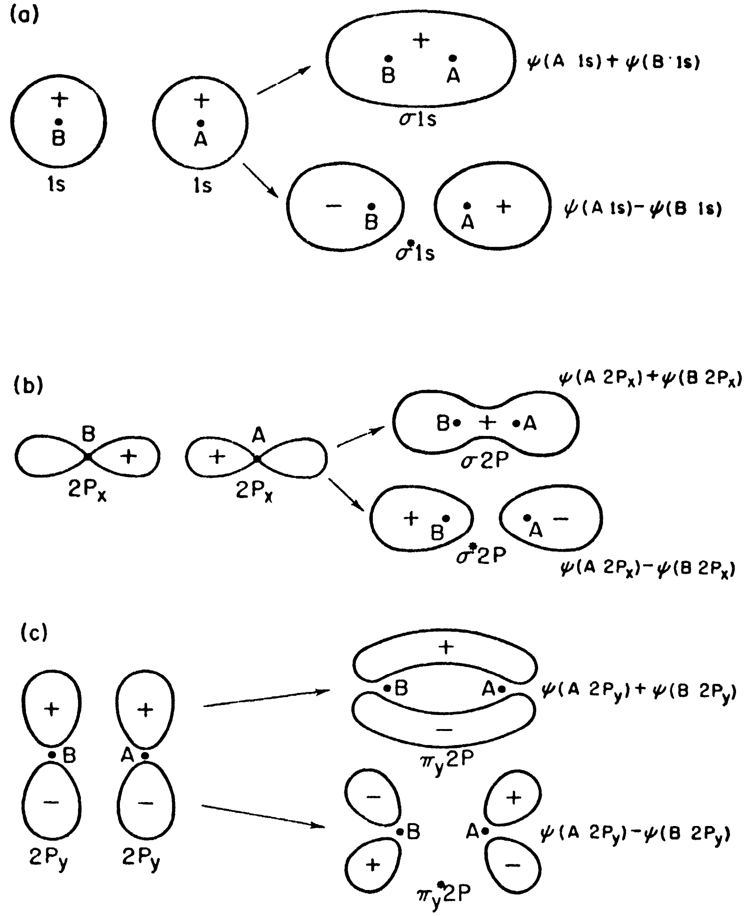


Fig. 11.5. Formation of molecular orbitals by linear combinations of atomic orbitals.

density between the nuclei. The subtractive one, ψ_u, has an empty space free of charge between the nuclei. Both these M.O.'s are completely symmetrical about the internuclear axis; the angular momentum about the axis is zero, and they are called σ orbitals. The first one is designated as a $\sigma 1s$ orbital. It is called a *bonding orbital*, for the piling up of charge between the nuclei tends to bind them together. The second one is written as $\sigma^* 1s$, and is an *antibonding orbital*, corresponding to a net repulsion, since there is no shielding between the positively charged nuclei. Antibonding orbitals will be designated with a star.

A further insight into the nature of these orbitals is obtained if we imagine the H nuclei squeezed so tightly together that they coalesce into the united nucleus of helium. Then the bonding orbital $\sigma 1s$ merges into the $1s$ atomic orbital of helium. The antibonding $\sigma^* 1s$ must merge into the next lowest A.O. in helium, the $2s$. This $2s$ level is 19.7 ev above the $1s$, and this energy difference is further evidence of the antibonding nature of the $\sigma^* 1s$.

The electron configurations of the molecules are built up just as in the atomic case, by feeding electrons one by one into the available orbitals. In accordance with the Pauli Principle, each M.O. can hold two electrons with opposite spins.

In the case of H_2, the two electrons enter the $\sigma 1s$ orbital. The configuration is $(\sigma 1s)^2$ and corresponds to a single electron pair bond between the H atoms.

The next possible molecule would be one with three electrons, He_2^+. This has the configuration $(\sigma 1s)^2(\sigma^* 1s)^1$. There are two bonding electrons and one antibonding electron, so that a net bonding is to be expected. The molecule has, in fact, been observed spectroscopically and has a dissociation energy of 3.0 ev.

If two helium atoms are brought together, the result is $(\sigma 1s)^2(\sigma^* 1s)^2$. Since there are two bonding and two antibonding electrons, there is no tendency to form a stable He_2 molecule. We have now used up all of our available M.O.'s and must make some more in order to continue the discussion.

The next possible A.O.'s are the $2s$, and these behave just like the $1s$ providing $\sigma 2s$ and $\sigma^* 2s$ M.O.'s with accommodations for four more electrons. If we bring together two lithium atoms with three electrons each, the molecule Li_2 is formed. Thus

$$\mathrm{Li}[1s^2 2s^1] + \mathrm{Li}[1s^2 2s^1] \rightarrow \mathrm{Li}_2[(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2]$$

Actually, only the outer-shell or valence electrons need be considered, and the M.O.'s of inner K-shell electrons need not be explicitly designated. The Li_2 configuration is therefore written as $[KK(\sigma 2s)^2]$. The molecule has a dissociation energy of 1.14 ev. The hypothetical molecule Be_2, with eight electrons, does not occur, since the configuration would have to be $[KK(\sigma 2s)^2(\sigma^* 2s)^2]$.

The next atomic orbitals are the $2p$'s shown in Fig. 10.14. There are three of these, p_x, p_y, p_z, mutually perpendicular and with a characteristic wasp-waisted appearance. The most stable M.O. that can be formed from the atomic p orbitals is one with the maximum overlap along the internuclear axis. This M.O. is shown in (b), Fig. 11.5, and with the corresponding antibonding orbital can be written

$$\psi_g = \psi(A : 2p_x) + \psi(B : 2p_x) \qquad \sigma 2p$$
$$\psi_u = \psi(A : 2p_x) - \psi(B : 2p_x) \qquad \sigma^* 2p$$

These orbitals have the same symmetry around the internuclear axis as the σ orbitals formed from atomic s orbitals. They also have a zero angular momentum around the axis.

The M.O.'s formed from the p_y and p_z A.O.'s have a distinctly different form, as shown in (c), Fig. 11.5. As the nuclei are brought together, the sides of the p_y or p_z orbitals coalesce, and finally form two streamers of charge density, one above and one below the internuclear axis. These are called π orbitals; they have an angular momentum of one unit.

We can summarize the available M.O.'s as follows, in order of increasing energy:

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p < \pi_y 2p = \pi_z 2p < \pi_y{}^* 2p = \pi_z{}^* 2p < \sigma^* 2p$$

With the good supply of M.O.'s now available, the configurations of other homonuclear molecules can be determined, by feeding pairs of electrons with opposite spins into the orbitals.

The formation of N_2 proceeds as follows:

$$\mathrm{N}[1s^2 2s^2 2p^3] + \mathrm{N}[1s^2 2s^2 2p^3] \rightarrow \mathrm{N}_2[KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p)^2(\pi 2p)^4]$$

There are six net bonding electrons, so that it can be said that there is a triple bond between the two N's. One of these bonds is a σ bond; the other two are π bonds at right angles to each other.

Molecular oxygen is an interesting case:

$$\mathrm{O}[1s^2 2s^2 2p^4] + \mathrm{O}(1s^2 2s^2 2p^4] \rightarrow \mathrm{O}_2[KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p)^2(\pi 2p)^4(\pi^* 2p)^2]$$

There are four net bonding electrons, or a double bond consisting of a σ and a π bond. Note that a single bond is usually a σ bond, but a double bond is not just two equivalent single bonds, but a σ plus a π. In O_2, the $(\pi^* 2p)$ orbital, which can hold 4 electrons, is only half filled. Because of electrostatic repulsion between the electrons, the most stable state will be that in which the electrons occupy separate orbitals and have parallel spins. Thus these two electrons are assigned as $(\pi_y{}^* 2p)^1(\pi_z{}^* 2p)^1$. The total spin of O_2 is then $\mathscr{S} = 1$, and its multiplicity, $2\mathscr{S} + 1 = 3$. The ground state of oxygen is $^3\Sigma$.

TABLE 11.1

PROPERTIES OF HOMONUCLEAR DIATOMIC MOLECULES

Molecule	Binding Energy (ev)	Internuclear Separation (Å)	Vibration Frequency (sec^{-1})	Bonding − Antibonding Electrons
B_2	3.6	1.59	3.15×10^{13}	2
C_2	5.5	1.31	4.92×10^{13}	4
N_2	7.4	1.09	7.08×10^{13}	6
O_2	5.1	1.20	4.74×10^{13}	4
F_2	3.0	1.30	3.40×10^{13}	2

In the M.O. method, all the electrons outside closed shells make a contribution to the binding energy between the atoms. The shared electron pair bond is not particularly emphasized. The way in which the excess of bonding over antibonding orbitals determines the tightness of binding may be seen by reference to the simple diatomic molecules in Table 11.1.

7. Heteronuclear diatomic molecules. If the two nuclei in a diatomic molecule are different, it is still possible to build up molecular orbitals by an L.C.A.O., but now the symmetry of the homonuclear case is lost. Consider, for example, the molecule HCl. The bond between the atoms is undoubtedly caused mainly by electrons in an M.O. formed from the 1*s* A.O. of H and a 3*p* A.O. of Cl.

The M.O. can be written as

$$\psi = \psi(\mathrm{H} : 1s) + \gamma\psi(\mathrm{Cl} : 3p)$$

Now γ is no longer ± 1, but there are still a bonding orbital for $+\gamma$ and an antibonding orbital for $-\gamma$. Actually, the chlorine has a greater tendency than the hydrogen to hold electrons, and thus the resulting M.O. partakes more of the chlorine A.O. than of the hydrogen A.O.

The larger γ, the more unsymmetrical is the orbital, or the more polar the bond. Thus in the series HI, HBr, HCl, HF, the value of γ increases as the halogen becomes more electronegative.

8. Comparison of M.O. and V.B. methods. Since the M.O. and the V.B. methods are the two basic approaches to the quantum theory of molecules, it is worth while to summarize the distinctions between them.

The V.B. treatment starts with individual atoms and considers the interaction between them. Consider two atoms *a* and *b* with two electrons (1) and (2). A possible wave function is $\psi_1 = a(1)b(2)$. Equally possible is $\psi_2 = b(1)a(2)$, since the electrons are indistinguishable. Then the valence bond (Heitler-London) wave function is

$$\psi_{\mathrm{VB}} = a(1)b(2) + a(2)b(1)$$

The M.O. treatment of the molecule starts with the two nuclei. If $a(1)$ is a wave function for electron (1) on nucleus (*a*), and $b(1)$ is that for electron (1) on nucleus (*b*), the wave function for the single electron moving in the field of the two nuclei is $\psi_1 = c_1a(1) + c_2b(1)$ (L.C.A.O.). Similarly for the second electron, $\psi_2 = c_1a(2) + c_2b(2)$. The combined wave function is the product of these two, or

$$\psi_{\mathrm{MO}} = \psi_1\psi_2 = c_1^2\, a(1)a(2) + c_2^2\, b(1)b(2) + c_1c_2[a(1)b(2) + a(2)b(1)]$$

Comparing the ψ_{VB} with the ψ_{MO}, we see that ψ_{MO} gives a large weight to configurations that place both electrons on one nucleus. In a molecule AB, these are the ionic structures A^+B^- and A^-B^+. The ψ_{VB} neglects these ionic terms. Actually, for most molecules, M.O. considerably overestimates the ionic terms, whereas V.B. considerably underestimates them. The true structure is usually some compromise between these two extremes, but the mathematical treatment of such a compromise is much more difficult.

9. Directed valence. In the case of polyatomic molecules, a rigorous M.O. treatment would simply set up the nuclei in their equilibrium positions and pour in the electrons. It is, however, more desirable to preserve the idea of definite chemical bonds, and to do this we utilize *bond orbitals*, or *localized molecular orbitals*.

For example, in the water molecule, the A.O.'s that take part in bond formation are the $1s$ orbitals of hydrogen, and the $2p_x$ and $2p_y$ of oxygen. The stable structure will be that in which there is maximum overlap of these orbitals. Since p_x and p_y are at right angles to each other, the situation in Fig. 11.6 is obtained. The observed valence angle in H_2O is not exactly 90°

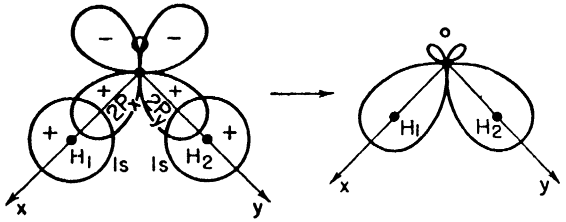


Fig. 11.6. Formation of a molecular orbital for H_2O.

but actually 105°. The difference can be ascribed in part[2] to the polar nature of the bond; the electrons are drawn toward the oxygen, and the residual positive charge on the hydrogens causes their mutual repulsion. In H_2S the bond is less polar and the angle is 92°. The important point is the straightforward fashion in which the directed valence is explained in terms of the shapes of the atomic orbitals.

The most striking example of directed valence is the tetrahedral orientation of the bonds formed by carbon in aliphatic compounds. To explain these bonds, it is necessary to introduce a new principle, the formation of *hybrid orbitals*. The ground state of the carbon atom is $1s^2 2s^2 2p^2$. There are two uncoupled electrons $2p_x$, $2p_y$, and one would therefore expect the carbon to be bivalent. In order to display a valence of four, the carbon atom must have four electrons with uncoupled spins. The simplest way to attain this condition is to *excite* or *promote* one of the $2s$ electrons into the p state, and to have all the resulting p electrons with uncoupled spins. Then the outer configuration would be $2s2p^3$, with $2s\uparrow 2p_x\uparrow 2p_y\uparrow 2p_z\uparrow$. This excitation requires the investment of about 65 kcal per mole of energy, but the extra binding energy of the four bonds that are formed more than compensates for the promotion energy, and carbon is normally quadrivalent rather than bivalent.

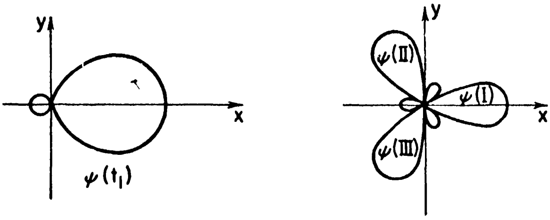
If these four $2s2p^3$ orbitals of carbon were coupled with the $1s$ orbitals

---

[2] A more detailed theory shows that the $2s$ electrons of the oxygen also take part in the bonding, forming hybrid orbitals like those discussed below for carbon.

of hydrogen to yield the methane molecule, it might at first be thought that three of the bonds would be different from the remaining one. Actually, of course, the symmetry of the molecule is such that all the bonds must be exactly the same.

Pauling[3] showed that in a case like this it is possible to form four identical ***hybrid orbitals*** that are a linear combination of the s and p orbitals. These are called *tetrahedral orbitals*, t_1, t_2, t_3, t_4, since they are spatially directed to the corners of a regular tetrahedron. One of them is shown in (a), Fig. 11.7. In terms of the $2s$ and $2p$ orbitals it has the form: $\psi(t_1) = \frac{1}{2}\psi(2s) + (\sqrt{3}/2)\psi(2p_x)$. The hybrid t orbitals then combine with the $1s$ orbitals of hydrogen to form a set of localized molecular orbitals for methane.



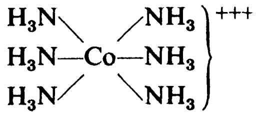
(o) (b)

Fig. 11.7. Hybrid atomic orbitals for carbon: (a) a single tetrahedral orbital; (b) three trigonal orbitals.

The tetrahedral orbitals are exceptionally stable since they allow the electron pairs to avoid one another to the greatest possible extent.

In addition to the tetrahedral hybrids, the four sp^3 orbitals of carbon can be hybridized in other ways. The so-called *trigonal hybrids* mix the $2s$, $2p_x$, and $2p_y$ to form three orbitals at angle of 120°. These hybrids are shown in (b), Fig. 11.7. For example, $\psi = \sqrt{\frac{1}{3}}\psi(2s) + \sqrt{\frac{2}{3}}\psi(2p_x)$. The fourth A.O., $2p_z$, is perpendicular to the plane of the others. This kind of hybridization is that used in the aromatic carbon compounds like benzene, and also in ethylene, which are treated separately in the next section.

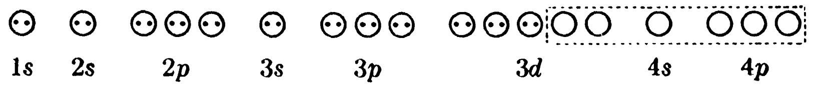
Hybrid orbitals are not restricted to carbon compounds. An interesting instance of their occurrence is in the compounds of the transition elements. It will be recalled that these elements have a d level that is only slightly lower than the outer s level. Cobalt, for example, has an outer configuration of $3d^7 4s^2$. The cobaltic ion, Co^{+++}, having lost three electrons, has $3d^6$. It is noted for its ability to form complexes, such as the hexamminocobaltic ion,



---

[3] L. Pauling, *Nature of the Chemical Bond* (Ithaca, N.Y.: Cornell Univ. Press, 1940), p. 85.

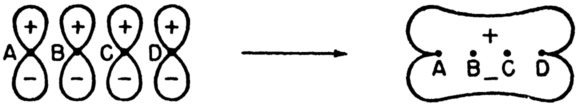
This characteristic can be explained by the fact that there are six low-lying empty orbitals, each of which can hold a pair of electrons:



These d^2sp^3 orbitals can be filled by taking twelve electrons from six NH_3 groups, forming the hexamminocobaltic ion with the stable rare gas configuration. Once again, hybridization takes place, and six identical orbitals are formed. Pauling's calculation showed that these orbitals should be oriented toward the vertices of an octahedron, and the octahedral arrangement is confirmed by the crystal structures of the compounds.

10. Nonlocalized molecular orbitals. It is not always possible to assign the electrons in molecules to molecular orbitals localized between two nuclei. The most interesting examples of delocalization are found in conjugated and aromatic hydrocarbons.

Consider, for example, the structure of butadiene, usually written $CH_2{=}CH{-}CH{=}CH_2$. The molecule is coplanar, and the C—C—C bond angles are close to 120°. The M.O.'s are evidently formed from hybrid carbon A.O.'s of the trigonal type. Three of these trigonal orbitals lie in a plane and are used to form localized bonds with C and H as follows: $CH_2{-}CH{-}CH{-}CH_2$. The fourth orbital is a p-shaped one, perpendicular to the others. These orbitals line up as shown in (a), Fig. 11.8, for the individual atoms. When the atoms are pushed together, the orbitals overlap to form a continuous sheet above and below the carbon nuclei as in (b). This typical nonlocalized orbital is called a *π orbital*, and it can hold four electrons.



(a) (b)

Fig. 11.8. Nonlocalized π orbital in butadiene.

It is important to note that the four π electrons are not localized in particular bonds, but are free to move anywhere within the region in the figure. Since a larger volume is available for the motion of the electrons, their energy levels are lowered, just as in the case of the particle in a box. Thus delocalization results in an extra binding energy, greater than would be achieved in the classical structure of alternating double and single bonds. In the case of butadiene, this *delocalization energy*, often called the *resonance energy*, amounts to about 7 kcal per mole.

Benzene and other aromatic molecules provide the most remarkable instances of nonlocalized orbitals. The discussion of benzene proceeds very similarly to that of butadiene. First the carbon A.O.'s are prepared as trigonal hybrids and then brought together with the hydrogens. The localized orbitals formed lie in a plane, as shown in (a), Fig. 11.9. The p orbitals extend their sausage-shaped sections above and below the plane, (b), and when they overlap they form two continuous bands, (c), the π orbitals, above and below the plane of the ring. These orbitals hold six mobile electrons, which are completely delocalized. The resulting resonance energy is about 40 kcal per mole.

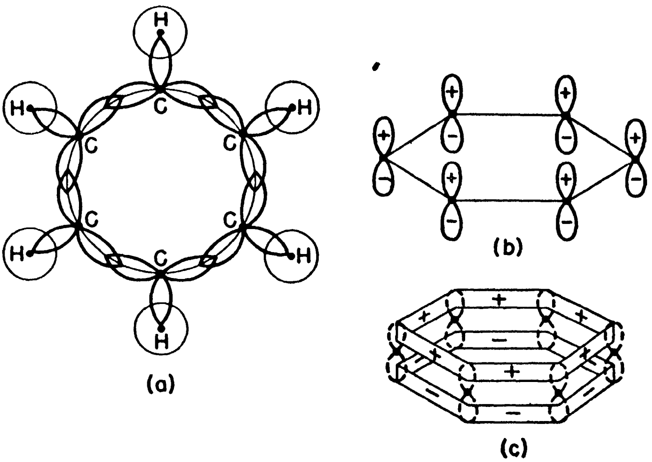
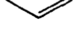


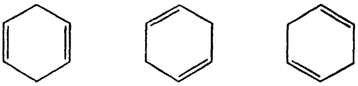
Fig. 11.9. Localized trigonal orbitals (a) and nonlocalized π orbitals (c) in benzene.

The properties of benzene bear out the existence of these mobile π electrons. All the C—C bonds in benzene have the same length, 1.39 Å compared to 1.54 in ethane and 1.30 in ethylene. The benzene ring is like a little loop of metal wire containing electrons; if a magnetic field is applied normal to the planes of the rings in solid benzene, the electrons are set in motion, and experimental measurements show that an induced magnetic field is caused that opposes the applied field.

11. Resonance between valence-bond structures. Instead of the M.O. method it is often convenient to imagine that the structure of a molecule is made up by the superposition of various distinct valence-bond structures. Applying this viewpoint to the case of benzene, one would say that the actual structure is formed principally by *resonance* between the two Kekulé structures,


and


with smaller contributions from the three Dewar structures,



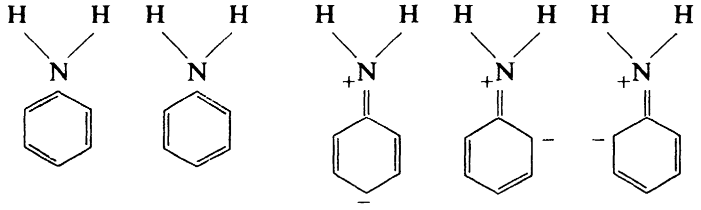
According to the resonance theory, the eigenfunction ψ describing the actual molecular structure is a linear combination of the functions for possible valence bond structures,

$$\psi = a_1\psi_1 + a_2\psi_2 + a_3\psi_3 + \ldots$$

This is an application of the general superposition principle for wave functions. Each eigenfunction ψ corresponds to some definite value E for the energy of the system. The problem is to determine the values of a_1, a_2, a_3, etc., in such a way as to make E a minimum. The relative magnitude of these coefficients when E is a minimum is then a measure of the contribution to the over-all structure of the different special structures represented by ψ_1, ψ_2, ψ_3, . . . It must be clearly understood that the resonance description does *not* mean that some molecules have one structure and some another. The structure of each molecule can only be described as a sort of weighted average of the resonance structures.

Two rules must be obeyed by possible resonating structures: (1) The structures can differ only in the position of electrons. Substances that differ in the arrangement of the atoms are ordinary isomers and are chemically and physically distinguishable as distinct compounds. (2) The resonating structures must have the same number of paired and unpaired electrons, otherwise they would have different total spins and be physically distinguishable by their magnetic properties.

In substituted benzene compounds, the contributions of various ionic structures must be included. For example, aniline has the following resonance structures:



covalent *ionic*

The ionic structures give aniline an additional resonance energy of 7 kcal, compared with benzene. The increased negative charge at the *ortho* and *para* positions in aniline accounts for the fact that the NH_2 group in aniline directs positively charged approaching substituents (NO_2^+, Br^+) to these positions.

The way in which the V.B. method would treat the hydrogen halides is instructive. Two important structures are postulated, one purely covalent and one purely ionic:

$$\mathrm{H^+}\quad :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:^- \qquad \text{and} \qquad \mathrm{H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:$$

The actual structure is visualized as a resonance hybrid somewhere between these two extremes. Its wave function is

$$\psi = \psi_{\text{covalent}} + a\psi_{\text{ionic}}$$

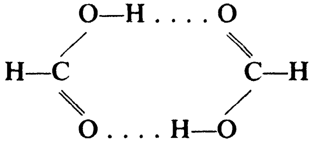
The value of a is adjusted until the minimum energy is obtained. Then $(a^2/1 + a^2)100$ is called the *per cent ionic character* of the bond. For the various halides the following results are found:

Molecule	HF	HCl	HBr	HI
% Ionic Character	60	17	11	5

The bond in HI is predominantly covalent; in HF, it is largely ionic. The distinction between these different bond types is thus seldom clearcut, and most bonds are of an intermediate nature.

The tendency of a pair of atoms to form an ionic bond is measured by the difference in their power to attract an electron, or in their *electronegativity*. Fluorine is the most, and the alkali metals are the least, electronegative of the elements. The fractional ionic character of a bond then depends upon the difference in electronegativity of its constituent atoms.

12. The hydrogen bond. It has been found that in many instances a hydrogen atom can act as if it formed a bond to two other atoms instead of to only one. A typical example is the dimer of formic acid, which has the structure



This hydrogen bond is not very strong, usually having a dissociation energy of about 5 kcal, but it is extremely important in many structures, such as the proteins. It occurs in general between hydrogen and the electronegative elements N, O, F, of small atomic volumes.

We know that hydrogen can form only one covalent bond, since it has only the single 1*s* orbital available for bond formation. Therefore the hydrogen bond is essentially an ionic bond. Since the proton is extremely small, its electrostatic field is very intense. A typical hydrogen-bonded structure is the ion $(HF_2)^-$, which occurs in hydrofluoric acid and in crystals such as KHF_2. It can be represented as a resonance hybrid of three structures,

$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{F}}}:\ \mathrm{H}\ \mathrm{F^-} \qquad \mathrm{F^-}\ \mathrm{H}\ :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{F}}}: \qquad \mathrm{F^-}\ \mathrm{H^+}\ \mathrm{F^-}$$

The ionic $F^-H^+F^-$ structure is the most important. It is noteworthy that electronegative elements with large ionic radii, *e.g.*, Cl, have little or no tendency to form hydrogen bonds, presumably owing to their less concentrated electrostatic fields.

13. Dipole moments. If a bond is formed between two atoms that differ in electronegativity, there is an accumulation of negative charge on the more electronegative atom, leaving a positive charge on the more electropositive atom. The bond then constitutes an *electric dipole*, which is by definition an equal positive and negative charge, $\pm q$, separated by a distance r. A dipole, as in (a), Fig. 11.10, is characterized by its *dipole moment*, a *vector* having the magnitude qr and the direction of the line joining the positive to the negative charge. The dimensions of a dipole moment are charge times length. Two charges with the magnitude of e (4.80×10^{-10} esu) separated by a distance of 1 Å would have a dipole moment of 4.80×10^{-18} esu cm. The unit 10^{-18} esu cm is called the *debye*, (*d*).

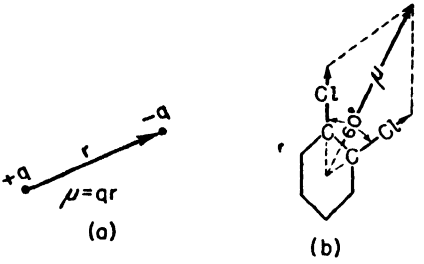


Fig. 11.10. (a) Definition of dipole moment; (b) vector addition of dipole moments in orthodichlorobenzene.

If a polyatomic molecule contains two or more dipoles in different bonds, the net dipole moment of the molecule is the resultant of the vector addition of the individual bond moments. An example of this is shown in (b), Fig. 11.10.

The measurement of the dipole moments of molecules provides an insight into their geometric structure and also into the character of their valence bonds. Before we can discuss the determination of dipole moments, however, it is necessary to review some aspects of the theory of dielectrics.

14. Polarization of dielectrics. Consider a parallel-plate capacitor with the region between the plates evacuated, and let the charge on one plate be $+\sigma$ and on the other $-\sigma$ per square centimeter. The electric field within the capacitor is then directed perpendicular to the plates and has the magnitude[4] $E_0 = 4\pi\sigma$. The capacitance is

$$C_0 = \frac{q}{U} = \frac{\sigma A}{4\pi d\sigma} = \frac{A}{4\pi d}$$

where A is the area of the plates, d the distance, and U the potential difference between them.

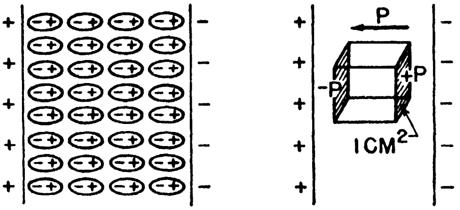
Now consider the space between the plates to be filled with some material substance. In general, this substance falls rather definitely into one of two classes, the conductors or the insulators. Under the influence of small fields, electrons move quite freely through conductors, whereas in insulators or

---

[4] See, for example, G. P. Harnwell, *Electricity and Magnetism* (New York: McGraw-Hill, 1949), p. 26.

dielectrics these fields displace the electrons only slightly from their equilibrium positions.

An electric field acting on a dielectric thus causes a separation of positive and negative charges. The field is said to *polarize* the dielectric. This polarizotion is shown pictorially in (a), Fig. 11.11. The polarization can occur in twa ways: the *induction* effect and the *orientation* effect. An electric field always *induces* dipoles in molecules on which it is acting, whether or not they contain dipoles to begin with. If the dielectric does contain molecules that are permanent dipoles, the field tends to align these dipoles along its own direction. The random thermal motions of the molecules oppose this orienting action.



(a) (b)

Fig. 11.11. (a) Polarization of a dielectric; (b) definition of the polarization vector, ***P***.

Our main interest is in the permanent dipoles, but before these can be studied, effects due to the induced dipoles must be clearly distinguished.

It is found experimentally that when a dielectric is introduced between the plates of a capacitor the capacitance is increased by a factor ε, called the *dielectric constant*. Thus if C_0 is the capacitance with a vacuum, the capacitance with a dielectric is $C = \varepsilon C_0$. Since the charges on the capacitor plates are unchanged, this must mean that the field between the plates is reduced by the factor ε, so that $E = E_0/\varepsilon$.

The reason why the field is reduced is clear from the picture of the polarized dielectric, for all the induced dipoles are aligned so as to produce an over-all dipole moment that cuts down the field strength. Consider in (b), Fig. 11.11, a unit cube of dielectric between the capacitor plates, and define a vector quantity $\boldsymbol{P}$ called the *polarization*, which is the *dipole moment per unit volume*. Then the effect of the polarization is equivalent to that which would be produced by a charge of $+P$ on one face and $-P$ on the other face (1 cm^2) of the cube. The field in the dielectric is now determined by the net charge on the plates, so that

$$\boldsymbol{E} = 4\pi(\sigma - \boldsymbol{P}) \tag{11.5}$$

A new vector has been defined, called the *displacement* $\boldsymbol{D}$, which depends only on the charge σ, according to $\boldsymbol{D} = 4\pi\sigma$. It follows that

$$\boldsymbol{D} = \boldsymbol{E} + 4\pi\boldsymbol{P}, \quad \text{and} \quad \boldsymbol{D}/\boldsymbol{E} = \varepsilon \tag{11.6}$$

It is apparent that in a vacuum, where $\varepsilon = 1$, $\boldsymbol{D} = \boldsymbol{E}$.

15. The induced polarization. Let us consider the *induced or distortion polarization*, $\boldsymbol{P}_D$, produced by an electric field acting on a dielectric that does not contain permanent dipoles.

The first problem to be solved is the magnitude of the dipole moment $\boldsymbol{m}$ induced in a molecule by the field acting on it. It may be assumed that this induced moment is proportional to the intensity of the field[5] $\boldsymbol{F}$, so that

$$\boldsymbol{m} = \alpha_0 \boldsymbol{F} \tag{11.7}$$

The proportionality constant α_0 is called the *distortion polarizability* of the molecule. It is the induced moment per unit field strength, and has the dimensions of a volume, since $q \cdot r/(q/r^2) = r^3 = v$.

At first it might seem that the field acting on a molecule should be simply the field $\boldsymbol{E}$ of eq. (11.5). This would be incorrect, however, for the field that polarizes a molecule is the *local field* immediately surrounding it, and this is different from the average field $\boldsymbol{E}$ throughout the dielectric. For an isotropic substance this local field can be calculated[6] to be

$$\boldsymbol{F} = \boldsymbol{E} + \frac{4\pi \boldsymbol{P}_D}{3} \tag{11.8}$$

In the absence of permanent dipoles, the polarization or dipole moment per unit volume is the number of molecules per cc, n, times the average moment induced in a molecule, $\bar{\boldsymbol{m}}$. Thus, from eqs. (11.7) and (11.8),

$$\boldsymbol{P}_D = n\bar{\boldsymbol{m}} = n\alpha_0 \boldsymbol{F} = n\alpha_0 \left(\boldsymbol{E} + \frac{4\pi \boldsymbol{P}_D}{3}\right)$$

Since, from eq. (11.6), $\boldsymbol{E}(\varepsilon - 1) = 4\pi \boldsymbol{P}_D$,

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi n\alpha_0}{3} \tag{11.9}$$

This is the Clausius-Mossotti equation.

Multiplying both sides by the ratio of molecular weight to density M/ρ,

$$\frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{\rho} = \frac{4\pi n M \alpha_0}{3\rho} = \frac{4}{3}\pi N \alpha_0 = P_M \tag{11.10}$$

The quantity P_M is called the *molar polarization*. So far it includes only the contribution from induced dipoles, and in order to obtain the complete molar polarization, a term due to permanent dipoles must be added.

16. Determination of the dipole moment. Having examined the effect of induced dipoles on the dielectric constant, we are in a position to consider

---

[5] This is true only for isotropic substances; otherwise, for example in nonisotropic crystals, the direction of the moment may not coincide with the field direction. This discussion therefore applies only to gases, liquids, and cubic crystals.

[6] A good derivation is given by Slater and Frank, *Introduction to Theoretical Physics* (New York: McGraw-Hill, 1933), p. 278; also, Syrkin and Dyatkina, *The Structure of Molecules* (New York: Interscience, 1950), p. 471.

the influence of permanent dipoles. If the bonds in a molecule are ionic or partially ionic, the molecule has a net dipole moment, unless the individual bond moments add vectorially to zero.

It is now possible to distinguish an *orientation polarization* of a dielectric, which is that caused by permanent dipoles, from the *distortion polarization*, caused by induced dipoles.

There will always be an induced moment. It is evoked almost instantaneously in the direction of the electric field. It is independent of the temperature, since if the molecule's position is disturbed by thermal collisions, the dipole is at once induced again in the field direction. The contribution to the polarization caused by permanent dipoles, however, is less at higher temperatures, since the random thermal collisions of the molecules oppose the tendency of their dipoles to line up in the electric field.

It is necessary to calculate the average component of a permanent dipole in the field direction as a function of the temperature. Consider a dipole with random orientation. If there is no field, all orientations are equally probable. This fact can be expressed by saying that the number of dipole moments directed within a solid angle $d\omega$ is simply $A\,d\omega$, where A is a constant depending on the number of molecules under observation.

If a dipole moment μ is oriented at angle θ to a field of strength F its potential energy[7] is $U = -\mu F \cos\theta$. According to the Boltzmann equation, the number of molecules oriented within the solid angle $d\omega$ is then

$$Ae^{-U/kT}\,d\omega = Ae^{\mu F\cos\theta/kT}\,d\omega$$

The average value of the dipole moment in the direction of the field, by analogy with eq. (7.39), can be written

$$\bar{m} = \frac{\int Ae^{\mu F\cos\theta/kT}\,\mu\cos\theta\,d\omega}{\int Ae^{\mu F\cos\theta/kT}\,d\omega}$$

To evaluate this expression, let $\mu F/kT = x$, $\cos\theta = y$; then $d\omega = 2\pi\sin\theta\,d\theta = 2\pi\,dy$.

Thus

$$\frac{\bar{m}}{\mu} = \frac{\int_{-1}^{+1} e^{xy}y\,dy}{\int_{-1}^{+1} e^{xy}\,dy} = \frac{dz/dx}{z}$$

Since

$$\int_{-1}^{+1} e^{xy}\,dy = \frac{(e^{x}-e^{-x})}{x},$$

$$\frac{\bar{m}}{\mu} = \frac{e^{x}+e^{-x}}{e^{x}-e^{-x}} - \frac{1}{x} = \coth x - \frac{1}{x} = L(x)$$

Here $L(x)$ is called the "Langevin function," in honor of the inventor of this treatment.

---

[7] Harnwell, *op. cit.*, p. 64.

In most cases $x = \mu F/kT$ is a very small number[8] so that on expanding $L(x)$ in a power series, only the first term need be retained, leaving $L(x) = x/3$, or

$$\bar{m} = \frac{\mu^2}{3kT} F \tag{11.11}$$

The total polarizability of a dielectric is found by adding this contribution due to permanent dipoles to the distortion polarizability, and may be written $\alpha = \alpha_0 + (\mu^2/3kT)$. Instead of eq. (11.10), the total polarization is therefore

$$P_M = \frac{4\pi}{3} N \left(\alpha_0 + \frac{\mu^2}{3kT}\right) \tag{11.12}$$

This equation was first derived by P. Debye.

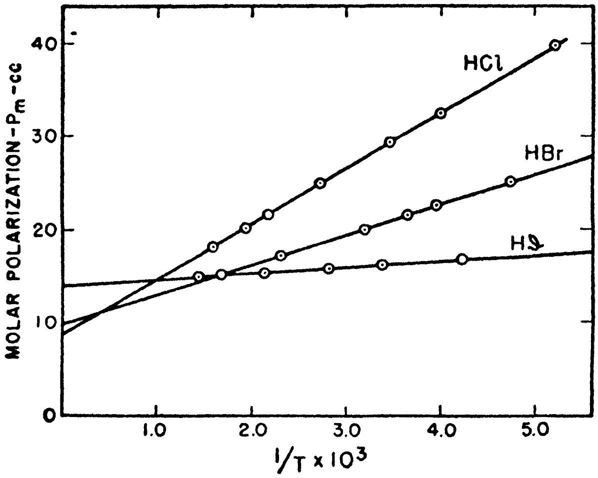


Fig. 11.12. Application of the Debye equation to the polarizations of the hydrogen halides.

When the Clausius-Mossotti treatment is valid,[9]

$$P_M = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{\rho}$$

For gases, ε is not much greater than 1, so that

$$P_M = \frac{\varepsilon - 1}{3} \frac{M}{\rho} = \frac{4\pi}{3} N \left(\alpha_0 + \frac{\mu^2}{3kT}\right) \tag{11.13}$$

---

[8] Values of μ range around 10^{-18} (esu) (cm). If a capacitor with 1 cm between plates is charged to 3000 volts, $\mu F = 10^{-18} \left(\frac{3 \times 10^3}{3 \times 10^2}\right) = 10^{-17}$ erg, compared with $kT = 10^{-14}$ erg at room temperature.

[9] This is the case only for gases or for dilute solutions of dipolar molecules in non-polar solvents. If there is a high concentration of dipolar molecules, as in aqueous solutions, there are localized polarization fields that cannot be treated by the Clausius-Mossotti method. In other words, the permanent dipoles tend to influence the induced polarization.

It is now possible to evaluate both α_0 and μ from the intercept and slope of P_M vs. $1/T$ plots, as shown in Fig. 11.12. The necessary experimental data are values of the dielectric constant over a range of temperatures. They are obtained by measuring the capacitance of a capacitor using the vapor or solution under investigation as the dielectric between the plates. A number of dipole-moment values are collected in Table 11.2.

TABLE 11.2

DIPOLE MOMENTS

Compound	Moment (debyes)	Compound	Moment (debyes)
HCl	1.03	CH_3Br	1.45
HBr	0.78	CH_3Cl	1.85
HI	0.38	CH_3I	1.35
H_2O	1.85	CH_3OH	1.68
H_2S	0.95	C_2H_5Cl	2.02
NH_3	1.49	$(C_2H_5)_2O$	1.14
SO_2	1.61	C_6H_5OH	1.70
CO_2	0.0	$C_6H_5NO_2$	4.08
CO	0.11	$C_6H_5.CH_2Cl$	1.85

17. Dipole moments and molecular structure. Two kinds of information about molecular structure are provided by dipole moments: (1) The extent to which a bond is permanently polarized, or its per cent ionic character; and (2) an insight into the geometry of the molecule, especially the angles between its bonds. Only a few examples of the applications will be mentioned.[10]

The H—Cl distance in HCl is 1.26 Å (found by methods described on page 334). If the structure were H^+Cl^-, the dipole moment would be

$$\mu = (1.26)(4.80) = 6.05d$$

The actual moment of 1.03 suggests therefore that the ionic character of the bond is equivalent to a separation of charges of about $\frac{1}{6}e$.

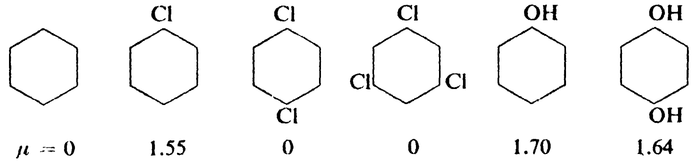
Carbon dioxide has no dipole moment, despite the difference in electronegativity between carbon and oxygen. It may be concluded that the molecule is linear, O—C—O; the moments due to the two C—O bonds, which are surely present owing to the difference in electronegativity of the atoms, exactly cancel each other on vector addition.

On the other hand, water has a moment of 1.85 d, and must have a triangular structure (see Fig. 11.6). It has been estimated that each O—H bond has a moment of 1.60 d and the bond angle is therefore about 105°, as shown by a vector diagram.

---

[10] R. J. W. LeFevre, *Dipole Moments* (London: Methuen, 1948) gives many interesting examples.

A final simple example is found in the substituted benzene derivatives:



The zero moments of *p*-dichloro- and sym-trichlorobenzene indicate that benzene is planar and that the C—Cl bond moments are directed in the plane of the ring, thereby adding to zero. The moment of *p*-di-OH benzene, on the other hand, shows that the O—H bonds are not in the plane of the ring, but directed at an angle to it, thus providing a net moment.

18. Polarization and refractivity. It may be recalled that one of the most interesting results of Clerk Maxwell's electromagnetic theory of light[11] was the relationship $\varepsilon = n_R^2$, where n_R is the index of refraction. Thus the refractive index is related through eq. (11.10) to the molar polarization.

The physical reason for this relationship can be understood without going into the details of the electromagnetic theory. The refractive index of a medium is the ratio of the speed of light in a vacuum to its speed in the medium, $n_R = c/c_m$. Light always travels more slowly through a material substance than it does through a vacuum. A light wave is a rapidly alternating electric and magnetic field. This field, as any other, acts to polarize the dielectric through which it passes, pulling the electrons back and forth in rapid alternation. The greater the polarizability of the molecules, the greater is the field induced in opposition to the applied field, and the greater therefore is the "resistance" to the transmission of the light wave. Thus high polarizability means low c_m and high refractive index. We have already seen that increasing the polarization increases the dielectric constant. The detailed theory leads to the Maxwell relation, $\varepsilon = n_R^2$.

This relation is experimentally confirmed only under certain conditions:

(1) The substance contains no permanent dipoles.

(2) The measurement is made with radiation of very long wavelength, in the infrared region.

(3) The refractive index is not measured in the neighborhood of a wavelength where the radiation is absorbed.

The first restriction arises from the fact that dielectric constants are measured at low frequencies (500 to 5000 kc), whereas refractive indices are measured with radiation of frequency about 10^{12} kc. A permanent dipole cannot line up quickly enough to follow an electric field alternating this rapidly. Permanent dipoles therefore contribute to the dielectric constant but not to the refractive index.

The second restriction is a result of the effect of high frequencies on the

---

[11] G. P. Harnwell, *op. cit.*, p. 579.

induced polarization. With high-frequency radiation (in the visible) only the electrons in molecules can adjust themselves to the rapidly alternating electric fields; the more sluggish nuclei stay practically in their equilibrium positions. With the lower-frequency infrared radiation the nuclei are also displaced.

It is customary, therefore, to distinguish, in the absence of permanent dipoles, an electronic polarization P_E and an atomic polarization P_A. The total polarization, $P_A + P_E$, is obtained from dielectric-constant measurements or infrared determinations of the refractive index. The latter are hard to make, but sometimes results with visible light can be successfully extrapolated. The electronic polarization P_E can be calculated from refractive index measurements with visible light. Usually P_A is only about 10 per cent of P_E, and may often be neglected.

When the Maxwell relation is satisfied, we obtain from eq. (11.10) the Lorenz-Lorentz equation:

$$\frac{n_R{}^2 - 1}{n_R{}^2 + 2} \cdot \frac{M}{\rho} = P_M \tag{11.14}$$

The quantity at the left of eq. (11.14) is often called the *molar refraction* R_M. When the Maxwell relation holds, $R_M = P_M$.

It will be noted that the molar refraction R_M has the dimensions of volume. It can indeed be shown from simple electrostatic theory[12] that a sphere of conducting material of radius r, in an electric field $\boldsymbol{F}$, has an induced electric moment of $\boldsymbol{m} = r^3\boldsymbol{F}$. According to this simple picture, the molar refraction should be equal to the true volume of the molecules contained in one mole. A comparison of some values of molecular volume obtained in this way from refractive index measurements with those obtained from van der Waal's b was shown in Table 7.5.

19. Dipole moments by combining dielectric constant and refractive index measurements. The Lorenz-Lorentz equation also provides an alternative method of separating the orientation and the distortion polarizations, and thereby determining the dipole moment. A solution of the dipolar compound in a nonpolar solvent—*e.g.*, nitrobenzene in benzene—is prepared at various concentrations. The dielectric constant is measured and the apparent molar polarization calculated from eq. (11.10). This quantity is made up of the distortion polarizations of both solute and solvent plus the orientation polarization of the polar solute. The molar polarizations due to distortion can be set equal to the molar refractions R_M, calculated from the refractive indices of the pure liquids. When these R_M are subtracted from the total apparent P_M, the remainder is the apparent molar orientation polarization for the solute alone. This polarization is plotted against the concentration in the solution and extrapolated to zero concentration.[13] A value is obtained in

---

[12] Slater and Frank, *op. cit.*, p. 275.

[13] E. A. Guggenheim, *Trans. Faraday Soc.*, *47*, 573 (1951), gives an improved method for extrapolation.

this way from which the effect of dipole interaction has been eliminated. From eq. (11.13), therefore, it is equal to $(4\pi/3)N(\mu^2/3kT)$ and the dipole moment of the polar solute can be calculated.

20. Magnetism and molecular structure. The theory for the magnetic properties of molecules resembles in many ways that for the electric polarization. Thus a molecule can have a permanent magnetic moment and also a moment induced by a magnetic field.

Corresponding to eq. (11.6), we have

$$\boldsymbol{B} = \boldsymbol{H} + 4\pi\boldsymbol{I} \tag{11.15}$$

where $\boldsymbol{B}$ is the magnetic induction, $\boldsymbol{H}$ is the field strength, and $\boldsymbol{I}$ is the intensity of magnetization or magnetic moment per unit volume. These quantities are the magnetic counterparts of the electrical $\boldsymbol{D}$, $\boldsymbol{E}$, and $\boldsymbol{P}$. In a vacuum $\boldsymbol{B} = \boldsymbol{H}$, but otherwise $\boldsymbol{B} = \epsilon'\boldsymbol{H}$, where ϵ', the *permeability*, is the magnetic counterpart of the dielectric constant ϵ. Usually, however, magnetic properties are discussed in terms of

$$\frac{\boldsymbol{I}}{\boldsymbol{H}} = \chi \tag{11.16}$$

where χ is called the *magnetic susceptibility* per unit volume of the medium. (Electric susceptibility would be $\boldsymbol{P}/\boldsymbol{E}$.)

The susceptibility per mole is $\chi_M = (M/\rho)\chi$. The magnetic analogue of eq. (11.13) is

$$\chi_M = N\left(\alpha_0 + \frac{\mu_M{}^2}{3kT}\right) \tag{11.17}$$

where α_0 is the induced moment and μ_M is the permanent magnetic dipole moment. Just as before, the two effects can be experimentally separated by temperature-dependence measurements.

An important difference from the electrical case now appears, in that χ, or χ_M, can be either positive or negative. If χ_M is negative, the medium is called *diamagnetic*; if χ_M is positive, it is called *paramagnetic*. For iron, nickel, and certain alloys, χ_M is positive and much larger than usual, by a factor of about a million. Such substances are called *ferromagnetic*. From eq. (11.15) it can be seen that the magnetic field in diamagnetic substances is weaker than in a vacuum, whereas in paramagnetic substances it is stronger.

An experimental measurement of susceptibility can be made with the *magnetic balance*. The specimen is suspended so that it is partly inside and partly outside a strong magnetic field. When the magnet is turned on, a paramagnetic substance tends to be drawn into the field region, a diamagnetic tends to be pushed out of the field. From the weight required to restore the original balance point, the susceptibility is calculated.

The phenomenon of diamagnetism is the counterpart of the distortion polarization in the electrical case. The effect is exhibited by all substances and is independent of the temperature. A simple interpretation is obtained if one imagines the electrons to be revolving around the nucleus. If a magnetic field is applied, the velocity of the moving electrons is changed, producing a magnetic field that, in accordance with Lenz's Law, is opposed in direction to the applied field. The diamagnetic susceptibility is therefore always negative.

When paramagnetism occurs, the diamagnetic effect is usually quite overshadowed, amounting to only about 10 per cent of the total susceptibility. Paramagnetism is associated with the orbital angular momentum and the spin of uncoupled electrons, *i.e.*, those that are not paired with others having equal but opposite angular momentum and spin.

An electron revolving in an orbit about the nucleus is like an electric current in a loop of wire, or a turn in a solenoid. The resultant magnetic moment is a vector normal to the plane of the orbit, and proportional to the angular momentum p of the revolving electron. In the MKS system of units (charge in coulombs) the magnetic moment is $(e/2m)p$ (weber meters).[14] Since p can have only quantized values, $m_l h/2\pi$, where m_l is an integer, the allowed values of the magnetic moment are $m_l(eh/4\pi m)$. It is evident, therefore, that there is a *natural unit of magnetic moment*, $eh/4\pi m$. It is called the *Bohr magneton*.

The ratio of magnetic moment to angular momentum is called the *gyromagnetic ratio*, R_g. For the orbital motion of an electron, $R_g = e/2m$. The spinning electron also acts as a little magnet. For electron spin, however, $R_g = e/m$. Since the intrinsic angular momentum of an electron can have only quantized values $\pm\frac{1}{2}(h/2\pi)$, the magnetic moment of an unpaired electron is $eh/4\pi m$, or one Bohr magneton.

In the case of molecules, only the contributions due to spin are very important. This is true because there is a strong internal field within a molecule. In a diatomic molecule, for example, this field is directed along the internuclear axis. This internal field holds the orbital angular momenta of the electrons in a fixed orientation. They cannot line up with an external magnetic field, and thus the contribution they would normally make to the susceptibility is ineffective. It is said to be *quenched*. There remains only the effect due to the electron spin, which is not affected by the internal field. Thus a measurement of the permanent magnetic moment of a molecule tells us how many unpaired spins there are in its structure.

There have been many applications of this useful method,[15] of which only one can be mentioned here. Let us consider two complexes of cobalt,

---

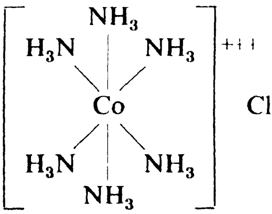
[14] A derivation is given by C. A. Coulson, *Electricity* (New York: Interscience, 1951), p. 91. In electrostatic units the magnetic moment is $(e/2mc)p$, where c is the speed of light *in vacuo*.

[15] P. W. Selwood, *Magnetochemistry* (New York: Interscience, 1943).

$\{Co(NH_3)_6\}\ Cl_3$ and $K_3\{CoF_6\}$. Two possible structures may be suggested for such complexes, one covalent and one ionic, as follows:

	3*d*					4*s*	4*p*			Unpaired Spins
Covalent .	⇅	⇅	⇅	⇅	⇅	⇅	⇅	⇅	⇅	0
Ionic . .	⇅	↑	↑	↑	↑	..	..	..	..	4

The hexammino complex is obviously covalent, but the structure of the hexafluoro complex is open to question. It is found that the hexammino complex has zero magnetic moment, whereas the $\{CoF_6\}^{\equiv}$ complex has a moment of 5.3 magnetons. The structures can thus be assigned as follows:



$Cl_3^{\equiv}$ and $[Co^{+++}(F^-)_6]K_3^{+++}$

21. Nuclear paramagnetism. In addition to the magnetism due to the electrons in an atom there is also magnetism due to the nuclei. We may consider a nucleus to be composed of protons and neutrons, and both these *nucleons* have intrinsic angular momenta or spins, and hence act as elementary magnets. In most nuclei these spins add to give a nonzero resultant nuclear spin. It was first predicted that the magnetic moment of the proton would be 1 *nuclear magneton*, $eh/4\pi M$, where M is the proton mass. Actually, however, the proton has a magnetic moment of 2.79245 nuclear magnetons, and the neutron moment is -1.9135. The minus sign indicates that the moment behaves like that of a negatively charged particle. Since M is almost 2000 times the electronic mass m, nuclear magnetic moments are less than electronic magnetic moments by a factor of about 1000.

The existence of nuclear magnetism was first revealed in the *hyperfine structure* of spectral lines. As an example consider the hydrogen atom, a proton with one orbital electron. The nucleus can have a spin $I = \pm\frac{1}{2}$, and the electron can have a spin $S = \pm\frac{1}{2}$. The nuclear and the electron spins can be either parallel or antiparallel to each other, and these two different alignments will differ slightly in energy, the parallel state being higher. Thus the ground state of the hydrogen atom will in fact be a closely spaced doublet, and this splitting is observed in the atomic spectra of hydrogen, if a spectrograph of high resolving power is employed. The spacing between the two levels, $\Delta E = h\nu$, corresponds to a frequency ν of 1420 megacycles. After the prediction of the astrophysicist van der Hulst, an intense emission of radiation at this frequency was observed from clouds of interstellar dust. The study of this phenomenon is an important part of the rapidly developing subject of radioastronomy, which is providing much information about hitherto uncharted regions of our universe.

If a nucleus with a certain magnetic moment is placed in a magnetic field, we can observe the phenomenon of *space quantization* (see page 267). The component of the moment in the direction of the field is quantized, and for each allowed direction there will be a slightly different energy level. For readily accessible magnetic fields, the frequencies $\nu = \Delta E/h$ for transitions between two such levels also lie in the microwave range of radio frequencies.

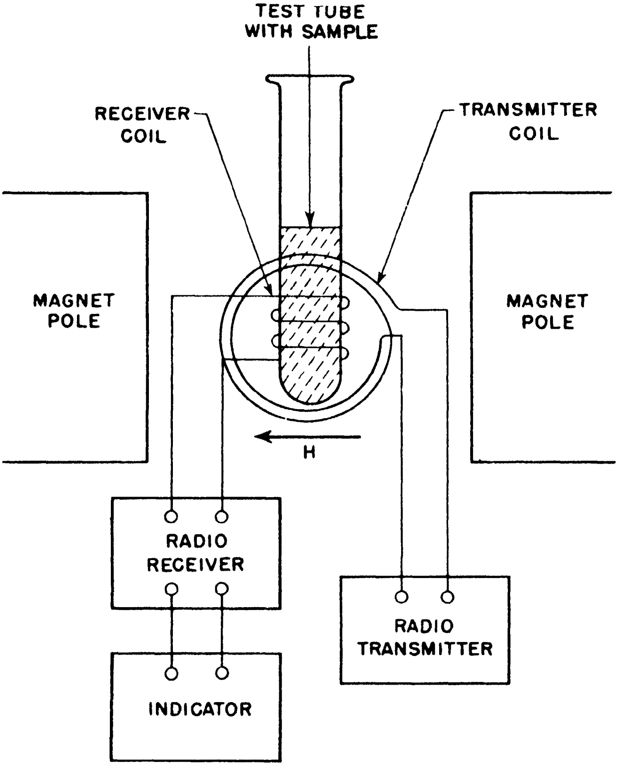


Fig. 11.13. Simplified apparatus for basic nuclear magnetic resonance experiment. (Drawing courtesy R. H. Varian.)

For example, at a field of 7050 gauss, the frequency for protons is 30 megacycles. The earlier attempts to detect these transitions were unsuccessful, but in 1946 E. M. Purcell and Felix Bloch independently developed the method of *nuclear magnetic resonance.*

The principle of this method is shown in Fig. 11.13. The field *H* of the magnet is variable from 0 to 10,000 gauss. This field produces an equidistant splitting of the nuclear energy levels which arise as a result of space quantization. The low-power radio-frequency transmitter operates at, for example, 30 megacycles. It causes a small oscillating magnetic field to be applied to the sample. This field induces transitions between the energy levels, by a resonance effect, when the frequency of the oscillating field equals that of the transitions. When such transitions occur in the sample, the resultant oscillation in magnetic field induces a voltage oscillation in the receiver coil, which can be amplified and detected.

Figure 11.14 shows an oscillographic trace of these voltage fluctuations over a very small range of magnetic fields (38 milligauss) around 7050 gauss, with ethyl alcohol as the sample. Note that each different kind of proton in the molecule $CH_3{\cdot}CH_2{\cdot}OH$ appears at a distinct value of H. The reason for this splitting is that the different protons in the molecule have a slightly different magnetic environment, and hence a slightly different resonant frequency. The areas under the peaks are in the ratio 3 : 2 : 1, corresponding to the relative number of protons in the different environments. Each peak also has a fine structure. The structural information that can be provided by this method is thus almost unbelievably detailed, and a new and deep insight into the nature of the chemical bond is provided. Applications have been made to problems ranging from isotope analysis to structure determinations.

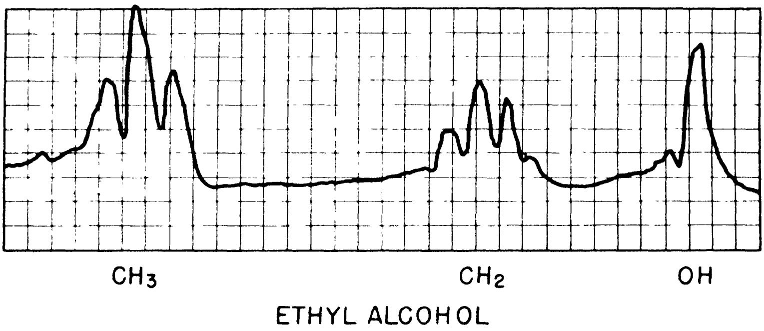


Fig. 11.14. Proton resonance under high resolution at 30 mc and 7050 gauss. Total sweep width 38 milligauss. Field decreases linearly from left to right.

22. Electron diffraction of gases. One of the most generally useful methods for measuring bond distances and bond angles has been the study of the diffraction of electrons by gases and vapors. The wavelength of 40,000 volt electrons is 0.06 Å, about one-tenth the order of magnitude of interatomic distances in molecules, so that diffraction effects are to be expected. The fact that the electron beam and the electrons in the scattering atoms both are negatively charged greatly enhances the diffraction.

On page 256 diffraction by a set of slits was discussed in terms of the Huygens construction. In the same way, if a collection of atoms at fixed distances apart (*i.e.*, a molecule) is placed in a beam of radiation, each atom can be regarded as a new source of spherical wavelets. From the interference pattern produced by these wavelets, the spatial arrangement of the scattering centers can be determined. The experimental apparatus for electron diffraction is illustrated in Fig. 11.15. The type of pattern found is a series of rings similar to those in Fig. 10.10 but somewhat more diffuse.

The electron beam traverses a collection of many gas molecules, oriented at random to its direction. It is most interesting that maxima and minima are observed in the diffraction pattern despite the random orientation of the molecules. This is because the scattering centers occur as groups of atoms with the same definite fixed arrangement within every molecule. A collection of individual atoms, *e.g.*, argon gas, would give no diffraction rings. Diffraction by gases was treated theoretically (for X rays) by Debye in 1915, but electron-diffraction experiments were not carried out till the work of Wierl in 1930.

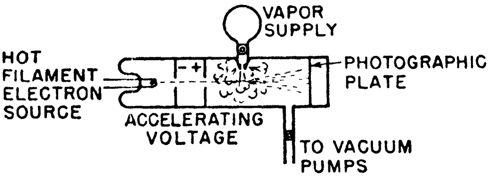


Fig. 11.15. Schematic diagram of electron diffraction apparatus.

We can show the essential features of the diffraction theory by considering the simplest case, that of a diatomic molecule.[16] The molecule is represented in Fig. 11.16 with one atom A, at the origin, and the other B, a distance r away. The electron beam enters along $Y'A$ and the diffracted beam, scattered through an angle θ, is picked up at P on a photographic film, a distance R from the origin. The angles α and ϕ give the orientation of AB to the primary beam.

The interference between the waves scattered from A and B depends on the difference between the lengths of the paths which they traverse. This path difference is $\delta = AP - CB - BP$. The difference in phase between the two scattered waves is $(2\pi/\lambda)\delta$.

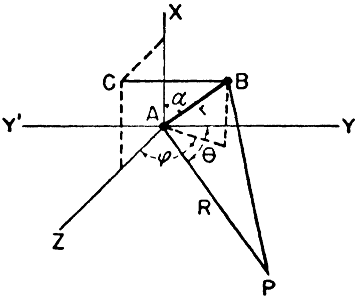


Fig. 11.16. Scattering of electrons by a diatomic molecule.

In order to add waves that differ in phase and amplitude, it is convenient to represent them in the complex plane and to add vectorially.[17] In our case we shall assume for simplicity that the atoms A and B are identical. Then the resultant amplitude at P is $A = A_0 + A_0 e^{-i2\pi\delta/\lambda}$. A_0, called the *atomic scattering factor*, depends on the number of electrons in the atom. The intensity of

---

[16] The treatment follows that given by M. H. Pirenne, *The Diffraction of X rays and Electrons by Free Molecules* (London: Cambridge, 1946), p. 7.

[17] See Courant and Robbins, *What Is Mathematics* ? (New York: Oxford, 1941), p. 94.

radiation is proportional to the square of the amplitude, or in this case to $A\bar{A}$, the amplitude times its complex conjugate. Thus

$$
\begin{aligned}
I \sim A\bar{A} &= A_0^2\,(1 + e^{-2\pi i\delta/\lambda})(1 + e^{2\pi i\delta/\lambda}) \\
&= A_0^2\,(2 + e^{-2\pi i\delta/\lambda} + e^{2\pi i\delta/\lambda}) \\
&= 2A_0^2\left(1 + \cos\frac{2\pi\delta}{\lambda}\right) = 4A_0^2\cos^2\frac{\pi\delta}{\lambda}
\end{aligned}
$$

It is now necessary to express δ in terms of r, R, θ, α, and ϕ. This can be done by referring to Fig. 11.16. We see first of all that $CB = r\sin\alpha\sin\phi$. Then $BP = \sqrt{R^2 + r^2 - 2rR\sin\alpha\sin(\theta + \phi)}$. Since r is a few Ångstroms while R is several cm, $r \ll R$, so that r^2 is negligible and the square root can be expanded[18] to yield $BP = R - r\sin\alpha\sin(\theta + \phi)$. Then we have $\delta = AP - CB - BP = r\sin\alpha\,[\sin(\theta + \phi) - \sin\phi] = 2r\sin\theta/2\sin\alpha\cos[\phi + (\theta/2)]$.

In order to obtain the required formula for the intensity of scattering of a randomly oriented group of molecules, it is necessary to average the expression for the intensity at one particular orientation (α, ϕ) over all possible orientations. The differential element of solid angle is $\sin\alpha\,d\alpha\,d\phi$, and the total solid angle of the sphere around AB is 4π. Hence the required average intensity becomes

$$
I_{av} \sim \frac{4A_0^2}{4\pi}\int_0^{\pi}\int_0^{2\pi}\cos^2\left[2\pi\frac{r}{\lambda}\sin\frac{\theta}{2}\sin\alpha\cos\left(\phi + \frac{2}{\theta}\right)\right]\sin\alpha\,d\alpha\,d\phi
$$

On integration,[19]

$$
I_{av} = 2\,A_0^2\left(1 + \frac{\sin xr}{xr}\right) \qquad (11.18)
$$

where

$$
x = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}
$$

---

[18] From the binomial theorem, $(1 + x)^{1/2} = 1 + \frac{1}{2}x - \frac{1}{8}x^2 + \ldots.$

[19] Let

$$
I_{av} = \frac{A_0^2}{\pi}\int_0^{2\pi}\int_0^{\pi}\cos^2(A\cos\beta)\,d\beta\sin\alpha\,d\alpha
$$

where

$$
A = \frac{2\pi r}{\lambda}\sin\frac{\theta}{2}\sin\alpha \qquad \text{and} \qquad \beta = \phi + \theta/2
$$

Then since $\cos^2\beta = (1 + \cos 2\beta)/2$, we obtain

$$
\begin{aligned}
I_{av} &= \frac{A_0^2}{\pi}\int_0^{2\pi}\int_0^{\pi}\left(\frac{d\beta}{2} + \cos(2A\cos\beta)d\beta\right)\sin\alpha\,d\alpha \\
&= A_0^2\int_0^{2\pi}(\tfrac{1}{2} + J_0(2A))\sin\alpha\,d\alpha
\end{aligned}
$$

where J_0 is the Bessel function of order zero (see Woods, *Advanced Calculus*, p. 282). This can now be integrated by introducing the series expansion of

$$
J_0(x) = \sum(-1)^k\frac{x^{2k}}{2^{2k}(k!)^2}
$$

In Fig. 11.17, I/A_0^2 is plotted against x, and the maxima and minima in the intensity are clearly evident.

In a more complex molecule with atoms j, k (having scattering factors A_j, A_k) a distance r_{jk} apart, the resultant intensity would be

$$I(\theta) = \sum_j \sum_k A_j A_k \frac{\sin xr_{jk}}{xr_{jk}} \tag{11.19}$$

This is called the "Wierl equation." The summation must be carried out over all pairs of atoms in the molecule.

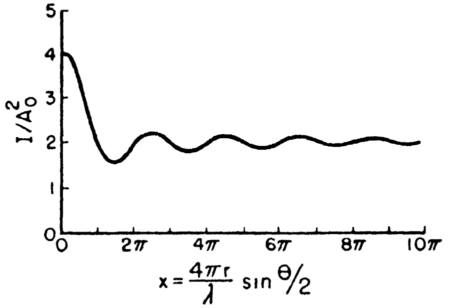


Fig. 11.17. Scattering curve for diatomic molecule—plot of eq. (11.18).

In the case of the homonuclear diatomic molecule already considered, eq. (11.19) becomes

$$I(\theta) = A_1 A_1 \frac{\sin xr_{11}}{xr_{11}} + A_1 A_2 \frac{\sin xr_{12}}{xr_{12}} + A_2 A_2 \frac{\sin xr_{22}}{xr_{22}} + A_1 A_2 \frac{\sin xr_{21}}{xr_{21}}$$

Since $r_{11} = r_{22} = 0$, and $(\sin x)/x \rightarrow 1$ as $x \rightarrow 0$, and $r_{12} = r_{21} = r$, this reduces to eq. (11.18).

23. Application of Wierl equation to experimental data. The scattering angles of maximum intensity are calculated from the positions of the dark rings on the picture and the geometry of the apparatus and camera. This gives an *experimental scattering curve*, whose general form resembles that of the theoretical curve shown in Fig. 11.17, although the positions of the maxima depend, of course, on the molecule being studied. Then a particular molecular structure is assumed and the *theoretical scattering curve* corresponding to it is calculated from eq. (11.19). For example, in the benzene structure there are three different carbon-carbon distances, six between *ortho* positions, six between *meta* positions, and three between *para* positions. Therefore the r_{jk} terms consist of $6r_{cc}$, $6(\sqrt{3}\, r_{cc})$, and $3(2\, r_{cc})$. The positions

---

where in our case $x = 2B \sin \alpha$, with $B = (2\pi r/\lambda) \sin \theta/2$. The required integral is given in Pierce's tables (No. 483) as

$$\int_0^{2\pi} \sin^n x\, dx = 2\sqrt{\pi} \frac{\Gamma[(n+1)/2]}{\Gamma[(n/2)+1]}$$

The series that results is that for $(\sin x)/x$. (Pierce No. 772.)

of hydrogen atoms are generally ignored because of their low scattering power.

It is often sufficiently accurate to substitute the atomic number Z for the atomic scattering factor A. For benzene, the Wierl equation would then become

$$\frac{I(\theta)}{Z^2} = \frac{6 \sin xr}{xr} + \frac{3 \sin 2xr}{2xr} + \frac{6 \sin \sqrt{3}\, xr}{\sqrt{3}\, xr}$$

This function is plotted for various choices of the parameter r, the interatomic distance, until the best agreement with the experimental curve is obtained. In other cases bond angles also enter as parameters to be adjusted to obtain the best fit between the observed and calculated curves. It may be noted that only the positions of the maxima and not their heights are used.

TABLE 11.3

THE ELECTRON DIFFRACTION OF GAS MOLECULES

Diatomic Molecules

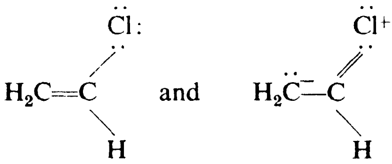
Molecule	Bond Distance (Å)	Molecule	Bond Distance (Å)
NaCl	2.51 ± 0.03	Cl_2	2.01 ± 0.03
NaBr	2.64 ± 0.01	Br_2	2.28 ± 0.02
NaI	2.90 ± 0.02	I_2	2.65 ± 0.10

Polyatomic Molecules

Molecule	Configuration	Bond	Bond Distance
CdI_2	Linear	Cd—I	2.60 ± 0.02
$HgCl_2$	Linear	Hg—Cl	2.34 ± 0.01
BCl_3	Planar	B—Cl	1.73 ± 0.02
SiF_4	Tetrahedral	Si—F	1.54 ± 0.02
$SiCl_4$	Tetrahedral	Si—Cl	2.00 ± 0.02
P_4	Tetrahedral	P—P	2.21 ± 0.02
Cl_2O	Bent, 115 ± 4°	Cl—O	1.68 ± 0.03
SO_2	Bent, 124 ± 15°	S—O	1.45 ± 0.02
CH_2O	Planar	C—O	1.15 ± 0.05
CO_2	Linear	C—O	1.13 ± 0.04
C_6H_6	Planar	C—C	1.390 ± 0.005

Some results of electron diffraction studies are collected in Table 11.3. As molecules become more complicated, it becomes increasingly difficult to determine an exact structure, since usually only a dozen or so maxima are visible, which obviously will not permit the exact calculation of more than five or six parameters. Each distinct interatomic distance or bond angle constitutes a parameter. It is possible, however, from measurements on simple compounds, to obtain quite reliable values of bond distances and angles, which may be used to estimate the structures of more complex molecules.

Some interesting effects of resonance on bond distances have been observed. For example, the C—Cl distance in CH_3Cl is 1.76 Å but in $CH_2{=}CHCl$ it is only 1.69 Å. The shortening of the bond is ascribed to resonance between the following structures:



The C—Cl bond in ethylene chloride is said to have about 18 per cent *double bond character.*

24. Molecular spectra. Perhaps the most widely useful of all methods for investigating molecular architecture is the study of molecular spectra. It affords information about not only the dimensions of molecules but also the possible molecular energy levels. Thus, other methods pertain to the ground state of the molecule alone, but the analysis of spectra also elucidates the nature of excited states.

It has been mentioned that the spectra of atoms consist of sharp lines, and those of molecules appear to be made up of bands in which a densely packed line structure is sometimes revealed under high resolving power.

Spectra arise from the emission or absorption of definite quanta of radiation when transitions occur between certain energy levels. In an atom the energy levels represent different allowed states for the orbital electrons. A molecule too can absorb or emit energy in transitions between different electronic energy levels. Such levels would be associated, for example, with the different molecular orbitals discussed on pages 303-311. In addition there are two other possible ways in which a molecule can change its energy level, which do not occur in atoms. These are by changes in the vibrations of the atoms within the molecule and by changes in the rotational energy of the molecule. These energies, like the electronic, are quantized, so that only certain distinct levels of vibrational and rotational energy are permissible.

In the theory of molecular spectra it is customary, as a good first approximation, to consider that the energy of a molecule can be expressed simply as the sum of electronic, vibrational, and rotational contributions. Thus,

$$E = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}} \tag{11.20}$$

This complete separation of the energy into three distinct categories is not strictly correct. For example, the atoms in a rapidly rotating molecule are separated by centrifugal forces, which thus affect the character of the vibrations. Nevertheless, the approximation of eq. (11.20) suffices to explain many of the observed characteristics of molecular spectra.

It will be seen in the following discussions that the separations between electronic energy levels are usually much larger than those between vibrational energy levels, which in turn are much larger than those between rotational levels. The type of energy-level diagram that results is shown in Fig. 11.18. Associated with each electronic level there is a series of vibrational levels, each of which is in turn associated with a series of rotational levels. The close packing of the rotational levels is responsible for the banded structure of molecular spectra.

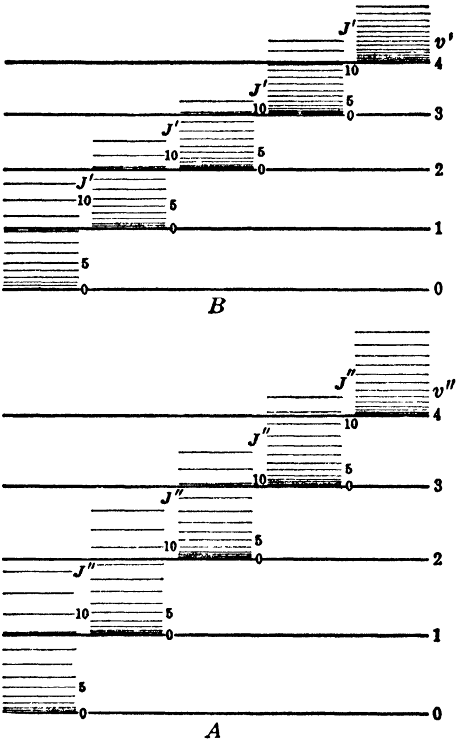


Fig. 11.18. Energy-level diagram for a molecule. Two electronic levels A and B, with their vibrational levels (v) and rotational levels (J)

Transitions between different electronic levels give rise to spectra in the visible or ultraviolet region; these are called *electronic spectra.* Transitions between vibrational levels within the same electronic state are responsible for spectra in the near infrared ($< 20\mu$), called *vibration-rotation spectra.* Finally, spectra are observed in the far infrared ($> 20\mu$) arising from transitions between rotational levels belonging to the same vibrational level; these are called *pure rotation spectra.*

25. Rotational levels—far-infrared spectra. The model of the rigid rotator, described on page 189, may be used for the interpretation of pure rotation spectra. The calculation of the allowed energy levels for such a system is a straightforward problem in quantum mechanics. The Schrödinger equation in this case is very similar to that for the motion of the electron about the nucleus in the hydrogen atom, except that for a diatomic molecule it is a question of the rotation of two nuclei about their center of mass. We recall that the rotation of a dumbbell model is equivalent to the rotation of the reduced mass μ at a distance r from the rotation axis. For a rigid rotator the potential energy U is zero, so that the wave equation becomes

$$\nabla^2\psi + \frac{8\pi^2\mu}{h^2}E\psi = 0 \tag{11.21}$$

Without too great difficulty this equation can be solved exactly.[20] It is then found that the eigenfunction ψ is single valued, continuous, and finite, as is required for physical meaning, only for certain values of the energy E, the allowed eigenvalues. These are

$$E_{\text{rot}} = \frac{h^2J(J+1)}{8\pi^2\mu r^2} = \frac{h^2J(J+1)}{8\pi^2 I} \tag{11.22}$$

Here I is the moment of inertia of the molecule and the rotational quantum number J can have only integral values, 0, 1, 2, 3, etc.

The value of J gives the allowed values of the rotational angular momentum p, in units of $h/2\pi$: $p = (h/2\pi)\sqrt{J(J+1)} \approx (h/2\pi)\cdot J$. This is exactly similar to the way in which the quantum number l in the hydrogen-atom system, and the corresponding λ in molecules, determine the orbital angular momenta of electrons.

The selection rule for rotational levels is found to be $\Delta J = 0$ or ± 1. Thus an expression for ΔE for the rigid-rotator model is readily derived from eq. (11.22). Writing $B = h/8\pi^2 I$, we obtain for two levels with quantum numbers J and J': $\Delta E = h\nu = hB[J(J+1) - J'(J'+1)]$. Since $\nu = (\Delta E/h)$, and $J - J' = 1$,

$$\nu = 2BJ \tag{11.23}$$

The spacing between energy levels increases linearly with J, as shown in Fig. 11.18. The absorption spectra due to pure rotation arise from transitions from each of these levels to the next higher one. By means of a spectrograph of good resolving power, the absorption band will be seen to consist of a series of lines spaced an equal distance apart. From eq. (11.23) this spacing is $\Delta\nu = \nu - \nu' = 2B$.

Pure rotation spectra occur only when the molecule possesses a permanent

---

[20] K. S. Pitzer, *Quantum Chemistry* (New York: Prentice-Hall, 1953), p. 53. An approximate formula is obtained directly from the Bohr hypothesis that the angular momentum is quantized in units of $h/2\pi$. Thus $I\omega = Jh/2\pi$, and the kinetic energy $\frac{1}{2}I\omega^2 = J^2h^2/8\pi^2 I$.

dipole moment. This behavior has been elucidated by quantum mechanical arguments, but it can be understood also in terms of the classical picture that radiation is produced when a rotating dipole sends out into space a train of electromagnetic waves. If a molecule has no dipole, its rotation cannot produce an alternating electric field.

We have discussed only the problem of the diatomic rotator. The rotational energy levels of polyatomic molecules are considerably more complex, but do not differ much from the diatomic case in the principles involved.

26. Internuclear distances from rotation spectra. The analysis of rotation spectra can give accurate values of the moments of inertia, and hence internuclear distances and shapes of molecules. Let us consider the example of HCl.

Absorption by HCl has been observed in the far infrared, around $\lambda = 50$ microns or $\nu' = 200\ \text{cm}^{-1}$. The spacing between successive lines is $\Delta\nu' = 20.1$ to $20.7\ \text{cm}^{-1}$. Analysis shows that the transition from $J = 0$ to $J = 1$ corresponds to a wave number of $\nu' = 1/\lambda = 20.6\ \text{cm}^{-1}$. The frequency is therefore

$$\nu = \frac{c}{\lambda} = (3.00 \times 10^{10})(20.6) = 6.20 \times 10^{11}\ \text{sec}^{-1}$$

The first rotational level, $J = 1$, lies at an energy of

$$h\nu = (6.20 \times 10^{11})(6.62 \times 10^{-27}) = 4.10 \times 10^{-15}\ \text{erg}$$

From eq. (11.22),

$$E = \frac{2h^2}{8\pi^2 I} = 4.10 \times 10^{-15}$$

so that

$$I = 2.72 \times 10^{-40}\ \text{g cm}^2$$

Since $I = \mu r^2$, where μ is the reduced mass, we can now determine the internuclear distance r. For HCl,

$$\mu = \left(\frac{(35.0)1}{35.0 + 1} \times \frac{1}{6.02 \times 10^{23}}\right) = 1.61 \times 10^{-24}\ \text{g}$$

Hence

$$r = \left(\frac{2.72 \times 10^{-40}}{1.61 \times 10^{-24}}\right)^{1/2} = 1.30 \times 10^{-8}\ \text{cm} = 1.30\ \text{Å}$$

27. Vibrational energy levels. Investigations in the far infrared are difficult to make, and a much greater amount of useful information has been obtained from the near-infrared spectra, arising from transitions between different vibrational energy levels.

The simplest model for a vibrating molecule is that of the harmonic oscillator, whose potential energy is given by $U = \frac{1}{2}\kappa x^2$, the equation of a parabola. The Schrödinger equation is therefore:

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2\mu}{h^2}(E - \tfrac{1}{2}\kappa x^2)\psi = 0 \qquad (11.24)$$

The solution to this equation can be obtained exactly by quite simple methods.[21] The result has already been mentioned as a consequence of uncertainty-principle arguments (page 275), being

$$E_{\text{vib}} = (v + \tfrac{1}{2})h\nu \tag{11.25}$$

The energy levels are equally spaced, and the existence of a zero point energy, $E_0 = \frac{1}{2}h\nu_0$ when $v = 0$, will be noted. The selection rule for transitions between vibrational energy levels is found to be $\Delta v = \pm 1$.

Actually, the harmonic oscillator is not a very good model for molecular vibrations except at low energy levels, near the bottom of the potential-energy curve. It fails, for example, to represent the fact that a molecule may dissociate if the amplitude of vibration becomes sufficiently large. The sort of potential-energy curve that should be used is one like that pictured for the hydrogen molecule in Fig. 11.2 on page 298.

Two *heats of dissociation* may be defined by reference to this curve. The *spectroscopic heat of dissociation*, D_e, is the height from the asymptote to the minimum. The *chemical heat of dissociation*, D_0, is measured from the ground state of the molecule, at $v = 0$, to the onset of dissociation. Therefore,

$$D_e = D_0 + \tfrac{1}{2}h\nu_0 \tag{11.26}$$

In harmonic vibration the restoring force is directly proportional to the displacement r. The potential-energy curve is parabolic and dissociation can never take place. Actual potential-energy curves, like that in Fig. 11.2, correspond to *anharmonic vibrations*. The restoring force is no longer directly proportional to the displacement. The force is given by $-\partial U/\partial r$, the slope of the potential curve, and this decreases to zero at large values of r, so that dissociation can occur as the result of vibrations of large amplitude.

The energy levels corresponding to an anharmonic potential-energy curve can be expressed as a power series in $(v + \frac{1}{2})$,

$$E_{\text{vib}} = h\nu[(v + \tfrac{1}{2}) - x_e(v + \tfrac{1}{2})^2 + y_e(v + \tfrac{1}{2})^3 - \ldots] \tag{11.27}$$

Considering only the first anharmonic term, with *anharmonicity constant*, x_e:

$$E_{\text{vib}} = h\nu(v + \tfrac{1}{2}) - h\nu x_e(v + \tfrac{1}{2})^2 \tag{11.28}$$

The energy levels are not evenly spaced, but lie more closely together as the quantum number increases. This fact is illustrated in the levels superimposed on the curve in Fig. 11.2. Since a set of closely packed rotational levels is associated with each of these vibrational levels, it is sometimes possible to determine with great precision the energy level just before the onset of the continuum, and so to calculate the heat of dissociation from the vibration-rotation spectra.

As an example of near-infrared spectra, let us consider some observations with hydrogen chloride. There is an intense absorption band at 2886 cm^{-1}.

---

[21] Pauling and Wilson, *loc. cit.*, p. 68. A student might well study this as a typical quantum mechanical problem, since it is about the simplest one available.

This arises from transitions from the state with $v = 0$ to that with $v = 1$, or $\Delta v = +1$. In addition, there are very much weaker bands at higher frequencies, corresponding to $\Delta v = +2, +3, \ldots$ etc., which are not completely ruled out for an anharmonic oscillator.

For the $v = 1$ band in HCl, we have, therefore,

$$\nu = (2886) \times 3 \times 10^{10} = 8.65 \times 10^{13}\ \text{sec}^{-1}$$

as the fundamental vibration frequency. This is about one hundred times the rotation frequency found from the far-infrared spectra.

The force constant of a harmonic oscillator with this frequency, from eq. (10.2), would be $\kappa = 4\pi^2\nu^2\mu = 4.81 \times 10^5$ dynes per cm. If the chemical bond is thought of as a spring, the force constant is a measure of its tightness.

Potential-energy curves of the type shown in Fig. 11.2 are so generally useful in chemical discussions that it is most convenient to have an analytical expression for them. An empirical function that fits very well is that suggested by P. M. Morse:

$$U = D_e(1 - e^{-\beta(r-r_0)})^2 \tag{11.29}$$

Here β is a constant that can be evaluated in terms of molecular parameters as $\beta = \nu_0\sqrt{2\pi^2\mu/D_e}$.

28. Microwave spectroscopy. Microwaves are those with a wavelength in or around the range from 1 mm to 1 cm. Their applications were rapidly advanced as a result of wartime radar research. In recent years, radar techniques have been applied to spectroscopy, greatly extending the accuracy with which we can measure small energy jumps within molecules.

In ordinary absorption spectroscopy, the source of radiation is usually a hot filament or high-pressure gaseous-discharge tube, giving in either case a wide distribution of wavelengths. This radiation is passed through the absorber and the intensity of the transmitted portion at different wavelengths is measured after analysis by means of a grating or prism. In microwave spectroscopy, the source is monochromatic, at a well defined single wavelength which can, however, be rapidly varied (frequency modulation). It is provided by an electronically controlled oscillator employing the recently developed klystron or magnetron tubes. After passage through the cell containing the substance under investigation, the microwave beam is picked up by a receiver, often of the crystal type, and after suitable amplification is fed to a cathode-ray oscillograph acting as detector or recorder. The resolving power of this arrangement is 100,000 times that of the best infrared grating spectrometer, so that wavelength measurements can be made to seven significant figures.

One of the most thoroughly investigated of microwave spectra has been that of the "umbrella" inversion of the ammonia molecule, the vibration in which the nitrogen atom passes back and forth through the plane of the three hydrogen atoms. The rotational fine structure of this transition has been beautifully resolved, over 40 lines having been catalogued for $^{14}NH_3$

and about 20 for $^{15}NH_3$. Such measurements provide an almost embarrassing wealth of experimental data, permitting the construction of extremely detailed theories for the molecular energy levels.

Pure rotational transitions in heavier molecules are inaccessible to ordinary infrared spectroscopy because, in accord with eq. (11.22), the large moments of inertia would correspond to energy levels at excessively long wavelengths. Microwave techniques have made this region readily accessible. From the moments of inertia so obtained, it is possible to calculate internuclear distances to better than ± 0.002 Å. A few examples are shown in Table 11.4.

TABLE 11.4
INTERNUCLEAR DISTANCES FROM MICROWAVE SPECTRA

Molecule	Distance (Å)	Molecule	Distance (Å)
ClCN	C—Cl 1.630	OCS	C—O 1.161
	C—N 1.163		C—S 1.560
BrCN	C—Br 1.789	N_2O	N—N 1.126
	C—N 1.160		N—O 1.191
		SO_2	S—O 1.433

By observing the spectra under the influence of an electric field (Stark effect) the dipole moments of gas molecules can be accurately determined. Microwave measurements also afford one of the best methods for finding nuclear spins.

29. Electronic band spectra. The energy differences ΔE between electronic states in a molecule are in general much larger than those between successive vibrational levels. Thus the corresponding electronic band spectra are observed in the visible or ultraviolet region. The ΔE's between molecular electronic levels are usually of the same order of magnitude as those between atomic energy levels, ranging therefore from 1 to 10 ev.

In Fig. 11.19 are shown the ground state of a molecule (Curve *A*), and two distinctly different possibilities for an excited state. In one (Curve *B*), there is a minimum in the potential energy curve, so that the state is a stable configuration for the molecule. In the other (Curve *C*), there is no minimum, and the state is unstable for all internuclear separations.

A transition from ground state to unstable state would be followed immediately by dissociation of the molecule. Such transitions give rise to a continuous absorption band in the observed spectra. Transitions between different vibrational levels of two stable electronic states also lead to a band in the spectra, but in this case the band can be analyzed into closely packed lines corresponding to the different upper and lower vibrational and rotational levels. The task of the spectroscopist is to measure the wavelengths of the various lines and interpret them in terms of the energy levels from which they arise. There is obviously a wealth of experimental data here, which should make possible a profound knowledge of the structure of molecules.

There is a general rule, known as the *Franck-Condon principle*, which is helpful in understanding electronic transitions. An electron jump takes place very quickly, much more quickly than the period of vibration of the atomic nuclei ($\sim 10^{-13}$ sec), which are heavy and sluggish compared with electrons. It can therefore be assumed that the positions and velocities of the nuclei are virtually unchanged during transitions,[22] which can thus be represented by vertical lines drawn on the potential energy curves, Fig. 11.19.

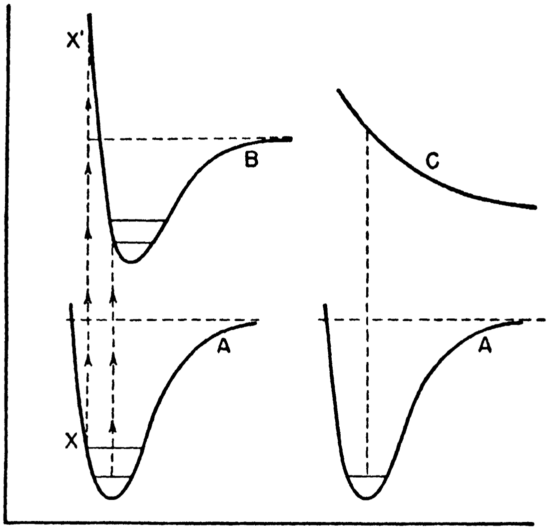


Fig. 11.19. Transitions between electronic levels in molecules.

By applying the Franck-Condon principle it is possible to visualize how transitions between stable electronic states may sometimes give rise to dissociation. For example, in Curve *A* of Fig. 11.19, the transition XX' leads to a vibrational level in the upper state that lies above the asymptote to the potential energy curve. Such a transition will lead to dissociation of the molecule.

If a molecule dissociates from an excited electronic state, the fragments formed, atoms in the diatomic case, are not always in their ground states. In order to obtain the heat of dissociation into atoms in their ground states, it is therefore necessary to subtract the excitation energy of the atoms. For

---

[22] It may be noted that the vertical line for an electronic transition is drawn from a point on the lower curve corresponding with the midpoint in the internuclear vibration. This is done because according to quantum mechanics the maximum in ψ in the ground state lies at the mid-point of the vibration. This is not true in higher vibrational states, for which the maximum probability lies closer to the extremes of the vibration. Classical theory predicts a maximum probability at the extremes of the vibration.

example, in the ultraviolet absorption spectrum of oxygen there is a series of bands corresponding to transitions from the ground state to an excited state. These bands converge to the onset of a continuum at 1759 Å, equivalent to 7.05 ev. The two atoms formed by the dissociation are found to be a normal atom ($3P$ state) and an excited atom ($1D$ state). The atomic spectrum of oxygen reveals that this $1D$ state lies 1.97 ev above the ground state. Thus the heat of dissociation of molecular oxygen into two normal atoms ($O_2 = 2\ O\ (3P)$) is $7.05 - 1.97 = 5.08$ ev or 117 kcal per mole.

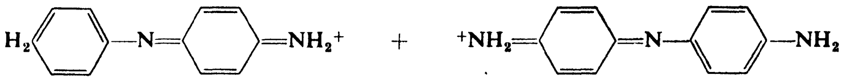
30. Color and resonance. The range of wavelengths from the red end of the visible spectrum at 8000 Å to the near ultraviolet at 2600 Å corresponds with a range of energy jumps from 34 to 114 kcal per mole. A compound with an absorption band in the visible or near ultraviolet must therefore possess at least one electronic energy level from 34 to 114 kcal above the ground level. This is not a large energy jump compared with the energy of binding of electrons in an electron pair bond. It is therefore not surprising that most stable chemical compounds are actually colorless. In fact, the appearance of color indicates that one of the electrons in the structure is loosely held and can readily be raised from the ground molecular orbital to an excited orbital.

For example, molecules containing an unpaired electron (odd molecules and free radicals) are usually colored (NO_2, ClO_2, triphenylmethyl, etc.). Groups such as —NO_2, —C=O, or N=N— often confer color on a molecule since they contain electrons, in π-type orbitals, that are readily raised to excited orbitals.

In other cases, resonance gives rise to a series of low-lying excited levels. The ground state in the benzene molecule can be assigned an orbital written as $\psi_A + \psi_B$, where A and B denote the two Kekulé structures shown on page 311. The first excited state is then $\psi_A - \psi_B$. This state lies 115 kcal above the ground level, and the excitation of an electron into this state is responsible for the near-ultraviolet absorption band of benzene around 2600 Å.

In a series of similar molecules such as benzene, naphthalene, anthracene, etc., the absorption shifts toward longer wavelength as the molecule becomes longer. The same effect is observed in the conjugated polyenes; butadiene is colorless but by the time the chain contains about twelve carbon atoms, the compounds are deeply colored. This behavior can be explained in terms of the increasing delocalization of the π-electrons as the length of the molecule increases. Let us recall the simple expression for the energy levels of an electron in a box, eq. (10.39), $E_n = h^2n^2/8ml^2$, where l is the length of the box. In a transition from n_1 to n_2 the energy jump is $(h^2/8ml^2)\ (n_1^2 - n_2^2)$. Thus not only the value of the energy but also the size of the energy jump falls markedly with increasing l. Now the molecular orbitals in organic molecules are of course not simple potential boxes, but the situation is physically very similar. Anything that increases the space in which the π-electron is free to move tends to decrease the energy gap between the ground state and excited states, and shifts the absorption toward the red.

Most dyes have structures that consist of two resonating forms. For instance, the phenylene blue ion is



A B

In this and similar cases, the transition responsible for the color can be ascribed to an electron jump between a $\psi_A + \psi_B$ and a $\psi_A - \psi_B$ orbital.

31. Raman spectra. If a beam of light is passed through a medium, a certain amount is absorbed, a certain amount transmitted, and a certain amount scattered. The scattered light can be studied by observations perpendicular to the direction of the incident beam. Most of the light is scattered without change in wavelength (Rayleigh scattering); but there is in addition a small amount of scattered light whose wavelength has been altered. If the incident light is monochromatic, *e.g.*, the Na_D line, the scattered spectrum will exhibit a number of faint lines displaced from the original wavelength. An example is shown in Fig. 11.20.

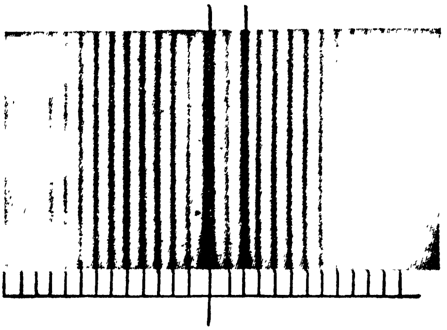


Fig. 11.20. Raman spectrum of O_2 excited by Hg 2537-Å line. (From Herzberg, *Molecular Spectra and Molecular Structure*, Van Nostrand, 1950.)

This effect was first observed by C. V. Raman and K. S. Krishnan in 1928. It is found that the Raman displacements, $\Delta\nu$, are multiples of vibrational and rotational quanta characteristic of the scattering substance. There are therefore rotational and vibration-rotational Raman spectra, which are the counterparts of the ordinary absorption spectra observed in the far and near infrared. Since the Raman spectra are studied with light sources in the visible or ultraviolet, they provide a convenient means of obtaining the same sort of information about molecular structure as is given by the infrared spectra. In many cases, the two methods supplement each other, since vibrations and rotations that are not observable in the infrared (*e.g.*, from molecules without permanent dipoles) may be active in the Raman.

32. Molecular data from spectroscopy. Table 11.5 is a collection of data derived from spectroscopic observations on a number of molecules.

TABLE 11.5

SPECTROSCOPIC DATA ON THE PROPERTIES OF MOLECULES*

Diatomic Molecules

Molecule	Equilibrium Internuclear Separation, r_e (Å)	Heat of Dissociation, D_0 (ev)	Fundamental Vibration Frequency (ω_e cm^{-1})	Moment of Inertia, (g cm^2 × 10^{-40})
Cl_2	1.989	2.481	564.9	114.8
CO	1.1284	9.144	2168	14.48
H_2	0.7414	4 777	4405	0.459
HD	0.7413	4.513	3817	0.611
D_2	0.7417	4 556	3119	0.918
HBr	1.414	3.60	2650	3.30
HCl^{35}	1.275	4.431	2989	2.71
I_2	2.667	1.542	214.4	748
Li_2	2.672	1 14	351.3	41.6
N_2	1.095	7 384	2360	13.94
NaCl	2 51	4 25	380	—
NH	1.038	3 4	3300	1.68
O_2	1 2076	5.082	1580	19.34
OH	0.971	4.3	3728	1 48

Triatomic Molecules

Molecule, X-Y-Z	Internuclear Separation (Å)		Bond Angle (deg)	Moments of Inertia (g cm^2 × 10^{40})			Fundamental Vibration Frequencies (cm^{-1})		
	r_{xy}	r_{yz}		I_A	I_B	I_C	ω_1	ω_2	ω_3
O=C=O	1.162	1 162	180	—	71 67	—	1320	668	2350
H—O—H	0 96	0 96	105	1 024	1 920	2 947	3652	1595	3756
D—O—D	0.96	0.96	105	1.790	3 812	5 752	2666	1179	2784
H—S—H	1.35	1.35	92	2 667	3 076	5.845	2611	1290	2684
O—S=O	1.40	1.40	120	12 3	73 2	85.5	1151	524	1361
N=N=O	1.15	1 23	180	—	66.9	—	1285	589	2224

* From G. Herzberg, *Molecular Spectra and Molecular Structure*, Vols. I and II (New York: D. Van Nostrand Co., 1950).

In this chapter we have not discussed the spectra of polyatomic molecules, one of the most active branches of modern spectroscopy. It is possible, however, to evaluate moments of inertia and vibration frequencies for polyatomic molecules by extensions of the methods described for diatomic molecules. Generally the high-frequency vibrations are those that *stretch* the bonds, and the lower frequencies are bond-*bending* vibrations.

It is often possible to characterize a given type of chemical bond by a *bond vibration frequency*, which is effectively constant in a large number of different compounds. For example, the stretching frequency of the —C=O bond is 1706 in acetone, 1715 in acetaldehyde, 1663 in actetic acid, and 1736 in methyl acetate.

The approximate constancy of these *bond* or *group frequencies* is the basis for the widespread application of infrared spectroscopy to the structure determination of new organic compounds and the detailed spectrum provides a method for characterizing a new compound which is as reliable as the finger-printing of a suspect citizen. Some typical bond frequencies are summarized in Table 11.6.

TABLE 11.6

BOND-FREQUENCY INTERVALS FOR INFRARED SPECTRA OF GASES*

Group	Frequency Interval cm^{-1}	Group	Frequency Interval cm^{-1}
H—O—	3500–3700	O=C<	1700–1850
H—N<	3300–3500	>C=C<	1550–1650
H—C≡C—	3300–3400	S=C<	1500–1600
H—C=C< |	3000–3100	F—C	1100–1300
		Cl—C	700–800
		Br—C	500–600
H—S—	2550–2650	I—C	400–500
N≡C—	2200–2300		
—C≡C—	2170–2270		

* After B. Bak, *Elementary Introduction to Molecular Spectra* (Amsterdam: North Holland Publ. Co., 1954).

33. Bond energies. In discussions of structure, thermodynamics, and chemical kinetics, it is often necessary to have some quantitative information about the strength of a certain chemical bond. The measure of this strength is the energy necessary to break the bond, the so-called *bond energy*. The energy of a bond between two atoms, *A—B*, depends on the nature of the rest of the molecule in which the bond occurs. There is no such thing as a strictly constant bond energy for *A—B* that persists through a varied series

TABLE 11.7

BOND ENERGIES (KCAL/MOLE)

Elements		Hydrides		Chlorides	
H—H	103.2	Li—H	58	C—Cl	78
Li—Li	26	C—H	98.2	O—Cl	49
C—C	80	N—H	92.2	Si—Cl	87
N—N	37	O—H	109.4	P—Cl	77
O—O	34	P—H	77	I—Cl	49.6
Cl—Cl	57.1	S—H	87 (?)		
I—I	35.6	Cl—H	102.1		
		Br—H	86.7		

	Single	Double	Triple
C—C	80	145	198
N—N	37	—	225
O—O	34	117	—
C—N	66	—	209

of compounds. Nevertheless, it is possible to strike an average from which actual *A—B* bonds do not deviate too widely.

Pauling has reduced a large amount of experimental data to a list of normal covalent single-bond energies.[23] If the actual bond is markedly polarized (partial ionic character), or if through resonance it acquires some double-bond character, its energy may be considerably higher than the norm.

Values from a recent compilation[24] are given in Table 11.7. These values are obtained by a combination of various methods: (1) spectroscopy, (2) thermochemistry, and (3) electron impact. The electron impact method employs a mass spectrometer and gradually increases the energy of the electrons from the ion gun until the molecule is broken into fragments.

An instance of the application of thermochemical data is the following determination of the O—H bond strength:

$$\begin{array}{rl}
H_2 = 2\,H & \Delta H = 103.4 \text{ kcal (spectroscopic)} \\
O_2 = 2\,O & \Delta H = 118.2 \text{ (spectroscopic)} \\
H_2 + \frac{1}{2}\,O_2 = H_2O & \Delta H = -\;57.8 \text{ (calorimetric)} \\
\hline
2\,H + O = H_2O & \Delta H = -220.3
\end{array}$$

This is ΔH for the formation of 2 O—H bonds, so that the bond strength is taken as 220.3/2 = 110 kcal.

PROBLEMS

1. Write down possible resonance forms contributing to the structures of the following: CO_2, CH_3COO^-, $CH_2{:}CH{\cdot}CH{:}CH_2$, CH_3NO_2, C_6H_5Cl, $C_6H_5NH_2$, naphthalene.

2. On the basis of molecular orbital theory, how would you explain the following? The binding energy of N_2^+ is 6.35 and that of N_2 7.38 ev, whereas the binding energy of O_2^+ is 6.48 and that of O_2, 5.08 ev.

3. The following results are found for the dielectric constant ε of gaseous sulfur dioxide at 1 atm as a function of temperature:

°K	267.6	297.2	336.9	443.8
ε	1.009918	1.008120	1.005477	1.003911

Estimate the dipole moment of SO_2, assuming ideal gas behavior.

4. M. T. Rogers[25] found the following values for the dielectric constant ε and density ρ of isopropyl cyanide at various mole fractions X in benzene solution at 25°C:

X	0.00301	0.00523	0.00956	0.01301	0.01834	0.02517
ε	2.326	2.366	2.442	2.502	2.598	2.718
ρ	0.87326	0.87301	0.87260	0.87226	0.87121	0.87108

For pure C_3H_7NC, $\rho = 0.76572$, refractive index $n_D = 1.3712$; for pure

---

[23] For a full discussion: L. Pauling, *op. cit.*, p. 53.

[24] K. S. Pitzer, *J. Am. Chem. Soc.*, *70*, 2140 (1948).

[25] *J. Am. Chem. Soc.*, *69*, 457 (1947).

benzene, $\rho = 0.87345$, $n_D = 1.5016$. Calculate the dipole moment μ of isopropyl cyanide.

5. Chlorobenzene has $\mu = 1.55$ d, nitrobenzene $\mu = 3.80$ d. Estimate the dipole moments of: metadinitrobenzene, orthodichlorobenzene, metachloronitrobenzene. The observed moments are 3.90, 2.25, 3.40 d. How would you explain any discrepancies?

6. The angular velocity of rotation $\omega = 2\pi\nu_{\text{rot}}$ where ν_{rot} is the rotation frequency of a diatomic rotor. The angular momentum is $(h/2\pi)\sqrt{J(J+1)}$. Calculate the rotation frequency of the HCl molecule for the state with $J = 9$. Calculate the frequency of the spectral line corresponding to the transition $J = 9$ to $J = 8$.

7. In the far infrared spectrum of HBr is a series of lines having a separation of 16.94 cm^{-1}. Calculate the moment of inertia and the internuclear separation in HBr from this datum.

8. In the near infrared spectrum of carbon monoxide there is an intense band at 2144 cm^{-1}. Calculate (a) the fundamental vibration frequency of CO; (b) the period of the vibration; (c) the force constant; (d) the zero-point energy of CO in cal per mole.

9. Sketch the potential-energy curve for the molecule Li_2 according to the Morse function, given $D_0 = 1.14$ ev, $\nu_0 = 351.35$ cm^{-1}, $r_e = 2.672$ Å.

10. The Schumann-Runge bands in the ultraviolet spectrum of oxygen converge to a well defined limit at 1759 Å. The products of the dissociation are an oxygen atom in the ground state and an excited atom. There are two low-lying excited states of oxygen, ^1D and ^1S at 1.967 and 4.190 volts above the ground state. By referring to the dissociation data in Table 4.4, page 81, decide which excited state is formed, and then calculate the spectroscopic dissociation energy of O_2 into two O atoms in the ground state.

11. In a diffraction investigation of the structure of CS_2 with 40-kv electrons, Cross and Brockway[26] found four sharp maxima (++) each followed by a weak maximum (+) and a deep minimum (—), at the following values of $4\pi/\lambda\ (\sin \theta/2)$

4.713	6.312	7.623	8.698	10.63	11.63	12.65	14.58	15.54	16.81
++	+	+	++	+	—	++	+	—	++

CS_2 is a linear molecule. Calculate the C—S distance from these data, using the approximation that the scattering factor is equal to the atomic number Z.

12. With data from Table 11.5, draw to scale the first five rotational levels in the molecule NaCl. At what frequency would the transition $J = 4$ to $J = 5$ be observed? In NaCl vapor at 1000°C what would be the relative numbers of molecules in the states with $J = 0$, $J = 1$, and $J = 2$.

---

[26] *J. Chem. Phys.*, *3*, 821 (1935).

13. In ions of the first transition series, the paramagnetism is due almost entirely to the unpaired spins, being approximately equal to $\mu = 2\sqrt{S(S+1)}$ magnetons where S is the total spin. On this basis, estimate μ for V^{+3}, Mn^{+2}, Co^{+2}, and Cu^{+}.

REFERENCES

BOOKS

1. Bates, L. F., *Modern Magnetism* (London: Cambridge, 1951).
2. Böttcher, C. J. F., *Theory of Electric Polarisation* (Amsterdam: Elsevier, 1952).
3. Burk, R. E., and O. Grummitt (editors), *Chemical Architecture* (New York: Interscience, 1948).
4. Coulson, C. A., *Valence* (New York: Oxford, 1952).
5. Debye, P., *Polar Molecules* (New York: Dover, 1945).
6. Gaydon, A. G., *Dissociation Energies* (London: Chapman and Hall, 1952).
7. Gordy, W., W. V. Smith, and R. F. Trambarulo, *Microwave Spectroscopy* (New York: Wiley, 1953).
8. Herzberg, G., *Infrared and Raman Spectra* (New York: Van Nostrand, 1945).
9. Herzberg, G., *Molecular Spectra and Molecular Structure* (New York: Van Nostrand, 1950).
10. Ketelaar, J. A. A., *Chemical Constitution* (Amsterdam: Elsevier, 1953).
11. Palmer, W. G., *Valency, Classical and Modern* (Cambridge, 1944).
12. Pauling, L., *The Nature of the Chemical Bond* (Ithaca: Cornell Press, 1940).
13. Pitzer, K. S., *Quantum Chemistry* (New York: Prentice-Hall, 1953).
14. Rice, F. O., and E. Teller, *The Structure of Matter* (New York: Wiley, 1949).

ARTICLES

1. Condon, E. U., *Am. J. Phys.*, *15*, 365–74 (1947), "The Franck-Condon Principle and Related Topics."
2. Klotz, I. M., *J. Chem. Ed.*, *22*, 328–36 (1945), "Ultraviolet Absorption Spectroscopy."
3. Mills, W. H., *J. Chem. Soc.*, 1942, 457–66 (1942), "The Basis of Stereochemistry."
4. Pake, G. E., *Am. J. Phys.*, *18*, 438–73 (1950), "Nuclear Magnetic Resonance."
5. Pauling, L., *J. Chem. Soc.*, 1461–67 (1948), "The Modern Theory of Valency."
6. Purcell, E. M., *Science*, *118*, 431–36 (1953), "Nuclear Magnetic Resonance."

7. Selwood, P. W., *J. Chem. Ed., 19,* 181–88 (1942), "Magnetism and Molecular Structure."
8. Spurr, R., and L. Pauling, *J. Chem. Ed., 18,* 458–65 (1941), "Electron Diffraction of Gases."
9. Sugden, S., *J. Chem. Soc.*, 328–33 (1943), "Magnetochemistry."
10. Thompson, H. W., *J. Chem. Soc.*, 183–92 (1944), "Infrared Measurements in Chemistry."
11. Wilson, E. B., *Ann. Rev. Phys. Chem., 2,* 151–76 (1951), "Microwave Spectroscopy of Gases".

CHAPTER 12

Chemical Statistics

1. The statistical method. If you take a deck of cards, shuffle it well, and draw a single card at random, it is not possible to predict what the card will be, unless you happen to be a magician. Nevertheless, a number of significant statements can be made about the result of the drawing. For example: the probability of drawing an ace is one in thirteen; the probability of drawing a spade is one in four; the probability of drawing the ace of spades is one in fifty-two. Similarly, if you were to ask an insurance company whether a certain one of its policyholders was going to be alive 10 years from now, the answer might be: "We cannot predict the individual fate of John Jones, but our actuarial tables indicate that the *chances* are nine out of ten that he will survive."

We are familiar with many statements of this kind and call them "statistical predictions." In many instances it is impossible to foretell the outcome of an individual event, but if a large number of similar events are considered, a statement based on probability laws becomes possible. An example from physics is found in the disintegration of radioactive elements. No one can determine *a priori* whether an isolated radium atom will disintegrate within the next 10 minutes, the next 10 days, or the next 10 centuries. If a milligram of radium is studied, however, we know that very close to 2.23×10^{10} atoms will explode in any 10-minute period.

Some applications of statistical principles to chemical systems were discussed in Chapter 7. It was pointed out that since the atoms and molecules of which matter is composed are extremely small, any large-scale body contains an enormous number of elementary particles. It is impossible to keep track of so many individual particles. Any theory that attempts to interpret the behavior of macroscopic systems in terms of atoms and molecules must therefore rely heavily on statistical considerations. But just because a system does contain so very many particles, its actual behavior will be practically indistinguishable from that predicted by statistics. If a man tossed 10 coins, the result might deviate widely from 50 per cent heads; if he tossed a thousand, the percentage deviation would be fairly small; but if some tireless player were to toss 10^{23} coins, the result would be to all intents and purposes exactly 50 per cent heads.

We have seen already that from the molecular-kinetic point of view the Second Law of Thermodynamics is a statistical law. It expresses the drive toward randomness or disorder in a system containing a large number of particles. Applied to an individual molecule it has no meaning, for in this case any distinction between heat (disordered energy) and work (ordered energy) disappears. Even for intermediate cases, such as colloidal particles in Brownian motion, the Second Law is inapplicable, since the particles contain only about 10^6 to 10^9 atoms.

Now that the structures and energy levels of atoms and molecules have been considered, in Chapters 8 through 11, it is possible to see how the behavior of macroscopic systems is determined by these atomic and molecular parameters. We shall confine our attention to systems in equilibrium, which are usually treated by thermodynamics. This is not, however, a necessary restriction for the statistical method, which is competent to handle also situations in which the system is changing with time. These are sometimes called "rate processes," and include transport phenomena, such as diffusion and thermal conductivity, as well as the kinetics of chemical reactions.

Statistical thermodynamics is still a very young science, and many fundamental problems remain to be solved. Thus the only systems that have been treated at all accurately are ideal gases and perfect crystals. Imperfect gases and liquids present unsurmounted difficulties.

2. Probability of a distribution. The discussion of statistical thermodynamics upon which we are embarking will not be distinguished for its mathematical precision, nor will any attempt be made to delve into the logical foundations of the subject.[1]

The general question to be answered is this: given a macroscopic physical system, composed of molecules (and/or atoms), and knowing from quantum mechanics the allowed energy states for these molecules, how will we distribute the large number of molecules among the allowed energy levels? The problem has already been discussed for certain special cases, the answers being expressed in the form of "distribution laws," for example, the Maxwell distribution law for the kinetic energies of molecules, the Planck distribution law for the energies of harmonic oscillators. We wish now to obtain a more general formulation.

The statistical treatment is based on an important principle: the most probable distribution in a system can be taken to be the equilibrium distribution. In a system containing a very large number of particles, deviations from the most probable distribution need not be considered in defining the equilibrium condition.[2]

We first require an expression for the probability P of a distribution. Then the expression for the maximum probability is obtained by setting the variation of P equal to zero, subject to certain restraining conditions imposed on the system.

---

[1] For such treatments, see R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (London: Cambridge, 1939); and R. C. Tolman, *Statistical Mechanics* (New York: Oxford, 1938).

[2] See J. E. Mayer and M. Mayer, *Statistical Mechanics* (New York: Wiley, 1940), for a good discussion of this point.

The method of defining the probability may be illustrated by an example that is possibly familiar to some students, the rolling of dice. The probability of rolling a certain number n will be defined as the number of different ways in which n can be obtained, divided by the total number of combinations that can possibly occur. There are six faces on each of two dice so that the total number of combinations is $6^2 = 36$. There is only one way of rolling a twelve; if the dice are distinguished as a and b, this way can be designated as $a(6)$—$b(6)$. Its probability $P(12)$ is equal to one in 36. For a seven, there are six possibilities:

$$\begin{array}{ll} a(6)\text{—}b(1) & a(1)\text{—}b(6) \\ a(5)\text{—}b(2) & a(2)\text{—}b(5) \\ a(4)\text{—}b(3) & a(3)\text{—}b(4) \end{array}$$

Therefore, $P(7) = \frac{6}{36} = \frac{1}{6}$.

Just as with the dice, the probability of a given distribution of molecules among energy levels could be defined as the number of ways of realizing the particular distribution divided by the total number of possible arrangements. For a given system, this total number is some constant, and it is convenient to omit it from the definition of the probability of the system. The new definition therefore is: the probability of a distribution is equal to the number of ways of realizing the distribution.

3. The Boltzmann distribution. Let us consider a system that has a total energy E and contains n identical particles. Let us assume that the allowed energy levels for the particles (atoms, molecules, etc.) are known from quantum mechanics and are specified as $\varepsilon_1, \varepsilon_2, \varepsilon_3, \cdots \varepsilon_K, \cdots$, etc. How will the total energy E be distributed among the energy levels of the n particles?

For the time being, we shall assume that each particle is distinguishable from all the others and that there are no restrictions on how the particles may be assigned to the various energy levels. These assumptions lead to the "classical" or Boltzmann distribution law. It will be seen later that this law is only an approximation to the correct quantum mechanical distribution laws, but the approximation is often completely satisfactory.

Now the n distinguishable particles are assigned to the energy levels in such a way that there are n_1 in level ε_1, n_2 in ε_2, or in general n_K in level ε_K. The probability of any particular distribution, characterized by a particular set of occupation numbers n, is by definition equal to the number of ways of realizing that distribution. Since permuting the particles within a given energy level does not produce a new distribution, the number of ways of realizing a distribution is the total number of permutations $n!$, divided by the number of permutations of the particles within each level, $n_1!\, n_2! \ldots n_K! \ldots$ The required probability is therefore

$$P = \frac{n!}{n_1!\, n_2! \ldots n_K! \ldots} = \frac{n!}{\prod\limits_K n_K!} \tag{12.1}$$

As an example of this formula, consider four particles *a*, *b*, *c*, *d* distributed so that two are in ε_1, none in ε_2, and one each in ε_3 and ε_4. The possible arrangements are as follows:

ε_1	ε_2	ε_3	ε_4
ab	—	*c*	*d*
ab	—	*d*	*c*
ac	—	*b*	*d*
ac	—	*d*	*b*
ad	—	*b*	*c*
ad	—	*c*	*b*
bc	—	*a*	*d*
bc	—	*d*	*a*
bd	—	*a*	*c*
bd	—	*c*	*a*
cd	—	*a*	*b*
cd	—	*b*	*a*

There are twelve arrangements as given by the formula [$0! = 1$]:

$$P = \frac{4!}{2!\,0!\,1!\,1!} = \frac{4 \cdot 3 \cdot 2 \cdot 1}{2 \cdot 1 \cdot 1 \cdot 1} = 12$$

Note that interchanges of the two particles *within* level ε_1 are not significant.

Returning to eq. (12.1), the equilibrium distribution is the one for which this probability is a maximum. The maximum is subject to two conditions, the constancy of the number of particles and the constancy of the total energy. These conditions can be written

$$\begin{gathered} \Sigma\, n_K = n \\ \Sigma\, n_K \varepsilon_K = E \end{gathered} \tag{12.2}$$

By taking the logarithm of both sides of eq. (12.1), the continued product is reduced to a summation.

$$\ln P = \ln n! - \sum_K \ln n_K!$$

The condition for a maximum in P is that the variation of P, and hence of $\ln P$, be zero. Since $\ln n!$ is a constant,

$$\delta \ln P = 0 = \Sigma\, \delta \ln n_K! \tag{12.3}$$

Stirling's formula[3] for the factorials of large numbers is

$$\ln n! = n \ln n - n \tag{12.4}$$

---

[3] For derivation see D. Widder, *Advanced Calculus* (New York: Prentice-Hall, 1947), p. 317.

Therefore eq. (12.3) becomes

$$\delta \sum n_K \ln n_K - \delta \Sigma n_K = 0$$

or

$$\Sigma \ln n_K \delta n_K = 0 \tag{12.5}$$

The two restraints in eq. (12.2), since n and E are constants, can be written

$$\begin{aligned} \delta n &= \Sigma\, \delta n_K = 0 \\ \delta E &= \Sigma\, \varepsilon_K\, \delta n_K = 0 \end{aligned} \tag{12.6}$$

These two equations are multiplied by two arbitrary constants,[4] α and β, and added to eq. (12.5), yielding

$$\Sigma\, \alpha\, \delta n_K + \Sigma\, \beta \varepsilon_K\, \delta n_K + \Sigma \ln n_K\, \delta n_K = 0 \tag{12.7}$$

The variations δn_K may now be considered to be perfectly arbitrary (the restraining conditions having been removed) so that for eq. (12.7) to hold, each term in the summation must vanish. As a result,

$$\ln n_K + \alpha + \beta \varepsilon_K = 0$$

or

$$n_K = e^{-\alpha} e^{-\beta \varepsilon_K} \tag{12.8}$$

This equation has the same form as the Boltzmann distribution law previously obtained and suggests that the constant β equals $1/kT$. It could have been calculated anew. Thus

$$n_K = e^{-\alpha} e^{-\varepsilon_K/kT} \tag{12.9}$$

It is convenient at this point to make one extension of this distribution law. It is possible that there may be more than one state corresponding with the energy level ε_K. If this is so, the level is said to be *degenerate* and should be assigned a *statistical weight* g_K, equal to the number of superimposed levels. The distribution law in this more general form is accordingly

$$n_K = g_K e^{-\alpha} e^{-\varepsilon_K/kT} \tag{12.10}$$

The constant α is evaluated from the condition

$$\Sigma n_K = n$$

whence

$$\Sigma e^{-\alpha} g_K e^{-\varepsilon_K/kT} = n$$

$$e^{-\alpha} = \frac{n}{\Sigma g_K e^{-\varepsilon_K/kT}}$$

Therefore eq. (12.10) becomes

$$\frac{n_K}{n} = \frac{g_K e^{-\varepsilon_K/kT}}{\sum\limits_K g_K e^{-\varepsilon_K/kT}} \tag{12.11}$$

---

[4] This is an application of Lagrange's method of undetermined multipliers, the standard treatment of constrained maxima problems. See, for example, D. Widder, *Advanced Calculus*, p. 113.

This is the Boltzmann distribution law in its most general form. The expression $\sum g_K e^{-\epsilon_K/kT}$ in the denominator of eq. (12.11) is very important in statistical mechanics. It is called the *partition function*, and will be denoted by the symbol

$$f \equiv \sum_K g_K e^{-\epsilon_K/kT} \tag{12.12}$$

The average energy $\bar{\epsilon}$ of a particle is given by (see eq. 7.38)

$$\bar{\epsilon} = \frac{\Sigma\, n_K \epsilon_K}{\Sigma\, n_K} = \frac{\Sigma\, g_K \epsilon_K e^{-\epsilon_K/kT}}{\Sigma\, g_K e^{-\epsilon_K/kT}}$$

or

$$\bar{\epsilon} = kT^2 \frac{\partial \ln f}{\partial T} \tag{12.13}$$

4. Internal energy and heat capacity. It is now possible to make use of the distribution law to calculate the various functions of thermodynamics. Thermodynamics deals not with individual particles, but with large-scale systems containing very many particles. The usual thermodynamic measure is the mole, 6.02×10^{23} molecules.

Instead of considering a large number of individual particles, let us consider a large number of systems, each containing a mole of the substance being studied. The average energy of these systems will be the ordinary internal energy E. We again use eq. (12.13), except that now a whole system takes the place of each particle. If the allowed energies of the whole system are $E_1, E_2, \ldots E_K$, the average energy will be

$$E = \frac{\Sigma\, n_K E_K}{\Sigma\, n_K} = \frac{\Sigma\, g_K E_K e^{-E_K/kT}}{\Sigma\, g_K e^{-E_K/kT}}$$

Writing

$$Z = \sum g_K e^{-E_K/kT} \tag{12.14}$$

then,

$$E = kT^2 \frac{\partial \ln Z}{\partial T} \tag{12.15}$$

We may call Z the *molar partition function* to distinguish it from the molecular partition function f. It is also called the *sum-over-states*

From eq. (12.15) the heat capacity at constant volume is

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(kT^2 \frac{\partial \ln Z}{\partial T}\right)$$

or

$$C_V = \frac{k}{T^2} \cdot \frac{\partial^2 \ln Z}{\partial (1/T)^2} \tag{12.16}$$

5. Entropy and the Third Law. Equation (12.16) can be employed to calculate the entropy in terms of the molar partition function Z. Thus:

$$S - S_0 = \int_0^T \frac{C_V}{T}\, dT = \int_0^T \frac{1}{T} \cdot \frac{\partial}{\partial T}\left(kT^2 \frac{\partial \ln Z}{\partial T}\right)_V dT$$

Integrating by parts, we find

$$S - S_0 = kT\left(\frac{\partial \ln Z}{\partial T}\right)_V + k\int_0^T \left(\frac{\partial \ln Z}{\partial T}\right)_V dT$$

$$= \frac{E}{T} + k \ln Z - k \ln Z|_{T=0}^{\text{at}} \qquad (12.17)$$

In this equation, only S_0 and $|k \ln Z|_{T=0}$ are temperature-independent terms. The constant term, S_0, the entropy at the absolute zero, is therefore

$$S_0 = k \ln Z|_{T=0} = k \ln g_0 \qquad (12.18)$$

Here g_0 is the statistical weight of the lowest possible energy state of the system. Equation (12.18) is the statistical-mechanical formulation of the Third Law of Thermodynamics.

If we consider, for example, a perfect crystal at the absolute zero, there will usually be one and only one equilibrium arrangement of its constituent atoms, ions, or molecules. In other words, the statistical weight of the lowest energy state is unity: the entropy at 0°K becomes zero. This formulation ignores the possible multiplicity of the ground state due to nuclear spin. If the nuclei have different nuclear-spin orientations, there will be a residual entropy at 0°K. In chemical problems such effects are of no importance, since in any chemical reaction the nuclear-spin entropy would be the same on both sides of the reaction equation. It is thus conventional to set $S_0 = 0$ for the crystalline elements and hence for all crystalline solids.

Many statistical calculations on this basis have been quantitatively checked by experimental Third-Law values based on heat-capacity data. Examples are given in Table 12.1.

TABLE 12.1

COMPARISON OF STATISTICAL (SPECTROSCOPIC) AND THIRD-LAW (HEAT-CAPACITY) ENTROPIES

Gas	Entropy as Ideal Gas at 1 atm, 298.2°K	
	Statistical	Third Law
N_2	45.78	45.9
O_2	49.03	49.1
Cl_2	53.31	53.32
H_2	31.23	29.74
HCl	44.64	44.5
HBr	47.48	47.6
HI	49.4	49.5
H_2O	45.10	44.28
N_2O	52.58	51.44
NH_3	45.94	45.91
CH_4	44.35	44.30
C_2H_4	52.47	52.48

In certain cases, however, it appears that even at absolute zero the particles in a crystal may persist in more than one geometrical arrangement. An example is crystalline nitrous oxide. Two adjacent molecules of N_2O can be oriented either as (ONN NNO) or as (NNO NNO). The energy difference ΔE between these alternative configurations is so slight that their relative probability $e^{\Delta E/RT}$ is practically unity even at low temperatures. By the time the crystal has been cooled to the *extremely low* temperature at which even a minute ΔE might produce a reorientation, the *rate* of rotation of the molecules within the crystal has become vanishingly slow. Thus the random orientations are effectively "frozen." As a result, heat-capacity measurements will not include a residual entropy S_0 equal to the entropy of mixing of the two arrangements. From eq. (3.42) this would amount to

$$S_0 = -R\,\Sigma\,X_i \ln X_i = -R(\tfrac{1}{2}\ln\tfrac{1}{2} + \tfrac{1}{2}\ln\tfrac{1}{2}) = R\ln 2 = 1.38 \text{ eu}$$

It is found that the entropy calculated from statistics is actually larger by 1.14 eu than the Third-Law value, which is within the experimental uncertainty of ±0.25 eu in S_0. A number of examples of this type have been carefully studied.[5]

If the substance at temperatures close to 0°K is not crystalline, but a glass, there is also a residual entropy owing to the randomness characteristic of vitreous structures.

Another instance of a residual entropy of mixing at 0°K arises from the isotopic constitution of the elements. This effect can usually be ignored since in most chemical reactions the isotopic ratios change very slightly.

As a result of this discussion, we shall set $S_0 = 0$ in eq. (12.18), obtaining

$$S = \frac{E}{T} + k\ln Z \tag{12.19}$$

6. Free energy and pressure. From the relation $A = E - TS$ and eqs. (12.15) and (12.19), the work function becomes

$$A = -kT\ln Z \tag{12.20}$$

The pressure, $-(\partial A/\partial V)_T$, is then

$$P = kT\frac{\partial \ln Z}{\partial V} \tag{12.21}$$

The Gibbs free energy is simply $F = A + PV$, and from ΔF° the equilibrium constants for a reaction can be calculated.

Expressions have now been obtained that enable us to calculate all thermodynamic properties of interest, once we know how to evaluate the molar partition function Z.

7. Evaluation of molar partition functions. The evaluation of the molar partition function Z has not yet been accomplished for all types of systems, which is of course hardly surprising, for the function Z contains in itself the

---

[5] For the interesting case of ice, see L. Pauling, *J. Am. Chem. Soc.*, *57*, 2680 (1935).

answer to all the equilibrium properties of matter. If we could calculate Z from the properties of individual particles, we could then readily calculate all the energies, entropies, free energies, specific heats, and so forth, that might be desired.

In many cases, it is a good approximation to consider that E_K, an energy of the system, can be represented simply as the sum of energies ε_K of non-interacting individual particles. This would be the case, for example, of a crystal composed of independent oscillators, or of an almost perfect gas in which the intermolecular forces were negligible. In such instances we can write

$$E_K = \varepsilon_1(1) + \varepsilon_2(2) + \varepsilon_3(3) + \ldots \varepsilon_N(N) \tag{12.22}$$

This expression indicates that particle (1) occupies an energy level ε_1, particle (2) an energy level ε_2, etc. Each different way of assigning the particles to the energy levels determines a distinct state of the system E_K.

The molar partition function, or sum over the states E_K, then becomes

$$Z = \sum_K e^{-E_K/kT} = \sum_K e^{-[\varepsilon_K(1)+\varepsilon_K(2)+\ldots\varepsilon_K(N)]/kT}$$

(The statistical weights g_K are omitted for convenience in writing the expressions.) The second summation must be taken over all the different ways of assigning the particles to the energy levels ε_K. It can be rewritten as

$$\sum e^{-\varepsilon_K(1)/kT} \cdot e^{-\varepsilon_K(2)/kT} \ldots e^{-\varepsilon_K(N)/kT}$$

Since each particle has the same set of allowed energy levels, this sum is equal[6] to

$$(\sum_K e^{-\varepsilon_K/kT})^N$$

Thus we find that $Z = f^N$.

The relation $Z = f^N$ applies to the case in which rearranging the particles among the energy levels in eq. (12.22) actually gives rise to different states that must be included in the summation for Z. This is the situation in a perfect crystal, the different particles (oscillators) occupying distinct localized positions in the crystal structure.

In the case of a gas, on the other hand, each particle is free to move throughout the whole available volume. States in the gas that differ merely

---

[6] It may be rather hard to see this equality at first. Consider therefore a simple case in which there are only two particles (1) and (2) and two energy levels ε_1 and ε_2. The ways of assigning the particles to the levels are:

$$E_1 = \varepsilon_1(1) + \varepsilon_2(2), \quad E_2 = \varepsilon_1(2) + \varepsilon_2(1), \quad E_3 = \varepsilon_1(1) + \varepsilon_1(2), \quad E_4 = \varepsilon_2(1) + \varepsilon_2(2)$$

The sum over states is:

$$Z = e^{-E_1/kT} + e^{-E_2/kT} + e^{-E_3/kT} + e^{-E_4/kT}$$

which is equal to

$$e^{-2\varepsilon_1/kT} + 2e^{-\varepsilon_1/kT}e^{-\varepsilon_2/kT} + e^{-2\varepsilon_2/kT}$$

Now it is evident that this is identical with

$$f^n = (\Sigma e^{-\varepsilon_K/kT})^2 = (e^{-\varepsilon_1/kT} + e^{-\varepsilon_2/kT})^2$$

by the interchange of two particles are not distinguishable and should be counted only once. If each level in eq. (12.22) contains only one particle,[7] the number of permutations of the particles among the levels is $N!$ We therefore divide the expression for Z by this factor, obtaining for the ideal gas case, $Z = (1/N!)f^N$.

Thus the relations between f and Z in the two extreme cases are

$$\begin{aligned} &\text{Ideal crystals} \quad Z = f^N \\ &\text{Ideal gases} \quad Z = \frac{1}{N!}f^N \end{aligned} \tag{12.23}$$

Intermediate kinds of systems, such as imperfect gases and liquids, are much more difficult to evaluate.

In proceeding to calculate the partition functions for an ideal gas, it is convenient to make use of a simplifying assumption. The energy of a molecule will be expressed as the sum of translational, rotational, vibrational, and electronic terms. Thus

$$\varepsilon = \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{elec}} \tag{12.24}$$

It follows that the partition function is the product of corresponding terms,

$$f = f_{\text{trans}} f_{\text{rot}} f_{\text{vib}} f_{\text{elec}} \tag{12.25}$$

The simplest case to be considered is that of the monatomic gas, in which there are no rotational or vibrational degrees of freedom; except at very high temperatures the electronic excitation is usually negligible.

8. Monatomic gases—translational partition function. In Section 10–20 it was shown that the translational energy levels for a particle in a one-dimensional box are given by

$$\varepsilon_n = \frac{n^2h^2}{8ml^2}$$

The statistical weight of each level is unity, $g_n = 1$. Therefore the molecular partition function becomes

$$f = \Sigma \exp\left(\frac{-n^2h^2/8ml^2}{kT}\right)$$

The energy levels are so closely packed together that they can be considered to be continuous, and the summation can be replaced by an integration,

$$f = \int_0^\infty \exp\left(\frac{-n^2h^2/8ml^2}{kT}\right) dn$$

---

[7] When the volume is large and the temperature not very low, there will be many more energy levels than there are particles. This will be evident on examination of eq. (10.39) for the levels of a particle in a box. Since there is no housing shortage, there is no reason for the particles to "double-up" and hence the assumption of single occupancy is a good one. For a further discussion, see Tolman, *loc. cit.*, pp. 569–572.

Letting
$$x^2 = \frac{n^2h^2}{8ml^2kT}$$

$$f = \frac{l}{h}(8mkT)^{1/2}\int_0^\infty e^{-x^2}dx = \frac{(2\pi mkT)^{1/2}l}{h} \tag{12.26}$$

For three degrees of translational freedom this expression is cubed, and since $l^3 = V$, we obtain

$$f = \frac{(2\pi mkT)^{3/2}V}{h^3} \tag{12.27}$$

This is the molecular partition function for translation.

The molar partition function is

$$Z = \frac{1}{N!}f^N = \frac{1}{N!}\left[\frac{(2\pi mkT)^{3/2}V}{h^3}\right]^N \tag{12.28}$$

The energy is therefore

$$E = NkT^2\frac{\partial \ln f}{\partial T} = RT^2\frac{\partial \ln f}{\partial T} = RT^2\cdot\frac{3}{2}\cdot\frac{1}{T} = \frac{3}{2}RT$$

This is, of course, the simple result to be expected from the equipartition principle.

The entropy is evaluated from eq. (12.19), using the Stirling formula, $N! = (N/e)^N$. It follows that

$$Z = \left[\frac{(2\pi mkT)^{3/2}eV}{Nh^3}\right]^N$$

$$\ln Z = N\ln\left[\frac{eV}{Nh^3}(2\pi mkT)^{3/2}\right]$$

The entropy is therefore

$$S = \frac{3}{2}R + R\ln\frac{eV}{Nh^3}(2\pi mkT)^{3/2}$$

$$S = R\ln\frac{e^{5/2}V}{Nh^3}(2\pi mkT)^{3/2} \tag{12.29}$$

This is the famous equation that was first obtained by somewhat unsatisfactory arguments by Sackur and Tetrode (1913). As an example, let us apply it to calculate the entropy of argon at 273.2°K and at one atmosphere pressure. Then

$R = 1.98$ cal per °C
$e = 2.718$
$V = 22{,}414$ cc
$N = 6.02 \times 10^{23}$
$h = 6.62 \times 10^{-27}$ erg sec

$\pi = 3.1416$
$m = 6.63 \times 10^{-23}$ g
$k = 1.38 \times 10^{-16}$ erg per °C
$T = 273.2$

On substituting these quantities into eq. (12.29), the entropy is found to be 36.2 cal per deg mole.

9. Diatomic molecules—rotational partition function. The energy levels for diatomic molecules, according to the rigid-rotator model, were given by eq. (11.22) as

$$\epsilon_{\text{rot}} = \frac{J(J+1)h^2}{8\pi^2 I}$$

If the moment of inertia I is sufficiently high, these energy levels become so closely spaced as to be practically continuous. This condition is, in fact, realized for all diatomic molecules except H_2, HD, and D_2. Thus for F_2, $I = 25.3 \times 10^{-40}$ g cm^2; for N_2, 13.8×10^{-40}; but for H_2, $I = 0.47 \times 10^{-40}$. These values are calculated from the interatomic distances and the masses of the molecules, since $I = \mu r^2$.

Now the multiplicity of the rotational levels requires some consideration. The number of ways of distributing J quanta of rotational energy between *two* axes of rotation equals $2J + 1$, for in every case except $J = 0$ there are *two* possible alternatives for each added quantum. The statistical weight of a rotational level J is therefore $2J + 1$.

The rotational partition function now becomes

$$f_{\text{rot}} = \Sigma\,(2J+1)e^{-J(J+1)h^2/8\pi^2 IkT} \tag{12.30}$$

Replacing the summation by an integration, since the levels are closely spaced, we obtain

$$f_{\text{rot}} = \int_0^\infty (2J+1)e^{-J(J+1)h^2/8\pi^2 IkT}dJ$$

$$f_{\text{rot}} = \frac{8\pi^2 IkT}{h^2} \tag{12.31}$$

One further complication remains. In homonuclear diatomic molecules ($N^{14}N^{14}$, $Cl^{35}Cl^{35}$, etc.) only all odd or all even J's are allowed, depending on the symmetry properties of the molecular eigenfunctions. If the nuclei are different ($N^{14}N^{15}$, HCl, NO, etc.) there are no restrictions on the allowed J's. A symmetry number σ is therefore introduced, which is either $\sigma = 1$ (heteronuclear) or $\sigma = 2$ (homonuclear). Then

$$f_{\text{rot}} = \frac{8\pi^2 IkT}{\sigma h^2} \tag{12.32}$$

As an example of the application of this equation, consider the calculation of the entropy of F_2 at 298.2°K, assuming translational and rotational contributions only. From eq. (12.29), the translational entropy is found to be 36.88 eu. Then the rotational part is

$$S_{\text{rot}} = RT\frac{\partial \ln f_{\text{rot}}}{\partial T} + k \ln f_{\text{rot}}^N = R + R \ln f_{\text{rot}} = R + R \ln \frac{8\pi^2 IkT}{2h^2}$$

Note that the rotational energy is simply RT in accordance with the equipartition principle. Substituting $I = 25.3 \times 10^{-40}$, $S_{\text{rot}} = 8.74$ eu. Adding the translational term, we have

$$S = S_{\text{rot}} + S_{\text{trans}} = 8.74 + 36.88 = 45.62 \text{ eu}$$

This compares with a total entropy of $S^{\circ}_{298} = 48.48$ eu. The vibrational contribution at 25°C is therefore small.

10. Polyatomic molecules—rotational partition function. The partition function in eq. (12.32) holds also for linear polyatomic molecules, with $\sigma = 2$ if the molecule has a plane of symmetry (such as O=C=O), and $\sigma = 1$ if it has not (such as N≡N=O).

For a nonlinear molecule, the classical rotational partition function has been found to be

$$f_{\text{rot}} = \frac{8\pi^2(8\pi^3 ABC)^{1/2}(kT)^{3/2}}{\sigma h^3} \tag{12.33}$$

In this equation A, B, C are the three principal moments of inertia of the molecule. The symmetry number σ is equal to the number of equivalent ways of orienting the molecule in space. For example: H_2O, $\sigma = 2$; NH_3, $\sigma = 3$; CH_4, $\sigma = 12$; C_6H_6, $\sigma = 12$.

11. Vibrational partition function. In evaluating a partition function for the vibrational degrees of freedom of a molecule, it is often sufficient to use the energy levels of the harmonic oscillator, which from eq. (11.25) are

$$\varepsilon_{\text{vib}} = (v + \tfrac{1}{2})h\nu \tag{12.34}$$

At low temperatures vibrational contributions are usually small and this approximation is adequate. For reasonably exact calculations at higher temperatures the anharmonicity of the vibrations must be considered. Sometimes the summation for f can be made by using energy levels obtained directly from molecular spectra.

The partition function corresponding to eq. (12.34) would be, for each vibrational degree of freedom,

$$f_{\text{vib}} = \sum_v e^{-(v+\frac{1}{2})h\nu/kT} = e^{-h\nu/2kT} \sum_v e^{-vh\nu/kT}$$

$$f_{\text{vib}} = e^{-h\nu/2kT}(1 - e^{-h\nu/kT})^{-1} \tag{12.35}$$

The total vibrational partition function is the product of terms such as eq. (12.35), one for each of the normal modes of vibration of the molecule,

$$f_{\text{vib}} = \prod_i f_{i,\text{vib}} \tag{12.36}$$

For the purposes of tabulation and facility in calculations, the vibrational contributions can be put into more convenient forms.

The vibrational energy, from eqs. (12.15), (12.23), and (12.35), is

$$E = RT^2 \frac{\partial \ln f}{\partial T} = N\frac{h\nu}{2} + \frac{Nh\nu\, e^{-h\nu/kT}}{1 - e^{-h\nu/kT}}$$

Now $Nh\nu/2$ is the zero point energy per mole E_0, whence, writing $h\nu/kT = x$,

$$\frac{E - E_0}{T} = \frac{Rx\,e^{-x}}{1 - e^{-x}} \tag{12.37}$$

Then the heat capacity

$$\left(\frac{\partial E}{\partial T}\right)_V = C_{V_{\text{vib}}} = \frac{Rx^2}{2(\cosh x - 1)} \tag{12.38}$$

From eq. (12.20), since for the vibrational contribution[8] $A = F$,

$$\frac{F - E_0}{T} = R \ln (1 - e^{-x}) \tag{12.39}$$

Finally the contribution to the entropy is

$$S = \frac{E - E_0}{T} - \frac{F - E_0}{T} \tag{12.40}$$

An excellent tabulation of these functions has been given by J. G. Aston.[9] A much less complete set of values is given in Table 12.2. If the vibration

TABLE 12.2

THERMODYNAMIC FUNCTIONS OF A HARMONIC OSCILLATOR

$x = \frac{h\nu}{kT}$	C_V	$\frac{(E - E_0)}{T}$	$\frac{-(F - E_0)}{T}$	$x = \frac{h\nu}{kT}$	C_V	$\frac{(E - E_0)}{T}$	$\frac{-(F - E_0)}{T}$
0.10	1.985	1.891	4.674	1.70	1.571	0.7551	0.4008
0.15	1.983	1.842	3.917	1.80	1.528	0.7070	0.3591
0.20	1.981	1.795	3.394	1.90	1.484	0.6640	0.3219
0.25	1.977	1.749	2.999	2.00	1.439	0.6221	0.2889
0.30	1.972	1.704	2.683	2.20	1.348	0.5448	0.2333
0.35	1.967	1.660	2.424	2.40	1.256	0.4758	0.1890
0.40	1.961	1.616	2.206	2.60	1.164	0.4145	0.1534
0.45	1.954	1.574	2.017	2.80	1.074	0.3603	0.1246
0.50	1.946	1.532	1.853	3.00	0.9860	0.3124	0.1015
0.60	1.929	1.450	1.581	3.50	0.7815	0.2166	0.0610
0.70	1.908	1.372	1.364	4.00	0.6042	0.1483	0.0367
0.80	1.884	1.297	1.186	4.50	0.4571	0.1005	0.0223
0.90	1.858	1.225	1.037	5.00	0.3393	0.0674	0.0133
1.00	1.830	1.157	0.9120	5.50	0.2477	0.0449	0.0081
1.10	1.798	1.091	0.8044	6.00	0.1782	0.0296	0.0050
1.20	1.765	1.028	0.7128	6.50	0.1266	0.0195	0.0030
1.30	1.729	0.9678	0.6321	7.00	0.0890	0.0127	0.0018
1.40	1.692	0.9106	0.5628	8.00	0.0427	0.0053	0.0006
1.50	1.653	0.8561	0.5016	9.00	0.0199	0.0022	0.0004
1.60	1.612	0.8043	0.4481	10.00	0.0090	0.0009	0.0001

---

[8] This is evident from eq. (12.21) since f_{vib} is not a function of V, $P = 0$, $F = A + PV = A$.

[9] H. S. Taylor and S. Glasstone, *Treatise on Physical Chemistry*, 3rd ed., vol. 1, p. 655 (New York: Van Nostrand, 1942).

frequency is obtainable from spectroscopic observations, these tables can be used to calculate the vibrational contributions to the energy, entropy, free energy, and heat capacity.

12. Equilibrium constant for ideal gas reactions. From the relation $-\Delta F^\circ = RT \ln K_p$, the equilibrium constant can be calculated in terms of the partition functions. From eqs. (12.20) and (12.23), $A = -kT \ln Z = -kT \ln (f^N/N!)$. From the Stirling formula, $N! = (N/e)^N$, and since for an ideal gas, $F = A + PV = A + RT$, we find that $F = -RT \ln (f/N)$. Let us write

$$f = f_{\text{int}} \frac{(2\pi mkT)^{3/2} V}{h^3} = f'V$$

where f_{int} denotes the internal partition functions, $f_{\text{rot}}\, f_{\text{vib}}\, f_{\text{elec}}$, and f' is the partition function per unit volume; *i.e.*, f/V. Then, the free energy $F = -RT \ln (f'V/N)$.

The standard free energy F° is the F at unit pressure of one atmosphere. The volume of a mole of ideal gas under standard conditions of 1 atm pressure is $V = RT/1$. The standard free energy is accordingly[10]

$$F^\circ = -RT \ln f'kT$$

For a typical reaction $aA + bB \rightleftarrows cC + dD$,

$$\Delta F^\circ = -RT \ln \frac{f'^{\,c}_{C} f'^{\,d}_{D}}{f'^{\,a}_{A} f'^{\,b}_{B}} (kT)^{c+d-a-b}$$

Therefore, $$K_p = \frac{f'^{\,c}_{C} f'^{\,d}_{D}}{f'^{\,a}_{A} f'^{\,b}_{B}} (kT)^{\Delta n}$$

From eq. (4.12), $$K_p = K_c (RT)^{\Delta n}$$

If the concentration terms in K_c are expressed in units of molecules per cc rather than the more usual moles per cc, we obtain the more concise expression,

$$K_c{}' = \frac{f'^{\,c}_{C} f'^{\,d}_{D}}{f'^{\,a}_{A} f'^{\,b}_{B}} \tag{12.41}$$

This equation can easily be given a simple physical interpretation. Consider a reaction $A \rightarrow B$, then $K_c{}' = f_B{}'/f_A{}'$. The partition function is the sum of the probabilities $e^{-\epsilon/kT}$ of all the different possible states of the molecules ($f = \Sigma\, e^{-\epsilon/kT}$). The equilibrium constant is therefore the ratio of the total probability of the occurrence of the final state to the total probability of the occurrence of the initial state.

13. The heat capacity of gases. The statistical theory that has now been outlined provides a very satisfactory interpretation of the temperature dependence of the heat capacity of gases.

The translational energy is effectively nonquantized. It makes a constant contribution $C_V = \frac{3}{2}R$, for all types of molecules.

---

[10] Note that k is in units of cc atm/°C.

Except in the molecules H_2, HD, and D_2, the rotational energy quanta are small comparėd to kT at temperatures greater than about 80°K. There is therefore a constant rotational contribution of $C_{r} = R$ for diatomic and linear polyatomic molecules or $C_{r} = \frac{3}{2}R$ for nonlinear polyatomic molecules. For example, with nitrogen at 0°C, $\Delta\epsilon_{rot} = 8 \times 10^{-16}$ erg compared to $kT = 377 \times 10^{-16}$ erg. At temperatures below 80°K the rotational heat capacity can be calculated from the partition function in eq. (12.30) and the general formula, eq. (12.16).

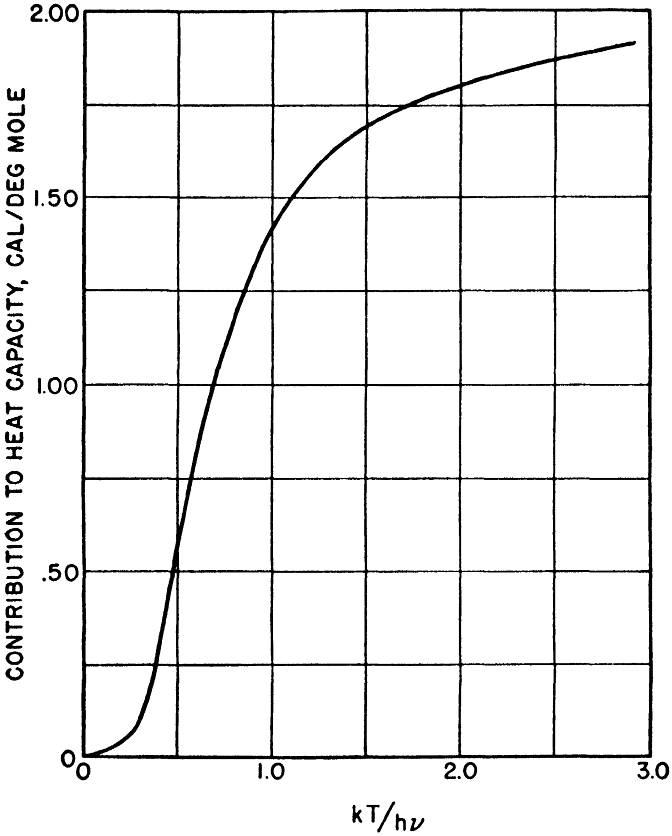


Fig. 12.1. Heat capacity contribution of a harmonic oscillator.

The magnitude of the quantum of vibrational energy $h\nu$ is usually quite large compared to kT at room temperatures. For example, the fundamental vibration frequency in N_2 is 2360 cm^{-1}, corresponding to ϵ_{vib} of 46.7×10^{-14} erg, whereas at 0°C kT 3.77×10^{-14}. Such values are quite usual and the vibrations therefore make relatively small contributions to low-temperature energies, entropies, and specific heats. The data in Table 7.6 (page 192) confirm this conclusion. In Fig. 12.1, the heat-capacity curve for a typical harmonic oscillator is shown as a function of T/θ_v, where $\theta_v = h\nu/k$ is called the *characteristic temperature of the vibration*. As the temperature is raised, vibrational excitation becomes more and more appreciable. If we know the fundamental vibration frequencies of a molecule, we can determine from Fig. 12.1 or Table 12.2 the corresponding contribution to C_V at any temperature. The sum of these contributions is the total vibrational heat capacity.

14. The electronic partition function. The electronic term in the partition function is calculated directly from eq. (12.12) and the observed spectroscopic data for the energy levels. Often the smallest quantum of electronic energy is so large compared to kT that at moderate temperatures the electronic energy acquired by the gas is negligible. In other cases, the ground state may be a multiplet, but have energy differences so slight that it may be considered simply as a degenerate single level.

There are, however, certain intermediate cases in which the multiplet splitting is of the order of kT at moderate temperatures. A notable example is NO, with a doublet splitting of around 120 cm^{-1} or 2.38×10^{-14} erg. An electronic contribution to the heat capacity is well marked in NO. Complications arise in these cases, however, owing to an interaction between the rotational angular momentum of the nuclei (quantum number J) and the electronic angular momentum (quantum number λ). The detailed analysis is therefore more involved than a simple separation of the internal energy into vibrational, rotational, and electronic contributions would indicate.[11]

15. Internal rotation. When certain polyatomic molecules are studied, it is found that the strict separation of the internal degrees of freedom into vibration and rotation is not valid. Let us compare, for example, ethylene and ethane, $CH_2{=}CH_2$ and $CH_3{-}CH_3$.

The orientation of the two methylene groups in C_2H_4 is fixed by the double bond, so that there is a torsional or twisting vibration about the bond but no complete rotation. In ethane, however, there is an *internal rotation* of the methyl groups about the single bond. Thus one of the vibrational degrees of freedom is lost, becoming an internal rotation. This rotation would not be difficult to treat if it were completely free and unrestricted, but such is not the case. There are potential-energy barriers, amounting to about 3000 calories per mole, which must be overcome before rotation occurs. The maxima in energy occur at positions where the hydrogen atoms on the two methyl groups are directly opposite to one another, the minima at positions where the hydrogens are "staggered."

The theoretical treatment of the problems of restricted internal rotation is still incomplete, but good progress is being made.[12]

16. The hydrogen molecules. Since the moment of inertia of the hydrogen molecule, H_2, is only 0.47×10^{-40} g cm^2, the quantum of rotational energy

---

[11] Fowler and Guggenheim, *op. cit.*, p. 102.

[12] J. G. Aston, *loc. cit.*, p. 590.

is too large for a classical treatment. To evaluate the partition function, the complete summation must be carried out. When this was first done, using eq. (12.30), modified with a symmetry number $\sigma = 2$, the calculated specific heats were in poor agreement with the experimental values. It was later realized that the discrepancy must be a result of the existence of the two nuclear-spin isomers for H_2.

The proton (nucleus of the H atom) has a nuclear spin $i = \frac{1}{2}$ in units of $h/2\pi$. The spins of the two protons in the H_2 molecule may either parallel or oppose each other. These two spin orientations give rise to the two spin isomers:

ortho H_2	spins parallel	resultant spin $= 1$
para H_2	spins antiparallel	resultant spin $= 0$

Spontaneous transitions between the *ortho* and *para* states are strictly prohibited. The *ortho* states are associated with only odd rotational levels ($J = 1, 3, 5 \ldots$), and *para* states have only even rotational levels ($J = 0, 2, 4 \ldots$). The nuclear-spin weights are $g_{NS} = 3$ for *ortho*, corresponding to allowed directions $+1, 0, -1$, and $g_{NS} = 1$ for *para*, whose resultant spin[13] is 0. At quite high temperatures ($\sim 0°C$), therefore, an equilibrium mixture of hydrogen consists of three parts *ortho* and one part *para*. At quite low temperatures (around 80°K, liquid-air temperature) the equilibrium condition is almost pure *para* hydrogen, with the molecules in the lowest rotational state, $J = 0$.

The equilibrium is attained very slowly in the absence of a suitable catalyst, such as oxygen adsorbed on charcoal, or other paramagnetic substance. It is thus possible to prepare almost pure p-H_2 by adsorbing hydrogen on oxygenated charcoal at liquid-air temperatures, and then warming the gas in the absence of catalyst.

The calculated heat capacities of pure p-H_2, pure o-H_2 and of the 1 : 3 normal H_2, are plotted in Fig. 12.2. Mixtures of o- and p-H_2 are conveniently analyzed by measuring their thermal conductivities, since these are proportional to their heat capacities.

A similar situation arises with deuterium, D_2. The nuclear spin of the D atom is 1. The possible resultant values for D_2 are therefore 0, 1, and 2. Of these, $i = 0$ and 2 belong to the *ortho* modification and $i = 1$ is the *para*. The weights $(2i + 1)$ are $1 + 5 = 6$, and 3, respectively. The high-temperature equilibrium mixture therefore contains two parts *ortho* to one part *para*.

In the molecule HD, which is not homonuclear, there are no restrictions on the allowed rotational energy levels. The partition function of eq. (12.30) is directly applicable.

Other diatomic molecules composed of like nuclei with nonzero nuclear spins may also be expected to exist in both *para* and *ortho* modifications.

---

[13] Compare the spatial quantization of the orbital angular momentum of an electron, page 268.

Any thermodynamic evidence for such isomers would be confined to extremely low temperatures, because their rotational energy quanta are small. The energy levels are so close together that in calculating heat capacities it is unimportant whether all odds or all evens are taken. It is necessary only to divide the total number of levels by $\sigma = 2$. Spectroscopic observations, however, will often reveal an alternating intensity in rotational lines caused by the different nuclear-spin statistical weights.

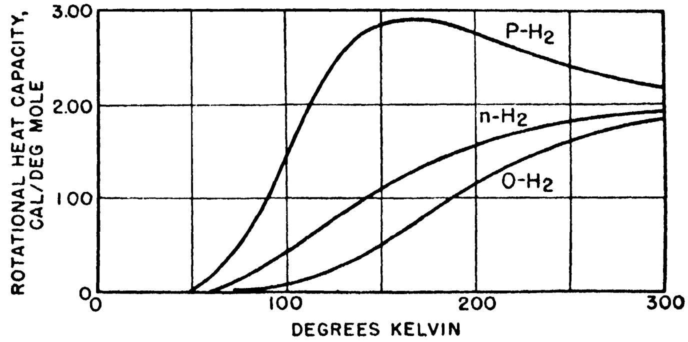


Fig. 12.2. Heat capacities of pure para-hydrogen, pure ortho-hydrogen, and 3-*o* to 1-*p* normal hydrogen.

17. Quantum statistics. In deriving the Boltzmann statistics, we assumed that the individual particles were distinguishable and that any number of particles could be assigned to one energy level. We know from quantum mechanics that the first of these assumptions is invalid. The second assumption is also incorrect if one is dealing with elementary particles or particles composed of an odd number of elementary particles. In such cases, the Pauli Exclusion Principle requires that no more than one particle can go into each energy level. If the particles considered are composed of an even number of elementary particles, any number can be accommodated in a single energy level.

Two different quantum statistics therefore arise, which are characterized as follows:

Name	*Obeyed by*	*Restrictions on n_K*
(1) Fermi-Dirac	Odd number of elementary particles (*e.g.*, electrons, protons)	Only one particle per state, $n_K \leq g_K$
(2) Bose-Einstein	Even number of elementary particles (*e.g.*, deuterons, photons)	Any number of particles per state

It is interesting to note that photons follow the Bose-Einstein statistics, indicating that they are complex particles and recalling the formation of electron-positron pairs from X-ray photons.

A schematic illustration of the two types of distribution would be

Distribution laws are calculated for these two cases by exactly the same sort of procedure as was used for the Boltzmann statistics.[14] The results are found to be very similar,

$$n_K = \frac{g_K}{e^{\alpha+\beta\epsilon_K} \pm 1} \tag{12.42}$$

F.D. case +

B.E. case −

Now in almost every case the exponential term is very large compared to unity, and the Boltzmann statistics are a perfectly good approximation for almost all practical systems. This can be seen by using the value of $e^\alpha = f/n$ from eq. (12.10). The condition for the Boltzmann approximation is then

$$e^\alpha e^{\beta\epsilon_K} \gg 1, \qquad \text{or} \qquad \frac{e^{\epsilon/kT} f}{n} \gg 1$$

Using the translational partition function f in eq. (12.27), we have

$$\frac{e^{\epsilon/kT}(2\pi mkT)^{3/2}V}{nh^3} \gg 1 \tag{12.43}$$

This condition is obviously realized for a gas at room temperature. It is interesting to note, however, the circumstances under which it would fail. If n/V, proportional to the density, became very high, the classical statistics would eventually become inapplicable. This is the situation in the interior of the stars, and forms the basis of R. H. Fowler's brilliant contribution to astrophysics. A more mundane case also arises, namely in the electron gas in metals. We shall consider this in the next chapter, with only a brief mention here. A metallic crystal, to a first approximation, may be considered as a regular array of positive ions, permeated by a gas of mobile electrons. In this case the density term in eq. (12.43) is exceptionally high and in addition the mass term m is lower by about 2×10^3 than in any molecular case. Thus the electron gas will not obey Boltzmann statistics; it must indeed follow the Fermi-Dirac statistics since electrons obey the Pauli Principle.

PROBLEMS

1. In the far infrared spectrum of HCl, there is a series of lines with a spacing of 20.7 cm^{-1}. In the near infrared spectrum, there is an intense band at 3.46 microns. Use these data to calculate the entropy of HCl as an ideal gas at 1 atm and 298°K.

---

[14] For these calculations, see, for example, Tolman, *op. cit.*, p. 388.

2. Estimate the equilibrium constant of the reaction $Cl_2 = 2\,Cl$ at 1000°K. The fundamental vibration frequency of Cl_2 is 565 cm^{-1} and the equilibrium Cl–Cl distance is 1.99 Å. Compare with the experimental value in Table 4.5.

3. The isotopic composition of zinc is: ^{64}Zn 50.9 per cent; ^{66}Zn 27.3 per cent; ^{67}Zn 3.9 per cent; ^{68}Zn 17.4 per cent; ^{70}Zn 0.5 per cent. Calculate the entropy of mixing per mole of zinc at 0°K.

4. Thallium forms a monatomic vapor. The normal electronic state of the atom is $^2P_{1/2}$ but there is a $^2P_{3/2}$ state lying only 0.96 ev. above the ground state. The statistical weights of the states are 2 and 4, respectively. Plot a curve showing the variation with temperature of the contribution to the specific heat of the vapor caused by the electronic excitation.

5. In a star whose temperature is 10^6 °K, calculate the density of material at which the classical statistics would begin to fail.

6. Calculate the equilibrium constant of the reaction $H_2 + D_2 = 2\,HD$ at 300°K given:

	H_2	HD	D_2
ω_e, cm^{-1}	4371	3786	3092
Reduced mass, μ, at. wt. units . .	0.5038	0.6715	1.0065
Moment of inertia, I, g $cm^2 \times 10^{40}$.	0.458	0.613	0.919

7. In Problem 4.10, heat-capacity data were listed for a calculation of the Third-Law entropy of nitromethane. From the following molecular data, calculate the statistical entropy S°_{298}. Bond distances (Å): N—O 1.21; C—N, 1.46; C—H, 1.09. Bond angles: O—N—O 127°; H—C—N 109½°. From these distances, calculate the principal moments of inertia, $I = 67.2$, 76.0, 137.9×10^{-40} g cm^2. The fundamental vibration frequencies[15] in cm^{-1} are: 476, 599, 647, 921, 1097, 1153, 1384, 1413, 1449, 1488, 1582, 2905, 3048 (2). One of the torsional vibrations has become a free rotation around the C—N bond with $I = 4.86 \times 10^{-40}$.

8. Calculate the equilibrium constant K_p at 25°C for $O_2{}^{18} + O_2{}^{16} = 2\,O^{16}O^{18}$. The nuclear spins of O^{18} and O^{16} are both zero. The vibration frequencies are given by $\nu = (1/2\pi)(\kappa/\mu)^{1/2}$, where κ is the same for all three molecules. For $O_2{}^{16}$, $\nu = 4.741 \times 10^{13}\ sec^{-1}$. The equilibrium internuclear distance, 1.2074 Å, does not depend on the isotopic species.

9. The ionization potential of Na is 5.14 ev. Calculate the degree of dissociation, $Na = Na^+ + e$, at 10^4 °K and 1 atm.

---

[15] A. J. Wells and E. B. Wilson, *J. Chem. Phys.*, *9*, 314 (1941).

REFERENCES

BOOKS

1. Born, M., *Natural Philosophy of Cause and Chance* (New York: Oxford, 1949).
2. Dole, M., *Introduction to Statistical Thermodynamics* (New York: Prentice-Hall, 1954).
3. Gurney, R. W., *Introduction to Statistical Mechanics* (New York: McGraw-Hill, 1949).
4. Khinchin, A. I., *Statistical Mechanics* (New York: Dover, 1949).
5. Lindsay, R. B., *Physical Statistics* (New York: Wiley, 1941).
6. Rushbrooke, G. S., *Introduction to Statistical Mechanics* (New York: Oxford, 1949).
7. Schrödinger, E., *Statistical Thermodynamics* (Cambridge, 1946).
8. Ter Haar, D., *Elements of Statistical Mechanics* (New York: Rinehart, 1954).

ARTICLES

1. Bacon, R. H., *Am. J. Phys.*, *14*, 84–98 (1946), "Practical Statistics for Practical Physicists."
2. Eyring, H., and J. Walter, *J. Chem. Ed.*, *18*, 73–78 (1941), "Elementary Formulation of Statistical Mechanics."

CHAPTER 13

Crystals

1. The growth and form of crystals. The symmetry of crystalline forms, striking a responsive chord in our aesthetic nature, has fascinated many men, from the lapidary polishing gems for a royal crown to the natural philosopher studying the structure of matter. Someone once said that the beauty of crystals lies in the planeness of their faces. It was also the measurement and explanation of these plane faces that first demanded scientific attention.

In 1669, Niels Stensen (Steno), Professor of Anatomy at Copenhagen and Vicar Apostolic of the North, compared the interfacial angles in various specimens of quartz rock crystals. An interfacial angle may be defined as the angle between lines drawn perpendicular to two faces. Steno found that the corresponding angles (in different crystals) were always equal. After the invention of the contact goniometer in 1780, this conclusion was checked and extended to other substances, and the constancy of interfacial angles has been called the "first law of crystallography."

It was a most important principle, for out of a great number of crystalline properties it isolated one that was constant and unchanging. Different crystals of the same substance may differ greatly in appearance, since corresponding faces may have developed to diverse extents as the crystals were growing. The interfacial angles, nevertheless, remain the same.

We can consider that a crystal grows from solution or melt by the deposition onto its faces of molecules or ions from the liquid. If molecules are deposited preferentially on a certain face, this face will not extend rapidly in area, compared with faces at angles to it on which deposition is less frequent. The faces with the largest area are therefore those on which added molecules are deposited most slowly.

Sometimes an altered rate of deposition can completely change the form, or *habit*, of a crystal. A well known case is sodium chloride, which grows from pure water solution as cubes, but from 15 per cent aqueous urea solution as octahedra. It is believed that urea is preferentially adsorbed on the octahedral faces, preventing deposition of sodium and chloride ions, and therefore causing these faces to develop rapidly in area.

The real foundations of crystallography may be said to date from the work of the Abbé Réné Just Haüy, Professor of the Humanities at the University of Paris. In 1784, he proposed that the regular external form of crystals was a reflection of an inner regularity in the arrangement of their constituent building units. These units were believed to be little cubes or polyhedra, which he called the *molécules intégrantes* of the substance This picture also helped to explain the *cleavage* of crystals along uniform planes. The Haüy model was essentially confirmed, 128 years later, by the work of Max von Laue with X-ray diffraction, the only difference being in a more advanced knowledge of the elementary building blocks.

2. The crystal systems. The faces of crystals, and also planes within crystals, can be characterized by means of a set of three noncoplanar axes. Consider in Fig. 13.1 three axes having lengths a, b, and c, which are cut by the plane ABC, making intercepts OA, OB, and OC. If a, b, c, are chosen as unit lengths, the lengths of the intercepts may be expressed as OA/a, OB/b, OC/c. The reciprocals of these lengths will then be a/OA, b/OB, c/OC. Now it has been established that it is always possible to find a set of axes on which the reciprocal intercepts of crystal faces are small whole numbers. Thus, if h, k, l are small integers:

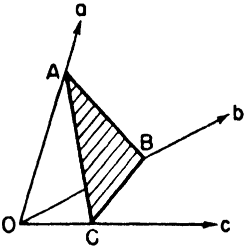


Fig. 13.1. Crystal axes.

$$\frac{a}{OA} = h, \quad \frac{b}{OB} = k, \quad \frac{c}{OC} = l$$

This is equivalent to the *law of rational intercepts*, first enunciated by Haüy. The use of the reciprocal intercepts (hkl) as indices defining the crystal faces was first proposed by W. H. Miller in 1839. If a face is parallel to an axis, the intercept is at ∞, and the Miller index becomes $1/\infty$ or 0. The notation is also applicable to planes drawn within the crystal. As an illustration of the Miller indices, some of the planes in a cubic crystal are shown in Fig. 13.2.

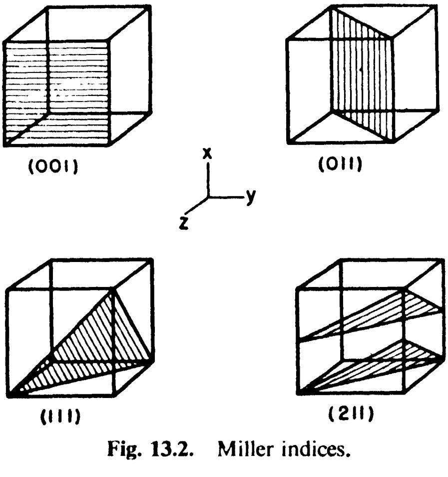


Fig. 13.2. Miller indices.

According to the set of axes used to represent their faces, crystals may be divided into seven systems. These are summarized in Table 13.1. They range from the completely general set of three unequal axes (a, b, c) at three unequal angles (α, β, γ) of the triclinic system, to the highly symmetrical set of three equal axes at right angles of the cubic system.

TABLE 13.1

THE SEVEN CRYSTAL SYSTEMS

System	Axes	Angles	Example
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Rock salt
Tetragonal	$a = b; c$	$\alpha = \beta = \gamma = 90^\circ$	White tin
Orthorhombic	$a; b; c$	$\alpha = \beta = \gamma = 90^\circ$	Rhombic sulfur
Monoclinic	$a; b; c$	$\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$	Monoclinic sulfur
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite
Hexagonal	$a = b; c$	$\alpha = \beta = 90^\circ; \gamma = 120^\circ$	Graphite
Triclinic	$a; b; c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	Potassium dichromate

3. Lattices and crystal structures. Instead of considering, as Haüy did, that a crystal is made of elementary material units, it is helpful to introduce a geometrical idealization, consisting only of a regular array of points in space, called a *lattice*. An example in two dimensions is shown in Fig. 13.3.

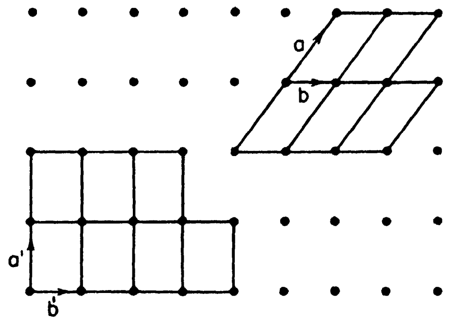


Fig. 13.3. Two-dimensional lattice with unit cells.

The lattice points can be connected by a regular network of lines in various ways. Thus the lattice is broken up into a number of *unit cells*. Some examples are shown in the figure. Each cell requires two vectors, a and b, for its description. A three-dimensional *space lattice* can be similarly divided into unit cells that require three vectors for their description.

If each point in a space lattice is replaced by an identical atom or group of atoms there is obtained a *crystal structure*. The lattice is an array of points; in the crystal structure each point is replaced by a material unit.

In 1848, A. Bravais showed that all possible space lattices could be assigned to one of only 14 classes.[1] The 14 Bravais lattices are shown in Fig. 13.4. They give the allowed different translational relations between points in an infinitely extended regular three-dimensional array. The choice of the 14 lattices is somewhat arbitrary, since in certain cases alternative descriptions are possible.

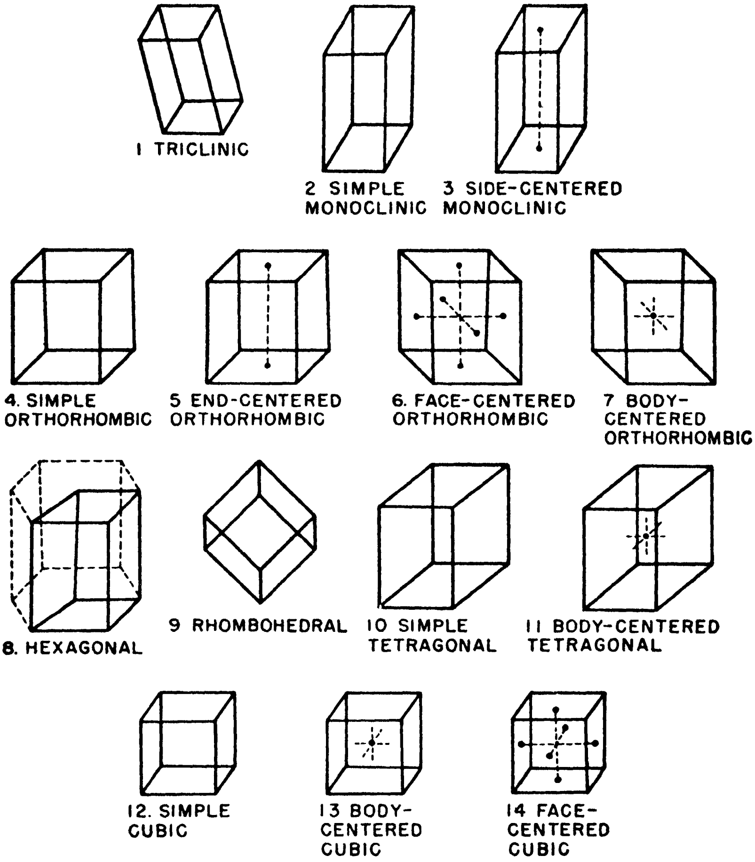


Fig. 13.4. The fourteen Bravais lattices.

4. Symmetry properties. The word "symmetry" has been used in referring to the arrangement of crystal faces. It is now desirable to consider the nature of this symmetry in more detail. If an actual crystal of a substance is studied, some of the faces may be so poorly developed that it is difficult or impossible to see its full symmetry just by looking at it. It is necessary therefore to

[1] A lattice that contains body-, face-, or end-centered points can always be reduced to one that does not (primitive lattice). Thus the face-centered cubic can be reduced to a primitive rhombohedral. The centered lattices are chosen when possible because of their higher symmetry.

consider an ideal crystal in which all the faces of the same kind are developed to the same extent. It is not only in face development that the symmetry of the crystal is evident but also in all of its physical properties, *e.g.*, electric and thermal conductivity, piezoelectric effect, and refractive index.

Symmetry is described in terms of certain *symmetry operations*, which are those that transform the crystal into an image of itself. The symmetry operations are imagined to be the result of certain *symmetry elements*: axes of rotation, mirror planes, and centers of inversion. The possible symmetry elements of finite figures, *i.e.*, actual crystals, are shown in Fig. 13.5 with schematic illustrations.

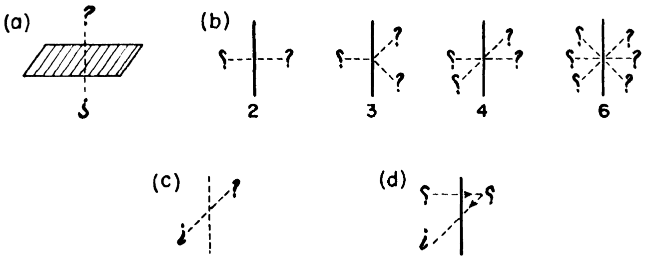


Fig. 13.5. Examples of symmetry elements: (a) mirror plane *m*; (b) rotation axes; (c) symmetry center $\bar{1}$; (d) twofold rotary inversion axis $\bar{2}$.

The possible combinations of these symmetry elements that can occur in crystals have been shown to number exactly 32. These define the 32 *crystallographic point groups*,[2] which determine the 32 *crystal classes*.

The symbols devised by Hermann and Mauguin are used to represent the symmetry elements. An axis of symmetry is denoted by a number equal to its multiplicity. The combination of a rotation about an axis with reflection through a center of symmetry is called an "axis of rotary inversion"; it is denoted by placing a bar above the symbol for the axis, *e.g.*, $\bar{2}$, $\bar{4}$. The center of symmetry alone is then $\bar{1}$. A mirror plane is given the symbol *m*.

All crystals necessarily fall into one of the *seven systems*, but there are several *classes* in each system. Only one of these, called the *holohedral* class, possesses the complete symmetry of the system. For example, consider two crystals belonging to the cubic system, rock salt (NaCl) and iron pyrites (FeS_2). Crystalline rock salt, Fig. 13.6, possesses the full symmetry of the cube: three 4-fold axes, four 3-fold axes, six 2-fold axes, three mirror planes perpendicular to the 4-fold axes, six mirror planes perpendicular to the 2-fold axes, and a center of inversion. The cubic crystals of pyrites might at first seem to possess all these symmetry elements too. Closer examination reveals,

---

[2] A set of symmetry operations forms a *group* when the consecutive application of any two operations in the set is equivalent to an operation belonging to the set (law of multiplication). It is understood that the identity operation, leaving the crystal unchanged, is included in each set; that the operations are reversible; and that the associative law holds, $A(BC) = (AB)C$.

however, that the pyrites crystals have characteristic striations on their faces, as shown in the picture, so that all the faces are not equivalent. These crystals therefore do not possess the six 2-fold axes with the six planes normal to them, and the 4-fold axes have been reduced to 2-fold axes.

In other cases, such departures from full symmetry are only revealed, as far as external appearance goes, by the orientation of etch figures formed by treating the surfaces with acids. Sometimes the phenomenon of pyroelectricity provides a useful symmetry test. When a crystal that contains no center of symmetry is heated, a difference in potential is developed across its faces. This can be observed by the resultant electrostatic attraction between individual crystals.

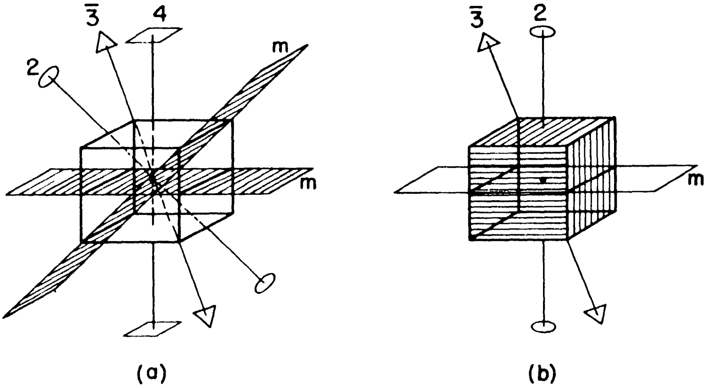


Fig. 13.6. (a) Rock salt. (b) Pyrites.

All these differences in symmetry are caused by the fact that the full symmetry of the point lattice has been modified in the crystal structure, as a result of replacing the geometrical points by groups of atoms. Since these groups need not have so high a symmetry as the original lattice, classes of lower than holohedral symmetry can arise within each system.

5. Space groups. The crystal classes are the various groups of symmetry operations of finite figures, *i.e.*, actual crystals. They are made up of operations by symmetry elements that leave at least one point in the crystal invariant. This is why they are called point groups.

In a crystal structure, considered as an infinitely extended pattern in space, new types of symmetry operation are admissible, which leave no point invariant. These are called space operations. The new symmetry operations involve *translations* in addition to rotations and reflections. Clearly only an infinitely extended pattern can have a space operation (translation) as a symmetry operation.

The possible groups of symmetry operations of infinite figures are called *space groups*. They may be considered to arise from combinations of the

14 Bravais lattices with the 32 point groups.[3] A space group may be visualized as a sort of crystallographic kaleidoscope. If one structural unit is introduced into the unit cell, the operations of the space group immediately generate the entire crystal structure, just as the mirrors of the kaleidoscope produce a symmetrical pattern from a few bits of colored paper.

The space group expresses the sum total of the symmetry properties of a crystal structure, and mere external form or bulk properties do not suffice for its determination. The inner structure of the crystal must be studied and this is made possible by the methods of X-ray diffraction.

6. X-ray crystallography. At the University of Munich in 1912, there was gathered a group of physicists interested in both crystallography and the behavior of X rays. P. P. Ewald and A. Sommerfeld were studying the passage of light waves through crystals. At a colloquium discussing some of this work, Max von Laue pointed out that if the wavelength of the radiation became as small as the distance between atoms in the crystals, a diffraction pattern should result. There was some evidence that X rays should have the right wavelength, and W. Friedrich agreed to make the experimental test.

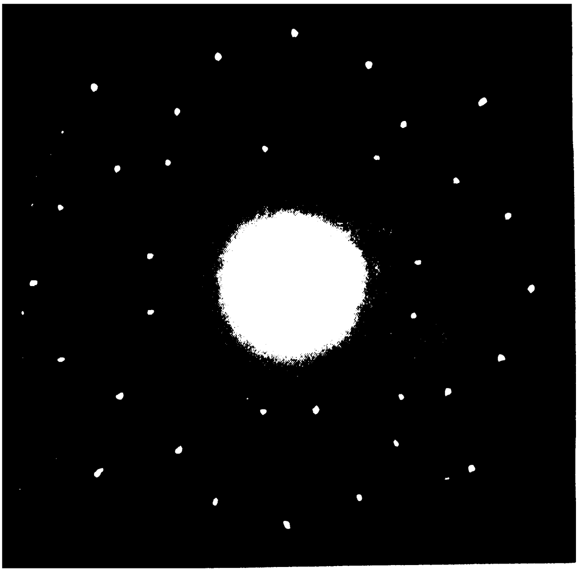


Fig. 13.7. A Laue photograph taken with X-rays. (From Lapp and Andrews, *Nuclear Radiation Physics*, 2nd Ed., Prentice-Hall, 1953.)

On passing an X-ray beam through a crystal of copper sulfate, there was obtained a diffraction pattern like that in Fig. 13.7, though not nearly so

---

[3] A good example of the construction of space groups is given by Sir Lawrence Bragg, *The Crystalline State* (London: G. Bell & Sons, 1933), p. 82. The space-group notation is described in *International Tables for the Determination of Crystal Structures*, Vol. I. There are exactly 230 possible crystallographic space groups.

distinct in these first trials. The wave properties of X rays were thus definitely established and the new science of X-ray crystallography began.

Some of the consequences of Laue's great discovery have already been mentioned, and on page 257 the conditions for diffraction maxima from a regular three-dimensional array of scattering centers were found to be

$$\begin{aligned}\cos(\alpha - \alpha_0) &= h\lambda \\ \cos(\beta - \beta_0) &= k\lambda \\ \cos(\gamma - \gamma_0) &= l\lambda\end{aligned} \qquad (13.1)$$

If monochromatic X rays are used, there is only a slim chance that the orientation of the crystal is fixed in such a way as to yield diffraction maxima. The Laue method, however, uses a continuous spectrum of X radiation with a wide range of wavelengths. This is the so-called *white radiation*, conveniently obtained from a tungsten target at high voltages. In this case, at least some of the radiation is at the proper wavelength to experience interference effects, no matter what the orientation of crystal to beam.

7. The Bragg treatment. When the news of the Munich work reached England, it was immediately taken up by W. H. Bragg and his son W. L. Bragg who had been working on a corpuscular theory of X rays. W. L. Bragg, using Laue-type photographs, analyzed the structures of NaCl, KCl, and ZnS (1912, 1913). In the meantime (1913), the elder Bragg devised a spectrometer that measured the intensity of an X-ray beam by the amount of ionization it produced, and he found that the characteristic X-ray line spectrum could be isolated and used for crystallographic work. Thus the Bragg method uses a monochromatic (single wavelength) beam of X rays.

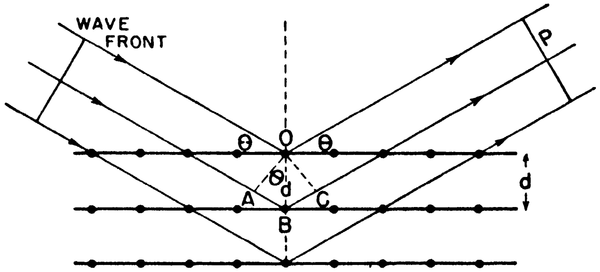


Fig. 13.8. Bragg scattering condition.

The Braggs developed a treatment of X-ray scattering by a crystal that was much easier to apply than Laue's theory, although the two are essentially equivalent. It was shown that the scattering of X rays could be represented as a "reflection" by successive planes of atoms in the crystal. Consider, in Fig. 13.8, a set of parallel planes in the crystal structure and a beam of X rays incident at an angle θ. Some of the rays will be "reflected" from the upper layer of atoms, the angle of reflection being equal to the angle of incidence. Some of the rays will be absorbed, and some will be "reflected" from the second layer, and so on with successive layers. All the waves "reflected" by a single crystal plane will be in phase. Only under certain strict conditions will the waves "reflected" by different underlying planes be in phase with one another. The condition is that the path difference between the waves scattered from successive planes must be an integral number of wavelengths, $n\lambda$. If we consider the "reflected" waves at the point P, this path distance for the first two planes is $\delta = \overline{AB} + \overline{BC}$. Since triangles AOB and COB are congruent, $\overline{AB} = \overline{BC}$ and $\delta = 2\,\overline{AB}$. Therefore $\delta = 2d \sin \theta$. The condition for reinforcement or Bragg "reflection" is thus

$$n\lambda = 2d \sin \theta \tag{13.2}$$

According to this viewpoint, there are different *orders* of "reflection" specified by the values $n = 1, 2, 3 \ldots$ The second order diffraction maxima from (100) planes may then be regarded as a "reflection" due to a set of planes (200) with half the spacing of the (100) planes.

The Bragg equation indicates that for any given wavelength of X rays there is a lower limit to the spacings that can give observable diffraction spectra. Since the maximum value of sin θ is 1, this limit is given by

$$d = \frac{n\lambda}{2 \sin \theta_{\max}} = \frac{\lambda}{2}$$

8. The structures of NaCl and KCl. Among the first crystals to be studied by the Bragg method were sodium and potassium chlorides. A single crystal was mounted on the spectrometer, as shown in Fig. 13.9, so that the X-ray beam was incident on one of the important crystal faces, (100), (110), or (111). The apparatus was so arranged that the "reflected" beam entered the ionization chamber, which was filled with methyl bromide. Its intensity was measured by the charge built up on an electrometer.

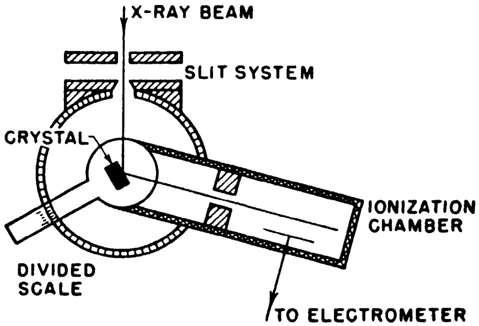


Fig. 13.9. Bragg X-ray spectrometer.

The experimental data are shown plotted in Fig. 13.10 as "intensity of scattered beam" vs. "twice the angle of incidence of beam to crystal." As the crystal is rotated, successive maxima "flash out" as the angles are passed conforming to the Bragg condition, eq. (13.2). In these first experiments the monochromatic X radiation was obtained from a palladium target. Both the wavelength of the X rays and the structure of the crystals were unknown to begin with.

It was known, of course, from external form, that both NaCl and KCl could be based on a cubic lattice, simple, body-centered, or face-centered. By comparing the spacings calculated from X-ray data with those expected for these lattices, a decision could be made as to the proper assignment.

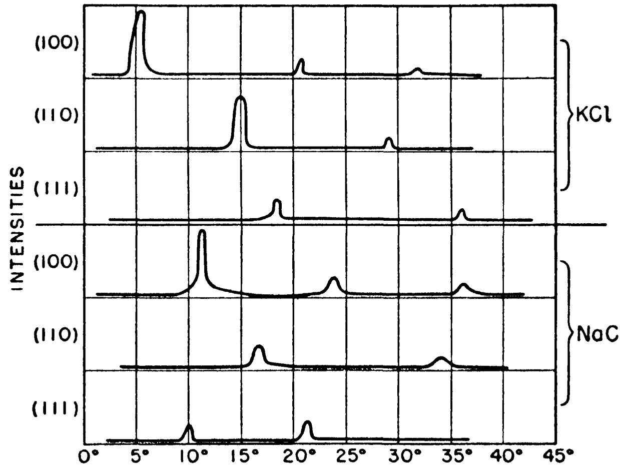


Fig. 13.10. Bragg spectrometer data, I vs. 2θ.

The general expression for the spacing of the planes (hkl) in a cubic lattice is

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$

When this is combined with the Bragg equation, we obtain

$$\sin^2 \theta = (\lambda^2/4a_0^2)(h^2 + k^2 + l^2)$$

Thus each observed value of $\sin \theta$ can be *indexed* by assigning to it the value of (hkl) for the set of planes responsible for the "reflection." For a simple cubic lattice, the following spacings are allowed:

(hkl) . . .	100	110	111	200	210	211	220	221, 300	etc.
$h^2 + k^2 + l^2$ . .	1	2	3	4	5	6	8	9	etc.

If the observed X-ray pattern from a simple cubic crystal was plotted as intensity vs. $\sin^2 \theta$ we would obtain a series of six equidistant maxima, with the seventh missing, since there is no set of integers hkl such that $h^2 + k^2 + l^2 = 7$. There would then follow seven more equidistant maxima, with the 15th missing; seven more, the 23rd missing; four more, the 28th missing; and so on.

In Fig. 13.11 (a) we see the (100), (110), and (111) planes for a simple cubic lattice. A structure may be based on this lattice by replacing each lattice point by an atom. If an X-ray beam strikes such a structure at the Bragg angle, $\theta = \sin^{-1}(\lambda/2a)$, the rays scattered from one (100) plane will be exactly in phase with the rays from successive (100) planes. The strong scattered beam may be called the "first-order reflection from the (100) planes." A similar result is obtained for the (110) and (111) planes. We shall obtain a diffraction maximum from each set of planes (hkl), since for any given (hkl) all the atoms will be included in the planes.

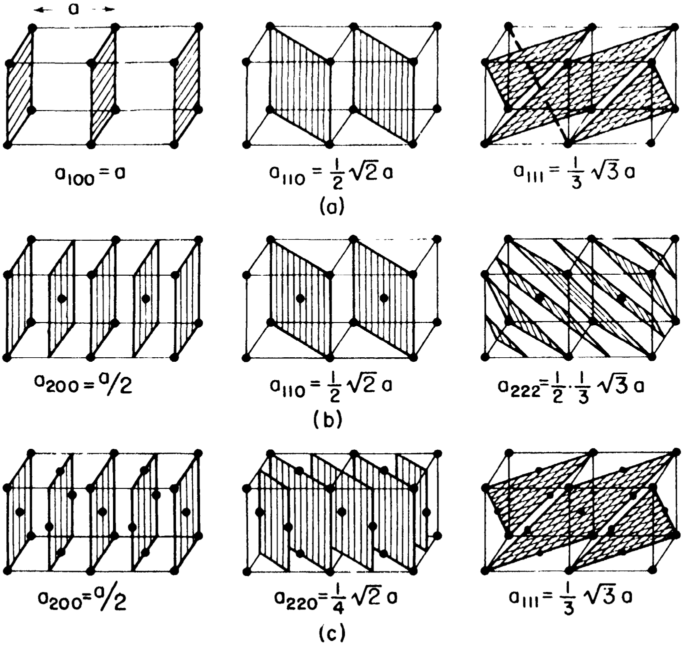


Fig. 13.11. Spacings in cubic lattices: (a) simple cubic; (b) body-centered cubic; (c) face-centered cubic.

Fig. 13.11 (b) shows a structure based on a body-centered cubic lattice. The (110) planes, as in the simple-cubic case, pass through all the lattice points, and a strong first-order (110) reflection will occur. In the case of the (100) planes, however, we find a different situation. Exactly midway between any two (100) planes, there lies another layer of atoms. When X rays scattered from the (100) planes are in phase and reinforce one another, the rays scattered by the interleaved atomic planes will be retarded by half a wavelength, and hence will be exactly out of phase with the others. The observed intensity will therefore be the difference between the scattering from the two sets of planes. If the atoms all have identical scattering powers, the resultant intensity will be reduced to zero by the destructive interference, and no first-order (100) reflection will appear. If, however, the atoms are different, the first-order (100) will still appear, but with a reduced intensity given by the difference between the scatterings from the two interleaved sets of planes.

The second-order diffraction from the (100) planes, occurring at the Bragg angle with $n = 2$ in eq. (13.2), can equally well be expressed as the scattering from a set of planes, called the (200) planes, with just half the spacing of the (100) planes. In the body-centered cubic structure, all the atoms lie in these (200) planes, so that all the scattering is in phase, and a strong scattered beam is obtained. The same situation holds for the (111) planes: the first-order (111) will be weak or extinguished, but the second-order (111), *i.e.* the (222) planes, will give strong scattering. If we examine successive planes (*hkl*) in this way, we find for the body-centered cubic structure the results shown in Table 13.2, in which planes missing due to extinction are indicated by dotted lines.

TABLE 13.2

CALCULATED AND OBSERVED DIFFRACTION MAXIMA

(*hkl*)	100	110	111	200	210	211		220	300 211	310
$h^2 + k^2 + l^2$ . .	1	2	3	4	5	6		8	9	10
simple cubic . .	|	|	|	|	|	|	—	|	|	|
body-centered cubic .	:	|		|		|	—	|	⋮	|
face-centered cubic .	:	·	|	|	·	.	—	|	:	⋮
Sodium Chloride .	·	·	|	|	:	⋮	—	|	⋮	⋮
Potassium Chloride .	200 |	220 |	222 |	400 |	420 |	422 |	—	440 |	600 422 |	620 |

In the case of the face-centered cubic structure, Fig. 13.11 (c), reflections from the (100) and (110) planes are weak or missing, and the (111) planes give intense reflection. The results for subsequent planes are included in Table 13.2.

In the first work on NaCl and KCl, the X-ray wavelength was not known, so that the spacings corresponding to the diffraction maxima could not be calculated. The values of $\sin^2 \theta$, however, can be used directly. The observed maxima are compared in Table 13.2 with those calculated for the different cubic lattices.

The curious result is now noted that apparently NaCl is face centered while KCl is simple cubic. The reason why the KCl structure behaves toward X rays like a simple cubic array is that the scattering powers of K^+ and Cl^- ions are indistinguishable since they both have an argon configuration with 18 electrons. In the NaCl structure the difference in scattering power of the Na^+ and Cl^- ions is responsible for the deviation from the simple cubic pattern.

The observed maxima from the (111) face of NaCl include a weak peak at an angle of about 10°, in addition to the stronger peak at about 20°, corresponding to that observed with KCl. These results are all explained by the NaCl structure shown in Fig. 13.12, which consists of a face-centered cubic array of Na^+ ions and an interpenetrating face-centered cubic array of Cl^- ions. Each Na^+ ion is surrounded by six equidistant Cl^- ions and each Cl^- ion by six equidistant Na^+ ions. The (100) and (110) planes contain an equal number of both kinds of ions, but the (111) planes consist of either all Na^+ or all Cl^- ions. Now if X rays are scattered from the (111) planes in NaCl, whenever scattered rays from successive Na^+ planes are exactly in phase, the rays scattered from the interleaved Cl^- planes are retarded by half a wavelength and are therefore exactly out of phase. The first-order (111) reflection is therefore weak in NaCl since it represents the difference between these two scatterings. In the case of KCl, where the scattering powers are the same, the first-order reflections are altogether extinguished by interference. Thus the postulated structure is in complete agreement with the experimental X-ray evidence.

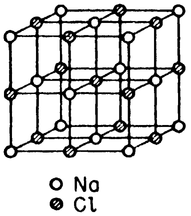


Fig. 13.12. Sodium chloride structure.

Once the NaCl structure was well established, it was possible to calculate the wavelength of the X rays used. From the density of crystalline NaCl, $\rho = 2.163$ g per cm³, the molar volume is $M/\rho = 58.45/2.163 = 27.02$ cc per mole. Then the volume occupied by each NaCl unit is $27.02 \div (6.02 \times 10^{23}) = 44.88 \times 10^{-24}$ cc. In the unit cell of NaCl, there are eight Na^+ ions at the corners of the cube, each shared between eight cubes, and six Na^+ ions at the face centers, each shared between two cells. Thus, per unit cell, there are $8/8 + 6/2 = 4$ Na^+ ions. There is an equal number of Cl^- ions, and therefore four NaCl units per unit cell. The volume of the unit cell is therefore $4 \times 44.88 \times 10^{-24} = 179.52$ (Å)³. The interplanar spacing for the (200) planes is $\frac{1}{2}a = \frac{1}{2}179.52^{1/3} = 2.82$ Å. Substituting this value and the observed diffraction angle into the Bragg equation, $\lambda = 2(2.82) \sin 5° 58'$; $\lambda = 0.586$ Å.

Once the wavelength has been measured in this way, it can be used to determine the interplanar spacings in other crystal structures. Conversely, crystals with known spacings can be used to measure the wavelengths of other X-ray lines. The most generally useful target material is copper, with

$\lambda = 1.537$ Å ($K_{\alpha 1}$), a convenient length relative to interatomic distances. When short spacings are of interest, molybdenum (0.708) is useful, and chromium (2.285) is often employed for study of longer spacings.

The Bragg spectrometer method is generally applicable but is quite time consuming. Most crystal structure investigations have used photographic methods to record the diffraction patterns. Improved spectrometers have been developed recently in which a Geiger-counter tube replaces the electrometer and ionization chamber.

9. The powder method. The simplest technique for obtaining X-ray diffraction data is the powder method, first used by P. Debye and P. Scherrer. Instead of a single crystal with a definite orientation to the X-ray beam, a mass of finely divided crystals with random orientations is used. The experimental arrangement is illustrated in (a), Fig. 13.13. The powder is contained in a thin-walled glass capillary, or deposited on a fiber. Polycrystalline metals are studied in the form of fine wires. The sample is rotated in the beam to average as well as possible the orientations of the crystallites.

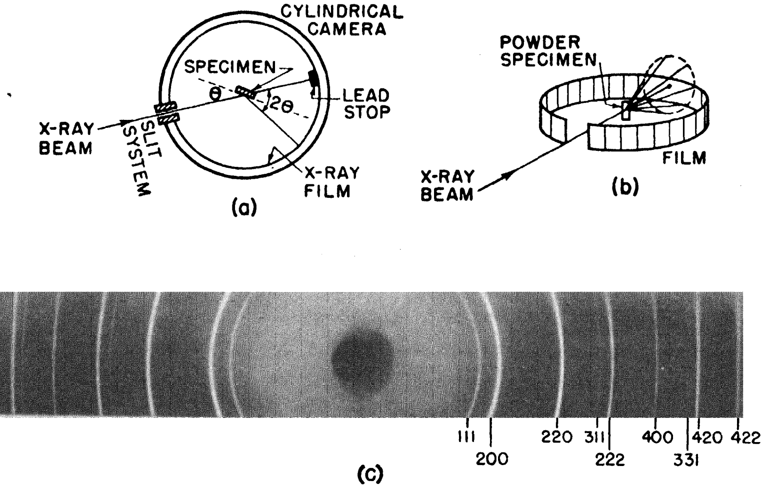


Fig. 13.13. The powder method. Powder picture of sodium chloride, Cu-K_α radiation, (c). (Courtesy Dr. Arthur Lessor, Indiana University.)

Out of the many random orientations of the little crystals, there will be some at the proper angle for X-ray reflection from each set of planes. The direction of the reflected beam is limited only by the requirement that the angle of reflection equal the angle of incidence. Thus if the incident angle is θ, the reflected beam makes an angle 2θ with the direction of the incident beam, (b), Fig. 13.13. This angle 2θ may itself be oriented in various directions around the central beam direction, corresponding to the various orientations of the individual crystallites. For each set of planes, therefore, the reflected beams outline a cone of scattered radiation. This cone, intersecting a cylindrical film surrounding the specimen, gives rise to the observed dark lines. On a flat plate film, the observed pattern consists of a series of concentric circles. A typical X-ray powder picture is shown in (c), Fig. 13.13. It may be compared with the electron-diffraction picture obtained by G. P. Thomson from a polycrystalline gold foil (page 272).

After obtaining a powder diagram, the next step is to index the lines, assigning each to the responsible set of planes. The distance x of each line from the central spot is measured carefully, usually by halving the distance between the two reflections on either side of the center. If the film radius is r, the circumference $2\pi r$ corresponds to a scattering angle of 360°. Then, $x/2\pi r = 2\theta/360°$. Thus θ is calculated and, from eq. (13.2), the interplanar spacing.

The spacing data are often used, without further calculation, to identify solids or analyze solid mixtures. Extensive tables are available[4] that facilitate the rapid identification of unknowns.

To index the reflections, one must know the crystal system to which the specimen belongs. This system can sometimes be determined by microscopic examination. Powder diagrams of monoclinic, orthorhombic, and triclinic crystals may be almost impossible to index. For the other systems straightforward methods are available. Once the unit-cell size is found, by calculation from a few large spacings (100, 110, 111, etc.), all the interplanar spacings can be calculated and compared with those observed, thus completing the indexing. Then more precise unit-cell dimensions can be calculated from high-index spacings. The general formulae giving the interplanar spacings are straightforward derivations from analytical geometry.[5]

10. Rotating-crystal method. The rotating-single-crystal method, with photographic recording of the diffraction pattern, was developed by E. Schiebold around 1919. It has been, in one form or another, the most widely used technique for precise structure investigations.

The crystal, which is preferably small and well formed, perhaps a needle a millimeter long and a half-millimeter wide, is mounted with a well defined axis perpendicular to the beam which bathes the crystal in X radiation. The film may be held in a cylindrical camera, and the crystal is rotated slowly during the course of the exposure. In this way, successive planes pass through the orientation necessary for Bragg reflection, each producing a dark spot on the film. Sometimes only part of the data is recorded on a single film, by oscillating through some smaller angle rather than rotating through 360°. An especially useful method employs a camera that moves the film back and forth with a period synchronized with the rotation of the crystal. Thus the position of a spot on the film immediately indicates the orientation of the crystal at which the spot was formed (Weissenberg method).

We cannot give here a detailed interpretation of these several varieties

---

[4] J. D. Hanawalt, *Ind. Eng. Chem. Anal.*, *10*, 457 (1938).

[5] C. W. Bunn, *Chemical Crystallography* (New York: Oxford, 1946), p. 376.

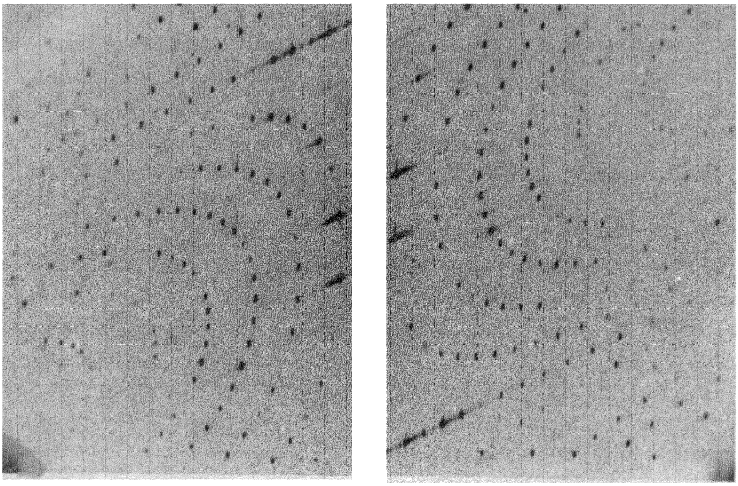


Fig. 13.14. Rotation picture of zinc oxine dihydrate—Weissenberg method. (Courtesy Prof. L. L. Merritt, Indiana University.)

of rotation pictures.[6] A typical example is shown in Fig. 13.14. Methods have been developed for indexing the various spots and also for measuring their intensities. These data are the raw material for crystal-structure determinations.

11. Crystal-structure determinations: the structure factor. The problem of reconstructing a crystal structure from the intensities of the various X-ray diffraction maxima is analogous in some ways to the problem of the formation of an image by a microscope. According to Abbé's theory of the microscope, the objective gathers various orders of light rays diffracted by the specimen and resynthesizes them into an image. This synthesis is possible because two conditions are fulfilled in the optical case: the phase relationships between the various orders of diffracted light waves are preserved at all times, and optical glass is available to focus and form an image with radiation having the wavelength of visible light. We have no such lenses for forming X-ray images (compare, however, the electron microscope), and the way in which the diffraction data are necessarily obtained (one by one) means that all the phase relationships are lost. The essential problem in determining a crystal structure is to regain this lost information in some way or other, and to resynthesize the structure from the amplitudes and phases of the diffracted waves.

We shall return to this problem in a little while, but first let us see how the intensities of the various spots on an X-ray picture are governed by the crystal structure.[7] The Bragg relation fixes the angle of scattering in terms of

---

[6] See Bragg, *loc. cit.*, p. 30. Also Bunn, *loc. cit.*, p. 137.

[7] This treatment follows that given by M. J. Buerger in *X-Ray Crystallography* (New York: Wiley, 1942), which should be consulted for more details.

the interplanar spacings, which are determined by the arrangement of points in the crystal lattice. In an actual structure, each lattice point is replaced by a group of atoms. It is primarily the arrangement and composition of this group that controls the intensity of the scattered X rays, once the Bragg condition has been satisfied.

As an example, consider in (a), Fig. 13.15, a lattice in which each point has been replaced by two atoms (*e.g.*, a diatomic molecule). Then if a set of lattice planes is drawn through the black atoms, another parallel but slightly displaced set can be drawn through the white atoms. When the Bragg condition is met, as in (b), Fig. 13.15, the reflections from all the black atoms are in phase, and the reflections from all the white atoms are in phase. The radiation scattered from the blacks is slightly out of phase with that from the whites, so that the resultant amplitude, and therefore intensity, is diminished by interference.

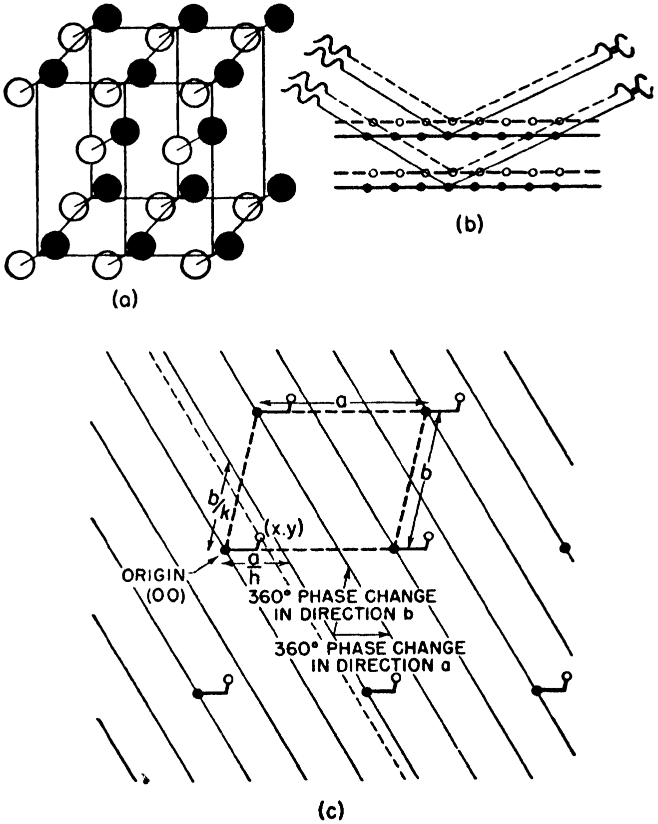


Fig. 13.15. X-ray scattering from a typical structure.

The problem now is to obtain a general expression for the phase difference. An enlarged view of the structure (two-dimensional) is shown in (c), Fig. 13.15, with the black atoms at the corners of a unit cell with sides a and b, and the whites at displaced positions. The coordinates of a black atom may be taken as (0, 0) and those of a white as (x, y). A set of planes (hk) is shown, for which it is assumed the Bragg condition is being fulfilled; these are actually the (32) planes in the figure. Now the spacings a/h along a and b/k along b correspond to positions from which scattering differs in phase by exactly 360° or 2π radians, *i.e.*, scattering from these positions is exactly in phase. The phase difference between these planes and those going through the white atoms is proportional to the displacement of the white atoms. The phase difference P_x for displacement x in the a direction is given by $x/(a/h) = P_x/2\pi$, or $P_x = 2\pi h(x/a)$. The total phase difference for displacement in both a and b directions becomes

$$P_x + P_y = 2\pi\left(h\frac{x}{a} + k\frac{y}{b}\right)$$

By extension to three dimensions, the total phase change that an atom at (xyz) in the unit cell contributes to the plane (hkl) is

$$P = 2\pi\left(\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c}\right) \tag{13.3}$$

We may recall (page 327) that the superposition of waves of different amplitude and phase can be accomplished by vectorial addition. If f_1 and f_2 are the amplitudes of the waves scattered by atoms (1) and (2), and P_1 and P_2 are the phases, the resultant amplitude is $F = f_1e^{iP_1} + f_2e^{iP_2}$. For any number of atoms,

$$F = \sum_K f_K\, e^{iP_K} \tag{13.4}$$

When this is combined with eq. (13.3), there is obtained an expression for the resultant amplitude of the waves scattered from the (hkl) planes by all the atoms in a unit cell:

$$F(hkl) = \Sigma f_K\, e^{2\pi i(hx/a + ky/b + lz/c)} \tag{13.5}$$

The expression $F(hkl)$ is called the *structure factor* of the crystal. Its value is determined by the exponential terms, which depend on the positions of the atoms, and by the *atomic scattering factors* f_K, which depend on the number and distribution of the electrons in the atom, and on the scattering angle θ.

The intensity of scattered radiation is proportional to the absolute value of the amplitude squared, $|F(hkl)|^2$. The crystal structure problem now becomes that of obtaining agreement between the observed intensities and those calculated from a postulated structure. Structure-factor expressions have been tabulated for all the space groups.[8]

---

[8] *International Tables for the Determination of Crystal Structures* (1952). It is usually possible to narrow the choice of space groups to two or three by means of study of missing reflections (hkl) and comparison with the tables.

As an example of the use of the structure factor let us calculate $F(hkl)$ for the 100 planes in a face-centered cubic structure, *e.g.*, metallic gold. In this structure there are four atoms in the unit cell ($Z = 4$), which may be assigned coordinates (x/a, y/b, z/c) as follows: (000), ($\frac{1}{2}\ \frac{1}{2}\ 0$), ($\frac{1}{2}\ 0\ \frac{1}{2}$), and ($0\ \frac{1}{2}\ \frac{1}{2}$). Therefore, from eq. (13.5)

$$F(100) = f_{Au}(e^{2\pi i\cdot 0} + e^{2\pi i\cdot\frac{1}{2}} + e^{2\pi i\cdot\frac{1}{2}} + e^{2\pi i\cdot 0})$$
$$= f_{Au}(2 + 2e^{\pi i}) = 0$$

since $$e^{\pi i} = \cos\pi + i\sin\pi = -1$$

Thus the structure factor vanishes and there is therefore zero intensity of scattering from the (100) set of planes. This is almost a trivial case, since inspection of the face-centered cubic structure immediately reveals that there is an equivalent set of planes interleaved midway between the 100 planes, so that the resultant amplitude of the scattered X rays must be reduced to zero by interference. In more complicated instances, however, it is essential to use the structure factor to obtain a quantitative estimation of the scattering intensity expected from any set of planes (hkl) in any postulated crystal structure.

12. Fourier syntheses. An extremely useful way of looking at a crystal structure was proposed by Sir William Bragg when he pointed out that it may be regarded as a periodic three-dimensional distribution of electron density, since it is the electrons that scatter the X rays. Any such density function may be expressed as a Fourier series, a summation of sine and cosine terms.[9] It is more concisely written in the complex exponential form. Thus the electron density in a crystal may be represented as

$$\rho(xyz) = \sum_{p=-\infty}^{+\infty}\sum_{q=-\infty}^{+\infty}\sum_{r=-\infty}^{+\infty} A_{pqr}\, e^{2\pi i(px/a + qy/b + rz/c)} \tag{13.6}$$

It is not hard to show[10] that the Fourier coefficients A_{pqr} are equal to the structure factors divided by the volume of the unit cell. Thus

$$\rho(xyz) = \frac{1}{V}\Sigma\Sigma\Sigma\ F(hkl)\, e^{-2\pi i(hx/a + ky/b + lz/c)} \tag{13.7}$$

This equation expresses the fact that the only Fourier term that contributes to the X-ray scattering by the set of planes (hkl) is the one with the coefficient $F(hkl)$, which appears intuitively to be the correct formulation.

Equation (13.7) summarizes the whole problem involved in structure determinations, since in a very real sense the crystal structure is simply $\rho(xyz)$. Positions of individual atoms are peaks in the electron density function ρ, and interatomic regions are valleys in the plot of ρ. Thus if we knew the $F(hkl)$'s we could immediately plot the crystal structure. All we know, however, are the intensities, which are proportional to $|F(hkl)|^2$. As

---

[9] See, for example, Widder, *Advanced Calculus*, p. 324.

[10] Bragg, *op. cit.*, p. 221.

stated earlier, we know the amplitudes but we have necessarily lost the phases in taking the X-ray pattern.

A trial structure is now assumed and the intensities are calculated. If the assumed arrangement is even approximately correct, the most intense observed reflections should have large calculated intensities. The observed F's for these reflections may be put into the Fourier series with the calculated signs.[11] The graph of the Fourier summation will give new positions for the atoms, from which new F's can be calculated, which may allow more of the signs to be determined. Gradually the structure is refined as more and more terms are included in the synthesis. In Fig. 13.16 are shown three Fourier summations for the structure of glycylglycine. As additional terms are included in the summation, the resolution of the structure improves, just as the resolution of a microscope increases with objectives that catch more and more orders of diffracted light.

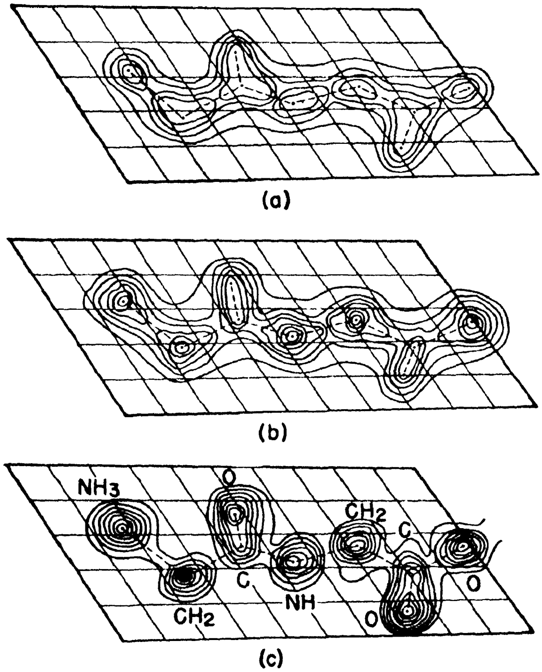


Fig. 13.16. Fourier map of electron density in glycylglycine projected on base of unit cell: (a) 40 terms; (b) 100 terms; (c) 200 terms.

Sometimes a heavy atom can be introduced into the structure, whose position is known from symmetry arguments. The large contribution of the heavy atom makes it possible to determine the phases of many of the F's.

---

[11] The complete Fourier series is rarely used; instead, various two-dimensional projections are preferred.

This was the method used with striking success by J. M. Robertson in his work on the phthalocyanine structures,[12] and in the determination of the structure of penicillin. This last was one of the great triumphs of X-ray crystallography, since it was achieved before the organic chemists knew the structural formula.

13. Neutron diffraction. Not only X-ray and electron beams, but also beams of heavier particles may exhibit diffraction patterns when scattered from the regular array of atoms in a crystal. Neutron beams have proved to be especially useful for such studies. The wavelength is related to the mass and velocity by the Broglie equation, $\lambda = h/mv$. Thus a neutron with a speed of 3.9×10^5 cm sec^{-1} (kinetic energy 0.08 ev) would have a wavelength of 1.0 Å. The diffraction of electron rays or X rays is caused by their interaction with the orbital electrons of the atoms in the material through which they pass; the atomic nuclei contribute practically nothing to the scattering. The diffraction of neutrons, on the other hand, is primarily caused by two other effects: (a) *nuclear scattering* due to interaction of the neutrons with the atomic nuclei, (b) *magnetic scattering* due to interaction of the magnetic moments of the neutrons with permanent magnetic moments of atoms or ions.

In the absence of an external magnetic field, the magnetic moments of atoms in a paramagnetic crystal are arranged at random, so that the magnetic scattering of neutrons by such a crystal is also random. It contributes only a diffuse background to the sharp maxima occurring when the Bragg condition is satisfied for the nuclear scattering. In *ferromagnetic materials*, however, the magnetic moments are regularly aligned so that the resultant spins of adjacent atoms are parallel, even in the absence of an external field. In *antiferromagnetic materials*, the magnetic moments are also regularly aligned, but in such a way that adjacent spins are always opposed. The neutron diffraction patterns distinguish experimentally between these different magnetic structures, and indicate the direction of alignment of spins within the crystal.

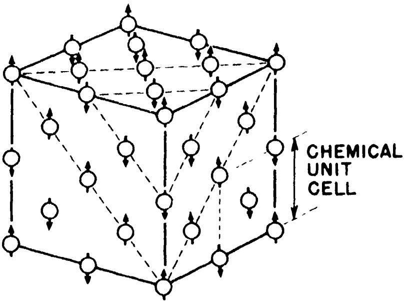


Fig. 13.17. Magnetic structure of MnO as found by neutron diffraction. Note that the "magnetic unit cell" has twice the length of the "chemical unit cell." [From C. G. Shull, E. O. Wollan, and W. A. Strauser, *Phys. Rev.*, *81*, 483 (1951).]

For example, manganous oxide, MnO, has the rock-salt structure (Fig. 13.12), and is antiferromagnetic. The detailed magnetic structure as revealed by neutron diffraction is shown in Fig. 13.17. The manganous ion, Mn^{+2}, has the electronic structure $3s^2 3p^6 3d^5$.

---

[12] *J. Chem. Soc.* (*London*), 1940, 36. For an account of the work on penicillin, see *Research*, *2*, 202 (1949).

The five $3d$ electrons are all unpaired, and the resultant magnetic moment is $2\sqrt{\frac{5}{2}(\frac{5}{2}+1)} = 5.91$ Bohr magnetons. If we consider Mn^{+2} ions in successive (111) planes in the crystal, the resultant spins are oriented so that they are alternately positively and negatively directed along the [100] direction.

Another useful application of neutron diffraction has been the location of hydrogen atoms in crystal structures. It is usually impossible to locate hydrogen atoms by means of X-ray or electron diffraction, because the small scattering power of the hydrogen is completely overshadowed by that of heavier atoms. The hydrogen nucleus, however, is a strong scatterer of neutrons. Thus it has been possible to work out the structures of such compounds as UH_3 and KHF_2 neutron-diffraction analysis.[13]

14. Closest packing of spheres. Quite a while before the first X-ray structure analyses, some shrewd theories about the arrangement of atoms and molecules in crystals were developed from purely geometrical considerations. From 1883 to 1897, W. Barlow proposed a number of structures based on the packing of spheres.

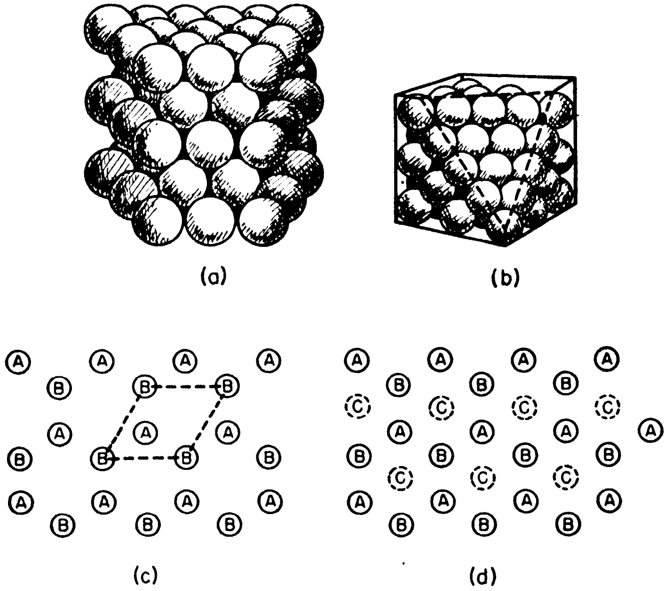


Fig. 13.18. (a) Hexagonal closest packing; (b) cubic closest packing (edge cut away to show closest packing normal to cube diagonals); (c) plan of hexagonal closest packing; (d) plan of cubic closest packing.

There are two different ways in which spheres of the same size can be packed together so as to leave a minimum of unoccupied volume, in each case 26 per cent voids. They are the hexagonal-closest-packed (hcp) and the

---

[13] S. W. Peterson and H. A. Levy, *J. Chem. Phys.*, *20*, 704 (1952).

cubic-closest-packed (ccp) arrangements depicted in Fig. 13.18. In ccp the layers repeat as ABC ABC ABC . . ., and in hcp the order is AB AB AB . . . It will be noted that the ccp structure may be referred to a face-centered-cubic unit cell, the (111) planes being the layers of closest packing.

The ccp structure is found in the solid state of the inert gases, in crystalline methane, etc.—symmetrical atoms or molecules held together by van der Waals forces. The high-temperature forms of solid H_2, N_2, and O_2 occur in hcp structures.

The great majority of the typical metals crystallize in the ccp, the hcp, or a body-centered-cubic structure. Some examples are collected in Table 13.3. Other structures include the following:[14] the diamond-type cubic of grey tin and germanium; the face-centered tetragonal, a distorted fcc, of γ-manganese and indium; the rhombohedral layered structures of bismuth, arsenic, and antimony; and the body-centered tetragonal of white tin. It will be noted that many of the metals are polymorphic (allotropic), with two or more structures depending on conditions of temperature and pressure.

TABLE 13.3
STRUCTURES OF THE METALS

Cubic Closest Packed (fcc) or (ccp)		Hexagonal Closest Packed (hcp)		Body-Centered Cubic (bcc)	
Ag	γFe	αBe	Os	Ba	Mo
Al	Ni	γCa	αRu	αCr	Na
Au	Pb	Cd	βSc	Cs	Ta
αCa	Pt	αCe	αTi	αFe	βTi
βCo	Sr	αCo	αTl	δFe	V
Cu	Th	βCr	Zn	K	βW
		Mg	αZr	Li	βZr

The nature of the binding in metal crystals will be discussed later. For the present, we may think of them as a network of positive metal ions packed primarily according to geometrical requirements, and permeated by mobile electrons. This so-called *electron gas* is responsible for the high conductivity and for the cohesion of the metal.

The ccp metals, such as Cu, Ag, Au, Ni, are all very ductile and malleable. The other metals, such as V, Cr, Mo, W, are harder and more brittle. This distinction in physical properties reflects a difference between the structure types. When a metal is hammered, rolled, or drawn, it deforms by the gliding of planes of atoms past one another. These *slip planes* are those that contain the most densely packed layers of atoms. In the ccp structure, the slip planes are therefore usually the (111), which occur in sheets normal to

---

[14] For descriptions see R. W. G. Wyckoff, *Crystal Structures* (New York: Interscience, 1948).

all four of the cube diagonals. In the hcp and other structures there is only one set of slip planes, *e.g.*, those perpendicular to the hexagonal axis. Thus the ccp metals are characteristically more ductile than the others, since they have many more glide ways.

15. Binding in crystals. The geometrical factors, seen in their simplest form in the closest packed structures of identical spheres, are always very important in determining the crystal structure of a substance. Once they are satisfied, other types of interaction must also be considered. Thus, for example, when directed binding appears, closest packing cannot be achieved.

Two different theoretical approaches to the nature of the chemical bond in molecules have been described in Chapter 11. In the method of atomic orbitals, the point of departure is the individual atom. Atoms are brought together, each with the electrons that "belong to it," and one considers the effect of an electron in one atomic orbital upon that in another. In the second approach, the electrons in a molecule are no longer assigned possessively to the individual atoms. A set of nuclei is arranged at the proper final distances and the electrons are gradually fed into the available molecular orbitals.

For studying the nature of binding in crystals, these two different treatments are again available. In one case, the crystal structure is pictured as an array of regularly spaced atoms, each possessing electrons used to form bonds with neighboring atoms. These bonds may be ionic, covalent, or intermediate in type. Extending throughout three dimensions, they hold the crystal together. The alternative approach is once again to consider the nuclei at fixed positions in space and then gradually to pour the electron cement into the periodic array of nuclear bricks.

Both these methods yield useful and distinctive results, displaying complementary aspects of the nature of the crystalline state. We shall call the first treatment, growing out of the atomic-orbital theory, the *bond model* of the solid state. The second treatment, an extension of the method of molecular orbitals, we shall call, for reasons to appear later, the *band model* of the solid state.

16. The bond model. If we consider that a solid is held together by chemical bonds, it is useful to classify the bond types. Even though the available classifications are as usual somewhat frayed at the edges, the following categories may be distinguished:

(1) *The van der Waals bonds.* These bonds are the result of forces between inert atoms or essentially saturated molecules. These forces are the same as those responsible for the *a* term in the van der Waals equation. Crystals held together in this way are sometimes called *molecular crystals.* Examples are nitrogen, carbon tetrachloride, benzene. The molecules tend to pack together as closely as their geometry allows. The binding between the molecules in van der Waals structures represents a combination of factors such as dipole-dipole and dipole-polarization interactions, and the quantum

mechanical *dispersion forces*, first elucidated by F. London, which are often the principal component.[15]

(2) *The ionic bonds*. These bonds are familiar from the case of the NaCl molecule in the vapor state (page 297). In a crystal, the coulombic interaction between oppositely charged ions leads to a regular three-dimensional structure. In rock salt, each positively charged Na$^+$ ion is surrounded by six negatively charged Cl$^-$ ions, and each Cl$^-$ is surrounded by six Na$^+$. There are no sodium-chloride molecules unless one wishes to regard the entire crystal as a giant molecule.

The ionic bond is spherically symmetrical and undirected; an ion will be surrounded by as many oppositely charged ions as can be accommodated geometrically, provided that the requirement of over-all electrical neutrality is satisfied.

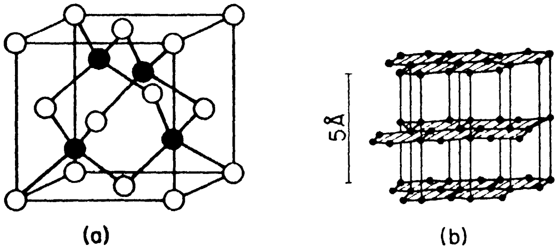


Fig. 13.19. (a) Diamond structure; (b) graphite structure.

(3) *The covalent bonds*. These bonds, we recall, are the result of spin valence (page 303), the sharing between atoms of two electrons with antiparallel spins. When extended through three dimensions, they may lead to a variety of crystal structures, depending on the valence of the constituent atoms, or the number of electrons available for bond formation.

A good example is the diamond structure in (a), Fig. 13.19. The structure can be based on two interpenetrating face-centered cubic lattices. Each point in one lattice is surrounded tetrahedrally by four equidistant points in the other lattice. This arrangement constitutes a three-dimensional polymer of carbon atoms joined together by tetrahedrally oriented sp^3 bonds. Thus the configuration of the carbon bonds in diamond is similar to that in the aliphatic compounds such as ethane. The C—C bond distance is 1.54 Å in both diamond and ethane. Germanium, silicon, and grey tin also crystallize in the diamond structure.

The same structure is assumed by compounds such as ZnS (zinc blende), AgI, AlP, and SiC. In all these structures, each atom is surrounded by four unlike atoms oriented at the corners of a regular tetrahedron. In every case the binding is primarily covalent. It is interesting to note that it is not necessary that each atom provide the same number of valence electrons; the

---

[15] See Chapter 14, Sect. 10.

structure can occur whenever the total number of outer-shell electrons is just four times the total number of atoms.

There is also a form of carbon, actually the more stable allotrope, in which the carbon bonds resemble those in the aromatic series of compounds. This is graphite, whose structure is shown in (b), Fig. 13.19. Strong bonds operate within each layer of carbon atoms, whereas much weaker binding joins the layers; hence the slippery and flaky nature of graphite. The C—C distance within the layers of graphite is 1.34 Å, identical with that in anthracene.

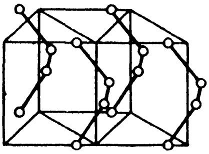


Fig. 13.20. Structure of selenium

Just as in the discussion of the nature of binding in aromatic hydrocarbons (page 311), we can distinguish two types of electrons within the graphite structure. The σ electrons are paired to form localized-pair (sp^2) bonds, and the π electrons are free to move throughout the planes of the C_6 rings.

Atoms with a spin valence of only 2 cannot form regular three-dimensional structures. Thus we have the interesting structures of selenium (Fig. 13.20), and tellurium, which consist of endless chains of atoms extending through the crystal, the individual chains being held together by much weaker forces. Another way of solving the problem is illustrated by the structure of rhombic sulfur, Fig. 13.21. Here there are well defined, puckered, eight-membered rings of sulfur atoms. The bivalence of sulfur is maintained and the S_8 "molecules" are held together by van der Waals attractions. Elements like arsenic and antimony that in their compounds display a covalence of 3 tend to crystallize in structures that contain well defined *layers* of atoms.

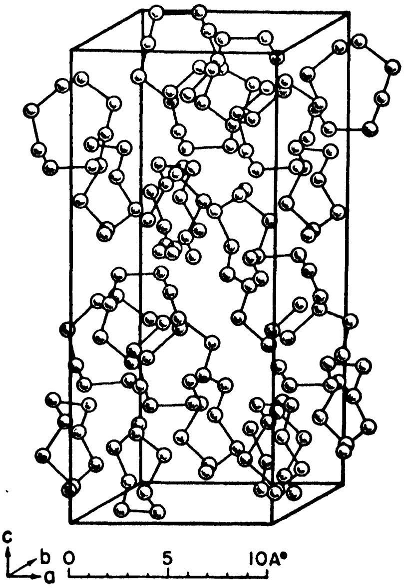


Fig. 13.21. Structure of rhombic sulfur.

(4) *The intermediate-type bonds.* Just as in individual molecules, these bonds arise from resonance between covalent and ionic contributions. Alternatively, one may consider the polarization of one ion by an oppositely charged ion. An ion is said to be polarized when its electron "cloud" is distorted by the presence of the oppositely charged ion. The larger an ion the more readily is it polarized, and the smaller an ion the more intense is its electric field and the greater

its polarizing power. Thus in general the larger anions are polarized by the smaller cations. Even apart from the size effect, cations are less polarizable than anions because their net positive charge tends to hold their electrons in place. The structure of the ion is also important: rare-gas cations such as K^+ have less polarizing power than transition cations such as Ag^+, since their positive nuclei are more effectively shielded.

The effect of polarization may be seen in the structures of the silver halides. AgF, AgCl, and AgBr have the rock-salt structure, but as the anion becomes larger it becomes more strongly polarized by the small Ag^+ ion. Finally, in AgI the binding has very little ionic character and the crystal has the zinc-blende structure. It has been confirmed spectroscopically that crystalline silver iodide is composed of atoms and not ions.

(5) *The hydrogen bond.* The hydrogen bond, discussed on page 313, plays an important role in many crystal structures, *e.g.*, inorganic and organic acids, salt hydrates, ice. The structure of ice is shown in Fig. 13.22. The coordination is similar to that in wurtzite, the hexagonal form of zinc sulfide. Each oxygen is surrounded tetrahedrally by four nearest neighbors at a distance of 2.76 Å. The hydrogen bonds hold the oxygens together, leading to a very open structure. By way of contrast, hydrogen sulfide, H_2S, has a ccp structure, each molecule having twelve nearest neighbors.

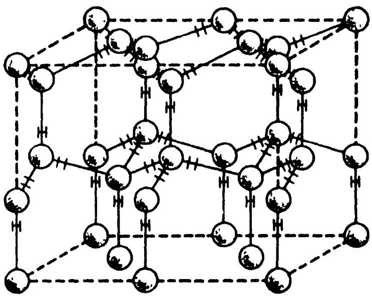


Fig. 13.22. Structure of ice.

(6) *The metallic bond.* The bond model has also been extended to metals. According to this picture, the metallic bond is closely related to the ordinary covalent electron-pair bond. Each atom in a metal forms covalent bonds by sharing electrons with its nearest neighbors. It is found that there are more orbitals available for bond formation than there are electrons to fill them. As a result the covalent bonds resonate among the available interatomic positions. In the case of a crystal this resonance extends throughout the entire structure, thereby producing great stability. The empty orbitals permit a ready flow of electrons under the influence of an applied electric field, leading to metallic conductivity.

Structures such as those of selenium and tellurium, and of arsenic and antimony, represent transitional forms in which the electrons are much more localized because the available orbitals are more completely filled. In a covalent crystal like diamond the four sp^3 tetrahedral orbitals are completely filled.

17. The band model. It was in an attempt to devise an adequate theory for metals that the *band* model had its origin. The high thermal and electrical conductivities of metals focused attention on the electrons as the important entities in their structures. If we use as a criterion the behavior of the electrons, three classes of solids may be distinguished:

(1) Conductors or metals, which offer a low resistance to the flow of electrons, an electric current, when a potential difference is applied. The resistivity of metals increases with the temperature.

(2) Insulators, which have a high electric resistivity.

(3) Semiconductors, whose resistivity is intermediate between that of typical metals and that of typical insulators, and decreases, usually exponentially, with the temperature.

The starting point of the band theory is a collection of nuclei arrayed in space at their final crystalline internuclear separations. The total number of available electrons is poured into the resultant field of force, a regularly periodic field. What happens?

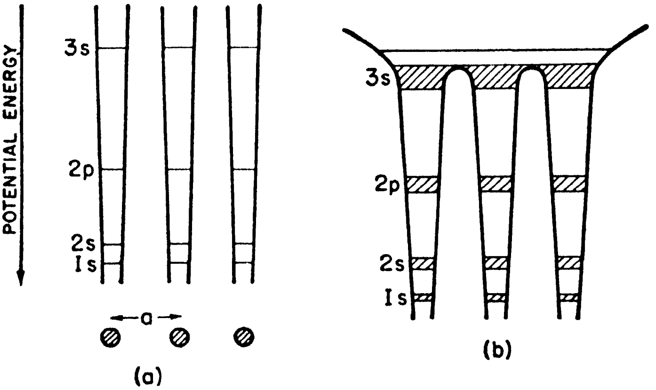


Fig. 13.23. Energy levels in sodium: (a) isolated atoms; (b) section of crystal.

Consider in Fig. 13.23 the simplified model of a one-dimensional structure. For concreteness, let us think of the nuclei as being those of sodium, therefore bearing a charge of +11. The position of each nucleus will represent a deep potential-energy well for the electrons, owing to the large electrostatic attraction. If these wells were infinitely deep, the electrons would all fall into fixed positions on the sodium nuclei, giving rise to $1s^2 2s^2 2p^6 3s^1$ configurations, typical of isolated sodium atoms. This is the situation shown in (a), Fig. 13.23. But the wells are not infinitely deep, or in other words the potential-energy barriers separating the electrons on different nuclei are not infinitely high. The actual situation is more like the one shown in (b), Fig. 13.23. Now the possibility of a quantum mechanical leakage of electrons through the barriers must be considered. Otherwise expressed, there will be a resonance of electrons between the large number of identical positions. There is always a possibility of an electron on one nucleus slipping through to occupy a position on a neighboring nucleus. We are thus no longer concerned with the energy levels of single sodium atoms but with levels of the crystal as a whole. Then the Pauli Principle comes into play, and tells us that no more than two electrons can occupy exactly the same energy level. Once the possibility of electrons moving through the structure is admitted, we can no longer consider the energy levels to be sharply defined. The sharp 1*s* energy level in an individual sodium atom is broadened in crystalline sodium into a band of closely packed energy levels. A similar situation arises for the other energy levels, each becoming a band of levels as shown in (b), Fig. 13.23.

Each atomic orbital contributes one level to a band. In the lower bands (1*s*, 2*s*, 2*p*) there are therefore just enough levels to accommodate the number of available electrons, so that the bands are completely filled. If an external electric field is applied, the electrons in the filled bands cannot move under its influence, for to be accelerated by the field they would have to move into somewhat higher energy levels. This is impossible for electrons in the interior of a filled band, since all the levels above them are already occupied, and the Pauli Principle forbids their accepting additional tenants. Nor can the electrons at the very top of a filled band acquire extra energy, since there are no higher levels for them to move into. Very occasionally, it is true, an electron may acquire a relatively terrific jolt of energy and be knocked completely out of its band into a higher unoccupied band.

So much for the electrons in the lower bands. The situation is very different in the uppermost band, the 3*s*, which is only half filled. An electron in the interior of the 3*s* band still cannot be accelerated because the levels directly above are already filled. Electrons toward the top of the band, however, can readily move up into unfilled levels within the band. This is what happens when an electric field is applied and a current flows. It will be noticed from the diagram that the topmost band has actually broadened sufficiently to overlap the tops of the potential-energy barriers, so that these electrons can move quite freely through the crystal structure.

According to this idealized model in which the nuclei are always arranged at the points of a perfectly periodic lattice, there would indeed be no resistance at all offered to the flow of an electric current. The resistance arises from deviations from perfect periodicity. An important loss of periodicity is caused by the thermal vibrations of the lattice nuclei. These vibrations destroy the perfect resonance between the electronic energy levels and cause a resistance to the free flow of electrons. As would be expected, the resistance therefore increases with the temperature. Another illustration of the same principle is found in the increased resistance that results when an alloying constituent is added to a pure metal, and the regular periodicity of the structure is diminished by the foreign atoms.

At this point the reader may well be thinking that this is a pretty picture for a univalent metal such as sodium, but what of magnesium with its two 3*s* electrons and therefore completely filled 3*s* bands? Why isn't it an insulator instead of a metal? The answer is that in this, and similar cases, detailed calculations show that the $3p$ band is low enough to overlap the top of the $3s$ band, providing a large number of available empty levels.

Thus conductors are characterized either by partially filled bands or by overlapping of the topmost bands. Insulators have completely filled lower bands with a wide energy gap between the topmost filled band and the lowest empty band. These models are represented schematically in Fig. 13.24.

The energy bands in solids can be studied experimentally by the methods of X-ray emission spectroscopy.[16] For example, if an electron is driven out of the $1s$ level in sodium metal (Fig. 13.23b) the K_α X-ray emission occurs when an electron from the $3s$ band falls into the hole in the $1s$ level. Since the $3s$ electron can come from anywhere within the band of energy levels, the X rays emitted will have a spread of energies (and hence frequencies) exactly corresponding with the spread of allowed energies in the $3s$ band. The following widths (in ev) were found for the conduction bands in a few of the solids investigated:

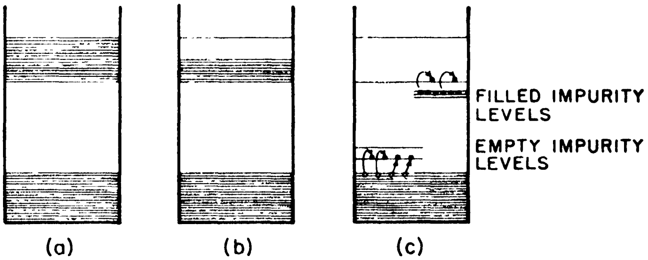


Fig. 13.24. Band models of solid types: (a) insulator; (b) metal; (c) semiconductor.

Li	Na	Be	Mg	Al
4.1	3.4	14.8	7.6	13.2

18. Semiconductors. Band models for semiconductors are also included in Fig. 13.24. These models possess, in addition to the normal bands, narrow *impurity bands*, either unfilled levels closely above a filled band or filled levels closely below an empty band. The extra levels are the result of either foreign atoms dissolved in the structure or a departure from the ideal stoichiometric composition. Thus zinc oxide normally contains an excess of zinc, whereas cuprous oxide normally contains an excess of oxygen. Both these compounds behave as typical semiconductors. Their conductivities increase approximately exponentially with the temperature, because the number of conduction electrons depends on excitation of electrons into or out of the impurity levels, and excitation is governed by an $e^{-\Delta E/RT}$ Boltzmann factor.

---

[16] A review by N. F. Mott gives further references. *Prog. Metal Phys. 3*, 76–114 (1952), "Recent Advances in the Electron Theory of Metals."

If the energy gap between the filled valence band and the empty conduction band is narrow enough, a crystal may be a semiconductor even in the absence of effects due to impurities. Germanium with an energy gap of 0.72 ev and grey tin with 0.10 ev are examples of such *intrinsic semiconductors.*

19. Brillouin zones. The band theory of the crystalline state leads to a system of allowed energy levels separated by regions of forbidden energy. In other words, electron waves having a forbidden energy cannot pass through the crystal. Those familiar with radio circuits would say that the periodic crystal structure acts as a band-pass filter for electron waves.

In this simple picture we have not considered the variety of periodic patterns that may be encountered by an electron wave, depending on the direction of its path through the crystal. When this is done, it is found that special geometrical requirements are imposed on the band structure, so that it is not necessarily the same for all directions in space. Now we can see qualitatively an important principle. If an electron wave with an energy in a forbidden region were to strike a crystal, it could not be transmitted, but would instead be strongly scattered or "reflected" in the Bragg sense. The Bragg relation therefore defines the geometric structure of the allowed energy bands. This principle was first enunciated by Leon Brillouin, and the energy bands constructed in this way are called the Brillouin zones of the crystal.

The quantitative application of the zone theory is still in its early stages. Qualitatively it is clear that the properties of crystals are determined by the nature of the zones and the extent to which they are filled with electrons. This interpretation is especially useful in elucidating the structures of metal alloys.

20. Alloy systems—electron compounds. If two pure metals crystallize in the same structure, have the same valence and atoms of about the same size, they may form a continuous series of solid solutions without undergoing any changes in structure. Examples are the systems Cu–Au and Ag–Au.

When these conditions are not fulfilled, a more complicated phase diagram will result. An example is that for the brass system, copper and zinc. Pure copper crystallizes in a face-centered-cubic structure and dissolves up to about 38 per cent zinc in this α phase. Then the body-centered-cubic β phase supervenes. At about 58 per cent zinc, a complex cubic structure begins to form, called "γ brass," which is hard and brittle. At about 67 per cent Zn, the hexagonal closest packed ε phase arises, and finally there is obtained the η phase having the structure of pure zinc, a distorted hcp arrangement.

It is most interesting that a sequence of structure changes very similar to these is observed in a wide variety of alloy systems. Although the compositions of the phases may differ greatly, the β, γ, and ε structures are quite typical. W. Hume-Rothery was the first to show that this regular behavior was related to a constant ratio of valence electrons to atoms for each phase.

Examples of these ratios are shown in Table 13.4. The transition metals Fe, Co, Ni follow the rule if the number of their valence electrons is taken as zero.[17] In all these cases, the zone structure determines the crystal structure, and the composition corresponding to each structure is fixed by the number of electrons required to fill the zone. Such alloys are therefore sometimes called *electron compounds.*

TABLE 13.4

ELECTRON COMPOUNDS ILLUSTRATING HUME-ROTHERY RULE

Alloy*	Electrons	Atoms	Ratio
β Phases (Ratio 3/2			
CuZn	1 + 2	2	3 : 2
AgCd	1 + 2	2	3 : 2
CuBe	1 + 2	2	3 : 2
AuZn	1 + 2	2	3 : 2
Cu_3Al	3 + 3	4	6 : 4
Cu_5Sn	5 + 4	6	9 : 6
CoAl	0 + 3	2	3 : 3
FeAl	0 + 3	2	3 : 2
γ Phases (Ratio 21/13)			
Cu_5Zn_8	5 + 2 × 8	13	21 : 13
Ag_5Zn_8	5 + 2 × 8	13	21 : 13
Fe_5Zn_{21}	0 + 2 × 21	26	42 : 26
Cu_9Ga_4	9 + 3 × 4	13	21 : 13
Cu_9Al_4	9 + 3 × 4	13	21 : 13
$Cu_{31}Sn_8$	31 + 4 × 8	39	63 : 39
ε Phases (Ratio 7/4)			
$CuZn_3$	1 + 2 × 3	4	7 : 4
$AgCd_3$	1 + 2 × 3	4	7 : 4
Cu_3Sn	3 + 4	4	7 : 4
Cu_3Ge	3 + 4	4	7 : 4
Au_5Al_3	5 + 3 × 3	8	14 : 8
Ag_5Al_3	5 + 3 × 3	8	14 : 8

* The alloy composition is variable within a certain range, but the nominal compositions listed always fall within the range.

The body-centered β brass structure illustrates another interesting property of some alloy systems, the *order-disorder transition.* At low temperatures, the structure is ordered; the copper atoms occupy only the

---

[17] Pauling has pointed out that it seems to be unreasonable to say that iron, which is famous for its great strength, contributes nothing to the bonding in iron alloys. From magnetic moments and other data he concludes that iron actually contributes between 5 and 6 bonding electrons per atom [*J. Am. Chem. Soc.*, *69*, 542 (1947)].

body-centered positions. At higher temperatures, the various positions are occupied at random by copper and zinc atoms.

21. Ionic crystals. The binding in most inorganic crystals is predominantly ionic in character. Therefore, since coulombic forces are undirected, the sizes of the ions play a most important role in determining the final structure. Several attempts have been made to calculate a consistent set of ionic radii, from which the internuclear distances in ionic crystals could be estimated. The first table, given by V. M. Goldschmidt in 1926, was modified by Pauling. These radii are listed in Table 13.5.

TABLE 13.5

IONIC CRYSTAL RADII (Å)*

Li^+	0.60	Na^+	0.95	K^+	1.33	Rb^+	1.48	Cs^+	1.69
Be^{++}	0.31	Mg^{++}	0.65	Ca^{++}	0.99	Sr^{++}	1.13	Ba^{++}	1.35
B^{3+}	0.20	Al^{3+}	0.50	Sc^{3+}	0.81	Y^{3+}	0.93	La^{3+}	1.15
C^{4+}	0.15	Si^{4+}	0.41	Ti^{4+}	0.68	Zr^{4+}	0.80	Ce^{4+}	1.01
O^{--}	1.40	S^{--}	1.84	Cr^{6+}	0.57	Mo^{6+}	0.62		
F^-	1.36	Cl^-	1.81	Cu^+	0.96	Ag^+	1.26	Au^+	1.37
				Zn^{++}	0.74	Cd^{++}	0.97	Hg^{++}	1.10
				Se^{--}	1.98	Te^{--}	2.21		
				Br^-	1.95	I^-	2.16		

* From L. Pauling, *The Nature of the Chemical Bond*, 2nd ed. (Ithaca: Cornell Univ. Press, 1940), p. 346.

First, let us consider ionic crystals having the general formula CA. They may be classified according to the *coordination number* of the ions; *i.e.*, the number of ions of opposite charge surrounding a given ion. The CsCl structure, body centered as shown in Fig. 13.25, has eightfold coordination. The NaCl structure (Fig. 13.12) has sixfold coordination. Although zinc blende (Fig. 13.19a) is itself covalent, there are a few ionic crystals, *e.g.*, BeO, with this structure which has fourfold coordination. The coordination number of a structure is determined primarily by the number of the larger ions, usually the anions, that can be packed around the smaller ion, usually the cation. It should therefore depend upon the *radius ratio*, $r_{\text{cation}}/r_{\text{anion}} = r_C/r_A$. The critical radius ratio is that obtained when the anions packed around a cation are in contact with both the cation and with one another.

Fig. 13.25. The cesium chloride structure.

Consider, for example, the structure of Fig. 13.25. If the anions are at the cube corners and have each a radius a, when they are exactly touching, the unit cube has a side $2a$. The length of the cube diagonal is then $\sqrt{3} \cdot 2a$, and the diameter of the empty hole in the center of the cube is therefore

$\sqrt{3}\cdot 2a - 2a = 2a(\sqrt{3} - 1)$. The radius of the cation exactly filling this hole is thus $a(\sqrt{3} - 1)$, and the critical radius ratio becomes $r_C/r_A = a(\sqrt{3} - 1)/a = 0.732$. By this simple theory, whenever the ratio falls below 0.732, the structure can no longer have eightfold coordination, and indeed should go over to the sixfold coordination of NaCl.

In the sixfold coordination, a given ion at the center of a regular octahedron is surrounded by six neighbors at the corners. The critical radius ratio for this structure may readily be shown to be $\sqrt{2} - 1 = 0.414$. The next lower coordination would be threefold, at the corners of an equilateral triangle, with a critical ratio of 0.225.

The structures and ionic-radius ratios of a number of CA compounds are summarized in Table 13.6. The radius-ratio rule, while not infallible, provides the principal key to the occurrence of the different structure types.

TABLE 13.6

STRUCTURES AND RADIUS RATIOS OF CA IONIC CRYSTALS

Cesium Chloride Structure		Sodium Chloride Structure						Zinc Blende or Wurtzite Structure	
Theoretical Range									
1.000–0.732		0.732–0.414						0.414–0.225	
CsCl	0.93	KF	0.98	RbI	0.69	NaBr	0.49	ZnS	0.40
CsBr	0.87	BaO	0.94	BaSe	0.68	MgO	0.46	MgTe	0.29
CsI	0.78	RbF	0.92	KBr	0.68	CaTe	0.45	BeO	0.22
		RbCl	0.82	SrS	0.61	LiF	0.44	BeS	0.17
		SrO	0.81	BaTe	0.61	NaI	0.44	BeSe	0.16
		CsF	0.80	KI	0.60	MgS	0.36	BeTe	0.14
		RbBr	0.76	SrSe	0.57	MgSe	0.33		
		BaS	0.73	CaS	0.58	LiBr	0.31		
		KCl	0.73	NaCl	0.53	LiCl	0.30		
		CaO	0.71	SrTe	0.51	LiI	0.28		
		NaF	0.70	CaSe	0.50				

The structures of CA_2 ionic crystals are found to be governed by the same coordination principles. Four common structures are shown in Fig. 13.26. In fluorite each Ca^{++} is surrounded by eight F^- ions at the corners of a cube, and each F^- is surrounded by four Ca^{++} at the corners of a tetrahedron. This is an example of 8 : 4 coordination. The structure of rutile illustrates a 6 : 3 coordination, and that of cristobalite a 4 : 2 type. Once again the coordination is determined primarily by the radius ratio.

The cadmium-iodide structure illustrates the result of a departure from typically ionic binding. The iodide ion is easily polarized, and one can distinguish definite CdI_2 groups forming a layerlike arrangement.

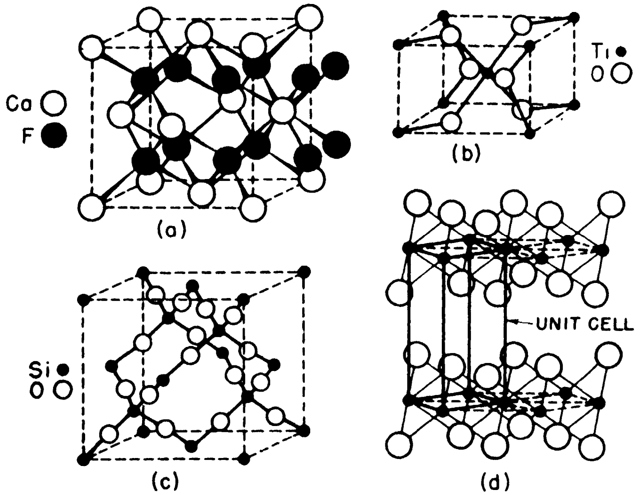


Fig. 13.26. CA$_2$ structures: (a) fluorite; (b) rutile; (c) β cristobalite; (d) cadmium iodide.

22. Coordination polyhedra and Pauling's Rule. Many inorganic crystals contain oxygen ions; their size is often so much larger than that of the cations that the structure is largely determined by the way in which they pack together. The oxygens are arranged in coordination polyhedra around the cations, some common examples being the following:

Around B: 3 O's at corners of equilateral triangle
Si, Al, Be, B, Zn: 4 O's at corners of tetrahedron
Al, Ti, Li, Cr: 6 O's at corners of octahedron

For complex structures, Pauling has given a general rule that determines how these polyhedra can pack together. Divide the valence of the positive ion by the number of surrounding negative ions; this gives the fraction of the valence of a negative ion satisfied by this positive ion. For each negative ion, the sum of the contributions from neighboring positive ions should equal its valence. This rule simply expresses the requirement that electrostatic lines of force, starting from a positive ion, must end on a negative ion in the immediate vicinity, and not be forced to wander throughout the structure seeking a distant terminus.

As an example of the application of the rule, consider the silicate group, (SiO_4). The valence of the positive ion, Si^{+4}, is $+4$. Therefore each O^{--} ion has one valence satisfied by the Si^{+4} ion, *i.e.*, one-half of its total valence of two. It is therefore possible to join each corner of a silicate tetrahedron to another silicate tetrahedron. It is also possible for the silicates to share edges and faces, although these arrangements are less favorable energetically, since they bring the central Si^{+4} ions too close together.

In the (AlO_6) octahedron, only a valence of $\frac{1}{2}$ for each O^{--} is satisfied by the central Al^{+3} ion. It is therefore possible to join two aluminum octahedra to each corner of a silicate tetrahedron.

The various ways of linking the silicate tetrahedra give rise to a great diversity of mineral structures. The following classification was given by W. L. Bragg:

(*a*) Separate SiO_4 groups
(*b*) Separate Si—O complexes
(*c*) Extended Si—O chains
(*d*) Sheet structures
(*e*) Three-dimensional structures

An example from each class is pictured in Fig. 13.27. In many minerals, other anionic groups and cations also occur, but the general principles that govern the binding remain the same. The structural characteristics are naturally reflected in the physical properties of the substances. Thus the

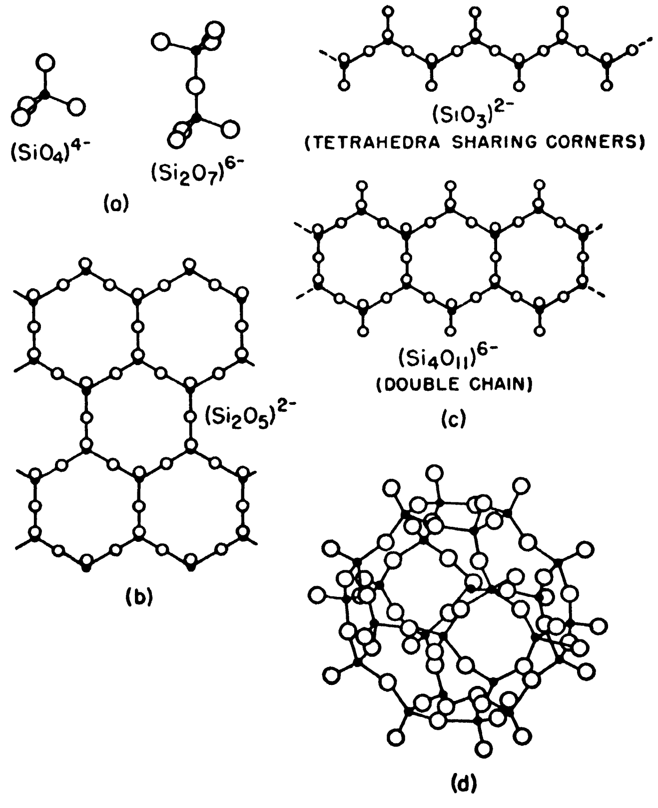


Fig. 13.27. Silicate structures: (a) isolated groups; (b) hexagonal-type sheets; (c) extended chains; (d) three-dimensional framework. (After W. L. Bragg, *The Atomic Structure of Minerals*, Cornell University Press, 1937.)

chainlike architecture is found in the asbestos minerals, the sheet arrangement in micas and talcs, and the feldspars and zeolites are typical three-dimensional polymers.

23. Crystal energy—the Born-Haber cycle. The binding energy in a purely ionic crystal can be calculated via ordinary electrostatic theory. The potential energy of interaction of two oppositely charged ions may be written

$$U = \frac{-z_1 z_2 e^2}{r} + \frac{be^2}{r^n} \tag{13.8}$$

where r is the internuclear separation and ze the ionic charge.

In calculating the electrostatic energy of a crystal, we must take into account not only the attraction between an ion and the oppositely charged ions coordinated around it, but also the repulsions between ions of like sign at somewhat larger separations, then attractions between the unlike ions once removed, and so on. Therefore, for each ion the electrostatic interaction will be a sum of terms, alternately attractive and repulsive, and diminishing in magnitude owing to the inverse-square law. For any given structure this summation amounts to little more than relating all the different internuclear distances to the smallest distance r. Thus, corresponding with eq. (13.8) for an ionic molecule, there is obtained for the potential energy of an ionic crystal per mole

$$U = \frac{-ANe^2 z_1 z_2}{r} + \frac{Be^2}{r^n} \tag{13.9}$$

The constant A, which depends on the type of crystal structure, is called the *Madelung constant*.[18] If e is in esu and U is in kcal per mole, one has the following typical A values: NaCl structure, $A = 1.74756$; CsCl, 1.76267; rutile, 4.816.

At the equilibrium internuclear distance r_0, the energy is a minimum, so that $(\partial U/\partial r)_{r_0} = 0$. Hence for the case $z_1 = z_2$,

$$\left(\frac{\partial U}{\partial r}\right) = 0 = \frac{ANe^2 z^2}{r_0^2} - \frac{nBe^2}{r_0^{n+1}}$$

$$r_0 = \left(\frac{nB}{ANz^2}\right)^{1/(n-1)}$$

$$B = \frac{r_0^{(n-1)} ANz^2}{n} \tag{13.10}$$

The value of the exponent n in the repulsive term can be estimated from the compressibility of the crystal, since work is done against the repulsive forces in compressing the crystal. Typical values of n range from 6 to 12, indicative of the rapid rise in repulsion as the internuclear separation is narrowed.

---

[18] J. Sherman, *Chem. Rev.*, *11*, 93 (1932).

The so-called *crystal energy* is obtained from eqs. (13.9) and (13.10) as

$$E_c = -U_0 = \frac{NAe^2z^2}{r_0}\left(1 - \frac{1}{n}\right) \tag{13.11}$$

This is the heat of reaction of gaseous ions to yield the solid crystal. For example, for rock salt:

$$\mathrm{Na^+(g) + Cl^-(g) = NaCl\,(c)} + E_c$$

Calculated values of E_c can be compared with other thermochemical quantities by means of the *Born-Haber cycle*. For the typical case of NaCl, this has the form:

$$\begin{tikzcd}
\mathrm{NaCl\,(c)} \arrow[r, dashed, "E_c"] & \mathrm{Na^+(g) + Cl^-\,(g)} \\
\mathrm{Na\,(c)} + \frac{1}{2}\,\mathrm{Cl_2\,(g)} \arrow[u, "Q"] \arrow[r, dashed, "(-S - \frac{1}{2}D)"] & \mathrm{Na\,(g) + Cl\,\;(g)} \arrow[u, "-I + A"']
\end{tikzcd}$$

The energetic quantities entering into the cycle are defined as follows, all per mole:

E_c = the crystal energy
Q = the standard heat of formation of crystalline NaCl
S = heat of sublimation of metallic Na
I = the ionization potential of Na
A = the electron affinity of Cl
D = the heat of dissociation of $\mathrm{Cl_2}$ (g) into atoms

For the cyclic process, by the First Law of Thermodynamics:

$$E_c = S + I + \tfrac{1}{2}D - A - Q \tag{13.12}$$

All the quantities on the right side of this equation can be evaluated, at least for alkali-halide crystals, and the value obtained for the crystal energy can be compared with that calculated from eq. (13.11). The ionization potentials I are obtained from atomic spectra, and the dissociation energies D can be accurately determined from molecular spectra. Most difficult to measure are the electron affinities A.[19]

A summary of the figures obtained for various crystals is given in Table 13.7. When the calculated crystal energy deviates widely from that obtained through the Born-Haber cycle, one may suspect nonionic contributions to the crystal binding.

24. Statistical thermodynamics of crystals: the Einstein model. If one could obtain an accurate partition function for a crystal, it would then be possible to calculate immediately all its thermodynamic properties by making use of the general formulas of Chapter 12.

For one mole of a crystalline substance, containing N atoms, there are

---

[19] See, for example, P. P. Sutton and J. E. Mayer, *J. Chem. Phys.*, *2*, 146 (1934); *3*, 20 (1935).

TABLE 13.7

THE BORN-HABER CYCLE

(Energy Terms in Kilocalories per Mole)

Crystal	$-Q$	I	S	D	A	E_c	E_c*
NaCl	99	117	26	54	88	181	190
NaBr	90	117	26	46	80	176	181
NaI	77	117	26	34	71	166	171
KCl	104	99	21	54	88	163	173
KBr	97	99	21	46	80	160	166
KI	85	99	21	34	71	151	159
RbCl	105	95	20	54	88	159	166
RbBr	99	95	20	46	80	157	161
RbI	87	95	20	34	71	148	154

* Calculated, Eq. (13.11).

$3N$ degrees of freedom. Except when there is rotation of the atoms within the solid, we can consider that there are $3N$ vibrational degrees of freedom, since $3N - 6$ is to all intents and purposes still $3N$. The precise determination of $3N$ normal modes of vibration for such a system would be an impossible task, and it is fortunate that some quite simple approximations give sufficiently good answers.

First of all, let us suppose that the $3N$ vibrations arise from independent oscillators, and then that these are harmonic oscillators, which is a good enough approximation at low temperatures, when the amplitudes are small. The model proposed by Einstein in 1906 assigned the same frequency ν to all the oscillators.

The crystalline partition function according to the Einstein model is, from eqs. (12.35) and (12.23),

$$Z = e^{-3N(h\nu/2kT)}(1 - e^{-h\nu/kT})^{-3N} \tag{13.13}$$

It follows immediately that,

$$E - E_0 = 3Nh\nu(e^{h\nu/kT} - 1)^{-1} \tag{13.14}$$

$$S = 3Nk\left[\frac{h\nu/kT}{e^{h\nu/kT} - 1} - \ln(1 - e^{-h\nu/kT})\right] \tag{13.15}$$

$$F - E_0 = 3NkT\ln(1 - e^{-h\nu/kT}) \tag{13.16}$$

$$C_V = 3Nk\left(\frac{h\nu}{2kT}\operatorname{csch}\frac{h\nu}{2kT}\right)^2 \tag{13.17}$$

Particularly interesting is the predicted temperature variation of C_V. We recall that Dulong and Petit, in 1819, noted that the molar heat capacities of the solid elements, especially the metals, were usually around $3R = 6$ calories per degree. Later measurements showed that this figure was merely a high-temperature limiting value, approached by different elements at different temperatures.

If we expand the expression in eq. (13.17) and simplify somewhat,[20] we obtain

$$C_V = \frac{3R}{1 + \frac{1}{12}(h\nu/kT)^2 + \frac{1}{360}(h\nu/kT)^4 + \ldots} \tag{13.18}$$

When T is large, this expression reduces to $C_V = 3R$. For smaller T's, a curve like the dotted line in Fig. 13.28 is obtained, the heat capacity being a universal function of (ν/T). The frequency ν can be determined from one experimental point at low temperatures and then the entire heat-capacity curve can be drawn for the substance. The agreement with the experimental data is good except at the lowest temperatures. It is clear that the higher the fundamental vibration frequency ν, the larger is the quantum of vibrational energy, and the higher the temperature at which C_V attains the classical value of $3R$. For example, the frequency for diamond is 2.78×10^{13} sec^{-1}, but for lead it is only 0.19×10^{13} sec^{-1}, so that C_V for diamond is only about 1.3 at room temperature, but C_V for lead is 6.0. The elements that follow Dulong and Petit's rule are those with relatively low vibration frequencies.

25. The Debye model. If, instead of a single fundamental frequency, a spectrum of vibration frequencies is taken for the crystal, the statistical problem becomes somewhat more complicated. One possibility is to assume that the frequencies are distributed according to the same law as that given on page 261 for the distribution of frequencies in black-body radiation. This problem was solved by P. Debye.

Instead of using eq. (13.14), the energy must be obtained by averaging over all the possible vibration frequencies ν_i of the solid, from 0 to ν_M the maximum frequency. This gives

$$\bar{E} - E_0 = \frac{1}{3N}\sum_{i=0}^{M} \frac{3Nh\nu_i}{e^{h\nu_i/kT} - 1} = \sum_{i=0}^{M} \frac{h\nu_i}{e^{h\nu_i/kT} - 1} \tag{13.19}$$

Since the frequencies form a virtual continuum the summation is replaced by an integration, by using the distribution function for the frequencies found in eq. (10.14) (multiplied by $\frac{3}{2}$ since we have one longitudinal and two transverse vibrations, instead of the two transverse of radiation). Thus

$$dn = f(\nu)d\nu = 12\pi \frac{V}{c^3} \nu^2 \, d\nu \tag{13.20}$$

where c is now the velocity of elastic waves in the crystal. Then eq. (13.19) becomes

$$\bar{E} - E_0 = \int_0^{\nu_M} \frac{h\nu}{e^{h\nu/kT} - 1} f(\nu) \, d\nu \tag{13.21}$$

---

[20] Recalling that $\operatorname{cosech} x = 2/(e^x - e^{-x})$, and $e^x = 1 + x + (x^2/2!) + (x^3/3!) + \ldots.$

Before substituting eq. (13.20) in (13.21) we eliminate c by using eq. (10.14), since when $n = 3N$, $\nu = \nu_M$, for each direction of vibration,

$$3N = \frac{4\pi}{c^3} V\nu_M^3, \quad c^3 = \frac{4\pi}{3N} V\nu_M^3, \quad f(\nu) = \frac{9N}{\nu_M^3}\nu^2\,d\nu$$

Then eq. (13.21) becomes

$$\bar{E} - E_0 = \frac{9Nh}{\nu_M^3}\int_0^{\nu_M} \frac{\nu^3\,d\nu}{e^{h\nu/kT} - 1} \tag{13.22}$$

By differentiation with respect to T,

$$C_V = \frac{9Nh^2}{kT^2\nu_M^3}\int_0^{\nu_M} \frac{\nu^4 e^{h\nu/kT}\,d\nu}{(e^{h\nu/kT} - 1)^2} \tag{13.23}$$

Let us set $x = h\nu/kT$, whereupon eq. (13.23) becomes

$$C_V = 3Nk\left(\frac{kT}{h\nu_M}\right)^3 \int_0^{h\nu_M/kT} \frac{e^x x^4\,dx}{(e^x - 1)^2} \tag{13.24}$$

The Debye theory predicts that the heat capacity of a solid as a function of temperature should depend only on the characteristic frequency ν_M. If the heat capacities of different solids are plotted against $kT/h\nu_M$, they should fall on a single curve. Such a plot is shown in Fig. 13.28, and the confirmation of the theory appears to be very good. Debye has defined a *characteristic temperature*, $\Theta_D = h\nu_M/k$, and some of these characteristic temperatures are listed in Table 13.8 for various solids. The theory of Debye is really adequate for isotropic solids only, and further theoretical work will be necessary

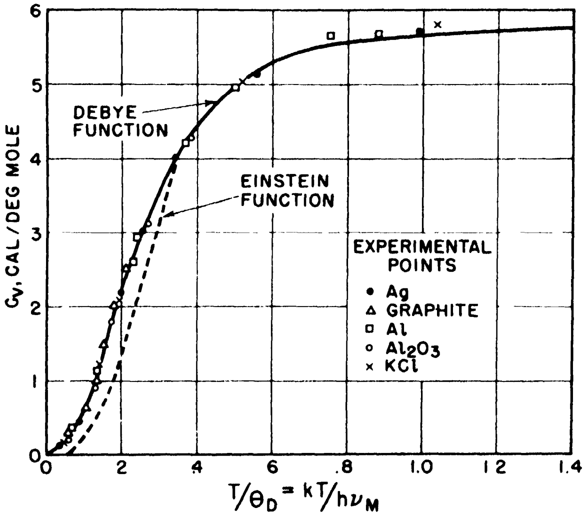


Fig. 13.28. The molar heat capacity of solids. (After F. Seitz, *The Modern Theory of Solids*, McGraw-Hill, 1940.)

before we have a comprehensive theory applicable to crystals with more complicated structures.

TABLE 13.8

DEBYE CHARACTERISTIC TEMPERATURES

Substance	Θ_D	Substance	Θ_D	Substance	Θ_D
Na	159	Be	1000	Al	398
K	100	Mg	290	Ti	350
Cu	315	Ca	230	Pb	88
Ag	215	Zn	235	Pt	225
Au	180	Hg	96	Fe	420
KCl	227	AgCl	183	CaF_2	474
NaCl	281	AgBr	144	FeS_2	645

The application of eq. (13.24) to the limiting cases of high and very low temperatures is of considerable interest. When the temperature becomes large, $e^{h\nu/kT}$ becomes small, and the equation may readily be shown to reduce to simply $C_V = 3R$, the Dulong and Petit expression. When the temperature becomes low, the integral may be expanded in a power series to show that

$$C_V = aT^3 \tag{13.25}$$

This T^3 law holds below about 30°K and is of great use in extrapolating heat-capacity data to absolute zero in connection with studies based on the Third Law of Thermodynamics (cf. page 90).

PROBLEMS

1. Show that a face-centered-cubic lattice can also be represented as a rhombohedral lattice. Calculate the rhombohedral angle α.

2. To the points in a simple orthorhombic lattice add points at $\frac{1}{2}\,\frac{1}{2}\,0$, $\frac{1}{2}\,0\,\frac{1}{2}$; *i.e.*, at the centers of a pair of opposite faces in each unit cell. Prove that the resulting arrangement of points in space is not a lattice.

3. Prove that the spacing between successive planes (hkl) in a cubic lattice is $a/\sqrt{h^2 + k^2 + l^2}$ where a is the side of the unit cell.

4. The structure of fluorite, CaF_2, is cubic with $Z = 4$, $a_0 = 5.45$ Å. The Ca^{++} ions are at the corners and face centers of the cube. The F^- ions are at $(\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4},\ \frac{3}{4}\,\frac{3}{4}\,\frac{3}{4},\ \frac{1}{4}\,\frac{3}{4}\,\frac{3}{4},\ \frac{1}{4}\,\frac{1}{4}\,\frac{3}{4},\ \frac{3}{4}\,\frac{3}{4}\,\frac{1}{4},\ \frac{1}{4}\,\frac{3}{4}\,\frac{1}{4},\ \frac{3}{4}\,\frac{1}{4}\,\frac{1}{4},\ \frac{3}{4}\,\frac{1}{4}\,\frac{3}{4})$. Calculate the nearest distance of approach of Ca—Ca, F—F, Ca—F. Sketch the arrangement of ions in the planes 100, 110, 111.

5. MgO has the NaCl structure and a density of 3.65 g per cc. Calculate the values of $(\sin \theta)/\lambda$ at which scattering occurs from the planes 100, 110, 111, 210.

6. Nickel crystallizes in the fcc structure with $a_0 = 3.52$ Å. Calculate the distance apart of nickel atoms lying in the 100, 110, and 111 planes.

7. A Debye-Scherrer powder picture of a cubic crystal with radiation of $\lambda = 1.539$ Å displayed lines at the following scattering angles:

No. of line	1	2	3	4	5	6	7	8	9
θ, deg Intensity	13.70 w	15.89 vs	22.75 s	26.91 vw	28.25 m	33.15 w	37.00 w	37.60 m	41.95 m

Note: w—weak; s—strong; m—medium; v—very.

Index these lines. Calculate a_0 for the crystal. Identify the crystal. Explain the intensity relation between lines 5 and 4 in terms of the structure factor.

8. Calculate the atomic volume for spheres of radius 1 Å in ccp and hcp structures. Give the unit cell dimensions, a_0 for cubic, a_0 and c_0 for hexagonal.

9. Show that the void volume for spheres in both ccp and hcp is 25.9 per cent. What would be the per cent void in a bcc structure with corner atoms in contact with the central atom?

10. White tin is tetragonal with $a_0 = b_0 = 5.819$ Å, and $c_0 = 3.175$ Å. Tin atoms are at 000, $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$, $\frac{1}{2}\,0\,\frac{1}{4}$, $0\,\frac{1}{2}\,\frac{3}{4}$. Calculate the density of the crystal. Grey tin has the diamond structure with $a_0 = 6.46$ Å. Describe how the tin atoms must move in the transformation from grey to white tin.

11. In a powder picture of lead with Cu—K_α radiation ($\lambda = 1.539$ Å) the line from the 531 planes appeared at $\sin\theta = 0.9210$. Calculate a_0 and the density of lead.

12. The Debye characteristic temperature of copper is $\Theta = 315$°K. Calculate the entropy of copper at 0°C and 1 atm assuming that $\alpha_0 = 4.95 \times 10^{-5}$ deg^{-1}, $\beta_0 = 7.5 \times 10^{-7}$ atm^{-1}, independent of the temperature.

13. Calculate the proton affinity of NH_3 from the following data (*i.e.*, the ΔE for reaction $NH_3 + H^+ \rightarrow NH_4^+$). NH_4F crystallizes in the ZnO type structure whose Madelung constant is 1.64. The Born repulsion exponent for NH_4F is 8, the interionic distance is 2.63 Å. The electron affinity of fluorine is 95.0 kcal. The ionization potential of hydrogen is 311.9 kcal. The heats of formation from the atoms are: $NH_3 = 279.6$; $N_2 = 225$; $H_2 = 104.1$; $F_2 = 63.5$ kcal. The heat of reaction $\frac{1}{2}\,N_2(g) + 2\,H_2(g) + \frac{1}{2}\,F_2(g) = NH_4^+F^-(c)$ is 111.9 kcal.

REFERENCES

BOOKS

1. Barrett, C. S., *Structure of Metals* (New York: McGraw-Hill, 1952).
2. Bragg, W. H., and W. L. Bragg, *The Crystalline State*, vol. I (London: Bell, 1934).
3. Buerger, M. J., *X-Ray Crystallography* (New York: Wiley, 1942).

4. Bunn, C. W., *Chemical Crystallography* (New York: Oxford, 1945).
5. Evans, R. C., *Crystal Chemistry* (London: Cambridge, 1939).
6. Hume-Rothery, W., *Atomic Theory for Students of Metallurgy* (London: Institute of Metals, 1947).
7. Kittel, C., *Introduction to Solid-State Physics* (New York: Wiley, 1953).
8. Lonsdale, K., *Crystals and X-Rays* (New York: Van Nostrand, 1949).
9. Phillips, F. C., *An Introduction to Crystallography* (New York: Longmans, 1946).
10. Wells, A. F., *Structural Inorganic Chemistry* (New York: Oxford, 1950).
11. Wilson, A. H., *Semiconductors and Metals* (London: Cambridge, 1939).
12. Wooster, W. A., *Crystal Physics* (London: Cambridge, 1938).

ARTICLES

1. Bernal, J. D., *J. Chem. Soc.*, 643–66 (1946), "The Past and Future of X-Ray Crystallography."
2. DuBridge, L. A., *Am. J. Phys.*, *16*, 191–98 (1948), "Electron Emission from Metal Surfaces."
3. Frank, F. C., *Adv. Phys.*, *1*, 91–109 (1952), "Crystal Growth and Dislocations."
4. Fuoss, R. M., *J. Chem. Ed.*, *19*, 190–93, 231–35 (1942), "Electrical Properties of Solids."
5. Lonsdale, K., *Endeavour*, *6*, 139–46 (1947), "X-Rays and the Carbon Atom."
6. Robertson, J. M., *J. Chem. Soc.*, 249–57 (1945), "Diffraction Methods in Modern Structural Chemistry."
7. Sidhu, S. S., *Am. J. Phys.*, *16*, 199-205 (1948), "Structure of Cubic Crystals."
8. Smoluchowski, R., and J. S. Koehler, *Ann. Rev. Phys. Chem.*, *2*, 187–216 (1951), "Band Theory and Crystal Structure."
9. Weisskopf, V. F., *Am. J. Phys.*, *11*, 111–12 (1943), "Theory of the Electrical Resistance of Metals."

CHAPTER 14

Liquids

1. The liquid state. The crystalline and the gaseous states of matter have already been surveyed in some detail. The liquid state remains to be considered. Not that every substance falls neatly into one of these three classifications—there is a variety of intermediate forms well calculated to perplex the morphologist: rubbers and resins, glasses and liquid crystals, fibers and protoplasm.

Gases, at least in the ideal approximation approached at high temperatures and low densities, are characterized by complete randomness on the molecular scale. The ideal crystal, on the other hand, is one of nature's most orderly arrangements. Because the extremes of perfect chaos and perfect harmony are both relatively simple to treat mathematically, the theory of gases and crystals is at a respectably advanced stage. Liquids, however, representing a peculiar compromise between order and disorder, have so far defied a comprehensive theoretical treatment.

Thus in an ideal gas, the molecules move independently of one another and interactions between them are neglected. The energy of the perfect gas is simply the sum of the energies of the individual molecules, their internal energies plus their translational kinetic energies; there is no intermolecular potential energy. It is therefore possible to write down a partition function such as that in eq. (12.23), from which all the equilibrium properties of the gas are readily derived.

In a crystalline solid, translational kinetic energy is usually negligible. The molecules, atoms, or ions vibrate about equilibrium positions to which they are held by strong intermolecular, interatomic, or interionic forces. In this case too, an adequate partition function, such as that in eq. (13.13), can be obtained.

In a liquid, on the other hand, the situation is much harder to define. The cohesive forces are sufficiently strong to lead to a condensed state, but not strong enough to prevent a considerable translational energy of the individual molecules. The thermal motions introduce a disorder into the liquid without completely destroying the regularity of its structure. It has therefore not yet been possible to devise an acceptable partition function for liquids.

It should be mentioned that in certain circles it is now considered indelicate to speak of individual molecules in condensed systems, such as liquids or solids. As James Kendall once put it, we may choose to imagine that "the whole ocean consists of one loose molecule and the removal of a fish from it is a dissociation process."

In studying liquids, it is often helpful to recall the relation between entropy and degree of disorder. Consider a crystal at its melting point. The crystal is energetically a more favorable structure than the liquid to which it melts. It is necessary to add energy, the latent heat of fusion, to effect the melting. The equilibrium situation, however, is determined by the free-energy difference, $\Delta F = \Delta H - T\Delta S$. It is the greater randomness of the liquid, and hence its greater entropy, that finally makes the $T\Delta S$ term large enough to overcome the ΔH term, so that the crystal melts when the following condition is reached:

$$T(S_{\text{liq}} - S_{\text{cry}}) = H_{\text{liq}} - H_{\text{cry}}$$

The sharpness of the melting point is noteworthy. There does not in general appear to be a continuous gradation of properties between liquid and crystal. The sharp transition is due to the extremely rigorous geometrical requirements that must be fulfilled by a crystal structure. It is not possible to introduce small regions of disorder into the crystal without at the same time seriously disturbing the structure over such a long range that the crystalline arrangment is destroyed. Two-dimensional models of the gaseous, liquid, and crystalline states are illustrated in Fig. 14.1. The picture of the liquid was constructed by J. D. Bernal by introducing around "atom" *A* only five other atoms instead of its normal close-packed coordination of six. Every effort was then made to draw the rest of the circles in the most ordered arrangement possible, with the results shown. The one point of abnormal coordination among some hundred atoms sufficed to produce the long-range disorder believed to be typical of the liquid state. We see that if there is to be any abnormal coordination at all, there has to be quite a lot of it. Herein probably lies an explanation of the sharpness of melting. When the thermal motions in one region of a crystal suffice to destroy the regular structure, the irregularity rapidly spreads throughout the entire specimen; thus disorder in a crystal may be contagious.

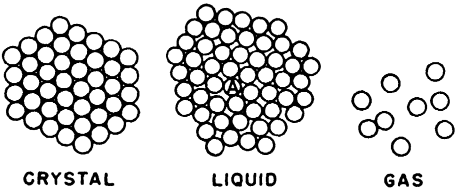


Fig. 14.1. Two-dimensional models.

These remarks should not be taken to imply that all crystals are ideally perfect, and admit of no disorder at all. It is only that the amount of disorder allowed is usually very limited. When the limit is exceeded, complete melting of the crystal occurs. There are two types of defect that occur in crystal structures. There may be vacant lattice positions or "holes," and there may be interstitial positions occupied by atoms or ions.

It is sometimes convenient to classify liquids, like crystals, from a rather chemical standpoint, according to the kind of cohesive forces that hold them together. Thus there are the ionic liquids such as molten salts, the liquid metals consisting of metal ions and fairly mobile electrons, liquids such as water held together mainly by hydrogen bonds, and finally molecular liquids in which the cohesion is due to the van der Waals forces between essentially saturated molecules. Many liquids fall into this last group, and even when other forces are present, the van der Waals contribution may be large. The nature of these forces will be considered later in this chapter.

2. Approaches to a theory for liquids. From these introductory remarks it may be evident that there are three possible ways of essaying a theory of the liquid state, two cautious ways and one direct way.

The cautious approaches are by way of the theory of gases and the theory of solids. The liquid may be studied as an extremely imperfect gas. This is a reasonable viewpoint, since above the critical point there is no distinction at all between liquid and gas, and the so-called "fluid state" of matter exists. On the other hand, the liquid may be considered as similar to a crystal, except that the well-ordered arrangement of units extends over a short range only, five or six molecular diameters, instead of over the whole specimen. This is sometimes called "short-range order and long-range disorder." This is a reasonable viewpoint, since close to the melting point the density of crystal and liquid are very similar; the solid usually expands about 10 per cent in volume, or only about 3 per cent in intermolecular spacing, when it melts. It should be realized too that whatever order exists in a liquid structure is continuously changing because of thermal motions of the individual molecules; it is the time average of a large number of different arrangements that is reflected in the liquid properties.

The imperfect-gas theory of liquids would be suitable close to the critical point; the disordered-crystal theory would be best near the melting point. At points between, they might both fail badly. A more direct approach to liquids would abandon these flanking attacks and try to develop the theory directly from the fundamentals of intermolecular forces and statistical mechanics. This is a very difficult undertaking, but a beginning has been made by Max Born, J. G. Kirkwood, and others.

We shall consider first some of the resemblances between liquid and crystal structures, as revealed by the methods of X-ray diffraction.

3. X-ray diffraction of liquids. The study of the X-ray diffraction of liquids followed the development of the method of Debye and Scherrer for powdered crystals. As the particle size of the powder decreases, the width of the lines in the X-ray pattern gradually increases. From particles around 100 Å in diameter, the lines have become diffuse halos, and with still further decrease in particle size the diffraction maxima become blurred out altogether.

If a liquid were completely amorphous, *i.e.*, without any regularity of structure, it should also give a continuous scattering of X rays without maxima or minima. This was actually not found to be the case. A typical pattern, that obtained from liquid mercury, is shown in (a), Fig. 14.2, as a microphotometer tracing of the photograph. This reveals the maxima and minima better than the unaided eye. One or two or sometimes more intensity maxima appear, whose positions often correspond closely to some of the larger interplanar spacings that occur in the crystalline structures. In the case of the metals, these are the close-packed structures. It is interesting that a crystal like bismuth, which has a peculiar and rather loose solid structure, is transformed on melting into a close-packed structure. We recall that bismuth is one of the few substances that contract in volume when melted.

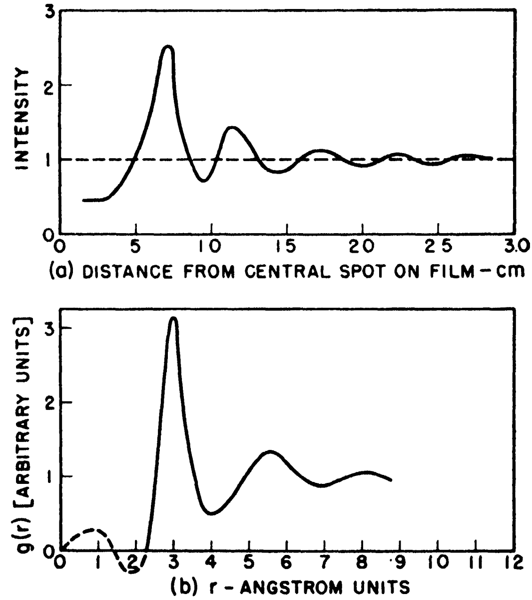


Fig. 14.2. (a) Photometric tracing of liquid-mercury picture; (b) radial distribution function for liquid mercury.

The fact that only a few maxima are observed in the diffraction patterns from liquids is in accord with the picture of short-range order and increasing disorder at longer range. In order to obtain the maxima corresponding to smaller interplanar spacings or higher orders of diffraction, the long-range order of the crystal must be present.

The diffraction maxima observed with crystals or liquids should be distinguished from those obtained by the X-ray or electron diffraction of gases. The latter arise from the fixed positions of the atoms within the molecules. The individual molecules are far apart and distributed at random. In deriving on page 327 the diffraction formula for gases, we considered only a single molecule and averaged over all possible orientations in space. With both solids and liquids the diffraction maxima arise from the ordered arrangement of the units (molecules or atoms) in the condensed three-dimensional structure. Thus gaseous argon, a monatomic gas, would yield no maxima, but liquid argon displays a pattern similar to that of liquid mercury.

It is possible to analyze the X-ray diffraction data from liquids by using the Bragg relation to calculate spacings. A more instructive approach, however, is to consider a liquid specimen as a single giant molecule, and then to use the formulas, such as eq. (11.19), derived for diffraction by single molecules. A simple theory is obtained only in the case of monatomic liquids, such as the metals and group O elements.

The arrangement of atoms in such a liquid is described by introducing the *radial distribution function* $g(r)$. Taking the center of one atom as origin, this $g(r)$ gives the probability of finding the center of another atom at the end of a vector of length r drawn from the origin. The chance of finding another atom between a distance r and $r + dr$, irrespective of angular orientation, is therefore $4\pi r^2 g(r)\,dr$ (cf. page 187). It is now possible to obtain, for the intensity of scattered X radiation, an expression similar to that in eq. (11.19), except that instead of a summation over individual scattering centers, there is an integration over a continuous distribution of scattering matter, specified by $g(r)$. Thus

$$I(\theta) \sim \int_0^\infty 4\pi r^2 g(r) \frac{\sin \mu r}{\mu r}\, dr \tag{14.1}$$

As before,

$$\mu = \frac{4\pi}{\lambda} \cdot \sin\left(\frac{\theta}{2}\right)$$

By an application of Fourier's integral theorem, this integral can be inverted,[1] yielding

$$4\pi r^2 g(r) \sim \frac{2}{\lambda} \int_0^\infty I(\theta) \frac{\sin \mu r}{\mu r}\, d\theta \tag{14.2}$$

By use of this relationship it is possible to calculate a radial-distribution curve, such as that plotted in (b), Fig. 14.2, from an experimental scattering curve, such as that in (a), Fig. 14.2. The regular coordination in the close-packed liquid-mercury structure is clearly evident, but the fact that maxima in the curve are rapidly damped out at larger interatomic distances indicates that the departure from the ordered arrangement becomes greater and greater as one travels outward from any centrally chosen atom.

4. Results of liquid-structure investigations. X-ray diffraction data from liquids are not sufficiently detailed to permit complete structure analyses like those of crystals. This situation is probably inevitable because the diffraction experiments reveal only an average or statistical structure, owing to the continual destruction and reformation of ordered arrangements by the thermal motions of the atoms or molecules in the liquid.

One view, however, proposed by G. W. Stewart (around 1930), is that

---

[1] See, for example, H. Bateman, *Partial Differential Equations of Mathematical Physics* (New York: Dover Publications, 1944), p. 207.

there are actually large regions in a liquid that are extremely well ordered. These are called *cybotactic groups*, and are supposed to contain up to several hundred molecules. These islands of order are dispersed in a sea of almost completely disordered molecules, whose behavior is essentially that of a very dense gas. There is a dynamic equilibrium between the cybotactic groups and the unattached molecules. This picturesque model is probably unsuitable for the majority of liquids and it is usually preferable to think of the disorder as being fairly well averaged throughout the whole structure.

The results with liquid metals have already been mentioned. They appear to have approximately close-packed structures quite similar to those of the solids, with the interatomic spacings expanded by about 5 per cent. The number of nearest neighbors in a close-packed structure is twelve. In liquid sodium, each atom is found to have on the average ten nearest neighbors.

One of the most interesting liquid structures is that of water. J. Morgan and B. E. Warren[2] have extended and clarified an earlier discussion by Bernal and Fowler. They studied the X-ray diffraction of water over a range of temperatures, and obtained the radial distribution curves.

The maximum of the large first peak occurs at a distance varying from about 2.88 Å at 1.5°C to slightly over 3.00 Å at 83°C. The closest spacing in ice is at 2.76 Å. It might at first be thought that this result is in disagreement with the fact that there is a contraction in volume of about 9 per cent when ice melts. Further analysis shows, however, that the coordination in liquid water is not exactly the same as the tetrahedral coordination of four nearest neighbors in ice. The number of nearest neighbors can be estimated from the area under the peaks in the radial-distribution curve, with the following results:

Temperature, °C:	1.5	13	30	62	83
Number nearest neighbors:	4.4	4.4	4.6	4.9	4.9

Thus the tetrahedral arrangement in ice is partially broken down in water, to an extent that increases with temperature. This breakdown permits closer packing, although water is of course far from being a closest-packed structure. The combination of this effect with the usual increase of intermolecular separation with temperature explains the occurrence of the maximum in the density of water at 4°C.

Among other structures that have been investigated, those of the long-chain hydrocarbons may be mentioned. These molecules tend to pack with parallel orientations of the chains, sometimes suggesting an approach to Stewart's cybotactic models.

5. Liquid crystals. In some substances the tendency toward an ordered arrangement is so great that the crystalline form does not melt directly to a

---

[2] *J. Chem. Phys.*, *6*, 666 (1938). This paper is recommended as a clear and excellent example of the X-ray method as applied to liquids.

liquid phase at all, but first passes through an intermediate stage (the *mesomorphic* or *paracrystalline* state), which at a higher temperature undergoes a transition to the liquid state. These intermediate states have been called *liquid crystals*, since they display some of the properties of each of the adjacent states. Thus some paracrystalline substances flow quite freely but are not isotropic, exhibiting interference figures when examined with polarized light; other varieties flow in a gliding stepwise fashion and form "graded droplets" having terracelike surfaces.

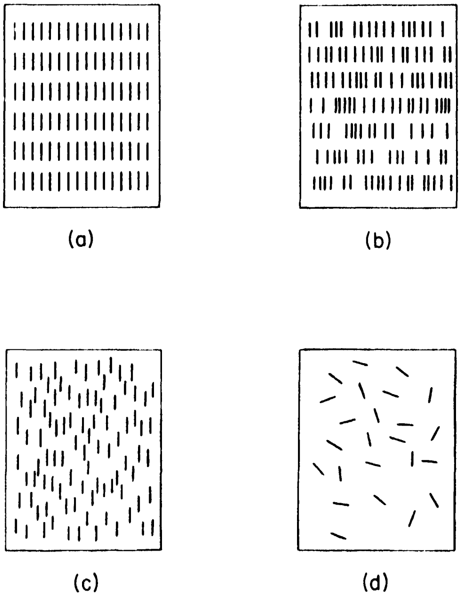
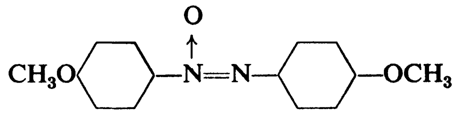
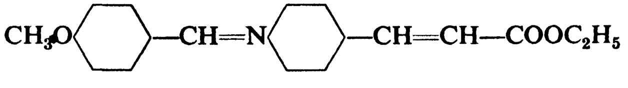


Fig. 14.3. Degrees of order: (a) crystalline—orientation and periodicity; (b) smectic—orientation and arrangement in equispaced planes, but no periodicity within planes; (c) nematic—orientation without periodicity; (d) isotropic fluid —neither orientation nor periodicity.

A compound frequently studied in its paracrystalline state is *p*-azoxyanisole,



The solid form melts at 84° to the liquid crystal, which is stable to 150° at which point it undergoes a transition to an isotropic liquid. The compound ethyl *p*-anisalaminocinnamate,



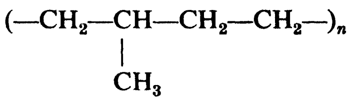
passes through three distinct paracrystalline phases between 83° and 139°. Cholesteryl bromide behaves rather differently.[3] The solid melts at 94° to an isotropic liquid, but this liquid can be supercooled to 67° where it passes over into a metastable liquid-crystalline form.

Liquid crystals tend to occur in compounds whose molecules are markedly unsymmetrical in shape. For example, in the crystalline state long-chain molecules may be lined up as shown in (a), Fig. 14.3. On raising the temperature, the kinetic energy may become sufficient to disrupt the binding between the ends of the molecules but insufficient to overcome the strong lateral attractions between the long chains. Two types of anisotropic melt might then be obtained, shown in (b) and (c), Fig. 14.3. In the *smectic* (σμηγμα, "soap") state the molecules are oriented in well-defined planes. When a stress is applied, one plane glides over another. In the *nematic* (νημα, "thread") state the planar structure is lost, but the orientation is preserved. With some substances, notably the soaps, several different phases, differentiated by optical and flow properties, can be distinguished between typical crystal and typical liquid.

It has been suggested that many of the secrets of living substances may be elucidated when we know more about the liquid-crystalline state. Joseph Needham[4] has written:

> Liquid crystals, it is to be noted, are not important for biology and embryology because they manifest certain properties which can be regarded as analogous to those which living systems manifest (models), but because living systems actually *are* liquid crystals, or, it would be more correct to say, the paracrystalline state undoubtedly exists in living cells. The doubly refracting portions of the striated muscle fibre are, of course, the classical instance of this arrangement, but there are many other equally striking instances, such as cephalopod spermatozoa, or the axons of nerve cells, or cilia, or birefringent phases in molluscan eggs, or in nucleus and cytoplasm of echinoderm eggs. . . .
>
> The paracrystalline state seems the most suited to biological functions, as it combines the fluidity and diffusibility of liquids while preserving the possibilities of internal structure characteristic of crystalline solids.

6. Rubbers. Natural rubber is a polymerized isoprene, with long hydrocarbon chains of the following structure:



$$(\text{—CH}_2\text{—}\underset{\substack{|\\ \text{CH}_3}}{\text{CH}}\text{—CH}_2\text{—CH}_2\text{—})_n$$

The various synthetic rubbers are also long, linear polymers, with similar structures. The elasticity of rubber is a consequence of the different degrees of ordering of these chains in the stretched and unstretched states. An idealized model of the rubber chains when stretched and when contracted

---

[3] J. Fischer, *Zeit. physik. Chem.*, *160A*, 110 (1932).

[4] Joseph Needham, *Biochemistry and Morphogenesis* (London: Cambridge, 1942), p. 661.

is shown in Fig. 14.4. Stretching forces the randomly oriented chains into a much more ordered alignment. The unstretched, disordered configuration is a state of greater entropy, and if the tension is released, the stretched rubber spontaneously reverts to the unstretched condition.

Robert Boyle and his contemporaries talked about the "elasticity of a gas," and although we hear this term infrequently today, it is interesting to note that the thermodynamic interpretations of the elasticity of a gas and of the elasticity of a rubber band are in fact the same. If the pressure is released on a piston that holds gas in a cylinder, the piston springs back as the gas expands. The expanded gas is in a state of higher entropy than the compressed gas: it is in a more disordered state since each molecule has a larger volume in which to move. Hence the compressed gas spontaneously expands for the same reason that the stretched rubber band spontaneously contracts.

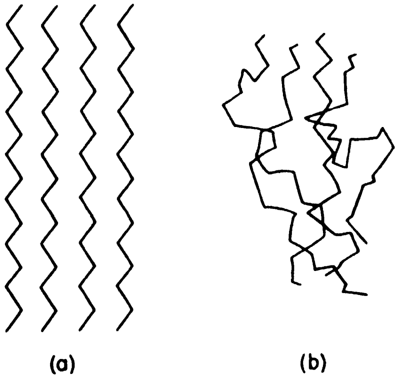


Fig. 14.4. Idealized models of chains in rubber: (a) stretched; (b) contracted.

From eq. (6) on page 65, the pressure is

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - \left(\frac{\partial E}{\partial V}\right)_T \tag{14.3}$$

For a gas, the $(\partial E/\partial V)_T$ term is small, so that effectively $P = T(\partial S/\partial V)_T$, and the pressure varies directly with T, and is determined by the change in entropy with the volume. The analog of eq. (14.3) for a rubber band of length L in which the tension is K is

$$-K = T\left(\frac{\partial S}{\partial L}\right)_T - \left(\frac{\partial E}{\partial L}\right)_T \tag{14.4}$$

It was found experimentally that K varies directly with T, so that, just as in the case of an ideal gas, the term involving the energy must be negligible. It was this observation that first led to the interpretation of rubber elasticity as an entropy effect.

7. Glasses. The glassy or vitreous state of matter is another example of a compromise between crystalline and liquid properties. The structure of a glass is essentially similar to that of an associated liquid such as water, so that there is a good deal of truth in the old description of glasses as supercooled liquids. The two-dimensional models in Fig. 14.5, given by W. H. Zachariasen, illustrate the differences between a glass and a crystal.

The bonds are the same in both cases, *e.g.*, in silica the strong electrostatic Si—O bonds. Thus both quartz crystals and vitreous silica are hard and mechanically strong. The bonds in the glass differ considerably in length and therefore in strength. Thus a glass on heating softens gradually rather than melts sharply, since there is no one temperature at which all the bonds become loosened simultaneously.

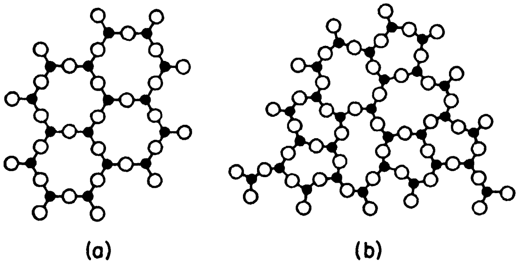


Fig. 14.5. Two-dimensional models for (a) crystal and (b) glass.

The extremely low coefficient of thermal expansion of some glasses, notably vitreous silica, is explicable in terms of a structure such as that in Fig. 14.5. The structure is a very loose one, and just as in the previously discussed case of liquid water, increasing the temperature may allow a closer coordination. To a certain extent, therefore, the structure may "expand into itself." This effect counteracts the normal expansion in interatomic distance with temperature.

8. Melting. In Table 14.1 are collected some data on the melting point, latent heat of fusion, latent heat of vaporization, and entropies of fusion and vaporization of a number of substances.

It will be noted that the heats of fusion are much less than the heats of vaporization. It requires much less energy to convert a crystal to liquid than to vaporize a liquid.

The entropies of fusion are also considerably lower than the entropies of vaporization. The latter are quite constant, around 21.6 eu (Trouton's rule). The constancy of the former is not so marked. For some classes of substances, however, notably the close-packed metals, the entropies of fusion are seen to be remarkably constant.

9. Cohesion of liquids—the internal pressure. We have so far been discussing the properties of liquids principally from the disordered-crystal point of view. Whatever the model chosen for the liquid state, the cohesive

TABLE 14.1

DATA ON MELTING AND VAPORIZATION

Substance	Heat of Fusion (kcal/mole)	Heat of Vaporization (kcal/mole)	Melting Point (°K)	Entropy of Fusion (cal/°)	Entropy of Vaporization (cal/°)
Metals					
Na	0.63	24.6	371	1.70	21.1
Al	2.55	67.6	932	2.73	29.0
K	0.58	21.9	336	1.72	21.0
Fe	3.56	96.5	1802	1.97	29.5
Ag	2.70	69.4	1234	2.19	27.8
Pt	5.33	125	2028	2.63	26.7
Hg	0.58	15.5	234	2.48	24.5
Ionic Crystals					
NaCl	7.22	183	1073	6.72	109
KCl	6.41	165	1043	6.15	93
AgCl	3.15	—	728	4.33	—
KNO_3	2.57	—	581	4.42	—
$BaCl_2$	5.75	—	1232	4.65	—
$K_2Cr_2O_7$	8.77	—	671	13.07	—
Molecular Crystals					
H_2	0.028	0.22	14	2.0	15.8
H_2O	1.43	11.3	273	5.25	30.1
A	0.280	1.88	83	3.38	21.6
NH_3	1.84	7.14	198	9.30	29.7
C_2H_5OH	1.10	10.4	156	7.10	29.6
C_6H_6	2.35	8.3	278	8.45	23.5

forces are of primary importance. Ignoring, for the time being, the origin of these forces, we can obtain an estimate of their magnitude from thermodynamic considerations. This estimate is provided by the so-called *internal pressure*.

We recall from eq. (3.43) that

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{14.5}$$

In the case of an ideal gas, the internal pressure term $P_i = (\partial E/\partial V)_T$ is zero since intermolecular forces are absent. In the case of an imperfect gas, the $(\partial E/\partial V)_T$ term becomes appreciable, and in the case of a liquid it may become much greater than the external pressure.

The internal pressure is the resultant of the forces of attraction and the forces of repulsion between the molecules in a liquid. It therefore depends markedly on the volume V, and thus on the external pressure P. This effect is shown in the following data for diethyl ether at 25°C.

P (atm):	200	800	2000	5300	7260	9200	11,100
P_i (atm):	2790	2840	2530	2020	40	−1590	−4380

For moderate increases in P, the P_i decreases only slightly, but as P exceeds 5000 atm, the P_i begins to decrease rapidly, and goes to large negative values as the liquid is further compressed. This behavior is a reflection, on a larger scale, of the law of force between individual molecules that was illustrated in Fig. 7.8. on page 181.

Internal pressures at 1 atm and 25°C are summarized in Table 14.2, taken from a compilation by J. H. Hildebrand. With normal aliphatic hydrocarbons there appears to be a gradual increase in P_i with the length of the chain. Dipolar liquids tend to have somewhat larger values than nonpolar liquids. The effect of dipole interaction is nevertheless not predominant. As might be expected, water with its strong hydrogen bonds has an exceptionally high internal pressure.

TABLE 14.2

INTERNAL PRESSURES OF LIQUIDS

(25°C and 1 atm)

Compound	P_i *atm*
Diethyl ether	2,370
n-Heptane	2,510
n-Octane	2,970
Tin tetrachloride	3,240
Carbon tetrachloride	3,310
Benzene	3,640
Chloroform	3,660
Carbon bisulfide	3,670
Mercury	13,200
Water	20,000

Hildebrand was the first to point out the significance of the internal pressures of liquids in determining solubility relationships. If two liquids have about the same P_i, their solution has little tendency toward positive deviations from Raoult's Law. The solution of two liquids differing considerably in P_i will usually exhibit considerable positive deviation from ideality, *i.e.*, a tendency toward lowered mutual solubility. Negative deviations from ideality are still ascribed to incipient compound or complex formation.

10. Intermolecular forces. It should be clearly understood from earlier discussions (cf. Chapter 11) that all the forces between atoms and molecules are electrostatic in origin. They are ultimately based on Coulomb's Law of the attraction between unlike, and the repulsion between like charges. One often speaks of long-range forces and short-range forces. Thus a force that depends on $1/r^2$ will be effective over a longer range than one dependent on $1/r^7$. All these forces may be represented as the gradient of a potential function, $f = -\partial U/\partial r$, and it is often convenient to describe the potential energies rather than the forces themselves (See Fig. 7.8, page 181.) The following varieties of intermolecular and interionic potential energies may then be distinguished:

(1) The coulombic energy of interaction between ions with net charges, leading to a long-range attraction, with $U \sim r^{-1}$.

(2) The energy of interaction between permanent dipoles, with $U \sim r^{-6}$.

(3) The energy of interaction between an ion and a dipole induced by it in another molecule, with $U \sim r^{-4}$.

(4) The energy of interaction between a permanent dipole and a dipole induced by it in another molecule, with $U \sim r^{-6}$.

(5) The forces between neutral atoms or molecules, such as the inert gases, with $U \sim r^{-6}$.

(6) The overlap energy arising from the interaction of the positive nuclei and electron cloud of one molecule with those of another. The overlap leads to repulsion at very close intermolecular separations, with an r^{-9} to r^{-12} potential.

The van der Waals attractions between molecules must arise from interactions belonging to classes (2), (4), and (5).

The first attempt to explain them theoretically was that of W. H. Keesom (1912), based on the interaction between permanent dipoles. Two dipoles in rapid thermal motion may sometimes be oriented so as to attract each other, sometimes so as to repel each other. On the average they are somewhat closer together in attractive configurations, and there is a net attractive energy. This energy was calculated[5] to be

$$U_{\mathrm{I}} = -\frac{2\mu^4}{3r^6}\cdot\frac{1}{kT} \tag{14.6}$$

where μ is the dipole moment. The observed r^{-6} dependence of the interaction energy, or r^{-7} dependence of the forces, is in agreement with deductions from experiment. This theory is of course not an adequate general explanation of van der Waals' forces, since there are considerable attractive forces between molecules, such as the inert gases, with no vestige of a permanent dipole moment.

Debye, in 1920, extended the dipole theory to take into account the *induction effect*. A permanent dipole induces a dipole in another molecule and a mutual attraction results. This interaction depends on the polarizability α of the molecules, and leads to a formula,

$$U_{\mathrm{II}} = -\frac{2\alpha\mu^2}{r^6} \tag{14.7}$$

---

[5] J. E. Lennard-Jones, *Proc. Phys. Soc.* (*London*), *43*, 461 (1931).

This effect is quite small and does not help us to explain the case of the inert gases.

In 1930, F. London solved this problem by a brilliant application of quantum mechanics. Let us consider a neutral molecule, such as argon. The positive nucleus is surrounded by a cloud[6] of negative charge. Although the time average of this charge distribution is spherically symmetrical, at any instant the distribution will be somewhat distorted. (This may be visualized very clearly in the case of the neutral hydrogen atom, in which the electron is sometimes on one side of the proton, sometimes on the other.) Thus a "snapshot" taken of an argon atom would reveal a little dipole with a certain orientation. An instant later the orientation would be different, and so on, so that over any macroscopic period of time the instantaneous dipole moments would average to zero.

Now it should not be thought that these little snapshot dipoles interact with those of other molecules to produce an attractive potential. This cannot happen since there will be repulsion just as often as attraction; there is no time for the instantaneous dipoles to line up with one another. There is, however, a snapshot-dipole—polarization interaction. Each instantaneous argon dipole induces an appropriately oriented dipole moment in neighboring atoms, and these moments interact with the original to produce an instantaneous attraction. The polarizing field, traveling with the speed of light, does not take long to traverse the short distances between molecules. Calculations show that this *dispersion interaction* leads to a potential,

$$U_{\text{III}} = -\tfrac{3}{4}h\nu_0 \frac{\alpha^2}{r^6} \tag{14.8}$$

where ν_0 is the characteristic frequency of oscillation of the charge distribution.[7]

The magnitudes of the contributions from the orientation, induction, and dispersion effects are shown in Table 14.3 for a number of simple molecules.

It is noteworthy that all the contributions to the potential energy of intermolecular attraction display an r^{-6} dependence. The complete expression for the intermolecular energy must include also a repulsive term, the overlap energy, which becomes appreciable at very close distances. Thus we may write

$$U = -Ar^{-6} + Br^{-n} \tag{14.9}$$

The value of the exponent n is from 9 to 12.

11. Equation of state and intermolecular forces. The calculation of the equation of state of a substance from a knowledge of the intermolecular

---

[6] At least a "probability cloud"—see p. 276.

[7] The r^{-6} dependence of the potential can be readily derived in this case from electrostatic theory. The field due to a dipole varies as $1/r^3$, and the potential energy of an induced dipole in a field F is $\frac{1}{2}\alpha F^2$. See Harnwell, *Electricity and Magnetism*, p. 59.

For a simple quantum-mechanical derivation of eq. (14.8), see R. H. Fowler, *Statistical Mechanics* (London: Cambridge, 1936), p. 296.

TABLE 14.3

RELATIVE MAGNITUDES OF INTERMOLECULAR INTERACTIONS*

Molecule	Dipole Moment $\mu \times 10^{18}$ (esu cm)	Polarizability $\alpha \times 10^{24}$ (cc)	Energy $h\nu_0$ (ev)	Orientation† $\frac{2}{3}\mu^4/kT$	Induction† $2\mu^2\alpha$	Dispersion† $\frac{3}{4}\alpha^2 h\nu_0$
CO	0.12	1.99	14.3	0.0034	0.057	67.5
HI	0.38	5.4	12	0.35	1.68	382
HBr	0.78	3.58	13.3	6.2	4.05	176
HCl	1.03	2.63	13.7	18.6	5.4	105
NH_3	1.5	2.21	16	84	10	93
H_2O	1.84	1.48	18	190	10	47
He	0	0.20	24.5	0	0	1.2
A	0	1.63	15.4	0	0	52
Xe	0	4.00	11.5	0	0	217

* J. A. V. Butler, *Ann. Rep. Chem. Soc. (London)*, *34*, 75 (1937).

† Units of erg cm^6 × 10^{-60}.

forces is in general a problem of great complexity. The method of attack may be outlined in principle, but so far the mathematical difficulties have proved so formidable that in practice a solution has been obtained only for a few drastically simplified cases.

We recall that the calculation of the equation of state reduces to calculating the partition function Z for the system. From Z the Helmholtz free energy A is immediately derivable, and hence the pressure, $P = -(\partial A/\partial V)_T$.

To determine the partition function, $Z = \Sigma\, e^{-E_i/kT}$, the energy levels of the system must be known. In the cases of ideal gases and crystals it is possible to use energy levels for individual constituents of the system, such as molecules or oscillators, ignoring interactions between them. In the case of liquids, this is not possible since it is precisely the interaction between different molecules that is responsible for the characteristic properties of a liquid. It would therefore be necessary to know the energy levels of the system as a whole, for example, one mole of liquid. So far this problem has not been solved.

An indication of the difficulties of a more general theory may be obtained by a consideration of the theory of imperfect gases. In this case we consider that the total energy of the system H can be divided into two terms, the kinetic energy E_K, and the intermolecular potential energy U: $H = E_K + U$.

For a mole of gas, U is a function of the positions of all the molecules. For the N molecules in a mole there are $3N$ positional coordinates, $q_1, q_2, q_3 \cdots q_{3N}$. Therefore, $U = U(q_1, q_2, q_3 \cdots q_{3N})$.

The partition function may now be written

$$Z = \Sigma\, e^{-(E_K+U)/kT} = \Sigma\, e^{-E_K/kT}\, \Sigma\, e^{-U/kT} \tag{14.10}$$

It is not necessary to consider quantized energy levels, and Z may be written in terms of an integration, rather than a summation over discrete levels.

$$Z = \Sigma\, e^{-E_K/kT} \int \ldots \int e^{-U(q_1,q_2\ldots q_{3N})/kT}\, dq_1, dq_2 \ldots dq_{3N} \qquad (14.11)$$

The theoretical treatment of the imperfect gas reduces to the evaluation of the so-called *configuration integral,*

$$\beta(T) = \int \ldots \int e^{-U(q_1,q_2\ldots q_{3N})/kT}\, dq_1, dq_2 \ldots dq_{3N} \qquad (14.12)$$

Since this is a repeated integral over $3N$ coordinates, q_i, it will be easily appreciated that its general evaluation is a matter of unconscionable difficulty, so that the general theory has ended in a mathematical cul-de-sac.

Physically, however, it is evident that the potential energy of interaction, even in a moderately dense gas, does not extend much beyond the nearest neighbors of any given molecule. This simplification still leaves a problem of great difficulty, which is at present the subject of active research.

The only simple approach is to consider interactions between *pairs* of molecules only. This would be a suitable approximation for a slightly imperfect gas. One lets $\phi(r_{ij})$ be the potential energy of interaction between two molecules i and j separated by a distance r_{ij}, and assumes that the total potential energy is the sum of such terms.

$$U = \sum_{\substack{ij \\ \text{over pairs}}} \phi(r_{ij})$$

When this potential is substituted in eq. (14.12), the configuration integral can be evaluated. The details of this very interesting, but rather long, calculation will not be given here.[8]

Efforts have been made to solve the configuration integral for more exact assumptions than the interaction between pairs. These important advances toward a comprehensive theory for dense fluids are to be found in the works of J. E. Lennard-Jones, J. E. Mayer, J. G. Kirkwood, and Max Born.

12. The free volume and holes in liquids. There have been many attempts to devise a workable theory for liquids that would avoid entanglement with the terrible intricacies of the configuration integral. One of the most successful efforts has been that of Henry Eyring, based on the concept of a *free volume.* The liquid is supposed to be in many respects similar to a gas. In a gas, the molecules are free to move throughout virtually the whole container, the excluded volume (four times van der Waals' b) being almost negligible at low densities. In a liquid, however, most of the volume is excluded volume, and only a relatively small proportion is a void space or free volume in which the centers of the molecules can manoeuvre.

Eyring then assumes that the partition function for a liquid differs from that for a gas in two respects: (1) the free volume V_f is substituted for the

---

[8] See J. C. Slater, *Introduction to Chemical Physics* (New York: McGraw-Hill, 1939), p. 191.

total volume V; (2) the zero point of energy is changed by the subtraction of the latent heat of vaporization from the energy levels of the gas. Thus, instead of eq. (12.28), one obtains

$$Z_{\text{liq}} = \frac{1}{N!}\left[\frac{(2\pi mkT)^{3/2}V_f}{h^3}\right]^N e^{\lambda_{\text{vap}}/RT} \tag{14.13}$$

The idea of a free volume in liquids is supported experimentally by Bridgman's studies of liquid compressibilities. These are high at low pressures, but after a compression in volume of about 3 per cent, the compressibility coefficient decreases markedly. The initial high compressibility corresponds to "taking up the slack" in the liquid structure or using up the free volume.

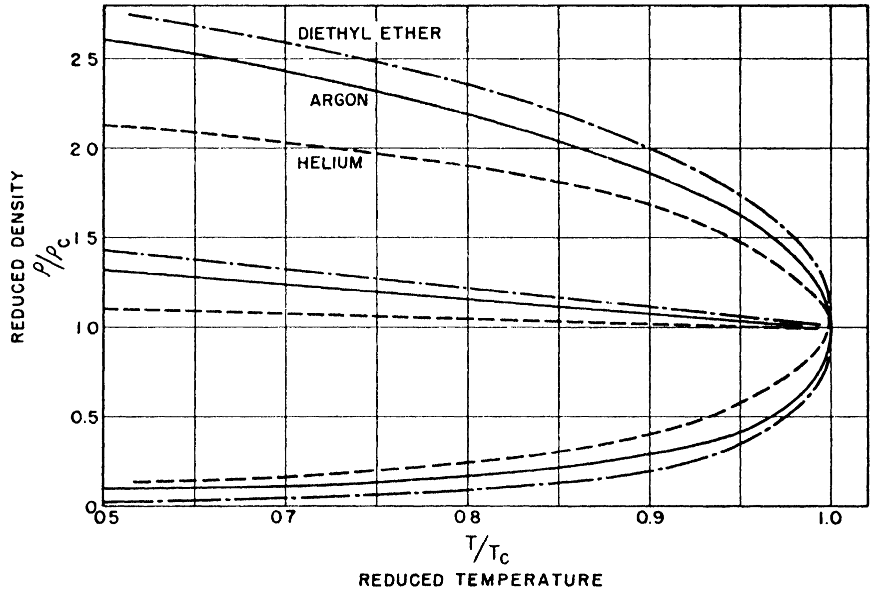


Fig. 14.6. Law of rectilinear diameters.

A useful model is sometimes provided by considering that the free volume is distributed throughout the liquid in the form of definite holes in a more closely packed structure. We should not think of these holes as being of molecular size, since there is probably a distribution of smaller holes of various sizes. The vapor is mostly void space with a few molecules moving at random. The liquid is a sort of inverse of this picture, being mostly material substance with a few holes moving at random.

As the temperature of a liquid is raised, the concentration of molecules in its vapor increases and the concentration of holes in the liquid also increases. Thus as the vapor density increases the liquid density decreases, until they become equal at the critical point. We might therefore expect the average density of liquid and vapor to be constant. Actually, there is a slight linear decrease with temperature. This behavior was discovered by L. Cailletet and E. Mathias (1886), and has been called the *law of rectilinear diameters*. It may be expressed as $\rho_{av} = \rho_0 - aT$, where ρ_{av} is the arithmetical mean of the densities of the liquid and the vapor in equilibrium with it, and ρ_0 and a are characteristic constants for each substance. The relationship is illustrated in Fig. 14.6 where the data for helium, argon, and ether are plotted in terms of reduced variables to bring them onto the same scale.

13. The flow of liquids. Perhaps most typical of all the properties of fluids is the fact that they begin to flow appreciably as soon as a shearing stress is applied. A solid, on the other hand, apparently supports a very considerable shear stress, opposing to it an elastic restoring force proportional to the strain, and given by Hooke's Law, $f = -\kappa x$.

Even a solid flows somewhat, but usually the stress must be maintained for a long time before the flow is noticeable. This slow flow of solids is called *creep*, and it can become a serious concern to designers of metal structural parts. Under high stresses, creep passes over into the *plastic deformation* of solids, for example, in the rolling, drawing, or forging of metals. These operations proceed by a mechanism involving the gliding of slip planes (page 391). Although creep is usually small, it must be admitted that the flow properties of liquids and solids differ in degree and not in kind.

The fact that liquids flow immediately under even a very small shear force does not necessarily mean that there are no elastic restoring forces within the liquid structure. These forces may exist without having a chance to be effective, owing to the rapidity of the flow process. The skipping of a thin stone on the surface of a pond demonstrates the elasticity of a liquid very well. An interesting substance, allied to the silicone rubbers, has been widely exhibited under the name of "bouncing putty." This curious material is truly a hybrid of solid and liquid in regard to its flow properties. Rolled into a sphere and thrown at a wall, it bounces back as well as any rubber ball. Set the ball on a table and it gradually collapses into a puddle of viscous putty. Thus under long-continued stress it flows slowly like a liquid, but under a sudden sharp blow it reacts like a rubber.

Some of the hydrodynamic theory of fluid flow was discussed in Chapter 7 (page 173) in connection with the viscosity of gases. It was shown how the viscosity coefficient could be measured from the rate of flow through cylindrical tubes. This is one of the most convenient methods for use with liquids as well as gases, the viscosity being calculated from the Poiseuille equation,

$$\eta = \frac{\pi \cdot \Delta P \cdot R^4}{8L\dot{V}}$$

Note that the equation for an incompressible fluid is suitable for liquids, whereas that for a compressible fluid is used for gases.

In the Ostwald type of viscometer, one measures the time required for a bulb of liquid to discharge through a capillary under the force of its own weight. It is usual to make relative rather than absolute measurements with these instruments, so that the dimensions of the capillary tube and volume of the bulb need not be known. The time t_0 required for a liquid of known viscosity η_0, usually water, to flow out of the bulb is noted. The time t_x for the unknown liquid is similarly measured. The viscosity of the unknown is

$$\eta_x = \frac{\rho_0}{\rho_x} \cdot \frac{t_x}{t_0} \cdot \eta_0$$

where ρ_0 and ρ_x are the densities of water and unknown.

Another useful viscometer is the Höppler type, based on Stokes' formula [eq. (8.11)]:

$$\eta = \frac{f}{6\pi r v} = \frac{(m - m_0)g}{6\pi r v}$$

By measuring the rate of fall in the liquid (terminal velocity v) of metal spheres of known radius r and mass m, the viscosity may be calculated, since the force f is equal to $(m - m_0)g$, where m_0 is the mass of liquid displaced by the ball.

14. Theory of viscosity. The hydrodynamic theories for the flow of liquids and gases are very similar. The kinetic-molecular mechanisms differ widely, as might be immediately suspected from the difference in the dependence of gas and liquid viscosities on temperature and pressure. In a gas, the viscosity increases with the temperature and is practically independent of the pressure. In a liquid, the viscosity increases with the pressure and decreases exponentially with increasing temperature.

The exponential dependence of liquid viscosity on temperature was first pointed out by J. deGuzman Carrancio in 1913. Thus the viscosity coefficient may be written

$$\eta = Ae^{\Delta E_{\mathrm{vis}}/RT} \tag{14.14}$$

The quantity ΔE_{vis} is a measure of the energy barrier that must be overcome before the elementary flow process can occur. It is expressed per mole of liquid. The term $e^{-\Delta E_{\mathrm{vis}}/RT}$ can then be explained as a Boltzmann factor giving the fraction of the molecules having the requisite energy to surmount the barrier.

In Table 14.4 are collected the values ΔE_{vis} for a number of liquids, together with values of ΔE_{vap} for purposes of comparison.[9] The energy required to create a hole of molecular size in a liquid is ΔE_{vap}. The fact that the ratio of ΔE_{vis} to ΔE is$_{\mathrm{vap}}$ about $\frac{1}{3}$ to $\frac{1}{4}$ for many liquids suggests that the viscous-flow process requires a free space about one-third to one-fourth the volume of a molecule. A noteworthy exception to the constancy of the $\Delta E_{\mathrm{vis}} : \Delta E_{\mathrm{vap}}$ ratio is provided by the liquid metals, for which the

---

[9] R. H. Ewell and Henry Eyring, *J. Chem. Phys.*, *5*, 726 (1937).

TABLE 14.4

VALUES OF ΔE_{vis}

Liquid	ΔE_{vis} (cal/mole)	ΔE_{vap} (cal/mole)	$\Delta E_{\text{vap}}/\Delta E_{\text{vis}}$
CCl_4	2500	6600	2.66
C_6H_6	2540	6660	2.62
CH_4	719	1820	2.53
A	516	1420	2.75
N_2	449	1210	2.70
O_2	398	1470	3.69
$CHCl_3$	1760	6630	3.76
C_2H_5Br	1585	6080	3.84
CS_2	1280	5920	4.63
Na	1450	23,400	16.1
K	1130	19,000	16.7
Ag	4820	60,700	12.5
Hg	650	13,600	20.8

values range from $\frac{1}{8}$ to $\frac{1}{20}$. This low ratio has been interpreted as indicating that the units that flow in liquid metals are ions, whereas the units that vaporize are the much larger atoms.

The pressure dependence of the viscosity follows an equation similar in form to eq. (14.14),

$$\eta = Be^{P\Delta V^*/RT} \tag{14.15}$$

The ΔV^* is the volume of the hole that must be created for the flow process to occur. As we have seen, ΔV^* for most liquids is about one-quarter of the molar volume, but for liquid metals ΔV^* is exceptionally small. Thus the viscosity of liquid metals increases only slowly with the pressure. Some properties of the earth provide an interesting confirmation of these ideas. To a depth of about 3500 km the earth consists of silicates. Except for a relatively thin solid crust, these must be molten, since the temperature is about 3000°C. The pressure is so high, however, that the molten silicates have the flow properties of a solid; this result is shown by the fact that seismic waves can pass through the material with little damping. The core of the earth, with a radius of about 3000 km, is believed to consist of molten metal. Although the pressures are even higher than in the silicate layer, the metallic core behaves as a typical liquid, and does not transmit seismic waves. In other words, the ΔV^* term for a molten metal is so small that the viscosity is not greatly increased even by very high pressures.

PROBLEMS

1. For CCl_4 the thermal pressure coefficient $(\partial P/\partial T)_V$ at 20.4°C and 1 atm is 11.63 atm per deg. Calculate the internal pressure in atmospheres.

2. The following values were found for the viscosity of liquid CCl_4:

t, °C	0	20	40	60	80
η millipoise	13.47	9.09	7.38	5.84	4.68

Plot these data and calculate ΔE_{vis}.

3. The liquid and vapor densities of ethanol in equilibrium at various temperatures are:

t, °C	100	150	200	220	240
ρ_{liq}, g/cc	0.7157	0.6489	0.5568	0.4958	0.3825
ρ_{vap}, g/cc	0.00351	0.0193	0.0508	0.0854	0.1716

The critical temperature is 243°C. What is the critical volume?

4. Suppose that the holes in liquid benzene are of the same order of size as the molecules. Estimate the number of holes per cc at 20°C where the vapor pressure is 77 mm. Hence estimate the free volume in liquid benzene in cc per mole. Van der Waals' b for benzene is 115 cc per mole. If b is four times the volume of the molecules and molecules are closely packed in liquid benzene, estimate the free volume on this basis. The density of benzene at 20°C is 0.879 g per cc.

5. The equation of state of a rubber band is $K = CT(L/L_0 - L_0^2/L^2)$, where K is the tension and L_0 is the length at zero tension. In a case with $L_0 = 20$ cm and $C = 1.33 \times 10^3$ dynes deg^{-1}, a band is stretched at 25°C to 40 cm. What is the decrease in entropy of the rubber band?

6. A certain glass at 800°C has a viscosity of 10^6 poise and a density of 3.5 g cm^{-3}. How long would a 5 mm diameter platinum ball require to fall 1.0 cm through the hot glass?

REFERENCES

BOOKS

1. Frenkel, J., *The Kinetic Theory of Liquids* (New York: Oxford, 1946).
2. Green, H. S., *The Molecular Theory of Fluids* (New York: Interscience, 1952).
3. Kimball, G. E., "The Liquid State," in *Treatise on Physical Chemistry*, vol. II, ed. by H. S. Taylor and S. Glasstone (New York: Van Nostrand, 1951).

ARTICLES

1. Condon, E. U., *Am. J. Phys.*, *22*, 310–17 (1954), "The Glassy State."
2. Hildebrand, J. H., *Proc. Phys. Soc. (London)*, *56*, 221–39 (1944), "The Liquid State."

3. Hirschfelder, J. O., *J. Chem. Ed.*, *16*, 540–44 (1939), "The Structure of Liquids."
4. Kirkwood, J. G., *Science in Progress*, vol. III (New Haven: Yale University Press, 1942), 208–221, "The Structure of Liquids."
5. Rowlinson, J. S., *Quart. Rev.*, *8*, 168–91 (1954), "Intermolecular Forces and Properties of Matter."
6. Ubbelohde, A. R., *Quart. Rev.*, *4*, 356–81 (1950), "Melting and Crystal Structure."

CHAPTER 15

Electrochemistry

1. Electrochemistry: coulometers. The subject of electrochemistry, the interrelations of electrical and chemical phenomena, is an exceedingly broad one since, as we have seen, all chemical interactions are fundamentally electrical in nature. In a more restricted sense, however, electrochemistry has come to mean the study of solutions of electrolytes and the phenomena occurring at electrodes immersed in such solutions. The electrochemistry of solutions may claim a special interest from physical chemists since it was in this field that physical chemistry first emerged as a distinct and characteristic science. Its first journal, *Die Zeitschrift für physikalische Chemie*, was founded in 1887 by Wilhelm Ostwald, and the early volumes are devoted mainly to the researches in electrochemistry of Ostwald, van't Hoff, Kohlrausch, Arrhenius, and others of their "school."

The early history of electrical science has already been discussed as an introduction to Chapter 8. Its culmination was Faraday's discovery of the quantitative laws of electrolysis.

These laws became the basis for the construction of *coulometers* for measuring quantity of electricity. A standard instrument is the silver coulometer, based on the mass of silver deposited at a platinum cathode by the passage of the electric current through an aqueous silver nitrate solution. One coulomb of electricity is equivalent to 0.00111800 g of silver. The iodine coulometer depends on the volumetric estimation of the iodine liberated by electrolysis of a potassium iodide solution. The experimental precautions needed for precise coulometry have been extensively studied.[1]

2. Conductivity measurements. From the very beginning one of the fundamental theoretical problems in electrochemistry was how the solutions of electrolytes conducted an electric current.

Metallic conductors were known to obey Ohm's Law,

$$I = \frac{\mathscr{E}}{R} \tag{15.1}$$

where I is the current (amperes), $\mathscr{E}$ is the electromotive force, emf (volts), and the proportionality constant R is called the *resistance* (ohms). The resistance depends on the dimensions of the conductor:

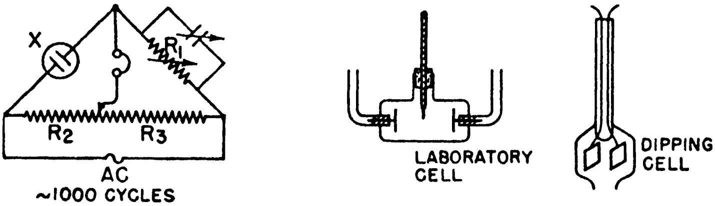
$$R = \frac{\rho l}{A} \tag{15.2}$$

---

[1] See, for example, H. S. Taylor, *Treatise on Physical Chemistry*, 2nd ed., pp. 591–598.

Here l is the length and A the cross-sectional area, and the specific resistance ρ (ohm cm) is called the *resistivity*. The reciprocal of the resistance is called the *conductance* (ohm^{-1}) and the reciprocal of the resistivity, the *specific conductance* or *conductivity* κ (ohm^{-1} cm^{-1}).

The earliest studies of the conductivity of solutions were made with rather large direct currents. The resulting electrochemical action was so great that erratic results were obtained, and it appeared that Ohm's Law was not obeyed; *i.e.*, the conductivity seemed to depend on the emf. This result was largely due to *polarization* at the electrodes of the conductivity cell, *i.e.*, a departure from equilibrium conditions in the surrounding electrolyte.



(a) (b)

Fig. 15.1. Conductivity measurement.

These difficulties were overcome by the use of an alternating-current bridge, such as that shown in (a), Fig. 15.1. With a-c frequencies in the audio range (1000–4000 cycles per sec) the direction of the current changes so rapidly that polarization effects are eliminated. One difficulty with the a-c bridge is that the cell acts as a capacitance in parallel with a resistance, so that even when the resistance arms are balanced there is a residual unbalance due to the capacitances. This effect can be partially overcome by inserting a variable capacitance in the other arm of the bridge, but for very precise work further refinements are necessary.[2] Microphones formerly were used to indicate the balance point of the bridge, but the preferred indicator is now the cathode-ray oscilloscope. The voltage from the bridge mid-point is filtered, amplified, and fed to the vertical plates of the oscilloscope. A small portion of the bridge input signal is fed to the horizontal plates of the scope through a suitable phase-shifting network. When the two signals are properly phased, the balance of capacitance is indicated by the closing of the loop on the oscilloscope screen, and the balance of resistance is indicated by the tilt of the loop from horizontal.

Typical conductivity cells are also shown in Fig. 15.1. Instead of measuring their dimensions, we now usually calibrate these cells before use with a solution of known conductivity, such as normal potassium chloride. The cell must be well thermostated since the conductivity increases with the temperature.

[2] T. Shedlovsky, *J. Am. Chem. Soc.*, *54*, 1411 (1932); W. F. Luder, *ibid.*, *62*, 89 (1940).

As soon as reliable conductivity data were available it became apparent that solutions of electrolytes followed Ohm's Law. The resistance was independent of the emf, and the smallest applied voltage sufficed to produce a current of electricity. Any conductivity theory would have to explain this fact: the electrolyte is always ready to conduct electricity and this capability is not something produced or influenced by the applied emf.

On this score, the ingenious theory proposed in 1805 by Baron C. J. von Grotthuss must be adjudged inadequate. According to his theory, the molecules of electrolyte were supposed to be very polar, with positive and negative ends. An applied field lined them up in a chain. Then the field caused the molecules at the end of the chain to dissociate, the free ions thus formed being discharged at the electrodes. Thereupon, there was an exchange of partners along the chain. Before further conduction could occur, each molecule had to rotate under the influence of the field to reform the original oriented chain.

Despite its shortcomings, the Grotthuss theory was valuable in emphasizing the necessity of having free ions in the solution to explain the observed conductivity. We shall see later that there are some cases in which a mechanism similar to that of Grotthuss may actually be followed.

In 1857, Clausius proposed that especially energetic collisions between undissociated molecules in electrolytes maintained at equilibrium a small number of charged particles. These particles were believed to be responsible for the observed conductivity.

3. Equivalent conductivities. From 1869 to 1880, Friedrich Kohlrausch and his coworkers published a long series of careful conductivity investigations. The measurements were made over a range of temperatures, pressures, and concentrations.

Typical of the painstaking work of Kohlrausch was his extensive purification of the water used as a solvent. After 42 successive distillations in vacuo, he obtained a *conductivity water* having a κ of 0.043×10^{-6} ohm^{-1} cm^{-1} at 18°C. Ordinary distilled water in equilibrium with the carbon dioxide of the air has a conductivity of about 0.7×10^{-6}.

To reduce his results to a common concentration basis, Kohlrausch defined a function called the *equivalent conductivity*,

$$\Lambda = \frac{\kappa}{c^*} \tag{15.3}$$

The concentration c^* is in units of equivalents per cc; the reciprocal $\phi = 1/c^*$ is called the *dilution*, in cc per equivalent. The equivalent conductivity would be the conductance of a cube of solution having one square centimeter cross section and containing one equivalent of dissolved electrolyte.

Some values for Λ are plotted in Fig. 15.2. On the basis of their conductivity behavior two classes of electrolytes can be distinguished. Strong electrolytes, such as most salts and acids like hydrochloric, nitric, and sulfuric, have high equivalent conductivities which increase only moderately with increasing dilution. Weak electrolytes, such as acetic and other organic acids and aqueous ammonia, have much lower equivalent conductivities at high concentrations, but the values increase greatly with increasing dilution.

The value of Λ extrapolated to zero concentration is called the *equivalent conductivity at infinite dilution*, Λ_0. The extrapolation is made readily for strong electrolytes but is impossible to make accurately for weak electrolytes

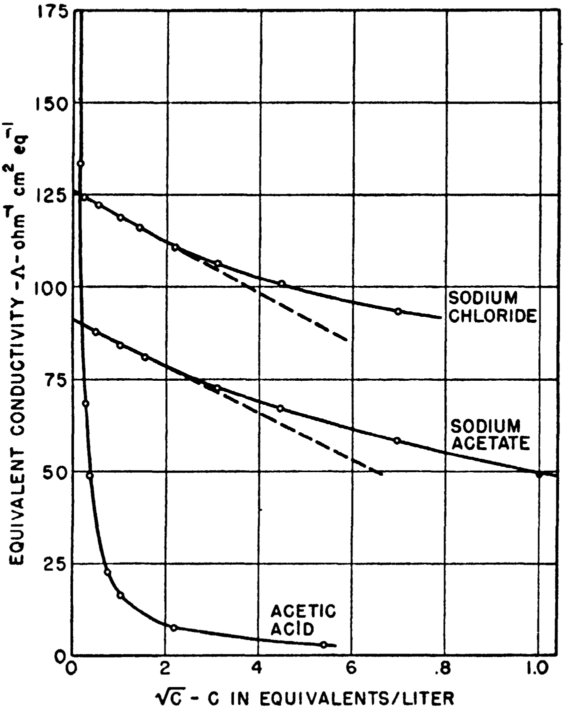


Fig. 15.2. Equivalent conductivities vs. square roots of concentration.

because of their tremendous increase in Λ at high dilutions, where the experimental measurements become very uncertain. It was found that the data were fairly well represented by the empirical equation

$$\Lambda = \Lambda_0 - k_c c^{1/2} \tag{15.4}$$

where k_c is an experimental constant.

Kohlrausch observed certain interesting relations between the values of Λ_0 for different electrolytes: the difference in Λ_0 for pairs of salts having a common ion was always nearly constant. For example (at 18°C):

	Λ_0		Λ_0		Λ_0
NaCl	108.99	$NaNO_3$	105.33	NaBr	111.10
KCl	130.10	KNO_3	126.50	KBr	132.30
Δ	21.11		21.17		21.20

Thus no matter what the anion might be, there was a constant difference between the conductivities of potassium and sodium salts. This behavior could be readily explained if Λ_0 is the sum of two independent terms, one characteristic of the anion and one of the cation. Thus

$$\Lambda_0 = \lambda_0^+ + \lambda_0^- \tag{15.5}$$

where λ_0^+ and λ_0^- are the *equivalent ionic conductivities* at infinite dilution. This is Kohlrausch's *law of the independent migration of ions*.

This rule made it possible to calculate the Λ_0 for weak electrolytes like organic acids from values for their salts, which are strong electrolytes. For example (at 18°C):

$$\begin{aligned}\Lambda_0\,(\text{HAc}) &= \Lambda_0\,(\text{NaAc}) + \Lambda_0\,(\text{HCl}) - \Lambda_0\,(\text{NaCl})\\ &= 87.4 + 379.4 - 109.0 = 357.8\end{aligned}$$

4. The Arrhenius ionization theory. From 1882 to 1886, Julius Thomsen published data on the heats of neutralization of acids and bases. He found that the heat of neutralization of a strong acid by a strong base in dilute solution was always very nearly constant, being about 13,800 calories per equivalent at 25°C. The neutralization heats of weak acids and bases were lower, and indeed the "strength" of an acid appeared to be proportional to its heat of neutralization by a strong base such as NaOH.

These results and the available conductivity data led Svante Arrhenius in 1887 to propose a new theory for the behavior of electrolytic solutions. He suggested that an equilibrium exists in the solution between undissociated solute molecules and ions which arise from these by *electrolytic dissociation*. Strong acids and bases being almost completely dissociated, their interaction was in every case simply $H^+ + OH^- = H_2O$, thus explaining the constant heat of neutralization.

While Arrhenius was working on this theory, the osmotic-pressure studies of van't Hoff appeared, which provided a striking confirmation of the new ideas. It will be recalled (page 132) that van't Hoff found that the osmotic pressures of dilute solutions of nonelectrolytes often followed the equation $\Pi = cRT$. The osmotic pressures of electrolytes were always higher than predicted from this equation, often by a factor of two, three, or more, so that a modified equation was written as

$$\Pi = icRT \tag{15.6}$$

Now it was noted that the van't Hoff "i factor" for strong electrolytes was very closely equal to the number of ions that would be formed if a solute molecule dissociated according to the Arrhenius theory. Thus for NaCl, KCl, and other uniunivalent electrolytes, $i = 2$; for $BaCl_2$, K_2SO_4, and other unibivalent species, $i = 3$; for $LaCl_3$, $i = 4$.

On April 13, 1887, Arrhenius wrote to van't Hoff as follows:

> It is true that Clausius had assumed that only a minute quantity of dissolved electrolyte is dissociated, and that all other physicists and chemists had followed

him; but the only reason for this assumption, as far as I can understand, is a strong feeling of aversion to a dissociation at so low a temperature, without any actual facts against it being brought forward. . . . At extreme dilution all salt molecules are completely dissociated. The degree of dissociation can be simply found on this assumption by taking the ratio of the equivalent conductivity of the solution in question to the equivalent conductivity at the most extreme dilution.

Thus Arrhenius would write the degree of dissociation α as

$$\alpha = \frac{\Lambda}{\Lambda_0} \tag{15.7}$$

The van't Hoff i factor can also be related to α. If one molecule of solute capable of dissociating into n ions per molecule is dissolved, the total number of particles present will be $i = 1 - \alpha + n\alpha$. Therefore

$$\alpha = \frac{i - 1}{n - 1} \tag{15.8}$$

Values of α for weak electrolytes calculated from eqs. (15.7) and (15.8) were found to be in good agreement.

Applying the mass-action principle to ionization, Ostwald obtained a *dilution law*, governing the variation of equivalent conductivity Λ with concentration. For a binary electrolyte AB with degree of dissociation α, whose concentration is c moles per liter:

$$\underset{c(1-\alpha)}{AB} \rightleftharpoons \underset{\alpha c}{A^+} + \underset{\alpha c}{B^-}$$

$$K = \frac{\alpha^2 c}{(1 - \alpha)}$$

From eq. (15.7), therefore,

$$K = \frac{\Lambda^2 c}{\Lambda_0(\Lambda_0 - \Lambda)} \tag{15.9}$$

This equation was closely obeyed by weak electrolytes in dilute solutions. An example is shown in Table 15.1. In this case, the "law" is obeyed at concentrations below about 0.1 molar, but discrepancies begin to appear at higher concentrations.

The accumulated evidence gradually won general acceptance for the Arrhenius theory, although to the chemists at the time it still seemed most unnatural that a stable molecule when placed in water should spontaneously dissociate into ions. This criticism was in fact justified and it soon became evident that the solvent must play more than a purely passive role in the formation of an ionic solution.

We now know that the crystalline salts are themselves formed of ions in regular array, so that there is no question of "ionic dissociation" when they are dissolved. The process of solution simply allows the ions to be separated from one another. The separation is particularly easy in aqueous solutions

TABLE 15.1

TEST OF OSTWALD'S DILUTION LAW

Acetic Acid at 25°C, $\Lambda_0 = 387.9$*

c (moles/liter)	Λ	Per Cent Dissociation $100\alpha = 100(\Lambda/\Lambda_0)$	Eq. (15.9) $K \times 10^5$
1.011	1.443	0.372	1.405
0.2529	3.221	0.838	1.759
0.06323	6.561	1.694	1.841
0.03162	9.260	2.389	1.846
0.01581	13.03	3.360	1.846
0.003952	25.60	6.605	1.843
0.001976	35.67	9.20	1.841
0.000988	49.50	12.77	1.844
0.000494	68.22	17.60	1.853

* D. A. MacInnes and T. Shedlovsky, *J. Am. Chem. Soc.*, *54*, 1429 (1932).

owing to the high dielectric constant of water, $\varepsilon = 82.0$. If we compare, for water and a vacuum, the work necessary to separate two ions, say Na^+ and Cl^-, from a distance of 2 Å to infinity, we find:[3]

Vacuum	*Water*
$w = \int_{2\text{Å}}^{\infty} f\,dr = \int_{2}^{\infty} \frac{e_1 e_2}{r^2}\,dr$	$w = \int_{2}^{\infty} \frac{e_1 e_2\,dr}{\varepsilon r^2}$
$= \frac{(4.80 \times 10^{-10})^2}{2 \times 10^{-8}} =$	$= \frac{(4.80 \times 10^{-10})^2}{82 \times 2 \times 10^{-8}} =$
1.15×10^{-11} erg	1.40×10^{-13} erg

Counteracting the energy necessary to separate the ions is the energy of hydration of the ions, which arises from the strong ion-dipole attractions. Thus in many cases the solution of ionic salts is an exothermic reaction. The equilibrium position is of course determined by the free-energy change. The increased randomness of the ions in solution, compared with the ionic crystal, leads to an increase in entropy, but this is sometimes outweighed by an entropy decrease due to the ordering effect of the ions on the water molecules.

In the case of acids such as HCl, the solution process probably occurs as follows: $HCl + H_2O = OH_3^+ + Cl^-$. In both HCl and H_2O the bonds are predominantly covalent in character. The ionization that occurs in solution is promoted by the high energy of hydration of the proton to form the hydronium ion, OH_3^+.

Whatever the detailed mechanisms may be, it has been clear since the work of Arrhenius that in electrolytic solutions the solute is ionized, and the

---

[3] This assumes that ε in the neighborhood of an ion is the same as ε for bulk water, which is an approximation.

transport of the ions in an electric field is responsible for the conductivity of the solutions.

5. Transport numbers and mobilities. The fraction of the current carried by a ~~given ionic species in~~ solution is called the *transport number* or *transference number* of that ion.

From Kohlrausch's law, eq. (15.5), the transference numbers t_0^+ and t_0^- of cation and anion at infinite dilution may be written

$$t_0^+ = \frac{\lambda_0^+}{\Lambda_0}, \qquad t_0^- = \frac{\lambda_0^-}{\Lambda_0} \tag{15.10}$$

The *mobility* l of an ion is defined as its velocity in an electric field of unit strength. The usual units are cm sec^{-1} per volt cm^{-1} (cm^2 sec^{-1} volt^{-1}).

Consider a one-square-centimeter cross section taken normal to the direction of the current in an electrolyte. The total current I passing through this area is the sum of that carried by the positive and that carried by the negative ions. Thus $I = n_+ v_+ z_+ e + n_- v_- z_- e$, where n_+ and n_- are the concentrations in ions per cc, z_+ and z_- are the number of charges on positive and negative ions, v_+ and v_- are the velocities of the ions, and e is the electronic charge. The requirement for over-all electrical neutrality is $n_+ z_+ = n_- z_-$, so that

$$I = n_+ z_+ e(v_+ + v_-) \tag{15.11}$$

For a unit cube of electrolyte, from eqs. (15.2) and (15.3): $I = \mathscr{E}/\rho = \kappa\mathscr{E} = \mathscr{E}\Lambda c^*$. Since $n_+ z_+ e$ is the charge in one cc and $\mathscr{F}$, the faraday, is the charge in one equivalent,

$$c^* = \frac{n_+ z_+ e}{\mathscr{F}} \tag{15.12}$$

From eqs. (15.11) and (15.12),

$$I = \mathscr{E}\Lambda \frac{n_+ z_+ e}{\mathscr{F}} = n_+ z_+ e(v_+ + v_-)$$

$$\frac{\Lambda}{\mathscr{F}} = \frac{v_+}{\mathscr{E}} + \frac{v_-}{\mathscr{E}}$$

Now $v_+/\mathscr{E}$ and $v_-/\mathscr{E}$ are the mobilities, l_+ and l_-. Therefore $\Lambda/\mathscr{F} = \lambda_+/\mathscr{F} + \lambda_-/\mathscr{F} = l_+ + l_-$, and

$$l_+ = \frac{\lambda_+}{\mathscr{F}}, \qquad l_- = \frac{\lambda_-}{\mathscr{F}} \tag{15.13}$$

It follows also from eq. (15.10) that

$$t_+ = \frac{l_+}{l_+ + l_-}, \qquad t_- = \frac{l_-}{l_+ + l_-} \tag{15.14}$$

6. Measurement of transport numbers—Hittorf method. The method of Hittorf is based on concentration changes in the neighborhood of the electrodes caused by the passage of current through the electrolyte. The principle of the method may be illustrated by reference to Fig. 15.3. Imagine a cell divided into three compartments as shown. The situation of the ions before the passage of any current is represented schematically as (a), each + or − sign indicating one equivalent of the corresponding ion.

Now let us assume that the mobility of the positive ion is three times that of the negative ion, $l_+ = 3l_-$. Let 4 faradays of electricity be passed through the cell. At the anode, therefore, four equivalents of negative ions are discharged, and at the cathode, four equivalents of positive ions. Four faradays must pass across any boundary plane drawn through the electrolyte parallel to the electrodes. Since the positive ions travel three times faster than the negative ions, 3 faradays are carried across the plane from left to right by the positive ions while one faraday is being carried from right to left by the negative ions. This transfer is depicted in panel (b) of the picture. The final situation is shown in (c). The change in number of equivalents around the anode, $\Delta n_a = 6 - 3 = 3$; around the cathode, $\Delta n_c = 6 - 5 = 1$. The ratio of these concentration changes is necessarily identical with the ratio of the ionic mobilities: $\Delta n_a/\Delta n_c = l_+/l_- = 3$.

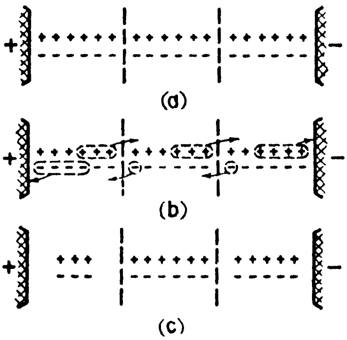


Fig. 15.3. Transport numbers (Hittorf method).

Suppose the amount of electricity passed through the cell has been measured by a coulometer in series, and found to be q faradays. Provided the electrodes are inert, q equivalents of cations have therefore been discharged at the cathode, and q equivalents of anions at the anode. The net *loss* of solute from the cathode compartment is

$$\Delta n_c = q - t_+ q = q(1 - t_+) = qt_-$$

Thus

$$t_- = \frac{\Delta n_c}{q}, \qquad t_+ = \frac{\Delta n_a}{q} \tag{15.15}$$

where Δn_a is the net loss of solute from the anode compartment. Since $t_+ + t_- = 1$, both transport numbers can be determined from measurements on either compartment, but it is useful to have both analyses as a check.

In the experiment just described, it is assumed that the electrodes are inert. In other cases ions may pass into the solution from the electrodes. Consider, for example, a silver anode in a silver nitrate solution. When electricity passes through the cell, there will be a net increase in the amount of electrolyte in the anode compartment, equal to the number of equivalents of silver entering the solution at the anode minus the number of equivalents of silver crossing the boundary of the anode compartment.

An experimental apparatus for carrying out these determinations is shown in Fig. 15.4. The apparatus is filled with a standardized electrolyte solution and a current, kept low to minimize thermal effects, is passed through the solution for some time. The total amount of electricity is measured with a coulometer. The solutions are drawn separately from the three sections of the cell and analyzed. Analysis gives the mass of solute and the mass of solvent in the solutions from the electrode compartments. Since the mass of solute originally associated with this mass of solvent is known, Δn_a and Δn_c can be found by difference. Ideally there should be no change in concentration in the middle compartment, but small changes arising from diffusion may detract from the accuracy of the determination.

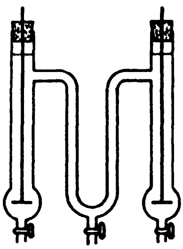


Fig. 15.4. Hittorf transport apparatus.

7. Transport numbers—moving boundary method. This method is based on the early work of Sir Oliver Lodge (1886) who used an indicator to follow the migration of ions in a conducting gel. For example, a solution of barium chloride may be placed around platinum electrodes serving as anode and cathode. The two sides of the cell are then connected by means of a tube filled with gelatin acidified with acetic acid to make it conducting and containing a small amount of dissolved silver sulfate as indicator. As the current is passed, the Ba^{++} and Cl$^-$ ions migrate into the gel from opposite ends, forming precipitates of $BaSO_4$ and AgCl, respectively. From the rate of progression of the white precipitate boundaries, the relative velocities of the ions may be estimated.

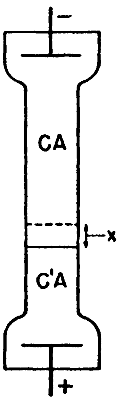


Fig. 15.5. Moving-boundary cell.

The more recent applications of this method discard the gel and indicator and use an apparatus such as that in Fig. 15.5, to follow the moving boundary between two liquid solutions. For example, the electrolyte to be studied, CA, is introduced into the apparatus in a layer above a solution of a salt with a common anion, $C'A$, and a cation whose mobility is considerably less than that of the ion C^+. When a current is passed through the cell, A^- ions move downwards toward the anode, while C^+ and C'^+ ions move upwards toward the cathode. A sharp boundary is preserved between the two solutions since the more slowly moving C'^+ ions never overtake the C^+ ions; nor do the following ions, C'^+, fall far behind, because if they began to lag, the solution behind the boundary would become more dilute, and its higher resistance and therefore steeper potential drop would increase the ionic velocity. Even with colorless solutions, the sharp boundary is visible owing to the different refractive indices of the two solutions.

Suppose the boundary moves a distance x for the passage of q coulombs. The number of equivalents transported is then $q/\mathcal{F}$, of which $t_+q/\mathcal{F}$ are carried by the positive ion. Recalling that c^* is the concentration in equivalents per cc, the volume of solution swept out by the boundary during the passage of q coulombs is $t_+q/\mathcal{F}c^*$. If a is the cross-sectional area of the tube, $xa = t_+q/\mathcal{F}c^*$, or

$$t_+ = \frac{\mathcal{F}xac^*}{q} \tag{15.16}$$

8. Results of transference experiments. Some of the measured transport numbers are summarized in Table 15.2. With these values it is possible to calculate from eq. (15.10) the equivalent ionic conductivities λ, some of which are given in Table 15.3. By the use of Kohlrausch's rule, they may

TABLE 15.2

TRANSPORT NUMBERS OF CATIONS IN WATER SOLUTIONS AT 25°C*

Normality Solution	$AgNO_3$	$BaCl_2$	LiCl	NaCl	KCl	KNO_3	$LaCl_3$	HCl
0.01	0.4648	0.440	0.3289	0.3918	0.4902	0.5084	0.4625	0.8251
0.05	0.4664	0.4317	0.3211	0.3876	0.4899	0.5093	0.4482	0.8292
0.10	0.4682	0.4253	0.3168	0.3854	0.4898	0.5103	0.4375	0.8314
0.50	—	0.3986	0.300	—	0.4888	—	0.3958	—
1.0	—	0.3792	0.287	—	0.4882	—	—	—

* L. G. Longsworth, *J. Am. Chem. Soc.*, *57*, 1185 (1935); *60*, 3070 (1938).

TABLE 15.3

EQUIVALENT IONIC CONDUCTIVITIES AT INFINITE DILUTION, λ_0, AT 25°C*

Cation	λ_0	Anion	λ_0
H^+	349.82	OH^-	198.0
Li^+	38.69	Cl^-	76.34
Na^+	50.11	Br^-	78.4
K^+	73.52	I^-	76.8
NH_4^+	73.4	NO_3^-	71.44
Ag^+	61.92	CH_3COO^-	40.9
$\frac{1}{2}\,Ca^{++}$	59.50	ClO_4^-	68.0
$\frac{1}{2}\,Ba^{++}$	63.64	$\frac{1}{2}\,SO_4^{=}$	79.8
$\frac{1}{2}\,Sr^{++}$	59.46		
$\frac{1}{2}\,Mg^{++}$	53.06		
$\frac{1}{3}\,La^{+++}$	69.6		

* D. MacInnes, *Principles of Electrochemistry* (New York: Reinhold, 1939).

be combined to yield values for the equivalent conductivities Λ_0 of a wide variety of electrolytes.

It has been mentioned that ions in solution are undoubtedly hydrated, so that the observed transport numbers are actually not those of the "bare ions" but of solvated ions. It was pointed out by Nernst that if a nonionized substance, such as urea or a sugar, is added to the solution in a Hittorf transference apparatus, its concentration in the end compartments should change as a result of the transport of water by the hydrated ions. This expectation was experimentally realized. From the equivalent ionic conductivities it is possible to calculate the mobilities of the ions by use of eq. (15.13). Some results are given in Table 15.4. The effect of hydration is shown in the set of values for Li^+, Na^+, K^+. Although Li^+ is undoubtedly the smallest ion, it has the lowest mobility; *i.e.*, the resistance to its motion through the solution is highest. This resistance must be partly due to a tightly held sheath of water molecules, bound by the intense electric field of the small ion.

TABLE 15.4

MOBILITIES OF IONS IN WATER SOLUTIONS AT 25°C

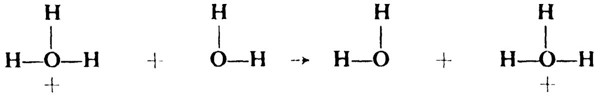
(cm^2 sec^{-1} volt^{-1})

Cations	Mobility	Anions	Mobility
H^+	36.30×10^{-4}	OH^-	20.50×10^{-4}
K^+	7.62×10^{-4}	$SO_4^{=}$	8.27×10^{-4}
Ba^{++}	6.59×10^{-4}	Cl^-	7.91×10^{-4}
Na^+	5.19×10^{-4}	NO_3^-	7.40×10^{-4}
Li^+	4.01×10^{-4}	HCO_3^-	4.61×10^{-4}

The passage of an ion through a liquid under the influence of an applied electric field $\boldsymbol{E}$ might be treated approximately as a hydrodynamic problem similar to the fall of a spherical body through a viscous medium under the influence of a gravitational field (cf. the oil drop experiment, page 210, and the Höppler viscometer, page 431). Then for steady flow the viscous resistance, given by the Stokes formula, would be balanced by the electric force: $6\pi\eta r v = ze\boldsymbol{E}$. Or, since $v = \boldsymbol{E}l$, $l\eta = ze/6\pi r$. From this follows the relation, $\eta\Lambda_0 =$ constant, known as "Walden's rule." It has a rather wide range of experimental validity when tested by measuring the Λ_0 of electrolytes in solutions of different viscosities. Its derivation from Stokes's Law is probably a specious one, for it seems unreasonable to apply the hydrodynamic equation, meant for a continuous fluid, to the motion of ions whose radii are about the same as those of the solvent molecules. Walden's rule may therefore simply imply that ionic conductance and viscous flow proceed by similar mechanisms. In water, for example, both have a temperature coefficient corresponding to an $e^{-\Delta E/RT}$ term with ΔE around 3500 calories per mole.

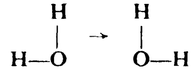
9. Mobilities of hydrogen and hydroxyl ions. An examination of Table 15.4 reveals that, with two exceptions, the ionic mobilities in aqueous solutions do not differ as to order of magnitude, being all around 6×10^{-4} cm^2 sec^{-1} volt^{-1}. The exceptions are the hydrogen and hydroxyl ions with the abnormally high mobilities of 36.2×10^{-4} and 20.5×10^{-4}.

The high mobility of the hydrogen ion is observed only in hydroxylic solvents such as water and the alcohols, in which it is strongly solvated, for example, in water to the hydronium ion, OH_3^+. It is believed to be an example of a Grotthuss type of conductivity, superimposed on the normal transport process. Thus the OH_3^+ ion is able to transfer a proton to a neighboring water molecule,



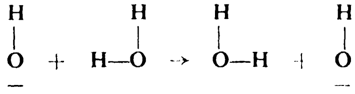
$$\mathrm{H{-}\underset{+}{\overset{H}{O}}{-}H} + \mathrm{\overset{H}{O}{-}H} \rightarrow \mathrm{H{-}\overset{H}{O}} + \mathrm{H{-}\underset{+}{\overset{H}{O}}{-}H}$$

This process may be followed by the rotation of the donor molecule so that it is again in a position to accept a proton:



$$\mathrm{H{-}\overset{H}{O}} \rightarrow \mathrm{\overset{H}{O}{-}H}$$

The high mobility of the hydroxyl ion in water is also believed to be caused by a proton transfer, between hydroxyl ions and water molecules,



$$\mathrm{\underset{-}{\overset{H}{O}}} + \mathrm{H{-}\overset{H}{O}} \rightarrow \mathrm{\overset{H}{O}{-}H} + \mathrm{\underset{-}{\overset{H}{O}}}$$

10. Diffusion and ionic mobility. The speed v of an ion of charge q in an electric field $\boldsymbol{E}$ is related to its mobility l by $v = q\boldsymbol{E}l$. The driving force in such ionic migration is the negative gradient of the *electric potential* U: $\boldsymbol{E} = -\partial U/\partial x$. Even in the absence of an external electric field, however, ions can migrate if there is a difference in *chemical potential* μ between different parts of the system. The migration of a substance under the action of a difference in chemical potential is called *diffusion*. Just as the electric force (per unit charge) on each particle equals the negative gradient of electric potential, so the diffusive force equals the negative gradient of chemical potential. In one dimension, therefore, the force on a particle of the ith kind is

$$f_i = -\frac{1}{N} \cdot \left(\frac{\partial \mu_i}{\partial x}\right)_T$$

Since μ refers to one mole of particles, it has been divided by Avogadro's Number N. The velocity under the action of unit force is the generalized mobility v_i, so that $v = (-v_i/N)(\partial \mu_i/\partial x)$. The net flow of material through unit cross section in unit time is therefore

$$s_{ix} = -v_i \frac{n_i}{N} \cdot \frac{\partial \mu_i}{\partial x}$$

where n_i is the number of particles in unit volume. For a sufficiently dilute solution, $\mu_i = RT \ln c_i + \mu_i^\circ$, and $\partial\mu_i/\partial x = (RT/c_i)(\partial c_i/\partial x)$. Hence,

$$s_{ix} = -kTv_i \frac{\partial c_i}{\partial x}$$

In 1855 Fick stated in his empirical "First Law of Diffusion" that the flow s_{ix} is proportional to the gradient of concentration:

$$s_{ix} = -D_i \frac{\partial c_i}{\partial x} \tag{15.17}$$

The proportionality factor D_i is called the *diffusion coefficient*. Thus $D_i = kTv_i$. Since the electric mobility $l_i = v_i q$, we have

$$D_i = \frac{kT}{q} l_i \tag{15.18}$$

This equation was derived by Nernst[4] in 1888. It indicates that diffusion experiments can yield much the same kind of information about ionic mobilities as that obtained from conductivity data. Equation (15.18) obviously applies to the diffusion of a single ionic species only. An experimental example would be the diffusion of a small amount of HCl dissolved in a solution of KCl. The Cl^- concentrations would be constant throughout the system, and the experiment would measure diffusion of the H^+ ions alone. In other cases, such as diffusion of salts from concentrated to dilute solution, it is necessary to use a suitable average value of the diffusion coefficients of the ions to represent the over-all D. For instance, Nernst showed that for electrolytes of type CA, the proper average is

$$D = \frac{2D_C D_A}{D_C + D_A} \tag{15.19}$$

11. A solution of the diffusion equation. Equation (15.17) gives only the steady-state condition for diffusion, but the way in which the concentration may change with time in any region of the solution can be found as follows. Consider a region of unit cross-section and of length dx, extending from x to $x + dx$. The increase in concentration within this region in unit time is the excess of material diffusing into the region over that diffusing out, divided by the volume dx:

$$\frac{\partial c}{\partial t} = \frac{1}{dx}\left[-D\left(\frac{\partial c}{\partial x}\right)_x + D\left(\frac{\partial c}{\partial x}\right)_{x+dx}\right]$$

But,
$$\left(\frac{\partial c}{\partial x}\right)_{x+dx} = \left(\frac{\partial c}{\partial x}\right)_x + \frac{\partial}{\partial x}\left(\frac{\partial c}{\partial x}\right) dx$$

Therefore
$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2}\right) \tag{15.20}$$

---

[4] *Z. physik. Chem.*, *2*, 613 (1888).

This equation is Fick's "Second Law of Diffusion." It has the same form as the equation for heat conduction, $\partial T/\partial x = K(\partial^2 T/\partial x^2)$, where K is the thermal conductivity divided by the heat capacity per unit volume. Thus all the solutions of heat conduction problems, which have been obtained for a great variety of boundary conditions, can be directly applied to problems of diffusion.

We shall consider one solution only, which illustrates very well the phenomena of interest. Suppose an extremely thin, effectively planar layer of the diffusing substance is introduced at the surface of the diffusion medium, $x = 0$. Thus at $t = 0$; $x = 0$, $c = c_0$; but at $t = 0$, for all $x > 0$, $c = 0$. It can readily be shown[5] that the solution of eq. (15.20) for these initial conditions is

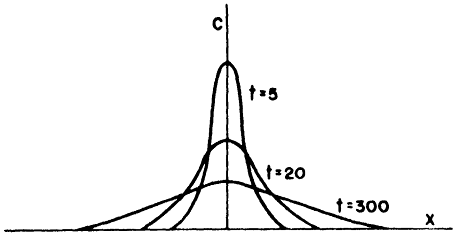


Fig. 15.6. Distribution of concentration of diffusing substance at various times. Plot of eq. (15.21) for both + and − x-direction. For diffusion from an interface between two regions, the c in eq. (15.21) must be divided by 2.

$$\frac{c}{c_0} = (\pi Dt)^{-1/2}\, e^{-x^2/4Dt} \tag{15.21}$$

The sort of concentration vs. distance curves that result for various times are shown in Fig. 15.6. The originally sharply defined source of diffusing material broadens with time; the resulting curves are in fact Gaussian error curves. The diffusion data can be evaluated from eq. (15.21) by plotting, for a given time, ln c vs. x^2; the slope of the straight line equals $(4Dt)^{-1}$.

The probability $p(x)dx$ that a given particle has diffused from $x = 0$ to a region between x and $x + dx$ is simply proportional to the concentration in this region. The average distance traversed by the diffusing particles is given by the mean square displacement[6]:

$$\overline{\Delta x^2} = \int_0^\infty x^2 p(x)dx = \int_0^\infty x^2 (\pi Dt)^{-1/2} e^{-x^2/4Dt}\, dx$$

Hence, $$\overline{\Delta x^2} = 2Dt \tag{15.22}$$

This useful expression can be applied directly to measure the diffusion coefficient of visible particles, *e.g.*, colloidal particles in Brownian motion.

---

[5] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (New York: Oxford, 1947), p. 33.

[6] One averages the square of the distance since in some cases diffusion in both the positive and the negative x directions can occur.

The displacements of a large number of individual particles after a time t are squared and averaged to give $\overline{\Delta x^2}$. Equation (15.22) is also often used to give a rapid estimate of the mean distance of diffusion in various solid and liquid systems.

12. Failures of the Arrhenius theory. After the controversies over the theory of ionic dissociation had somewhat abated, it began to be realized that the Arrhenius theory was unsatisfactory on a number of points, none of which was among those urged against it by its fierce original opponents.

The behavior of strong electrolytes presented many anomalies. The Ostwald dilution law was not closely followed by moderately strong electrolytes like dichloroacetic acid, although it agreed well with the data for weak acids like acetic. Also values for the degree of dissociation α of strong electrolytes obtained from conductance ratios were not in agreement with those from van't Hoff i factors, and the "dissociation constants" calculated by the mass-action law were far from constant.

Another discrepancy was in the neutralization heats of strong acids and bases. Although one of the first supports for the ionization theory was the constancy of these ΔH values for different acid-base pairs, more critical examination indicated that the ΔH values were actually too concordant to satisfy the theory. According to Arrhenius, there should have been small differences in the extents of ionization of acids such as HCl, H_2SO_4, HNO_3, etc., at any given concentration, and these differences should have been reflected in corresponding differences in the ΔH values, but such distinctions were not in fact observed.

Another flaw was the variation of transport numbers with concentration c. At low concentrations, these numbers were found to follow an equation of the form $t = t_0 - A\sqrt{c}$, where t_0 is the value at infinite dilution and A is a constant. The Arrhenius theory would predict that the numbers of both positive and negative current carriers should increase equally with increasing dilution. It provided no explanation of why their relative mobilities should vary.

A very striking argument against the partial dissociation of strong electrolytes was provided by the ionic structure of crystalline salts.

Finally, studies of the absorption spectra of solutions of strong electrolytes failed to reveal any evidence for undissociated molecules.

As early as 1902, a possible explanation of many of the above deficiencies of the dissociation theory was suggested by van Laar, who called attention to the strong electrostatic forces that must be present in an ionic solution and their influence on the behavior of the dissolved ions. In 1912, a detailed but highly mathematical discussion of this problem was given by S. R. Milner.

In 1923 the problem was taken up by P. Debye and E. Hückel, whose theory provided the basis for the modern treatment of strong electrolytes. It starts with the assumption that in strong electrolytes the solute is completely dissociated into ions. The observed deviations from ideal behavior, *e.g.*, apparent degrees of dissociation of less than 100 per cent, are to be ascribed entirely to the electrical interactions of the ions in solution. These deviations are therefore greater with more highly charged ions and in more concentrated solutions.

The electrical interaction theory can be applied to equilibrium problems, and also to the important transport problems in the theory of electrical conductivity. Before describing these applications we shall discuss the nomenclature and conventions employed for the thermodynamic properties of electrolytic solutions.

13. Activities and standard states. The thermodynamic description of nonideal solutions was discussed in Section 6–21. The activity a_A and activity coefficient γ_A of a component A in solution were defined by means of the equation:

$$\mu_A = \mu_A^{\circ\prime} + RT \ln \gamma_A X_A = \mu_A^{\circ\prime} + RT \ln a_A$$

It should be emphasized that the activity is a dimensionless quantity, being the ratio of the fugacity of the substance in a given system to its fugacity in some standard state ($a_A = f_A/f_A^{\circ\prime}$). The choice of the standard state is not dictated by any physical principles; it is subject only to the convenience of the person who is using the thermodynamic theory. Thus, in Section 6–21, we defined the standard state as the state of the pure solvent A at the temperature and pressure at which we investigate the variation in concentration of the solution. As the composition of the solution approaches closer and closer to pure A, deviations from ideality (Raoult's Law) become less and less. Our choice of standard state is convenient for this situation, since it requires that in the limit as $X_A \rightarrow 1, f_A \rightarrow f_A^{\circ}$, and hence $a_A = f_A/f_A^{\circ} \rightarrow 1$. The chemical potential $\mu_A^{\circ\prime}$ is therefore the free energy of pure A at the specified temperature and pressure, *i.e.*, F_A. We also note that as $X_A \rightarrow 1$, $\gamma_A \rightarrow 1$. The deviation from unity of the activity coefficient defined in this way is a measure of the deviation of component A from the ideal behavior expressed in Raoult's Law.

An inconvenient feature of this definition is also evident, however, in that it makes $\mu_A^{\circ\prime}$, the chemical potential in the standard state, and hence f_A°, functions of pressure as well as of temperature. A somewhat different definition is therefore usually employed, which takes as the standard state the pure substance *at unit pressure*. Thus the chemical potential in the standard state μ_A° is the same as F_A°, the standard free energy as ordinarily defined. Also, f_A° is a function only of temperature, which is more convenient. Every silver lining has its cloud, however, and we must note that with this new definition, it is only in the special case of unit pressure that $a_A \rightarrow X_A$ as $X_A \rightarrow 1$.

For work with dilute solutions it is often convenient to define a standard state different from that just described. As a solution is progressively diluted, the component designated as solvent A tends to obey Raoult's Law, but only for an ideal solution does the solute B also follow Raoult's Law. At sufficiently low concentrations, however, the solute always tends to follow Henry's Law. An alternative convention for activity coefficients is based on this fact. The activity coefficient γ_B is defined so that, at unit pressure, it approaches unity as the mole fraction of solute X_B approaches zero. Thus as $X_B \rightarrow 0$, $\gamma_B \rightarrow 1$, and $a_B \rightarrow X_B$. The departure of γ_B from unity (at unit pressure) is a measure of the departure of the solute behavior from that in an extremely dilute solution.

Instead of eq. (6.32) we have

$$\mu_B = \mu_B^s + RT \ln \gamma_B X_B = \mu_B^s + RT \ln a_B \tag{15.23}$$

Now μ_B^s is no longer the chemical potential of pure solute B; it is the chemical potential of B in a standard state consistent with our new definition

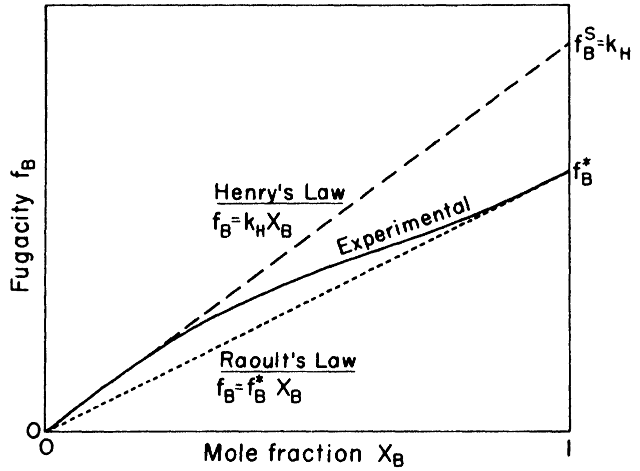


Fig. 15.7. Definition of standard state for a solute B, based on Henry's Law in dilute solution.

of activity coefficients. The activity is, of course, given by $a_B = f_B/f_B^s$, where f_B^s is the fugacity in the new standard state.

The determination of this standard state will be made clear by a reference to Fig. 15.7, which shows a plot of the fugacity of the solute B, f_B, against its mole fraction X_B. In dilute solution (as $X_B \rightarrow 0$) the fugacity follows Henry's Law, $f_B = k_H X_B$, where k_H is the Henry's Law constant. (We may recall that f_B differs from the partial vapor pressure P_B only by the correction for nonideality of the vapor.) As the solution becomes more concentrated, the experimental f_B deviates from the straight line graph of Henry's Law. Therefore the actual value of f_B at $X_B = 1$ (denoted by f_B^*) may differ widely from the extrapolated value f_B^s, obtained by assuming that Henry's Law holds all the way to $X_B = 1$. The extrapolation, shown as a dashed line in the figure, leads to the value $f_B^s = k_H$. We should note that this standard state is not an actual physical state of the solution. It is the *hypothetical state* that the solute would have if its mole fraction were unity, while at the same time it existed in an environment typical of a solution so very dilute that each solute molecule was free from any interaction with neighboring solute molecules. That this definition of standard state does indeed lead to Henry's Law at low concentrations can easily be seen as follows:

$$a_B = \frac{f_B}{f_B^{\,s}}, \quad f_B^{\,s} = k_H, \quad \text{and} \quad a_B = \gamma_B X_B$$

therefore, $f_B = k_H \gamma_B X_B$, and as $\gamma_B \to 1$, $f_B \to k_H X_B$. These activity coefficients based on Henry's Law and mole fractions are sometimes called *rational activity coefficients.*

In dealing with dilute solutions of electrolytes it is more usual to express concentrations in terms of molalities m or molarities c, instead of mole fractions X. If M_A and M_B are the molecular weights of solvent and solute, and ρ is the density of the solution, these quantities are related by

$$X_B = \frac{mM_A}{1000 + mM_A} = \frac{cM_A}{1000\rho - cM_B + cM_A} \tag{15.24}$$

In dilute solutions, mM_A, cM_B, cM_A become negligible compared to 1000, and ρ approaches ρ_A, the density of pure solvent. Then, eq. (15.24) reduces to

$$X_B \approx \frac{mM_A}{1000} \approx \frac{cM_A}{1000\rho_A}$$

For use with m and c as concentration units, two new activity coefficients and activities have been defined as follows:

$$\mu = \mu^{sm} + RT \ln \gamma^m m = \mu^{sm} + RT \ln a^m \tag{15.25}$$

$$\mu = \mu^{sc} + RT \ln \gamma^c c = \mu^{sc} + RT \ln a^c \tag{15.25a}$$

In dilute aqueous solutions, the molar and molal concentrations are nearly equal, so that $\gamma^m \approx \gamma^c$. In solutions more dilute than about 0.01 M, even γ^x (the rational activity coefficient) does not differ appreciably from the other two. At unit pressure, all the activity coefficients approach unity as the solution approaches infinite dilution, and their departures from unity are a convenient measure of the departures from Henry's Law.[7] The standard states corresponding to μ^{sm} and μ^{sc} in eqs. (15.25) and (15.25a) are determined in each case by a graph similar to Fig. 15.7. The fugacities at low concentrations are plotted against m (or c) and extrapolated to $m = 1$ (or $c = 1$) with the aid of the appropriate form of Henry's Law, $f_B = k_H{}' m$ (or $f_B = k_H{}'' c$). One further important practical point remains to be noted. In a dilute solution of an electrolyte, the solute will be dissociated to yield two or more ions from each solute molecule. The correct form of Henry's Law

---

[7] Because m and c are not proportional to X at higher concentrations, γ^m and γ^c are not unity for an ideal solution unless it is dilute. The molal concentration m is frequently used because m does not vary with temperature, whereas c is temperature dependent because it varies with the density of the solution.

must take into account this dissociation. For a uniunivalent electrolyte like HCl, for example, Henry's Law in molal concentration units will be $f_{HCl} = k_H' m^2$. Therefore, in order to find $k_H' = f^{\circ m}$, f_{HCl} must be plotted against m^2, instead of m.

14. Ion activities. In dealing with electrolytic solutions it would apparently be most convenient to use the activities of the different ionic species present in the solution. There are serious difficulties in the way of such a procedure. The requirement of over-all electrical neutrality in the solution prevents any increase in the charge due to positive ions without an equal increase in the charge due to negative ions. For example, we can change the concentration of a solution of sodium chloride by adding an equal number of sodium ions and of chloride ions. If we were to add sodium ions alone or chloride ions alone, the solution would acquire a net electric charge. The properties of ions in such a charged solution would differ considerably from their properties in the normal uncharged solution. There is in fact no conceivable way of *measuring* the individual ion activities, for there is no way of separating effects due to positive ions from those due to the accompanying negative ions in an uncharged solution.

It is nevertheless convenient to have an expression for the activity of an electrolyte in terms of the ions into which it dissociates. Consider the strong electrolyte CA, dissociated in solution according to $CA = C^+ + A^-$. Its activity a may be arbitrarily written as $a = a_+ a_- = a_\pm^2$. Now $a_\pm$ defined in this way is called the *mean activity* of the ions, and a_+ and a_- are the *conventional individual ion activities.*

For the general case, $C_{\nu_+} A_{\nu_-} = \nu_+ C^+ + \nu_- A^-$. The ion activities are then written

$$a = a_+^{\nu_+} a_-^{\nu_-} = a_\pm^{\nu} \qquad (15.26)$$

with

$$\nu_+ + \nu_- = \nu$$

Mean ionic activity coefficients and mean ionic concentrations can be similarly defined. Note that the mean values are *geometric means* of the individual ion values.[8]

In terms of the molal concentrations m, $a_\pm = \gamma_\pm m_\pm$. Now $m_\pm^\nu = m_+^{\nu_+} m_-^{\nu_-}$. Since the ionic concentrations are related to m by $m_+ = \nu_+ m$ and $m_- = \nu_- m$, we can write

$$m_\pm^\nu = (\nu_+ m)^{\nu_+} (\nu_- m)^{\nu_-} = m^\nu (\nu_+^{\nu_+} \nu_-^{\nu_-})$$

For the special case of a uniunivalent electrolyte, $m_\pm = m$.

---

[8] Sometimes *estimates* of single ion activities are made by various approximate methods. For example, the potassium ion and the chloride ion in KCl both have the argon configuration and are therefore nearly the same size. In a KCl solution it should be a good approximation to set $a_{K^+} = a_{Cl^-}$ so that $a_K^2 = a_{Cl}^2 = a_\pm^2$. Having obtained values for two ion activities in this way, we could construct a consistent set of values for others.

In a following section we shall see that it is possible to *calculate* single ion activities from electrostatic and statistical theory (method of Debye and Hückel). So far such theories are valid only in extremely dilute solutions. Comparison with experiment is always made in terms of the mean activities.

The activities can be determined by several different methods. Among the most important are measurements of the colligative properties of solutions, like freezing point depression and osmotic pressure, measurements of the solubilities of sparingly soluble salts, and methods based on the emf of electrochemical cells. We shall describe the first two methods now, postponing consideration of the emf method until cell reactions have been considered in more detail.

15. Activity coefficients from freezing points. For a two-component solution with solute (1) and solvent (0), the Gibbs-Duhem equation may be written

$$n_1\, d\mu_1 + n_0\, d\mu_0 = 0$$

Combination with eq. (15.25) yields

$$n_1\, d\ln a_1 + n_0\, d\ln a_0 = 0$$

Equation (6.18) applies to an ideal solution. For a dilute, nonideal solution, we have instead

$$\frac{d\ln a_0}{dT} = \frac{\lambda}{RT^2}$$

The freezing point depression $\Delta T = T_0 - T$, and since $T^2 \approx T_0^{\,2}$,

$$-d\ln a_0 = \left(\frac{\lambda}{RT_0^{\,2}}\right) d(\Delta T)$$

Therefore $$d\ln a_1 = -\left(\frac{n_0}{n_1}\right) d\ln a_0 = \left(\frac{n_0}{n_1}\right)\left(\frac{\lambda}{RT_0^{\,2}}\right) d(\Delta T)$$

If M_0 is the molecular weight of solvent, we have in 1000 g of solvent:

$$n_0 = \frac{1000}{M_0}, \qquad \frac{n_0}{n_1} = \frac{1000}{n_1 M_0}$$

Thus, $$d\ln a_1 = \left(\frac{1000}{n_1 M_0}\right)\left(\frac{\lambda}{RT_0^{\,2}}\right) d(\Delta T) = \left(\frac{1}{m_1 K}\right) d(\Delta T)$$

Here K is the molal freezing point depression constant (page 130), and the number of moles of (1) in 1000 g solvent is $n_1 = m_1$.

From eq. (15.26)

$$a_1 = a_\pm^{\,\nu} = \gamma_\pm^{\,\nu}\, m^\nu (\nu_+^{\,\nu_+}\, \nu_-^{\,\nu_-})$$

so that $$d\ln a_\pm = d\ln \gamma_\pm m = d\ln \gamma_\pm + d\ln m = \frac{d(\Delta T)}{\nu m K} \tag{15.27}$$

Let $j = 1 - (\Delta T/\nu m K)$, whereupon

$$dj = \frac{-d(\Delta T)}{\nu m K} + \left(\frac{\Delta T}{\nu K m^2}\right) dm$$

or $$\frac{d(\Delta T)}{\nu m K} = -dj + (1 - j)\frac{dm}{m}$$

By comparing this with eq. (15.27):

$$d \ln \gamma_{\pm} + d \ln m = -dj + (1 - j)\frac{dm}{m}$$

or

$$d \ln \gamma_{\pm} = -dj - j\, d \ln m \tag{15.28}$$

As m approaches 0, the solution approaches ideality, and $\gamma_{\pm} \rightarrow 1$ while $j \rightarrow 0$. (Since for an ideal solution $\Delta T/\nu mK = 1$.) Therefore, on integration of eq. (15.28), we obtain

$$\int_1^{\gamma_{\pm}} d \ln \gamma_{\pm} = \int_0^m -j\, d \ln m - \int_0^j dj$$

$$\ln \gamma_{\pm} = -j - \int_0^m \left(\frac{j}{m}\right) dm \tag{15.29}$$

The integration in this expression can be carried out graphically from a series of measurements of the freezing point depression in solutions of low known concentrations. We plot j/m vs. m, extrapolate to zero concentration, and measure the area under the curve.

A treatment exactly similar to the above is applicable to osmotic-pressure data. The activity coefficient determined from eq. (15.29) is that in terms of molal concentrations, $\gamma_{\pm}{}^m$.

16. Activity coefficients from solubilities. This method, applicable to sparingly soluble salts, may be illustrated by the typical example of silver chloride, AgCl. For the solution of AgCl in water we may write: $AgCl \rightleftharpoons Ag^+ + Cl^-$. The equilibrium constant becomes $K' = a_+a_-/a_s$ but since a_s is invariable owing to the presence of the solid phase, we usually write the so-called *solubility product constant* as

$$K_{sp} = a_{Ag}a_{Cl} = a_+a_- = \gamma_+\gamma_-c_+c_- \tag{15.30}$$

where c is the molar concentration. The solubility s_0 of AgCl is simply $s_0 = c_+ = c_-$. The solubility product constant may therefore be written $K_{sp} = \gamma_{\pm}{}^2 s_0{}^2$, whence

$$\gamma_{\pm} = \frac{K_{sp}{}^{1/2}}{s_0} \tag{15.31}$$

Note that this is the activity coefficient in terms of molar concentrations, $\gamma_{\pm}{}^c$. If we can find the constant K_{sp}, we can at once obtain activity coefficients from the measured solubilities s_0.

At infinite dilution, or zero concentration, the activity coefficient $\gamma_{\pm}$ approaches 1, and thus as the concentration approaches 0, s_0 approaches $K_{sp}{}^{1/2}$. The procedure adopted is therefore to measure the solubility, of AgCl for example, in a series of solutions containing decreasing concentrations of an added electrolyte, such as KNO_3. The solubilities may then be plotted against the salt concentration, and an extrapolation to zero concentration gives K_{sp}.

Extrapolations like this are most accurate if the functions plotted can be chosen so as to give a linear graph. In this case a linear graph can be obtained if we plot the log of the solubility against the square root of a quantity s, called the *ionic strength* of the solution. This is defined by

$$s = \tfrac{1}{2}\Sigma m_i z_i^2 \tag{15.32}$$

The summation is carried out over all the ionic species in the solution, with molalities m_i and charges z_i.

TABLE 15.5

MOLAL ACTIVITY COEFFICIENTS OF ELECTROLYTES

m	0.001	0.002	0.005	0.01	0.02	0.05	0.1	0.2	0.5	1.0	2.0	4.0
HCl	0.966	0.952	0.928	0.904	0.875	0.830	0.796	0.767	0.758	0.809	1.01	1.76
HNO_3	0.965	0.951	0.927	0.902	0.871	0.823	0.785	0.748	0.715	0.720	0.783	0.982
H_2SO_4	0.830	0.757	0.639	0.544	0.453	0.340	0.265	0.209	0.154	0.130	0.124	0.171
NaOH	—	—	—	—	—	0.82	—	0.73	0.69	0.68	0.70	0.89
$AgNO_3$	—	—	0.92	0.90	0.86	0.79	0.72	0.64	0.51	0.40	0.28	—
$CaCl_2$	0.89	0.85	0.785	0.725	0.66	0.57	0.515	0.48	0.52	0.71	—	—
$CuSO_4$	0.74	—	0.53	0.41	0.31	0.21	0.16	0.11	0.068	0.047	—	—
KCl	0.965	0.952	0.927	0.901	—	0.815	0.769	0.719	0.651	0.606	0.576	0.579
KBr	0.965	0.952	0.927	0.903	0.872	0.822	0.777	0.728	0.665	0.625	0.602	0.622
KI	0.965	0.951	0.927	0.905	0.88	0.84	0.80	0.76	0.71	0.68	0.69	0.75
LiCl	0.963	0.948	0.921	0.89	0.86	0.82	0.78	0.75	0.73	0.76	0.91	1.46
NaCl	0.966	0.953	0.929	0.904	0.875	0.823	0.780	0.730	0.68	0.66	0.67	0.78

17. Results of activity-coefficient measurements. Activity coefficients obtained by various methods[9] are summarized in Table 15.5 and plotted in Fig. 15.8. It will be noted that quite typically the coefficients decline markedly with increasing concentration in dilute solution, but then pass through

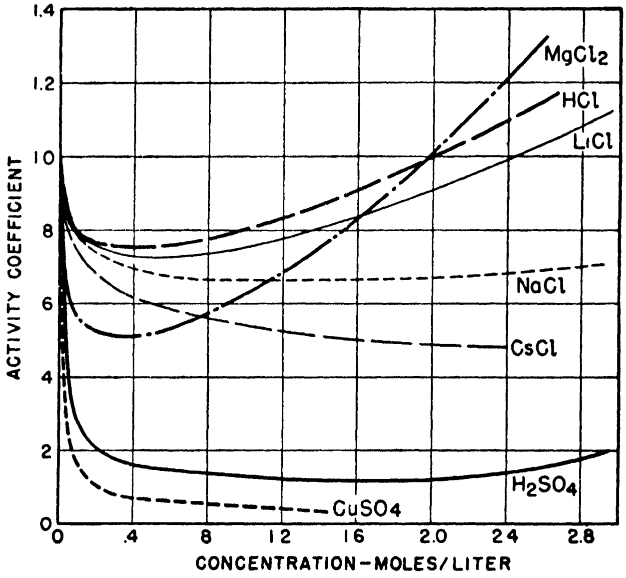


Fig. 15.8. Activity coefficients of electrolytes.

---

[9] A very complete tabulation is given by W. M. Latimer, *Oxidation Potentials* (New York: Prentice-Hall, 2nd ed., 1952).

minima and rise again in more concentrated solutions. The interpretation of this behavior constitutes one of the principal problems in the theory of strong electrolytes, to which we shall now turn our attention.

18. The Debye-Hückel theory. The theory of Debye and Hückel is based on the assumption that strong electrolytes are completely dissociated into ions. Observed deviations from ideal behavior are then ascribed to electrical interactions between the ions. To obtain theoretically the equilibrium properties of the solutions, it is necessary to calculate the extra free energy arising from these electrostatic interactions.

If the ions were distributed completely at random, the chances of finding a positive or a negative ion in the neighborhood of a given ion would be identical. In such a random distribution there would be no electrostatic energy, since on the average attractive configurations would be exactly balanced by repulsive configurations. It is evident that this cannot be the physical situation, since in the immediate neighborhood of a positive ion, a negative ion is more likely to be found than another positive ion. Indeed, were it not for the fact that the ions are continually being batted about by molecular collisions, an ionic solution might acquire a well ordered structure similar to that of an ionic crystal. The thermal motions effectively prevent any complete ordering, but the final situation is a dynamic compromise between the electrostatic interactions tending to produce ordered configurations and the kinetic collisions tending to destroy them.

The electrolyte is assumed to be completely dissociated and all deviations from ideal behavior are ascribed to the electrical interactions. Our problem is to calculate the average electric potential U of a given ion in the solution due to all the other ions. Knowing U we can calculate the work that must be expended to charge the ions reversibly to this potential, and this work will be the free energy due to electrostatic interactions. The extra electric free energy is simply related to the ionic activity coefficient, since both are a measure of the deviation from ideality.

19. Poisson's equation. The starting point in the calculation of the potential U is an expression for the average distribution of the ions, which we shall obtain in the next section. Let us call the average density of electric charge in any region of the solution ρ, *e.g.*, in units of esu per cc. Those conversant with electrical theory will recall that the potential U is related to ρ by Poisson's differential equation:

$$\nabla^2 U = -\frac{4\pi\rho}{\varepsilon} \tag{15.33}$$

where ε is the dielectric constant. We can, however, obtain quite simply the form of this equation that we need, by an application of Gauss's theorem of electrostatics.[10]

---

[10] For a further discussion see, for example, Harnwell, *Electricity and Magnetism*, p. 16. If the charge is in MKS units (coulombs), a factor ε_0 appears in Coulomb's Law and all expressions derived from it, *e.g.*, $f = q_1q_2/\varepsilon_0\varepsilon r^2$.

In (a), Fig. 15.9, is shown an electric point charge q, surrounded by a surface S. The electric field intensity at any point is by definition the force exerted on a unit charge placed at that point, so that in this case it is by Coulomb's Law:

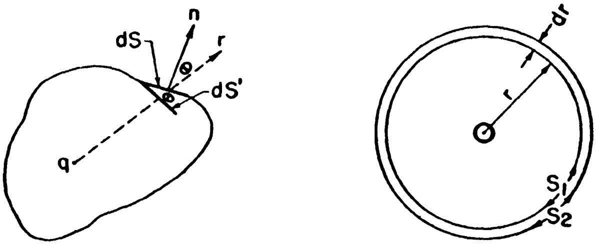
$$E_r = \frac{1 \cdot q}{\varepsilon r^2} = \frac{q}{\varepsilon r^2}$$

It is a component of a vector in the direction of the line joining the two charges.

Consider a small element dS of the surface S. The component of the field strength normal to dS is

$$E_n = E_r \cos(\boldsymbol{n}, \boldsymbol{r}) = \frac{q}{\varepsilon r^2} \cos(\boldsymbol{n}, \boldsymbol{r})$$

where $\cos(\boldsymbol{n}, \boldsymbol{r})$ is the cosine of the angle between the normal $\boldsymbol{n}$ to dS and the radius $\boldsymbol{r}$ giving the direction of the spherically symmetric field.



(a) (b)

Fig. 15.9. The Poisson equation.

The component of the area dS in the direction $\boldsymbol{r}$ is

$$dS' = dS \cos(\boldsymbol{n}, \boldsymbol{r})$$

Now the area dS' is related to $\boldsymbol{r}$ and the solid angle $d\omega$ by $dS' = r^2 d\omega$. Therefore

$$dS = \frac{r^2\, d\omega}{\cos(\boldsymbol{n}, \boldsymbol{r})}$$

It follows that $E_n\, dS = q\, d\omega/\varepsilon$. Integrating this over the entire solid angle subtended by a sphere of radius r, which is 4π, we obtain

$$\int_S E_n\, dS = \frac{q}{\varepsilon} \int_0^{4\pi} d\omega = \frac{4\pi q}{\varepsilon} \tag{15.34}$$

This is Gauss's theorem: the integral of the normal component of the electric field intensity over a closed surface equals $4\pi/\varepsilon$ times the charge enclosed within the surface.

Let us now apply this theorem to the special situation of two concentric spheres, Fig. 15.9 (b). The problem is to find the field due to the charges contained in an annular shell of thickness dr between the two spheres. For the two spherical surfaces S_1 and S_2:

$$\int_{S_1} E_n\, dS_1 + \int_{S_2} E_n\, dS_2 = \frac{4\pi}{\varepsilon} \times \text{(total charge within shell)} \tag{15.35}$$

The total charge within the shell, for the case of interest, may be expressed as a charge density ρ times the volume of the shell $4\pi r^2\, dr$; *i.e.*, $4\pi r^2 \rho\, dr$. Then eq. (15.35) becomes

$$-E_r 4\pi r^2 + E_{r+dr} 4\pi (r + dr)^2 = \frac{4\pi}{\varepsilon} 4\pi r^2 \rho\, dr$$

Now,

$$E_{r+dr} = E_r + \frac{dE}{dr}\, dr$$

Ignoring terms containing the product of two differentials, we find

$$d(r^2 E_r) = r^2 dE_r + 2rE_r\, dr = \frac{4\pi}{\varepsilon} r^2 \rho\, dr$$

or

$$\frac{1}{r^2} \cdot \frac{d}{dr}(r^2 E_r) = \frac{4\pi\rho}{\varepsilon} \tag{15.36}$$

The field strength may be represented as the negative gradient of the potential, $E_r = -dU/dr$, so that eq. (15.36) becomes

$$\frac{1}{r^2} \cdot \frac{d}{dr}\left(r^2 \frac{dU}{dr}\right) = -\frac{4\pi\rho}{\varepsilon} \tag{15.37}$$

This expression is the special form of Poisson's equation (15.33) for a spherically symmetrical problem; *i.e.*, when ρ is a function only of r. This is the situation of interest since on the average a given ion will be surrounded by a spherically symmetrical distribution of oppositely charged ions, forming the so-called *ionic atmosphere*. We wish to calculate the average electrostatic potential due to a central ion and its surrounding atmosphere. The solutions of eq. (15.37) give the potential in any region as a function of the charge density ρ. The next step is therefore to calculate ρ for the array of ions.

20. The Poisson-Boltzmann equation. The Boltzmann theorem (page 183) informs us that if n_i is the average number of ions of kind i in unit volume in the solution, the number n_i' in any particular region of the solution whose potential energy is E_p above the average is

$$n_i' = n_i e^{-E_p/kT}$$

If an ion of charge q_i is brought to a region of potential U, its potential energy is $q_i U$. For such ions the Boltzmann equation is therefore

$$n_i' = n_i e^{-q_i U/kT} \tag{15.38}$$

The charge density in a region whose potential is U is simply the summation of this expression over the different kinds of ion that may be present in the solution, each multiplied by its appropriate charge q_i.

$$\rho = \Sigma\, n_i' q_i = \Sigma\, n_i q_i e^{-q_i U/kT} \tag{15.39}$$

The Debye-Hückel treatment now considers a solution so dilute that ions will rarely be very close together. This condition implies that the interionic potential energy is small, and indeed much less than the average thermal energy, so that $q_i U \ll kT$. Then the exponential factor in eq. (15.39) may be expanded as follows:

$$e^{-q_i U/kT} = 1 - \frac{q_i U}{kT} + \frac{1}{2!}\left(\frac{q_i U}{kT}\right)^2 - \ldots$$

Terms higher than the second being negligible, eq. (15.39) becomes

$$\rho \quad \Sigma\, n_i q_i - \frac{U}{kT}\Sigma\, n_i q_i^2$$

The first term vanishes by virtue of the requirement of over-all electrical neutrality, and with $q_i = z_i e$,

$$\rho = -\frac{e^2 U}{kT}\Sigma\, n_i z_i^2 \tag{15.40}$$

It should be noted that $\Sigma\, n_i z_i^2$ is closely related to the *ionic strength*, which was defined as $s = \frac{1}{2}\Sigma\, m_i z_i^2$.

By substituting eq. (15.40) into eq. (15.37), there is obtained the Poisson-Boltzmann equation.

$$\frac{1}{r^2}\cdot\frac{d}{dr}\left(r^2\frac{dU}{dr}\right) = \frac{4\pi e^2 U}{\varepsilon kT}\Sigma\, n_i z_i^2$$

or

$$\frac{d}{dr}\left(r^2\frac{dU}{dr}\right) = b^2 r^2 U \tag{15.41}$$

where

$$b^2 = \frac{4\pi e^2}{\varepsilon kT}\Sigma\, n_i z_i^2 \tag{15.42}$$

The quantity $1/b$ has the dimensions of a length, and is called the *Debye length*. It may be thought of as an approximate measure of the *thickness of the ionic atmosphere, i.e.*, the distance over which the electrostatic field of an ion extends with appreciable strength. For example, in a one-molar aqueous solution of uniunivalent electrolyte at 25°C, $1/b = 3.1$ Å.

The Poisson-Boltzmann equation (15.41) can be readily solved by making the substitution $u = rU$, whence $d^2u/dr^2 = b^2 u$, so that

$$u = Ae^{-br} + Be^{br} \tag{15.43}$$

or

$$U = \frac{A}{r}e^{-br} + \frac{B}{r}e^{br}$$

A and B are the constants of integration, to be determined from the boundary conditions. In the first place, U must vanish as r goes to infinity, so that

$$0 = \frac{Ae^{-\infty}}{\infty} + \frac{Be^{\infty}}{\infty}$$

This can be true only if $B = 0$, since the limit of e^r/r as r goes to infinity is not zero. We then have left

$$U = \frac{A}{r} e^{-br}$$

The constant A can be determined by the fact that when $b = 0$, the concentration is zero, and therefore the potential is simply that of a single ion in the absence of any other charges, namely $U = ze/\varepsilon r$. Thus $ze/\varepsilon r = A/r$ and $A = ze/\varepsilon$. Therefore the final solution becomes

$$U = \frac{ze}{\varepsilon r} e^{-br} \tag{15.44}$$

Once again, for the case of the very dilute solution (since b is a function of the concentration) the exponential may be expanded, giving

$$U = \frac{ze}{\varepsilon r} e^{-br} \approx \frac{ze}{\varepsilon r}(1 - br)$$

$$U \approx \frac{ze}{\varepsilon r} - \frac{zeb}{\varepsilon} \tag{15.45}$$

Here it is evident that the first term $ze/\varepsilon r$ is simply the potential at a distance r due to an ion of charge ze in a medium of dielectric constant ε. The term $-zeb/\varepsilon$ is then the potential due to the other ions, those forming the ionic atmosphere of the given ion. It is this extra potential that is related to the extra free energy of the ionic solution.

21. The Debye-Hückel limiting law. For a single given ion the extra free energy is equal to the work that must be expended to charge the ion reversibly to the required potential $U = -zeb/\varepsilon$.

$$\Delta F = w = \int_0^U ze\, dU' = \int_0^U \left(\frac{-\varepsilon U'}{b}\right) dU'$$

$$\Delta F = \frac{-\varepsilon U^2}{2b} = \frac{-b}{2\varepsilon} z^2e^2 \tag{15.46}$$

Now, on the assumption that deviations of the dilute ionic solution from ideality are caused entirely by the electrical interactions, it can be shown that this extra electric free energy per ion is simply $kT \ln \gamma$, where γ is the conventional ion activity coefficient. Let us write for the chemical potential of an ionic species i,

$$\mu_i = RT \ln a_i + \mu_i^\circ$$

$$\mu_i = \mu_i\,(\text{ideal}) + \mu_i\,(\text{electrical})$$

Since $\mu_i\,(\text{ideal}) = RT\ln c_i + \mu_i^\circ$

and $a_i = \gamma_i c_i$

$$\mu_i\,(\text{electric}) = RT\ln\gamma_i$$

This is the extra electric free energy per mole. The extra free energy per ion is therefore equal to $kT\ln\gamma_i$, but this is equal to the expression in eq. (15.46). Therefore

$$\ln\gamma_i = -\frac{z_i^2 e^2 b}{2\epsilon kT} \tag{15.47}$$

We may substitute for b from eq. (15.42):

$$b = \left(\frac{4\pi e^2}{\epsilon kT}\sum n_i z_i^2\right)^{1/2}$$

Since n_i (ions per cc) and c_i (moles per liter) are related by $n_i = c_i N/1000$:

$$b = \left(\frac{4\pi N^2 e^2}{1000\epsilon RT}\sum c_i z_i^2\right)^{1/2}$$

In the dilute solutions being considered, $c_i = m_i\rho$, where ρ is the solvent density, so that the ionic strength, eq. (15.32), may be introduced:

$$b = \left(\frac{8\pi N^2 e^2\rho}{1000\epsilon RT}\right)^{1/2} s^{1/2} = Bs^{1/2} \tag{15.48}$$

Since the individual ion activity coefficients cannot be measured, the mean activity coefficient is calculated in order to obtain an expression that can be compared with experimental data. From eq. (15.26),

$$(\nu_+ + \nu_-)\ln\gamma_\pm = \nu_+\ln\gamma_+ + \nu_-\ln\gamma_-$$

Therefore from eq. (15.47),

$$\ln\gamma_\pm = -\left(\frac{\nu_+ z_+^2 + \nu_- z_-^2}{\nu_+ + \nu_-}\right)\frac{e^2 b}{2\epsilon kT}$$

Since $\nu_+ z_+ = \nu_- z_-$, $\ln\gamma_\pm = -z_+ z_-\left(\dfrac{e^2 b}{2\epsilon kT}\right)$ (15.49)

The valence factor can be evaluated as follows for the different electrolyte types:

Type	Example	Ionic Charges	Valence factor z_+z_-
uniunivalent	NaCl	$z_+ = 1, z_- = 1$	1
unibivalent	$MgCl_2$	$z_+ = 2, z_- = 1$	2
unitrivalent	$LaCl_3$	$z_+ = 3, z_- = 1$	3
bibivalent	$MgSO_4$	$z_+ = 2, z_- = 2$	4
bitrivalent	$Fe_2(SO_4)_3$	$z_+ = 3, z_- = 2$	6

Let us now transform eq. (15.49) into base-10 logarithms and introduce the values of the universal constants. If e is taken as 4.80×10^{-10} esu, R must be 8.31×10^7 erg per °C. mole. The result is the Debye-Hückel *limiting law* for the activity coefficient,

$$\log \gamma_\pm = -1.825 \times 10^6 z_+ z_- \left(\frac{s}{\varepsilon^3 T^3 \rho}\right)^{1/2} = -A z_+ z_- s^{1/2} \qquad (15.50)$$

For water at 25°C, $\varepsilon = 78.54$, $\rho = 0.997$, and the equation becomes

$$\log \gamma_\pm = -0.509\, z_+ z_- \sqrt{s} \qquad (15.51)$$

In the derivation of the limiting law it was consistently assumed that the analysis applied only to dilute solutions. It is not to be expected therefore that the equation should hold for concentrated solutions, nor does it. As solutions become more and more dilute, however, the equation should represent the experimental data more and more closely. This expectation has been fulfilled by numerous measurements, so that the Debye-Hückel theory for very dilute solutions may be considered to be well substantiated.

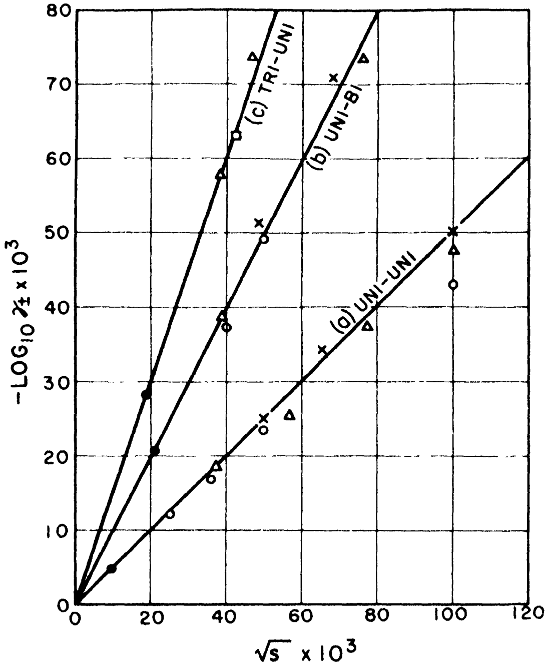


Fig. 15.10. Activity coefficients of sparingly soluble salts in salt solutions [After Brønsted and LaMer, *J. Am. Chem. Soc.*, *46*, 555 (1924).]

For example, in Fig. 15.10 some experimental activity coefficients are plotted against the square roots of the ionic strengths. These data were obtained by applying the solubility method to sparingly soluble complex salts in the presence of added salts such as NaCl, $BaCl_2$, KNO_3. The straight lines indicate the theoretical curves predicted by the limiting law, and it is evident that these limiting slopes are followed at low ionic strengths.

Another successful experimental test has been the measurement of activity coefficients for the same electrolyte in solvents with various dielectric constants.[11]

22. Advances beyond the Debye-Hückel theory. It would of course be desirable to have a theory that could be applied to solutions more concentrated than those for which the D-H treatment is valid, solutions usually so dilute that they have been uncharitably called slightly contaminated distilled water. Like the general theory of liquids, this is one of the major unsolved problems in physical chemistry, for when the simplifying assumption of extreme dilution is abandoned, the mathematical treatment becomes discouragingly messy.

In 1928, Gronwall, LaMer, and Sandved carried the Debye-Hückel theory one step further. Instead of assuming in eq. (15.39) that Uq is much less than kT, they retained the exponential factor and solved the resulting Poisson-Boltzmann equation in terms of a series expansion. Their results, though cumbersome, appeared to be valid at higher concentrations than those of the original D-H theory.

A clearer physical picture of what may be happening in more concentrated solutions has been provided by the *ionic association theory*, developed independently by N. Bjerrum, and by R. M. Fuoss and C. Kraus. As solutions become more concentrated it is likely that definite though transient *ion pairs* are formed, held together by electrostatic attraction. This tendency to pair formation will be greater the lower the dielectric constant of the solvent and the smaller the ionic radii, both of these factors tending to increase the electrostatic attractions.

We may be inclined to suspect that with this theory an historical circle has been completed, returning us to the original Arrhenius concept. There is, however, a real distinction, albeit a somewhat subtle one. Arrhenius presumed that in strong electrolytes there were neutral molecules, which *ionized* to an extent increasing with the dilution. According to the new theory, the solution contains nothing but ions, which are electrostatically associated to an extent that increases with the concentration.

The degree of association may become very appreciable even in a solvent of high dielectric constant ε, such as water. Bjerrum has calculated that in one-normal aqueous solution uniunivalent ions having a diameter of 2.82 Å are 13.8 per cent associated; of 1.76 Å, 28.6 per cent associated. For solvents of lower ε the association would be still greater. Such association into ion pairs would lower the values of the ionic activity coefficients.

There are two other factors, not considered in the D-H treatment, that tend to become important in concentrated solutions. One is the effect of

---

[11] H. S. Harned *et al.*, *J. Am. Chem. Soc.*, *61*, 49 (1939).

repulsive forces between ions at close distances of approach, called the *ionic size effect*. It is analogous to the b factor in van der Waals' equation, and tends to cut down the electrostatic interactions by preventing very close approaches between charges. In the derivation of the limiting law, eq. (15.50), it was assumed that the ions were point charges. Debye and Hückel made an improved theory which took into account the finite sizes of the ions. The resulting expression for the mean activity coefficient is

$$\log \gamma_{\pm} = \frac{-Az_{+}z_{-}\sqrt{s}}{1 + dB\sqrt{s}} \tag{15.52}$$

where A and B have the same significance as in eqs. (15.48) and (15.50), and d is the *average effective diameter* of the ions. The product dB is usually close to unity.

Probably of greater importance is the effect of the ions on the solvent molecules. It is known from transference experiments that ions in solution are solvated, especially in polar solvents like water. This is confirmed by the well known *salting-out effect*, by which added electrolytes decrease the solubility of nonelectrolytes. Some of the solvent molecules appear to be held so tightly by the ions that they are not able to participate in the solution of neutral solutes. For example, the solubility (25°C) of diethyl ether in pure water is 0.91 mole per liter, but in 15 per cent sodium chloride solution it is reduced to 0.13 mole per liter.

The solvent molecules surrounding an ion are highly oriented and polarized. It is likely, therefore, that the dielectric constant of the solvent is considerably enhanced. As a result interionic attractions decrease; consequently the ionic activity coefficients increase. In Fig. 15.8 it was noted that the observed γ's finally rise at higher concentrations. Both the ionic size effect and the polarization effect contribute to this rise.

23. Theory of conductivity. The interionic attraction theory was also applied by Debye and Hückel to the electric conductivity of solutions. An improved theory was given by Lars Onsager (1926–1928). The calculation of the conductivity is a difficult problem, and we shall content ourselves with a qualitative discussion.[12]

Under the influence of an electric field an ion moves through a solution not in a straight line, but in a series of zigzag steps similar to those of Brownian motion. The persistent effect of the potential difference ensures an average drift of the ions in the field direction.

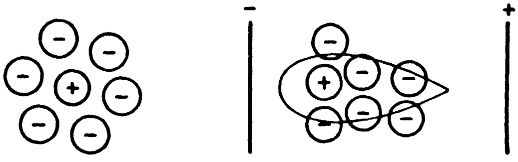
Opposing the electric force on the ion is first of all the frictional drag of the solvent. Although the solvent is not a continuous medium, Stokes's Law is frequently used to estimate this effect (cf. page 446 and Walden's rule). Since the molecules of solvent and the ions are about the same size, it is

---

[12] See H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions* (New York: Reinhold, 1943).

more likely that the ion moves by jumping from one "hole" to another in the liquid.

In addition to the *viscous effect*, two important electrical effects must be considered. As shown in (a), Fig. 15.11, an ion in any static position is surrounded by an ionic atmosphere of opposite charge. If the ion jumps to a new position, it will tend to drag with it this oppositely charged aura. The ionic atmosphere, however, has a certain inertia, and cannot instantaneously readjust itself to the new position of its central ion. Thus around a moving ion the atmosphere becomes asymmetric, as in (b), Fig. 15.11. Behind the ion there is a net accumulation of opposite charge, which exerts an electrostatic drag, decreasing the ionic velocity in the field direction. This retardation is called the *asymmetry effect*. It will obviously be greater at higher ionic concentrations.



(a) (b)

Fig. 15.11. (a) Ionic atmosphere surrounding ion at rest; (b) asymmetric cloud around moving ion.

A second electrical action that lowers the mobility of the ions is called the *electrophoretic effect*. The ions comprising the atmosphere around a given central ion are themselves moving, on the average in the opposite direction, under the influence of the applied field. Since they are solvated, they tend to carry along with them their associated solvent molecules, so that there is a net flow of solvent in a direction opposite to the motion of any given (solvated) central ion, which is thus forced to swim "upstream" against this current.

The steady state of motion of an ion can be found by equating the electric driving force to the sum of the frictional, asymmetric, and electrophoretic retardations. Onsager calculated each of the terms in this relationship, and thereby obtained a theoretical equation for the equivalent conductivity of a uniunivalent electrolyte in the limiting case of dilute solutions:

$$\Lambda = \Lambda_0 - \left[\frac{82.4}{(\epsilon T)^{1/2}\eta} + \frac{8.20 \times 10^5}{(\epsilon T)^{3/2}} \Lambda_0\right] \sqrt{c} \qquad (15.53)$$

Here c is the concentration of ionized electrolyte in moles per liter, which if dissociation is not complete must be calculated from the degree of dissociation α. Similar equations were derived for electrolytes of other valence types.[13]

---

[13] See S. Glasstone, *Introduction to Electrochemistry* (New York: Van Nostrand, 1942), p. 89.

The Onsager equations provide good agreement with the experimental conductivity data at low concentrations. Their range of validity is greater for uniunivalent electrolytes than for those whose ions bear higher charges, but as limiting laws they hold at extreme dilutions for all valence types. Further confirmation of the essential correctness of the Debye-Hückel-Onsager picture is obtained from two interesting effects occurring in conductivity measurements.

The *Debye-Falkenhagen effect* is observed when conductivities are studied at high a-c frequencies, of the order of 3 × 10^6 cycles per sec. As the frequency of the electric field is increased, a point is eventually reached at which the ionic atmosphere no longer can follow the rapidly changing field at all. Then the ions move practically independently of one another as the influence of their atmospheres becomes unimportant. Thus at high enough frequencies an increase in the conductivity of a solution is expected, and has been actually observed.

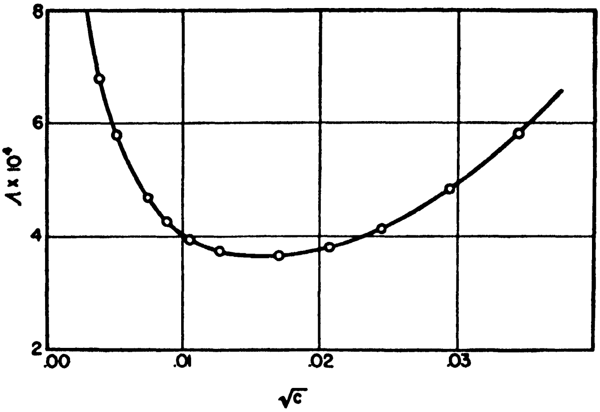


Fig. 15.12. Conductance of tetraisoamyl-ammonium nitrate in dioxane-water. [Fuoss and Kraus, *J. Am. Chem. Soc.* *55*, 2387 (1933).]

A second support for the ionic atmosphere model is found in the *Wien effect.* At sufficiently high field strengths, of the order of 10^5 volts per cm, the conductivity is also observed to increase. The explanation is that the velocities of the ions become so high, with these large fields, that the ionic atmospheres are left behind entirely, and the ions move independently.

In more concentrated solutions marked deviations from the Onsager equation are found, so that one may even obtain equivalent conductivity vs. concentration curves like that in Fig. 15.12. An interesting interpretation of the minima in such curves has been based on the ion-association theory.[14] The ion pairs (+ −) are electrically neutral and do not contribute to the equivalent conductivity, which therefore falls as more pairs are formed. As

[14] R. Fuoss and C. Kraus, *J. Am. Chem. Soc.*, *55*, 21 (1933).

the solution becomes still more concentrated, triple ions, either (+ − +) or (− + −), begin to be formed from some of the pairs, and since these triplets bear a net charge, they contribute to the conductivity, which therefore increases from its minimum value.

24. Acids and bases.[15] The concepts "acid" and "base" have had a long and interesting share in the history of chemistry. The distinctive behavior of these substances has always presented a challenge to theoretical interpretation.

Arrhenius's solution of the problem was to define an acid as a compound that dissociated in solution to yield a hydrogen ion, and a base as a compound yielding a hydroxyl ion. Then the process of neutralization was simply $H^+ + OH^- = H_2O$. These definitions relied exclusively on the phenomena observed in aqueous solutions, and it was evident that they would have to be broadened in some way.

In 1922–1923, J. N. Brønsted and M. Lowry advanced a new set of criteria. They proposed to define an acid as any compound that can lose a proton, and a base as any compound that can accept a proton. Thus

$$\underset{acid}{A} = \underset{proton}{H^+} + \underset{base}{B}$$

The compound B was called the *conjugate base* of the acid A. Some examples would be

$$HAc = H^+ + Ac^-$$

$$NH_4^+ = H^+ + NH_3$$

Bases and acids might be either neutral molecules or ions.

It was soon realized that the free proton probably never occurs in solution, the solvent itself acting as a proton acceptor—in other words, as a base. Therefore, the typical reactions should be written in the symmetrical form:

$$\begin{array}{lclclcl} \textit{Acid (I)} & + & \textit{Base (II)} & = & \textit{Acid (II)} & + & \textit{Base (I)} \\ HAc & + & H_2O & = & H_3O^+ & + & Ac^- \\ NH_4^+ & + & H_2O & = & H_3O^+ & + & NH_3 \\ H_2O & + & CN^- & = & HCN & + & OH^- \end{array}$$

Note that, depending on its partner, a compound, such as water in these examples, can act either as an acid or as a base. The complete similarity between the ammonium ion, NH_4^+, and the hydronium ion, H_3O^+, is apparent.

An interesting application of the Brønsted concept is found in the study of a series of strong acids: $HClO_4$, H_2SO_4, HNO_3, HBr, HCl, etc. In aqueous solution these acids are all about equally strong. That is to say, the equilibrium, $HX + H_2O = H_3O^+ + X^-$, lies in every case extremely far to the

---

[15] For a comprehensive treatment of this important subject, see W. F. Luder and S. Zuffanti, *The Electronic Theory of Acids and Bases* (New York: Wiley, 1946).

right, mainly owing to the large hydration energy of the proton. When the acids are dissolved in glacial acetic acid, very distinct differences in their strengths become apparent. Then the equilibria are: $HX + CH_3COOH = CH_3COOH_2^+ + X^-$. The acetic-acid molecule is not very anxious to accept a proton, and only when the other acid is a particularly insistent donor does the equilibrium lie sufficiently toward the right to produce a considerable number of ions. In a 0.005 molar solution in glacial acetic acid the equivalent conductivity of $HClO_4$ is more than fifty times that of HNO_3. It is therefore evident that $HClO_4$ is a much stronger acid than HNO_3, once the *leveling effect* of a solvent such as water is eliminated.[16]

The Brønsted picture still does not represent the full generality of acid-base phenomena. Further investigations in nonaqueous solutions, notably by C. A. Kraus and E. C. Franklin, revealed that familiar acid-base properties could be displayed by solutions that contained no protons at all. For example, the following typical neutralization reaction can be followed in chlorobenzene solution with crystal violet as an indicator:

$$\underset{\textit{acid}}{BCl_3} + \underset{\textit{base}}{(C_2H_5)_3N} \quad (C_2H_5)_3N:BCl_3$$

The indicator is yellow in the presence of excess acid, and violet in basic solutions.

In 1923 G. N. Lewis advanced a new concept of acids and bases derived from the electronic theory of valence. This generalized theory is indeed so broad that it removes the problem from the confines of the chemistry of ions into the domain of the formation of covalent bonds. Lewis defined an acid as a substance that can accept a pair of electrons from a donor substance, the base. The process called "neutralization" is therefore the formation of a covalent bond in which both electrons of the shared pair are provided by the base. It may be recalled that this is the type of bond that used to be called the "dative bond" or the "coordinate link." For example:

$$\begin{array}{ccccc}
H^+ & + & :\underset{\cdot\cdot}{\ddot{O}}:H^- & = & H:\underset{\cdot\cdot}{\ddot{O}}:H \\
Cl & & H & & Cl\ H \\
Cl:\underset{\cdot\cdot}{\ddot{B}} & + & :\underset{\cdot\cdot}{\ddot{N}}:H & = & Cl:\underset{\cdot\cdot}{\ddot{B}}:\underset{\cdot\cdot}{\ddot{N}}:H \\
Cl & & H & & Cl\ H \\
\textit{acid} & + & \textit{base} & = & \textit{covalent compound}
\end{array}$$

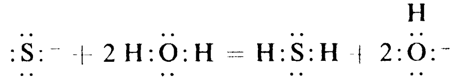
The close relationship between acid-base and oxidation-reduction reactions is now apparent. Both acids and oxidizing agents tend to accept electrons. They are said to be *electrophilic* or electron-loving reagents. An acid accepts a share in a pair of electrons held by a base, forming a coordinate covalent bond. An oxidizing agent accepts electrons provided by a reducing agent, but keeps them all to itself instead of sharing them with

---

[16] I. M. Kolthoff and A. Willman, *J. Am. Chem. Soc.*, *56*, 1007 (1934).

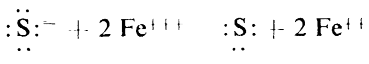
the donor. Bases and reducing agents are called *electrodotic* or electron-giving reagents.

The same reactant can display either acid-base or oxidation-reduction properties depending upon its reaction partner. Thus the sulfide ion behaves as a base toward water:



$$:\underset{..}{\overset{..}{S}}:^{-} + 2\,H:\underset{..}{\overset{..}{O}}:H = H:\underset{..}{\overset{..}{S}}:H + 2:\underset{..}{\overset{\overset{H}{..}}{O}}:^{-}$$

On the other hand, it behaves as a reductant toward an oxidizing agent like ferric ion:



$$:\underset{..}{\overset{..}{S}}:^{-} + 2\,Fe^{+++} \quad :\underset{..}{S}: + 2\,Fe^{++}$$

25. Dissociation constants of acids and bases. A typical acid HA reacts as follows when dissolved in water: $HA + H_2O \quad H_3O^+ + A^-$. The equilibrium constant may be written:

$$K_a' \quad \frac{a_{H_3O^+}a_{A^-}}{a_{HA}a_{H_2O}}$$

If the solution is dilute, the activity of the water a_{H_2O} may be taken to be the same as its concentration c, which will effectively be a constant equal to the number of moles of water in one liter. This constant may be divided out of the equilibrium constant K_a' to give the simpler expression:

$$K_a = \frac{a_{H_3O^+}a_{A^-}}{a_{HA}}$$

For a base B, the reaction is $B + H_2O = BH^+ + OH^-$. The equilibrium constant becomes

$$K_b = \frac{a_{BH^+}a_{OH^-}}{a_B}$$

These constants, K_a and K_b, are sometimes called the *dissociation constants* for the acid and base, and they provide a measure of their "strengths." The constants can be obtained from conductance measurements or by measurements of hydrogen-ion concentrations combined with appropriate activity coefficients. The hydrogen-ion concentration can be measured colorimetrically with *indicators*, but more precise values are obtained by potentiometric methods that will be described later.

Let us write, using the notation H^+ instead of H_3O^+

$$K_a = \frac{c_{H^+}c_{A^-}}{c_{HA}} \cdot \frac{\gamma_{H^+}\gamma_{A^-}}{\gamma_{HA}}$$

In dilute solution the molecule HA, being uncharged and therefore not subject to electrical interactions, may be assigned an activity coefficient of unity. Then

$$K_a = \left(\frac{c_{H^+}c_{A^-}}{c_{HA}}\right)\gamma_{H^+}\gamma_{A^-}$$

From the Ostwald dilution law,[17] eq. (15.9), this would become

$$K_a = \frac{\alpha^2 c}{(1-\alpha)}(\gamma_{H^+}\gamma_{A^-})$$

with $\alpha = \Lambda/\Lambda_0$. Thus the constant K_a can be evaluated by combining conductivity measurements in dilute solution with suitable activity-coefficient values, obtained experimentally or from the Debye-Hückel theory.

Some measured constants for acids and bases are summarized in Table 15.6, in the form of pK_a or pK_b values; by analogy with the definition of pH, $pK = -\log K$.

TABLE 15.6*

DISSOCIATION OF ACIDS AND BASES IN WATER SOLUTION AT 25°C

Acids	pK_a	Bases	pK_b
Formic	3.752	Ammonia	4.77
Acetic	4.756	Methylamine	3.36
Propionic	4.874	Aniline	9.39
Trimethylacetic	5.05	Methylaniline	9.70
Chloroacetic	2.861	Pyridine	8.80
Benzoic	4.20	Diphenylamine	13.16
p-Nitrobenzoic	3.43	Piperidine	2.88
Phenol	9.50		

Dibasic Acids	pK_1	pK_2
Oxalic	1.30	4.286
Carbonic	6.35	10.25
Hydrogen Sulfide	7.2	11.9
Phthalic	2.89	5.42
Maleic	2.00	6.27

* H. S. Harned and B. B. Owen, *Chem. Rev.*, *25*, 31 (1939); J. F. J. Dippy, *ibid.*, 151.

For an acid and its conjugate base we have the relationship

$$K_a K_b = K_s \tag{15.54}$$

where K_s is the dissociation constant of the solvent. For example, consider acetic acid HAc, and its conjugate base Ac⁻:

$$\mathrm{HAc + H_2O = H_3O^+ + Ac^-}$$

$$\mathrm{Ac^- + H_2O = OH^- + HAc}$$

Then,

$$K_a K_b = \frac{a_{H_3O^+} a_{Ac^-}}{a_{HAc}} \cdot \frac{a_{OH^-} a_{HAc}}{a_{Ac^-}} = a_{H_3O^+} a_{OH^-} = K_w$$

K_w is the dissociation constant of the solvent water.

---

[17] More exact methods are based on the Onsager conductivity theory. See Glasstone, *op. cit.*, pp. 163–169.

The value of K_w can be calculated from the measurements of Kohlrausch and Heydweiller[18] on the conductivity of extremely pure water. These data are given in Table 15.7 at various temperatures. The degree of dissociation α is calculated from the relation $\alpha = \Lambda/\Lambda_0$, Λ_0 being the sum of the equivalent ionic conductivities of H^+ and OH^- at infinite dilution. From Table 15.3 this sum at 25° is $349.8 + 198 = 547.8$. From eq. (15.3), $\Lambda = \kappa/c^*$, where c^* is the number of moles of water in one cc, 0.0553. Thus $\Lambda = 0.062 \times 10^{-6}/0.0553 = 1.05 \times 10^{-6}$. Since the ionic concentrations are very low, the activity coefficients may be taken as unity, so that $K_w = c_{H^+}c_{OH^-} = \alpha^2 c_w^2$, where c_w is the number of moles of liquid water in one liter. The calculated ion products are included in Table 15.7. At 25°, $K_w \approx 10^{-14}$, so that the hydrogen ion concentration $c_{H^+} \approx 10^{-7}$ moles per liter, or the pH ≈ 7.

TABLE 15.7

Conductivity and Ion Product of Water

Temperature, °C	0	18	25	34	50
Conductivity, κ ohm^{-1} cm^{-1} × 10^6	0.015	0.043	0.062	0.095	0.187
$10^{14} \cdot K_w = (c_{H^+}c_{OH^-}) \cdot 10^{14}$	0.12	0.61	1.04	2.05	5.66

When an acid and base are mixed, neutralization occurs, but except in the case of strong acids and bases, *i.e.*, those for which dissociation is essentially complete, the compound formed may react with the solvent. This process is called *solvolysis*, or in the special case of water, *hydrolysis*. For a compound BA in water:

$$BA + H_2O = HA + BOH$$

The *hydrolysis constant* is

$$K_h' = \frac{a_{HA}a_{BOH}}{a_{BA}a_{H_2O}}, \quad \text{or} \quad K_h = \frac{a_{HA}a_{BOH}}{a_{BA}} \tag{15.55}$$

It can easily be shown that the hydrolysis constants are related to the dissociation constants as follows:

$$\left.\begin{array}{ll} \text{Salt of weak acid and strong base:} & K_h = K_w/K_a \\ \text{Salt of weak base and strong acid:} & K_h = K_w/K_b \\ \text{Salt of weak acid and weak base:} & K_h = K_w/K_aK_b \end{array}\right\} \tag{15.56}$$

26. Electrode processes: reversible cells. So far we have been considering only those aspects of electrochemistry that deal with the state of affairs within solutions of electrolytes. The second important branch of the subject is concerned with what happens when electrodes are immersed in these solutions and connected via an external metallic conductor.

An electrode dipping into a solution is said to constitute a *half cell*; the

---

[18] *Z. physik. Chem.*, *14*, 317 (1894).

combination of two half cells is a typical *electrochemical cell.* An example is the Clark cell of Fig. 4.2.

We shall be interested primarily in the class of cells called *reversible cells.* These may be recognized by the following criterion: The cell is connected with a potentiometer arrangement for emf measurement by the compensation method (page 73). The emf of the cell is measured: (a) with a minute current flowing through the cell in one direction; (b) then with an imperceptible flow of current; (c) and finally with a minute flow in the opposite direction. If a cell is reversible its emf may change only slightly during this sequence, and there should be no discontinuity in the emf value at the point of balance (b). Reversibility implies that any chemical reaction occurring in the cell can proceed in either direction, depending on the flow of current, and at the null point the driving force of the reaction is just balanced by the compensating emf of the potentiometer. If a cell is reversible, it follows that the half cells comprising it are both reversible.

27. Types of half cells. A great many chemical reactions can be carried out in cells so as to yield electric energy, and there is a corresponding variety in the types of available half cells.

One of the simplest consists of a *metal electrode* in contact with a solution containing ions of the metal, *e.g.*, silver in silver-nitrate solution. Such a half cell is represented as $Ag|Ag^+(c)$, where c is the silver-ion concentration, and the vertical bar denotes the phase boundary. The reaction occurring at this electrode is the solution or deposition of the metal, according to $Ag = Ag^+ + e$.

It is sometimes convenient to form a metal electrode by using an amalgam instead of the pure metal. A liquid amalgam has the advantage of eliminating nonreproducible effects due to strains in the solid metals or traces of impurities at the electrode surface. In some instances a dilute amalgam electrode can be successfully employed while the pure metal would react violently with the solution, for example in the sodium amalgam half cell, $NaHg(c_1)|Na^+(c_2)$. If the amalgam is saturated with the solute metal, the electrode is equivalent to a pure metal electrode, since the chemical potential of a component in its saturated solution equals the chemical potential of pure solute. If the amalgam is not saturated, methods are available for calculating the emf of a pure metal electrode from a series of measurements at different amalgam concentrations.

Gas electrodes can be constructed by placing a strip of nonreactive metal, usually platinum or gold, in contact with both the solution and a gas stream. The hydrogen electrode consists of a platinum strip exposed to a current of hydrogen, and partially immersed in an acid solution. The hydrogen is probably dissociated into atoms at the catalytic surface of the platinum, the electrode reactions being

$$\begin{array}{rl} & \frac{1}{2}\,H_2 = H \\ & H = H^+ + e \\ \hline \text{over-all:} & \frac{1}{2}\,H_2 = H^+ + e \end{array}$$

The chlorine electrode operates similarly, negative chloride ions being formed in the solution: $e + \frac{1}{2}Cl_2 = Cl^-$.

An *oxidation-reduction electrode* is formed by an inert metal dipping into a solution containing ions in two different oxidation states, *e.g.*, ferric and ferrous ions in the half cell $Pt|Fe^{++}, Fe^{+++}$. When electrons are supplied to the electrode, the reaction is $Fe^{+++} + e = Fe^{++}$. Since it is the function of electrodes either to accept electrons from, or to donate electrons to ions in the solution, they are all in a sense oxidation-reduction electrodes. The difference between the silver electrode and the ferric-ferrous electrode is that in the former the concentration of the lower oxidation state, metallic silver, cannot be varied.

All the electrodes so far considered are examples of what are sometimes called "electrodes of the first kind." Electrodes of the "second kind" consist of a metal in contact with one of its slightly soluble salts; in the half cell, this salt is in turn in contact with a solution containing a common anion. An example is the silver-silver chloride half cell: $Ag|AgCl|Cl^-(c_1)$. The electrode reaction can be considered to proceed in two steps:

$$\begin{array}{rl} & AgCl\,(s) = Ag^+ + Cl^- \\ & Ag^+ + e = Ag\,(s) \\ \hline \text{or over-all:} & AgCl\,(s) + e = Ag\,(s) + Cl^- \end{array}$$

It is interesting to note that such an electrode is thermodynamically equivalent to a chlorine electrode ($Cl_2|Cl^-$) in which the gas is at a pressure corresponding to the dissociation pressure of AgCl according to $AgCl = Ag + \frac{1}{2}Cl_2$. This is an especially useful fact in view of the experimental difficulties involved in the use of reactive gas electrodes.

28. Electrochemical cells. When two suitable half cells are connected one obtains an electrochemical cell. The connection is made by bringing the solutions of the half cells into contact, so that ions can pass between them. If the two solutions are the same, no problems arise, but if they are different they must be kept from mixing appreciably by interdiffusion. At the interface between the two solutions there is a *liquid junction.* We shall postpone consideration of cells of this kind, and consider first of all some cells without liquid junctions.

It is necessary to adopt some standard notation for writing down a cell, the chemical reaction occurring in it, and the sign of its emf. Two sign conventions are in common use in the scientific literature, one used by American chemists and the other used by the rest of the world, including American electroplaters. With some misgivings, we shall follow the former.

We therefore decide that *a positive emf represents a tendency for positive ions to pass spontaneously from left to right through the cell as written*, or of negative ions to pass from right to left. If the electrodes are connected through a metallic conductor, electrons flow through the external circuit from left to right.

From eq. (4.2) the relation between the reversible emf and the maximum work, $-\Delta F$, for the cell reaction is $-\Delta F = z\mathscr{E}\mathscr{F}$. Thus a positive emf corresponds with a negative ΔF and therefore a positive driving force for the reaction.

Consider, for example, the Weston cell, which is universally used as a *standard cell.* It has a voltage of $\mathscr{E} = 1.01810$ volts at 25°C and a very small temperature coefficient. The cell may be written

$$\text{Cd (12.5\% amalgam)}|\text{CdSO}_4\cdot\tfrac{8}{3}\,\text{H}_2\text{O (s)}|\text{CdSO}_4\text{ (sat)}|\text{Hg}_2\text{SO}_4\text{ (s)}|\text{Hg}$$

Now for positive emf the positive ions proceed from left to right through the cell; the electrons proceed from left to right through the external circuit. Thus the reaction at the left-hand electrode must be an oxidation, the loss of electrons according to $Cd = Cd^{++} + 2e$. These electrons flow through the metallic conductor to the right-hand electrode, where they are given up to the mercurous ion, reducing it to mercury: $Hg_2^{++} + 2e = 2\ Hg$. The net cell reaction is the sum of the two electrode processes, or $Cd + Hg_2^{++} = Cd^{++} + 2\ Hg$. In terms of the salts present, this reaction might be written $Cd + Hg_2SO_4 = CdSO_4 + 2\ Hg$. The cell reaction is a displacement.

An example in which the reaction is a combination is found in the cell,

$$\text{Pt}|\text{H}_2\text{ (1 atm)}|\text{HCl (0.1 m)}|\text{Cl}_2\text{ (1 atm)}|\text{Pt}$$

The emf of the cell is 1.485 volts, so that the direction of the current flow is the same as before. The electrode processes are

$$\tfrac{1}{2}\,H_2 = H^+ + e$$
$$\tfrac{1}{2}\,Cl_2 + e = Cl^-$$
$$\text{Over-all reaction: } \tfrac{1}{2}\,H_2 + \tfrac{1}{2}\,Cl_2 = HCl\ (0.1\ m)$$

29. The standard emf of cells. Let us consider the generalized cell reaction: $a\,A + b\,B = c\,C + d\,D$. By comparison with eq. (4.8) the free-energy change in terms of the activities a of the reacting species is

$$\Delta F = \Delta F^\circ + RT\ln\frac{a_C{}^c\,a_D{}^d}{a_A{}^a\,a_B{}^b}$$

Since $\Delta F = -z\mathscr{E}\mathscr{F}$, division by $-z\mathscr{F}$ gives

$$\mathscr{E} = \mathscr{E}^\circ - \frac{RT}{z\mathscr{F}}\ln\frac{a_C{}^c\,a_D{}^d}{a_B{}^b\,a_A{}^a} \qquad (15.57)$$

When the activities of all the products and reactants are unity, the value of the emf is $\mathscr{E}^\circ = -\Delta F^\circ/z\mathscr{F}$. This $\mathscr{E}^\circ$ is called the *standard emf* of the cell. It is related to the equilibrium constant of the cell reaction, since

$$\mathscr{E}^\circ = -\frac{\Delta F^\circ}{z\mathscr{F}} = \frac{RT}{z\mathscr{F}}\ln K_a \qquad (15.58)$$

The determination of the standard emf's of cells is therefore one of the most important procedures in electrochemistry. We shall illustrate a useful method by means of a typical example.

Consider the cell shown in Fig. 15.13, consisting of a hydrogen electrode and a silver-silver chloride electrode immersed in a solution of hydrochloric acid:

$$\text{Pt}\,(\text{H}_2)|\text{HCl}\,(m)|\text{AgCl}|\text{Ag}$$

The electrode reactions are

$$\tfrac{1}{2}\,\text{H}_2 = \text{H}^+ + e$$

$$\text{AgCl} + e = \text{Ag} + \text{Cl}^-$$

The over-all reaction is accordingly

$$\text{AgCl} + \tfrac{1}{2}\,\text{H}_2 = \text{H}^+ + \text{Cl}^- + \text{Ag}$$

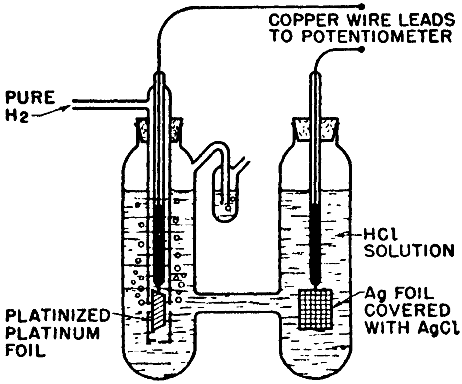


Fig. 15.13. Hydrogen electrode and silver-silver chloride electrode in arrangement for standard emf determination.

From eq. (15.57) the emf of the cell is

$$\mathscr{E} = \mathscr{E}^\circ - \frac{RT}{\mathscr{F}} \ln \frac{a_{\text{Ag}}a_{\text{H}^+}a_{\text{Cl}^-}}{a_{\text{AgCl}}a_{\text{H}_2}{}^{1/2}}$$

Setting the activities of the solid phases equal to unity, and choosing the hydrogen pressure so that $a_{\text{H}_2} = 1$ (for ideal gas $P = 1$ atm), we obtain the equation

$$\mathscr{E} = \mathscr{E}^\circ - \frac{RT}{\mathscr{F}} \ln a_{\text{H}^+}a_{\text{Cl}^-}$$

Introducing the mean activity of the ions defined by eq. (15.26), we have

$$\mathscr{E} = \mathscr{E}^\circ - \frac{2RT}{\mathscr{F}} \ln a_\pm = \mathscr{E}^\circ - \frac{2RT}{\mathscr{F}} \ln \gamma_\pm m \qquad (15.59)$$

On rearrangement,

$$\mathscr{E} + \frac{2RT}{\mathscr{F}} \ln m = \mathscr{E}^\circ - \frac{2RT}{\mathscr{F}} \ln \gamma_\pm$$

According to the Debye-Hückel theory, in dilute solutions $\ln \gamma_{\pm} = A\sqrt{m}$, where A is a constant. Hence the equation becomes

$$\mathscr{E} + \frac{2RT}{\mathscr{F}} \ln m = \mathscr{E}^{\circ} - \left(\frac{2RTA}{\mathscr{F}}\right) \sqrt{m}$$

If the quantity on the left is plotted against $\sqrt{m}$, and extrapolated back to $m = 0$, the intercept at $m = 0$ gives the value of $\mathscr{E}^{\circ}$.[19] For this cell one obtains $\mathscr{E}^{\circ} = 0.2225$ volt at 25°C.

Once the standard emf has been determined in this way, eq. (15.59) can be used to calculate mean activity coefficients for HCl from the measured emf's $\mathscr{E}$ in solutions of different molalities m.

30. Standard electrode potentials. Rather than tabulate data for all the numerous cells that have been measured, it would be much more convenient to make a list of "single-electrode potentials" of the various half cells. Cell emf's could then be obtained simply by taking differences between these electrode potentials. The status of single-electrode potentials is similar to that of single-ion activities. In 1899 Gibbs[20] pointed out that it is not possible to devise any experimental procedure that will measure a difference in *electric potential* between two points in media of different chemical composition—for instance, a metal electrode and the surrounding electrolyte. What we always in fact measure is a difference in potential between two points at the same chemical composition, such as two brass terminals of a potentiometer.

Consider an ion of copper, (a) in metallic copper, (b) in a solution of copper sulfate. Its state is determined by its chemical environment, usually expressed by its chemical potential μ, and by its electrical environment, expressed by its electric potential U. But there is no way of experimentally separating these two factors, as indeed is apparent from the facts that there is no way of separating electricity from matter, and that the phenomena we call "chemical" are all "electrical" in origin. Thus we can measure only the *electrochemical potential* of an ion, $\mu' = \mu + U$. It may sometimes be convenient to make an arbitrary separation of this quantity into two parts; such conventional separations seem to be helpful in some theoretical discussions.

Although absolute single-electrode potentials are not measurable, the problem of reducing the cell emf's to a common basis may be solved by expressing all the values relative to the same reference electrode. The choice of a conventional reference state does not affect the values of differences between the electrode potentials, *i.e.*, the cell emf's. The reference electrode is taken to be the *standard hydrogen electrode*, which is assigned by conven-

---

[19] A. S. Brown and D. A. MacInnes, *J. Am. Chem. Soc.*, *57*, 1356 (1935). In practice an extended form of the Debye-Hückel theory is often used to give a somewhat better extrapolation function.

[20] *Collected Works*, vol. 1, p. 429. See also E. A. Guggenheim, *J. Phys. Chem.*, *33*, 842 (1929).

tion the value $\mathscr{E}^\circ = 0$. It is the hydrogen electrode in which (a) the pressure of hydrogen is 1 atm (strictly, unit fugacity, but the gas may be taken to be ideal), (b) the solution is a hydrogen acid in which the mean ionic activity is $a_\pm = 1$. Thus: $\text{Pt}|\text{H}_2\,(1\text{ atm})|(\text{H}^+\,(a_\pm = 1)$.

The emf of the cell formed by combining any electrode with the standard hydrogen electrode gives the *electrode potential on the hydrogen scale*, $\mathscr{E}_\text{H}$. If the emf is the standard emf $\mathscr{E}^\circ$, it gives the *standard electrode potential on the hydrogen scale* $\mathscr{E}^\circ{}_\text{H}$.

To maintain the usual sign convention, always write down the complete cell with the electrode to be measured at the left and the hydrogen electrode at the right. For example, in the previous section, the cell $\text{Pt}(\text{H}_2)|\text{HCl}|\text{AgCl}|\text{Ag}$ was found to have a standard potential $\mathscr{E}^\circ = 0.2225$ v. The cell $\text{Ag}|\text{AgCl}|\text{HCl}|(\text{H}_2)\text{Pt}$ would have $\mathscr{E}^\circ = -0.2225$ v. The standard potential of the $\text{Ag}|\text{AgCl}$ electrode would thus be $\mathscr{E}^\circ{}_\text{H} = -0.2225 - 0.0 = -0.2225$ v.

Instead of measuring an electrode directly against the standard hydrogen electrode, it can be measured against any other electrode whose $\mathscr{E}^\circ{}_\text{H}$ has been determined. The normal calomel electrode is frequently used in this way as a subsidiary reference standard: $\text{Hg}|\text{Hg}_2\text{Cl}_2|\text{KCl}$ (1 normal), $\mathscr{E}^\circ{}_\text{H} = -0.2802$ v (25°C). We must subtract 0.2802 v from emf's measured against the normal calomel electrode to bring them onto the standard hydrogen scale.[21]

A summary of standard electrode potentials is given in Table 15.8. These may be called *oxidation potentials*, because the magnitude of the positive potential represents the tendency of oxidation, *i.e.*, loss of electrons, to occur at the electrode. A positive value for $\mathscr{E}^\circ{}_\text{H}$ indicates that the reduced form of the half cell is a better reducing agent than hydrogen. For example:

$$\text{Cd} = \text{Cd}^{++} + 2e, \qquad \mathscr{E}^\circ{}_\text{H} = 0.402$$

Therefore the reaction $\text{Cd} + 2\,\text{H}^+ \rightarrow \text{Cd}^{++} + \text{H}_2$ will proceed with a potential of $\mathscr{E} = \mathscr{E}^\circ{}_\text{H} - 0 = 0.402$ v. The positive potential corresponds to a negative ΔF° and therefore a spontaneous reaction. The cell would be written:

$$\text{Cd}|\text{Cd}^{++},\quad \text{H}^+\,(a_\pm = 1)|\text{H}_2\,(1\text{ atm})$$

Two half-cell reactions and potentials may be subtracted to obtain the $\mathscr{E}^\circ$ for a complete chemical reaction. For example:

$$\begin{array}{rcll}
\text{Cd} & = & \text{Cd}^{++} + 2e & \mathscr{E}^\circ = 0.403 \\
2\,\text{Ag} & = & 2\,\text{Ag}^+ + 2e & \mathscr{E}^\circ = -0.799 \\
\hline
\text{Cd} + 2\,\text{Ag}^+ & = & \text{Cd}^{++} + 2\,\text{Ag} & \mathscr{E}^\circ = 1.202
\end{array}$$

Sometimes it is necessary to add or subtract two half reactions to obtain the $\mathscr{E}^\circ$ of a third half reaction. Then one must be careful to add or subtract

---

[21] The symbol $\mathscr{E}^\circ{}_\text{H}$ is often written simply $\mathscr{E}^\circ$. Unless otherwise stated it will be understood that the potential is given on the hydrogen scale.

TABLE 15.8

STANDARD OXIDATION POTENTIALS*

Electrode Reaction	$\mathscr{E}^\circ_{\mathrm{H}}$
Acid Solutions	
$Li = Li^+ + e$	3.045
$K = K^+ + e$	2.925
$Cs = Cs^+ + e$	2.923
$Ba = Ba^{++} + 2e$	2.90
$Ca = Ca^{++} + 2e$	2.87
$Na = Na^+ + e$	2.714
$Mg = Mg^{++} + 2e$	2.37
$H^- = \frac{1}{2} H_2 + e$	2.25
$Al = Al^{+++} + 3e$	1.66
$Zn = Zn^{++} + 2e$	0.763
$Fe = Fe^{++} + 2e$	0.440
$Cr^{++} = Cr^{+++} + e$	0.41
$Cd = Cd^{++} + 2e$	0.403
$Sn = Sn^{++} + 2e$	0.136
$Pb = Pb^{++} + 2e$	0.126
$Fe = Fe^{+++} + 3e$	0.036
$D_2 = 2D^+ + 2e$	0.0034
$H_2 = 2H^+ + 2e$	0.000
$H_2S = S + 2\,H^+ + 2e$	−0.141
$Sn^{++} = Sn^{+4} + 2e$	−0.15
$Cu^+ = Cu^{++} + e$	−0.153
$2\,S_2O_3^{=} = S_4O_6^{=} + 2e$	−0.17
$Fe(CN)_6^{-4} = Fe(CN)_6^{-3} + e$	−0.36
$Cu = Cu^{++} + 2e$	−0.337
$2\,I^- = I_2 + 2e$	−0.5355
$Fe^{++} = Fe^{+++} + e$	−0.771
$Ag = Ag^+ + e$	−0.7991
$Hg = Hg^{++} + 2e$	−0.854
$Hg_2^{++} = 2\,Hg^{++} + 2e$	−0.92
$2\,Br^- = Br_2\,(l) + 2e$	−1.0652
$Mn^{++} + 2\,H_2O = MnO_2 + 4\,H^+ + 2e$	−1.23
$2\,Cr^{+3} + 7\,H_2O = Cr_2O_7^{=} + 14\,H^+ + 6e$	−1.33
$Cl^- = \frac{1}{2} Cl_2 + e$	−1.3595
$Ce^{+3} = Ce^{+4} + e$	−1.61
$Co^{++} = Co^{+++} + e$	−1.82
$2\,SO_4^{=} = S_2O_8^{=} + 2e$	−1.98
$2\,F^- = F_2 + 2e$	−2.65
Basic Solutions	
$2\,OH^- + Ca = Ca(OH)_2 + 2e$	3.03
$3\,OH^- + Cr = Cr(OH)_3 + 3e$	1.3
$4\,OH + Zn = ZnO_2^{=} + 2\,H_2O + 2e$	1.216
$2\,OH^- + CN^- = CNO^- + H_2O + 2e$	0.97
$2\,OH^- + SO_3^{=} = SO_4^{=} + H_2O + 2e$	0.93
$H_2 + 2\,OH^- = 2\,H_2O + 2e$	0.828
$2\,OH^- + Ni = Ni(OH)_2 + 2e$	0.72
$OH^- + Fe(OH)_2 = Fe(OH)_3 + e$	0.56
$O_2 + 2\,OH^- = O_3 + H_2O + 2e$	−1.24

---

* W. M. Latimer, *Oxidation Potentials* (New York: Prentice-Hall, 2nd ed., 1952).

the actual free energies in volt equivalents so that the different numbers of electrons are properly accounted for. For example:

	$\mathscr{E}°$	*Volt Equivalents*
$4\,H_2O + Mn^{++} = MnO_4^- + 8\,H^+ + 5e^-$	-1.52	-7.60
$2\,H_2O + Mn^{++} = MnO_2 + 4\,H^+ + 2e^-$	-1.28	-2.56
$2\,H_2O + MnO_2 = MnO_4^- + 4\,H^+ + 3e^-$	-1.68	-5.04

31. Standard free energies and entropies of aqueous ions. Closely related to the standard electrode potential on the hydrogen scale is the *standard free energy of an ion.* Once again, all values are referred to a conventional reference standard, the hydrogen ion at $a_\pm = 1$, which is taken to have a standard free energy of zero. Consider again the reaction

$$Cd + 2\,H^+ \rightarrow Cd^{++} + H_2 \qquad \mathscr{E}°_H = 0.403\ (25°C)$$

If all the reactants are in their standard states:[22]

$$-z\mathscr{E}°\mathscr{F} = \Delta F° = \bar{F}°_{Cd^{++}} + F°_{H_2} - F°_{Cd} - 2\bar{F}°_{H^+}$$

Now $F°_{H_2}$ and $F°_{Cd}$ are zero because the free energies of the elements are taken as zero in their standard states at 25°C, and $\bar{F}°_{H^+}$ is zero by our convention. It follows that

$$\bar{F}°_{Cd^{++}} = \Delta F° = -z\mathscr{F}\mathscr{E}° = -\frac{2 \times 0.403 \times 96{,}520}{4.184} = -18.59 \text{ kcal per mole}$$

In addition to the standard ionic free energies, it is useful to obtain also the standard ionic entropies, $\bar{S}°$. These are the partial molar entropies of the ions in solution relative to the conventionally chosen standard that sets the entropy of the hydrogen ion at unit activity equal to zero, $\bar{S}°_{H^+} = 0$. These ionic entropies provide a measure of the ordering effect produced by an ion on the surrounding water molecules. Small ions like Li^+ and F^- have lower entropies than larger ions like Na^+ and Cl^-. This difference is in accord with the data from transference experiments discussed on page 446. Ions bearing a multiple charge are found to have especially low entropies in aqueous solution, as a result of their strong electrostatic attraction for the water dipoles and correspondingly large ordering effect on the solvent.

One method for calculating the ionic entropies may be illustrated in terms of our example, the Cd^{++} ion. Consider again the reaction: $Cd + 2\,H^+ = Cd^{++} + H_2$. The standard entropy change is $\Delta S° = \bar{S}°_{Cd^{++}} + S°_{H_2} - 2\,\bar{S}°_{H^+} - S°_{Cd}$. Now $S°_{Cd}$ and $S°_{H_2}$ have been evaluated from Third-Law measurements and statistical calculations, being 31.23 and 12.3 cal per deg at 25°C. By our convention, $\bar{S}°_{H^+}$ is zero. Therefore $\bar{S}°_{Cd^{++}} = \Delta S° + 18.93$. The value of $\Delta S°$ can be obtained from $\Delta S° = (\Delta H° - \Delta F°)/T$. If cadmium is dissolved in a large excess of very dilute acid, the heat of solution per mole of cadmium is the standard enthalpy change $\Delta H°$, since in the extremely

---

[22] The free energies are written $\bar{F}$ because for species in solution they are the partial molar free energies or chemical potentials.

dilute solution all the activity coefficients approach unity. This experiment yields the value $\Delta H^\circ = -16{,}700$ cal. The ΔF° from the cell emf was found to be $-18{,}580$ cal. Therefore $\Delta S^\circ = (-16{,}700 + 18{,}580)/298.2 = 6.22$ cal per deg. It follows that $\bar{S}^\circ_{\text{Cd}^{++}} = -12.7$ cal per deg.

The methods described for determining the thermodynamic properties of ions in solution represent only a few examples of many possible ways of combining thermodynamic data. Latimer's book, *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, should be consulted for a thorough survey of this important field and extensive tables of the thermodynamic quantities.

32. Measurement of solubility products. Standard electrode potentials can be combined to yield the $\mathscr{E}^\circ$ and thus the ΔF° and equilibrium constant for the solution of salts. It is thus possible to calculate solubilities for salts even in cases where an extremely low solubility would make direct measurements very difficult. As an example, consider silver iodide, which dissolves according to: $\text{AgI} = \text{Ag}^+ + \text{I}^-$. The *solubility product constant* is $K_{sp} = a_{\text{Ag}^+}a_{\text{I}^-}$.

A cell whose net reaction corresponds to the solution of solid silver iodide can be formed by combining a silver electrode with a silver-silver iodide electrode, $\text{Ag}|\text{Ag}^+,\text{I}^-|\text{AgI (s)}|\text{Ag}$. The electrode reactions are

$$\begin{array}{lrcl} & \text{Ag} = \text{Ag}^+ + e & \mathscr{E}^\circ = & -0.7995 \\ & e + \text{AgI (s)} = \text{Ag} + \text{I}^- & \mathscr{E}^\circ = & -0.1510 \\ \hline \text{Over-all:} & \text{AgI (s)} = \text{Ag}^+ + \text{I}^- & \mathscr{E}^\circ = & -0.9505 \end{array}$$

Then, from $\Delta F^\circ = -z\mathscr{F}\mathscr{E}^\circ = -RT\ln K_{sp}$,

$$\log_{10} K_{sp} = \frac{(-0.951 \times 96{,}520)}{(2.303 \times 8.31 \times 298.2)} = -16.05$$

Assuming unit activity coefficients in the very dilute solution of AgI, this K_{sp} corresponds to a solubility of 2.47×10^{-6} g per liter.

33. Electrolyte-concentration cells. The cells so far described have all been *chemical cells*, producing electrical energy from chemical changes. There is also an important class of cells in which no net chemical change occurs. These are called *concentration cells*, because they owe their emf to concentration changes either in the electrolyte or in the electrodes (*e.g.*, in amalgams).

For the cell, $\text{Pt}|\text{H}_2|\text{HCl}\,(c)|\text{AgCl}|\text{Ag}$, the cell reaction is $\frac{1}{2}\text{H}_2 + \text{AgCl} = \text{Ag} + \text{HCl}\,(c)$. Measurements with two different hydrochloric acid concentrations c yielded the following results:

c	$\mathscr{E}$	$-\Delta F$ (*joules*)
0.0010	0.6095	58,820
0.0483	0.3870	37,340

If two such cells are set up so as to oppose each other, the combination constitutes a cell that can be written as follows:

$$\text{Ag}|\text{AgCl}|\text{HCl}\,(c_2)|\text{H}_2|\text{HCl}\,(c_1)|\text{AgCl}|\text{Ag}$$

The over-all change in this cell is simply the difference between the changes in the two separate cells: for the passage of each faraday the transfer of one mole of HCl from concentration c_2 to c_1, $\mathrm{HCl}\,(c_2) \rightarrow \mathrm{HCl}\,(c_1)$. Note, however, that there can be no direct transport of electrolyte from one side to the other. The HCl is removed from the left side by the reaction, $\mathrm{HCl} + \mathrm{Ag} = \mathrm{AgCl} + \mathrm{H_2}$. It is added to the right side by the reverse of this reaction. From the data above, if $c_1 = 0.001$ and $c_2 = 0.0483$, the free energy of dilution is $\Delta F = -21{,}480$, and $= 21{,}480/96{,}520 = 0.2225$.

34. Electrode-concentration cells. An example of an electrode-concentration cell would be one consisting of two hydrogen electrodes operating at different pressures and dipping into a hydrochloric-acid solution:

$$\mathrm{Pt}|\mathrm{H_2}\,(P_1)|\mathrm{HCl}\,(a)|\mathrm{H_2}\,(P_2)|\mathrm{Pt}$$

At the left electrode: $\frac{1}{2}\,\mathrm{H_2}\,(P_1) = \mathrm{H^+}\,(a_{\mathrm{H^+}}) + e$

At the right: $\mathrm{H^+}\,(a_{\mathrm{H^+}}) + e = \frac{1}{2}\,\mathrm{H_2}\,(P_2)$

The over-all change is accordingly $\frac{1}{2}\,\mathrm{H_2}\,(P_1) \rightarrow \frac{1}{2}\,\mathrm{H_2}\,(P_2)$, the transfer of one equivalent of hydrogen from pressure P_1 to P_2. The emf of the cell is

$$\mathcal{E} = -\frac{RT}{\mathcal{F}} \ln \frac{P_2}{P_1}$$

An interesting type of electrode concentration cell is one in which two amalgam electrodes of different concentrations dip into a solution containing the solute metal ions. For example:

$$\mathrm{Cd\text{-}Hg}\,(a_1)|\mathrm{CdSO_4}|\mathrm{Cd\text{-}Hg}\,(a_2)$$

The emf of this cell arises from the net work obtained in transferring cadmium from an amalgam where its activity is a_1 to one with activity a_2. The emf is therefore:

$$\mathcal{E} = \frac{RT}{2\mathcal{F}} \ln \frac{a_1}{a_2}$$

If the amalgams are considered to be ideal solutions, one may replace the activities by mole fractions. In Table 15.9 are some experimental data for

TABLE 15.9

CADMIUM AMALGAM ELECTRODE-CONCENTRATION CELLS*

Grams Cadmium per 100 grams Mercury		Emf Observed	Emf Calculated
Electrode (1)	Electrode (2)		
1.000	0.1000	0.02966	0.02950
0.1000	0.01000	0.02960	0.02950
0.01000	0.001000	0.02956	0.02950
0.001000	0.0001000	0.02950	0.02950

* G. Hulett, *J. Am. Chem. Soc.*, *30*, 1805 (1908).

these cells, together with the calculated emf's based on ideal solutions. The approach to the theoretical values with increasing dilution may be noted. Electrode-concentration cells are especially useful in studying the thermodynamics of alloys.[25]

35. Cells with liquid junctions. If the two electrodes of a cell are immersed in two different solutions, these solutions must be brought into contact in order to complete the electrical circuit. The contact can be made either directly or through a *salt bridge*, a connecting tube filled with salt solution.

The liquid-to-liquid junctions are designed so as to minimize mixing of the solutions by interdiffusion. Sometimes a flowing junction is used for greater reproducibility.

As was pointed out in Section 30, it is not possible to measure a difference in electrical potential between two chemically different media. Therefore liquid-junction potentials cannot be directly measured.

Attempts have been made to calculate liquid-junction potentials by solving diffusion equations for the ions in solution. Consider, for example, a junction between a solution of HCl and a solution of KCl. If the concentrations are about the same, one would expect the HCl solution to lose H^+ ions by diffusion more rapidly than the KCl solution loses K^+ ions, because the H^+ ion has a much higher mobility. Thus the HCl side of the contact would become negatively charged relative to the KCl side. Semi-quantitative estimates based on this picture have led to junction potentials of from 5 to 30 millivolts, not large compared with the usual cell emf's.

Attempts have been made to eliminate the liquid-junction potential by using a salt bridge. Concentrated solutions of KCl or NH_4NO_3 are often used in the bridge. The ions in these solutions have nearly the same transport numbers, and one may hope that the two cell-solution–bridge-solution potentials will be nearly equal numerically but opposite in sign.

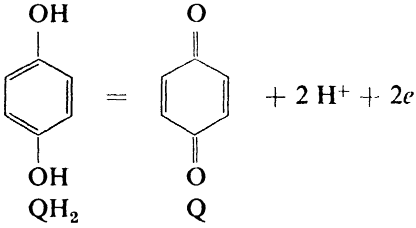
The most encouraging thing about cells with liquid junctions is that standard emf's obtained from them, when careful procedures are followed, often agree very closely with the results from cells without liquid junctions. We thus can feel considerable confidence in the necessary approximations. Cells without liquid junctions are used wherever possible, but in some applications, such as the measurements of *p*H, or of oxidation-reduction potentials of organic compounds, it is necessary to employ liquid junctions.

36. Oxidation-reduction reactions. Cells with liquid junctions are frequently used to study the equilibrium in oxidation-reduction reactions. Special interest has been focused on the oxidations of organic substances occurring in living cells, in view of the importance of such processes in cellular metabolism and respiration. Although the particular example is not

---

[25] J. Chipman, *Discussions of the Faraday Soc.*, *4*, 23 (1948).

a biological reaction, the principles involved can be illustrated by the oxidation of hydroquinone to quinone. The reaction is[26]



If an inert metal electrode (Au or Pt) is placed in a solution containing a mixture of hydroquinone and quinone, the reaction can be made to proceed in either direction by supplying or removing electrons at the electrode.

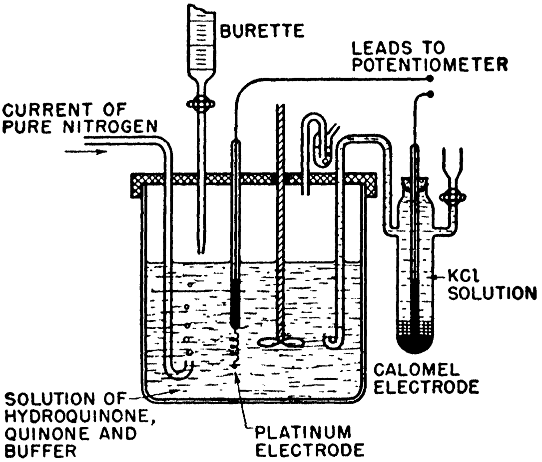


Fig. 15.14. Experimental arrangement for measuring emf of an oxidation-reduction reaction, or for a potentiometric titration.

A complete cell can be formed by coupling this hydroquinone electrode with a calomel electrode or other reference half cell. A typical experimental arrangement is shown in Fig. 15.14. The cell may be written

$$\mathrm{Au}|\mathrm{QH_2},\ \mathrm{Q}\ (\text{buffer: } \mathrm{H^+})|\mathrm{KCl},\ \mathrm{Hg_2Cl_2}|\mathrm{Hg_2Cl_2}\ (s)|\mathrm{Hg}$$

The cell reaction is

$$\begin{array}{ll} \text{At the left:} & QH_2 = Q + 2\,H^+ + 2e \\ \text{At the right:} & \underline{Hg_2Cl_2 + 2e = 2\,Hg + 2\,Cl^-} \\ \text{Over-all:} & QH_2 + Hg_2Cl_2 = Q + 2\,Hg + 2\,H^+ + 2\,Cl^- \end{array}$$

---

[26] Hydroquinone is a weak acid but in moderately acid solutions its dissociation is negligible. Under certain conditions the reaction proceeds in two steps, removal of one electron forming a highly colored *semiquinone*. See L. Michaelis, *Chem. Revs.*, *22*, 437 (1938).

The emf can be written

$$\mathscr{E} = \mathscr{E}^{\circ} - \frac{RT}{2\mathscr{F}} \ln \frac{a_{\mathrm{Q}}\, a_{\mathrm{H}^+}^{2}\, a_{\mathrm{Cl}^-}^{2}}{a_{\mathrm{QH}_2}}$$

$$\mathscr{E} = \mathscr{E}^{\circ} - \frac{RT}{2\mathscr{F}} \ln \frac{a_{\mathrm{Q}}}{a_{\mathrm{QH}_2}} - \frac{RT}{\mathscr{F}} \ln a_{\mathrm{HCl}} \tag{15.60}$$

Since Q and QH_2 are uncharged species, it is a good approximation to replace their activity ratio by a concentration ratio. Then from measured values of $\mathscr{E}$ at known acid strength, it is possible to calculate $\mathscr{E}^{\circ}$ and hence the equilibrium constant of the oxidation-reduction reaction. Note that the $\mathscr{E}$ of the cell and therefore the driving force of the reaction depend on the acid concentration.

By adding an oxidizing agent from the burette, it is possible to titrate the reduced form. As the concentration of QH_2 approaches zero, it is evident from eq. (15.60) that $\mathscr{E}$ approaches minus infinity. Consequently, when the amount of QH_2 remaining unoxidized becomes very small, the change in the measured cell emf becomes very steep. Of course $\mathscr{E}$ does not actually go to $-\infty$, because as the end point of the titration is approached the concentration of unreacted oxidizing agent (titrant) becomes appreciable, so that a new oxidation-reduction equilibrium is set up with an emf characteristic of the titrant system. The course of a typical *potentiometric titration* is shown in Fig. 15.15. If the standard potentials of the titrated system and the titrant system are sufficiently far apart, a good end point can be readily determined.

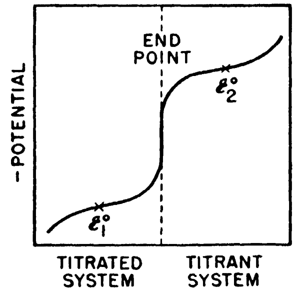


Fig. 15.15. Course of emf in a potentiometric titration.

37. Measurement of *p*H. We often need to know the concentration of hydrogen ions in aqueous solution. In 1909 S. P. Sørensen invented the symbol *p*H as a convenient expression for this quantity, defined by $p\mathrm{H} = -\log_{10} c_{\mathrm{H}^+}$, where c_{H^+} is the molar concentration.

In 1909 strong electrolytes like HCl were believed to be only partially dissociated even in dilute solutions. The degree of dissociation was believed to be given by $\alpha = \Lambda/\Lambda_0$. Values of c_{H^+} were accordingly calculated from the equivalent conductivities, and Sørensen set up his *p*H scale on this basis. It now appears that strong electrolytes are completely dissociated in dilute solutions, so that the Sørensen *p*H scale is unsatisfactory.

For most practical purposes the *p*H is a number determined by potentiometric measurement of a cell emf. Since cell emf's depend on activities and not on concentrations it is probably wise to abandon the definition of *p*H by a concentration scale, except as a first approximation. It might seem logical to define pH as $-\log_{10} a_{\text{H}^+}$, but this definition has the considerable drawback that a_{H^+} is not itself an experimentally measurable quantity.

The best procedure seems to be to define a pH scale by reference to the measured emf of a cell consisting of a hydrogen electrode combined with some reference electrode. Such a cell might be

$$(\text{Pt})\text{H}_2,\ 1\ \text{atm}|\text{H}^+X^-\vdots\text{KCl (saturated)}\vdots\text{Hg}_2\text{Cl}_2,\ \text{KCl}|\text{Hg}_2\text{Cl}_2|\text{Hg}$$

This cell contains two liquid junctions at the KCl salt bridge, so that we cannot separate the hydrogen electrode potential from the measured emf. If such a separation were possible we could write the emf as

$$\mathscr{E} = \mathscr{E}_{\text{ref}} - \frac{RT}{\mathscr{F}} \ln a_{\pm}$$

We now arbitrarily define the pH by writing

$$\mathscr{E} = \mathscr{E}_{\text{ref}} + 2.303\frac{RT}{\mathscr{F}}\,p\text{H} \tag{15.61}$$

We choose a value for $\mathscr{E}_{\text{ref}}$ that will give a pH value in accord with other thermodynamic data, such as the dissociation constants of weak acids. For the 0.1 normal KCl-calomel electrode this value at 25°C is $\mathscr{E}_{\text{ref}} = 0.3358$ v. Therefore eq. (15.61), defining the pH, can be written (at 25°C)

$$p\text{H} = \frac{\mathscr{E} - 0.3358}{2.303\ RT/\mathscr{F}} = \frac{\mathscr{E} - 0.3358}{0.0592}$$

The hydrogen electrode is not well suited for routine pH measurements because it requires a source of gaseous hydrogen and it is sensitive to various "poisons" that inhibit the catalytic activity of the platinized platinum surface. The most convenient method of measuring pH is undoubtedly by means of the *glass electrode*. The operation of this interesting device depends upon the difference in potential across a glass membrane separating solutions of different pH.[27]

38. Concentration cells with transference. In electrolyte-concentration cells without liquid junctions, the type previously described, there is no direct flow of electrolyte from one solution to the other. An example of a concentration cell that does have direct contact between the solutions is

$$\begin{array}{ccc} \text{H}_2\ (1\ \text{atm})|\text{HCl}\ (a_1) & \vdots & \text{HCl}\ (a_2)|\text{H}_2\ (1\ \text{atm}) \\ \tfrac{1}{2}\,\text{H}_2 \rightarrow \text{H}^+ & t_+\text{H}^+ & \text{H}^+ \rightarrow \tfrac{1}{2}\,\text{H}_2 \\ & \rightleftarrows & \\ & t_-\text{Cl}^- & \end{array}$$

The t's are the ionic transport numbers. For the passage of each faraday of charge, the following changes occur in the cell:

A. At the electrodes. (1) One equivalent of H^+ is formed at the left, by the reaction $\tfrac{1}{2}\,\text{H}_2 \rightarrow \text{H}^+(a_1)$. (2) One equivalent of H^+ is removed at the

---

[27] M. Dole, *The Glass Electrode* (New York: Wiley, 1941).

right, by the reaction $H^+(a_2) \rightarrow \frac{1}{2} H_2$. The net result of the electrode processes is $H^+(a_2) \rightarrow H^+(a_1)$.

B. At the liquid junction. (1) t_- equivalents of Cl^- ions pass from right to left, from the solution of activity a_2 to that of activity a_1. (2) $t_+ = 1 - t_-$ equivalents of H^+ ions pass from left to right, from activity a_1 to a_2.

The net result of these changes at the electrodes and at the junction is

$$t_-(\mathrm{HCl}) \text{ at } a_2 \rightarrow t_-(\mathrm{HCl}) \text{ at } a_1$$

Since the electrodes are reversible with respect to the cation H^+, the transport number t of the anion occurs in the expression for the net change.

Such a cell is called a *concentration cell with transference.* Note that it requires electrodes reversible with respect to only one of the ions. Concentration cells without transference require one electrode reversible with respect to the anion and one with respect to the cation.

The free-energy change of the cell reaction is $\Delta F = t_- 2RT \ln (a_1/a_2)$. The emf of the cell is accordingly

$$\mathscr{E}_t = t_- \frac{2RT}{\mathscr{F}} \ln \frac{a_2}{a_1}$$

The same process, dilution of HCl from a_2 to a_1, can be carried out in the cell without transference whose emf is

$$\mathscr{E} = \frac{2RT}{\mathscr{F}} \ln \frac{a_2}{a_1}$$

It follows that
$$t_- = \frac{2\mathscr{E}_t}{\mathscr{E}} \qquad (15.62)$$

From the ratio of the emf of concentration cells with and without transference, transport numbers can be obtained that are in good agreement with those measured in other ways. The result in eq. (15.62) is, however, an approximation based on the assumption that the transport numbers do not depend on the concentration.

39. Electrolysis and polarization: decomposition voltages. So far we have been considering electrode processes that are essentially reversible. These processes provide values for the equilibrium emf's of cells, which are related to the thermodynamic functions. The condition of reversibility is practically attained by balancing the cell emf against an external emf until only an imperceptible current flows through the cell, so that the cell reactions proceed extremely slowly. For many of the applications of electrochemistry, it is obviously necessary to consider more rapid reaction rates. Then there is necessarily a departure from the equilibrium situation. Either the cell reactions proceed spontaneously to generate electric energy, or an external source of electric energy is used to effect chemical reactions (electrolyses).

Let us consider, for example, the electrolysis of a dilute solution of hydrochloric acid. Platinum electrodes are introduced into the solution and connected, through a device for varying the voltage, to an external source of emf, such as a storage battery. The arrangement in (a), Fig. 15.16, may conveniently be used. If the applied voltage is gradually increased and the current flowing through the cell is measured as a function of the potential difference across the electrodes, the typical result shown in (b), Fig. 15.16, is obtained. The current is extremely small until a certain definite voltage is reached; thereafter the current-voltage curve rises steeply. The voltage at which the current begins to flow freely corresponds to that at which bubbles of gas are first discharged from the electrodes. It is called the *decomposition voltage* of the solution.

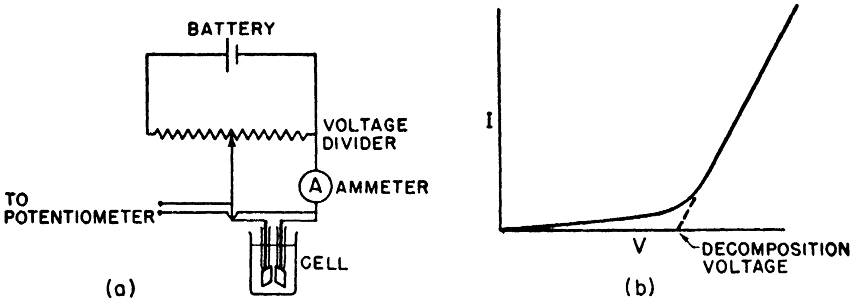


Fig. 15.16. (a) Measurement of decomposition voltage; (b) current-voltage curve.

The reason for the occurrence of a definite decomposition voltage in this instance is quite evident. As soon as the potential difference is set up between the electrodes, hydrogen ions migrate to the cathode and chloride ions to the anode. The ions are discharged, forming layers of adsorbed gas on the inert metal surfaces. Instead of having two platinum electrodes we now have a hydrogen electrode and a chlorine electrode. The result is a typical chemical cell:

$$\mathrm{Pt}|\mathrm{H_2}|\mathrm{H^+{\cdot}Cl^-}\ (a)|\mathrm{Cl_2}|\mathrm{Pt}$$

The cell produces a *back emf*, which counterbalances the external emf. Its reversible emf at 25° is given by

$$\mathscr{E} = \mathscr{E}^\circ + 0.059 \log_{10} (a_{\mathrm{H^+}} a_{\mathrm{Cl^-}})$$

From Table 15.8 the standard electrode potential $\mathscr{E}^\circ = 1.3583$. If the solution is taken to be one normal, the activity coefficient of HCl is 0.82, so that the reversible emf would be $\mathscr{E} = 1.3583 - 0.0051 \doteq 1.3532$.

The observed decomposition voltage is close to this value, being 1.31 v at 25°C in the 1 *N* solution. It is evident that in this case decomposition begins when the applied voltage reaches the reversible emf of the cell set up by the electrolysis of the solution. In other cases, however, the decomposition voltage actually required may be considerably above the calculated reversible decomposition voltage.

The small current that flows before the decomposition voltage is reached is caused by the slow diffusion of ions away from the gas electrodes. A certain expenditure of external electric energy is necessary to counterbalance this back diffusion and keep the electrodes polarized.

40. Polarization and overvoltage. When an electrochemical cell is working under irreversible conditions, its emf necessarily departs from the equilibrium value. If the cell is acting as a battery or source of electricity, its voltage falls below the equilibrium value. If the cell is the site of electrolysis, the voltage supplied must exceed the equilibrium value.

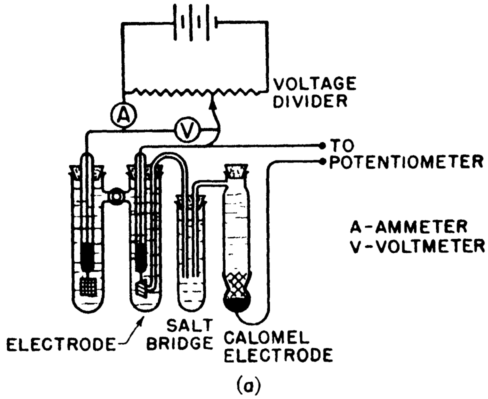
Part of this voltage difference is necessary to overcome the resistance of the cell and is equal to the IR product. The corresponding electric energy I^2R is dissipated as heat. It is analogous to the frictional losses in irreversible mechanical processes.

In addition to this, there are two other sources of voltage difference that are usually distinguished. One has its origin within the electrolyte of the cell, and the other is referred to rate processes occurring at the electrodes. The first is called *concentration polarization* and the second is called *overvoltage.*

As its name suggests, concentration polarization arises from concentration gradients within the electrolyte of the working cell. For example, consider a cell consisting of a copper anode and a platinum cathode in a solution of copper sulfate. When a current flows, copper is dissolved at the anode and deposited upon the cathode. If the current is appreciable the solution around the cathode becomes relatively depleted of copper ions. Thus a concentration gradient is set up within the cell. This gradient is equivalent to a concentration cell of the type discussed on page 482. The concentration cell may be considered to produce a *back emf* opposing the applied voltage. Concentration polarization of this sort can often be practically eliminated by vigorous stirring of the electrolyte, which destroys the concentration gradients caused by the electrolysis. Increase in temperature also tends to decrease the polarization, by accelerating the diffusion of electrolyte ions within the cell.

The phenomenon of *overvoltage* arises from a slow attainment of equilibrium at the electrodes, *i.e.*, either a slowness in the transfer of electrons to, or the acceptance of electrons from, ions in the solution. The effect may be observed for most electrode processes, but for deposition or solution at metal electrodes it is usually small. Much more noteworthy are the overvoltages required for the liberation of gaseous hydrogen or oxygen, which may amount to a volt or more on certain metals.

The overvoltage can be measured with an experimental arrangement like that shown in (a), Fig. 15.17. An auxiliary reference electrode, *e.g.*, normal calomel, is placed close to the electrode being investigated (to minimize IR drop) and the potential of the electrode at which the gas is being discharged is measured as a function of the current density. The solution is well stirred to eliminate concentration polarization. Some of the results with various metals are shown in (b), Fig. 15.17. Only in the case of platinized platinum is the hydrogen overvoltage small at all current densities. The oxygen overvoltage behaves very similarly, except that here the value is appreciable even on platinized platinum.



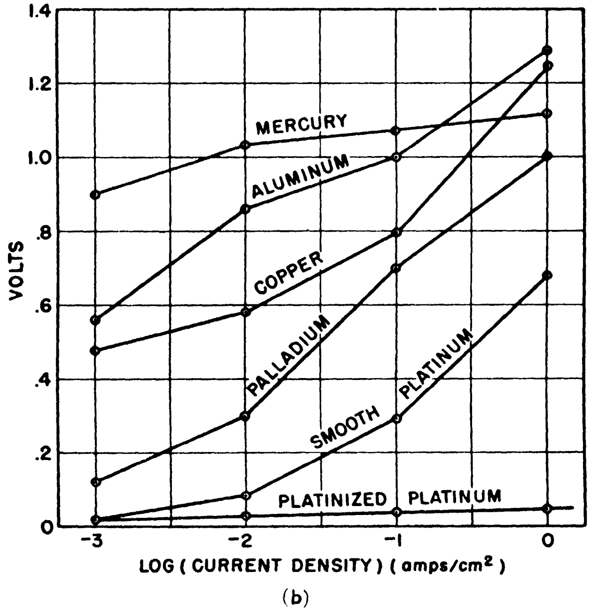


Fig. 15.17. (a) Apparatus for measuring overvoltage of an electrode as a function of current density; (b) hydrogen overvoltage at 25°C.

The importance of the overvoltage in practical applications of electrochemistry is very great. Because of the high hydrogen overvoltage, it is possible to plate metals from solutions in which their reversible discharge potentials are well below that of the hydrogen ion. For example, consider a cell consisting of platinum electrodes in a solution of zinc ions and hydrogen ions at unit activity. The reversible potentials of the half cells are

of the zinc: $\frac{1}{2}\,\mathrm{Zn} = \frac{1}{2}\,\mathrm{Zn}^{++} + e \qquad \mathscr{E}_0 = 0.762$

of the hydrogen: $\frac{1}{2}\,\mathrm{H}_2 = \mathrm{H}^+ + e \qquad \mathscr{E}_0 = 0$

If hydrogen were discharged at its reversible potential, it should be liberated at the cathode at a much lower voltage than that required to plate out zinc. The overvoltage of hydrogen on zinc, however, amounts to about 1.0 v, so that in an actual electrolysis, zinc will first be deposited on the cathode. The hydrogen ion will not be discharged until the zinc concentration has fallen to such a point that the emf of the zinc half cell lies above the hydrogen overvoltage.

Many theories have been proposed to account for the overvoltage.[28] They agree in postulating a slow step in the electrode reaction, which requires the surmounting of a considerable potential energy barrier. For a charged particle (ion) the applied emf serves to lower the energy barrier.

PROBLEMS

1. After passage of an electric current for 45 minutes, 7.19 mg of silver are found to be deposited in a silver coulometer. Calculate the average current.

2. A conductivity cell filled with a 0.1 molar solution of potassium chloride at 25°C has a measured resistance of 24.96 ohms. Calculate the cell constant if the conductivity κ for 0.1 molar KCl is 0.011639 ohm^{-1} cm^{-1} and conductivity water with $\kappa = 7.5 \times 10^{-8}$ ohm^{-1} cm^{-1} is used to make up the solutions. Filled with a 0.01 molar solution of acetic acid the cell resistance is 1,982 ohms. Calculate the equivalent conductivity of acetic acid at this concentration.

3. The following are the conductivities of chloroacetic acid in aqueous solution at 25°C:

$1/c$ (liter/mole)	16	32	64	128	256	512	1,024
equiv. cond., Λ	53.1	72.4	96.8	127.7	164	205.8	249.2

If $\Lambda_0 = 362$, are these values in accord with the Ostwald Dilution Law?

4. If the purest water has a conductivity of 6.2×10^{-8} ohm^{-1} cm^{-1} at 25°C, calculate the κ of a saturated solution of CO_2 in water at 25°C if the CO_2 pressure is maintained at 20 mm and the equilibrium constant for the reaction, $H_2O\,(l) + CO_2\,(aq) = HCO_3^- + H^+$, is 4.16×10^{-7}. The solubility of CO_2 in water follows Henry's Law with a constant $k' = 0.0290$ mole lit^{-1} atm^{-1} [cf. MacInnes and Belek, *J. Am. Chem. Soc.*, *55*, 2630 (1933)].

5. The conductivity of a saturated solution of silver chloride in pure

---

[28] J. Bockris, *Chem. Rev.*, *43*, 525 (1948).

water at 20°C is 1.26×10^{-6} ohm^{-1} cm^{-1} higher than that for the water used. Calculate the solubility of AgCl in water.

6. Draw a calculated curve showing how the conductivity of the solution varies as 10 ml of 0.1 N NaOH is titrated with 11 ml of 0.1 N HCl.

7. An 0.01 N silver nitrate solution is used with silver electrodes in a determination of the transference number of the Ag^+ ion by the Hittorf method; 32.10 mg of silver are deposited in a silver coulometer in series with the Hittorf cell. At the end of the run the 20.09 g of solution in the anode compartment are found to contain 39.66 mg of Ag; the 27.12 g of solution in the cathode compartment contain 11.14 mg of Ag. Calculate the Ag^+ transference number.

8. E. W. Washburn [*J. Am. Chem. Soc.*, *31*, 322 (1909)] measured the transference of the ions in a KCl solution to which was added an inert compound, raffinose, in order to detect the transport of water by the hydrated ions. The original concentration of the KCl was 1.24 molal, of raffinose 0.1 molal (formula: $C_{18}H_{32}O_{16}$). Ag-AgCl electrodes were used. In a run with 5.3685 g silver deposited in the coulometer the following data were obtained: Anode compartment, 103.21 g solution containing 6.510 per cent KCl, 4.516 per cent raffinose. Cathode compartment, 85.280 g, 10.030 per cent KCl, 4.290 per cent raffinose. If Δn_w is number of moles of water transported from anode to cathode for passage of one faraday of electricity, n_s and n_w are number of moles of salt and of water in original solution, show that $t - t_H = (n_s/n_w)\Delta n_w$. Here t_H is the apparent (Hittorf) transference number and t is the true transference number corrected for the transport of water. Calculate t_H and t in this experiment. If all the water of hydration is assumed to be held by the K^+ ion and none by the Cl^- ion, calculate the mean number of molecules of water held by each K^+ ion.

9. In a transport experiment in 0.02 molar NaCl solution at 25°C by the moving boundary method, Longsworth [*J. Am. Chem. Soc.*, *54*, 2741 (1932)] found the boundary between NaCl and $CdCl_2$ solutions to move 6.0 cm in 2,070 seconds with a current of 0.00160 amp. (Tube cross section 0.12 cm^2.) Calculate t^+.

10. From data in Table 15.4, calculate the transport number of the K^+ ion in K_2SO_4.

11. From the following freezing-point depressions for aqueous solutions of sodium chloride, calculate the activity coefficient γ_m of NaCl in 0.05 molal solution [G. N. Lewis and M. Randall *J. Am. Chem. Soc.*, *43*, 1112 (1921)].

molality, m . . .	0.01	0.02	0.05	0.10	0.20	0.50
f. pt. dep. °C . .	0.0361	0.0714	0.1758	0.3470	0.6850	1.677

12. From the molal activity coefficients in Table 15.5, calculate the mean ionic activity in 0.1 molal solution of $AgNO_3$, $CuSO_4$, $CaCl_2$.

13. The solubility of $AgIO_3$ in KNO_3 solutions has been measured by Kolthoff and Lingane [*J. Phys. Chem.*, *42*, 133 (1938)] at 25°C:

KNO_3, m/l	0	0.001301	0.003252	0.006503	0.01410
$AgIO_3$, m/l $\times 10^4$ . . .	1.761	1.813	1.863	1.908	1.991

Compare these results with the Debye-Hückel limiting law for solubilities and calculate the activity coefficients of $AgIO_3$ in the solutions.

14. Calculate the ionic strengths of one-molal solutions of KNO_3, K_2SO_4, $K_4Fe(CN)_6$.

15. Calculate the "thickness of the ionic atmosphere" according to the Debye-Hückel theory in 0.1 and 0.01 molar solutions of a uniunivalent electrolyte in (a) water at 25°C with dielectric constant $\varepsilon = 78$; (b) 70 per cent ethanol in water at 25°C with $\varepsilon = 38.5$.

16. The solubility of barium sulfate in water at 25°C is 0.957×10^{-5} m per liter. Using the Debye-Hückel theory, calculate ΔF° for the change: $BaSO_4\,(s) = Ba^{++} + SO_4^{--}\,(aq)$.

17. The solubility-product constant of AgCl at 25°C is $K_{sp} = (Ag^+)(Cl^-) = 1.20 \times 10^{-10}$. Calculate from the Debye-Hückel theory (limiting law) the solubility of AgCl in water and in a 0.01 *M* solution of (a) NaCl, (b) $NaNO_3$.

18. For an incompletely dissociated electrolyte the Onsager equation is: $\Lambda = \alpha[\Lambda_0 - (A + B\Lambda_0)\sqrt{\alpha c}]$. If we let $\Lambda' = [\Lambda_0 - (A + B\Lambda_0)\sqrt{\alpha c}]$ be the equivalent conductivity at the actual ionic concentration (αc) in the solution, it is evident that $\alpha = \Lambda/\Lambda'$. For dichloroacetic acid in 0.03 molar solution at 25°, $\Lambda = 273\ \text{ohm}^{-1}\,\text{cm}^{-1}$. Λ_0 is 388.5. Calculate the degree of dissociation α from the Onsager expression. (*Hint:* use a procedure of successive approximations to find Λ', starting with $\alpha = \Lambda/\Lambda_0$.)

19. Use the value of α calculated in problem 18 to obtain the thermodynamic equilibrium constant for the dissociation of dichloroacetic acid. The solution is so dilute that the activity of the undissociated acid can be set equal to its concentration and the mean ionic activity can be calculated from the Debye-Hückel limiting law.

20. A 0.1 molar H_3PO_4 solution is titrated with NaOH using methyl orange as an indicator to an endpoint at *p*H 4.3. The dissociation constants of H_3PO_4 are 7.5×10^{-3}, 6×10^{-8}, and 3.6×10^{-13}. Calculate the fractions of acid converted to $H_2PO_4^-$ and HPO_4^{--}.

21. Calculate the *p*H of a 0.1 *M* solution of ammonium lactate at 25°C. Lactic acid, $pK_a = 3.86$; ammonia, $pK_b = 4.76$.

22. In water solution, amino acids exist mainly as zwitterions, *e.g.*, glycine as $^+NH_3CH_2COO^-$. For $^+NH_3CH_2COOH = {}^+NH_3CH_2COO^- + H^+$, $pK_a = 2.35$; for $^+NH_3CH_2COO^- = NH_2CH_2COO^- + H^+$, $pK_b = 9.78$. Calculate the *p*H of a 0.1 *M* glycine solution.

23. The *p*H at which an amphoteric electrolyte yields an equal concentration of positive and negative ions is called the isoelectric point. Show that if the activity coefficients of all the ions are taken as unity, this $pH = \frac{1}{2}(pK_a + pK_b)$. Hence estimate the isoelectric point of glycine from the data in the previous problem.

24. Devise cells in which the cell reactions are the following:

(a) $2\,AgBr + H_2 = 2\,Ag + 2\,HBr$
(b) $H_2 + I_2 = 2\,HI$
(c) $S_2O_8^{--} + 2\,I^- = I_2 + 2\,SO_4^{--}$
(d) $2\,Fe^{+3} + CH_3CHO + H_2O = 2\,Fe^{+2} + CH_3COOH + 2\,H^+$
(e) $Ni + 2\,H_2O = Ni(OH)_2 + H_2$

Write down the cells with proper regard for the sign convention. Calculate the $\mathscr{E}^\circ$ for these cells from the standard electrode potentials. Assume any liquid-junction potentials are eliminated. The solubility of AgBr is 2.10×10^{-6} mole per liter.

25. Mercuric nitrate and ferrous nitrate, each in 0.01 molar solution, are mixed in equal volumes at 25°C. From the standard potentials in Table 15.8, find the equilibrium concentration of ferric ion in the solution. Activity coefficients may be estimated from the Debye-Hückel Limiting Law.

26. Calculate the values of the oxidation potential $\mathscr{E}$ of the electrode $Pt/Fe^{++}, Fe^{+++}$ as a function of the per cent oxidized form. Use concentrations in place of activities. Plot the results.

27. A solution 0.1 molar in lactic acid is mixed with an equal volume of a 0.1 molar methylene blue solution. Calculate the equilibrium concentration of lactic acid given the following oxidation potentials at 25°C:

methylene white = methylene blue + 2 H^+ + $2e^-$ $\mathscr{E}^\circ = -0.53$ v
lactic acid = pyruvic acid + 2 H^+ + $2e^-$ $\mathscr{E}^\circ = -0.20$ v

28. The emf's of the cell $H_2/HCl\,(m)/AgCl/Ag$ at 25°C are as follows [cf. Harned and Ehlers, *J. Am. Chem. Soc.*, *54*, 1350 (1932)]:

m (molal conc)	$\mathscr{E}$ *(volts)*	*m*	$\mathscr{E}$
0.01002	0.46376	0.05005	0.38568
0.01010	0.46331	0.09642	0.35393
0.01031	0.46228	0.09834	0.35316
0.04986	0.38582	0.20300	0.31774

Calculate $\mathscr{E}^\circ$ for the cell by the following method of graphical extrapolation. We can write $\mathscr{E} = \mathscr{E}^\circ - A \log a_{HCl}$ where $A = 2.303\,RT/\mathscr{F}$. This becomes $\mathscr{E} + 2A \log m = \mathscr{E}^\circ - 2A \log \gamma_\pm$. From Debye-Hückel theory, $\log \gamma_\pm = -B\sqrt{m}$. Thus: $\mathscr{E} + 2A \log m = \mathscr{E}^\circ + 2AB\sqrt{m}$. Plot the left side of this expression vs. $\sqrt{m}$ and extrapolate to $m = 0$, the intercept giving $\mathscr{E}^\circ$. (See Harned's paper for a more precise method of extrapolation.)

29. From the value of $\mathscr{E}^\circ$ obtained above and the measured emf's, calculate the mean activity coefficients $\gamma_\pm$ of HCl at the various concentrations.

30. The cell, Sn(liq)/$SnCl_2$ in molten KCl + LiCl/Sn-Sb liquid solution, was measured at 905°K at various mole fractions of tin in the solution with antimony:

X_{Sn}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$\mathcal{E}$ (v)	0.11984	0.08379	0.05905	0.04545	0.03705	0.02845	0.01725	0.00992	0.00523

If pure liquid tin is chosen as the standard state, $\Delta F = \bar{F}_A - F_A^\circ = -z\mathcal{E}\mathcal{F} = RT \ln a_A$, where a_A is the activity of tin in the electrode solution. Plot γ_{Sn} and γ_{Sb} as functions of X_{Sn}.

31. The emf of the cell $H_2(P)$/0.1 *m* HCl/HgCl/Hg was studied as a function of the hydrogen pressure at 25°:

P (atm)	1.0	37.9	51.6	110.2	286.6	731.8	1035.2
$\mathcal{E}$ (mv)	399.0	445.6	449.6	459.6	473.4	489.3	497.5

Calculate the activity coefficients of hydrogen gas ($\gamma = f/P$) and plot them as a function of the pressure over the given range.

32. For the cell H_2/HCl/AgCl/Ag, $\mathcal{E}^\circ = 0.222$ v. If the measured emf is 0.385 v what is the *p*H of the HCl solution?

33. Copper is being plated onto a platinum electrode from a 0.5 molar copper sulfate solution, 0.01 molar in H_2SO_4. If the hydrogen overvoltage on copper is 0.23 v, what will be the residual Cu^{++} concentration in the solution when H_2 evolution begins at cathode?

34. It is desired to separate Cd^{++} and Zn^{++} by electrolytic deposition of the Cd^{++}. The $\mathcal{E}^\circ$ for the cadmium electrode is 0.402 v, for the zinc 0.762 v. The overvoltages are Cd = 0.48 v; Zn = 0.70 v. Discuss the feasibility of the separation in a solution originally 0.1 molar in Zn^{++} and Cd^{++}.

REFERENCES

BOOKS

1. Butler, J. A. V., *Electrical Phenomena at Interfaces* (London: Methuen, 1951).
2. Glasstone, S., *Introduction to Electrochemistry* (New York: Van Nostrand, 1942).
3. Gurney, R. W., *Ionic Processes in Solution* (New York: McGraw-Hill, 1953).
4. Harned, H. H., and B. B. Owen, *Physical Chemistry of Electrolytic Solutions* (New York: Reinhold, 1943).
5. Kolthoff, I. M., and H. A. Laitenan, *pH and Electrotitrations* (New York: Wiley, 1941).
6. Latimer, W. M., *Oxidation Potentials* (New York: Prentice-Hall, 1952).
7. Luder, W. F., and S. Zuffanti, *The Electronic Theory of Acids and Bases* (New York: Wiley, 1946).
8. MacInnes, D. A., *The Principles of Electrochemistry* (New York: Reinhold, 1939).

ARTICLES

1. Audrieth, L. F., and T. Moeller, *J. Chem. Ed.*, *20*, 219–222 (1943), "Acid-Base Relationships at Higher Temperatures."
2. Bockris, J. O., *Chem. Rev.*, *43*, 525–575 (1948), "The Hydrogen Overpotential."
3. Denbigh, K. G., *J. Chem. Ed.*, *18*, 126–130 (1941), "Theory of the Solubility Product."
4. Hamer, W. J., *J. Electrochem. Soc.*, *99*, 331c–343c (1952), "Fifty Years of Electrochemical Theory."
5. Harned, H. S., *Chem. Rev.*, *40*, 461–522 (1947), "Diffusion in Electrolyte Solutions."
6. Luder, W. F., and A. A. Vernon, *J. Chem. Ed.*, *22*, 63–67 (1945), "Electrochemical Conventions."
7. MacInnes, D. A., *Science in Progress*, vol. II (New Haven: Yale Univ. Press, 1940), 197–231, "Motion of Ions and Proteins in Electric Fields."
8. Merrill, R. C., *J. Chem. Ed.*, *27*, 312–328 (1950), "Colloidal Electrolytes."
9. Owen B. B., *J. Chem. Ed.*, *21*, 59–63 (1944), "Effect of Pressure on the Properties of Electrolytic Solutions."
10. van Rysselberghe, P., and A. H. Gropp, *J. Chem. Ed.*, *21*, 96–99 (1944), "Solubility Products of Metallic Sulfides."

CHAPTER 16

Surface Chemistry

1. Surfaces and colloids. When in Chapter 5 we defined the concept of phase and discussed the thermodynamic treatment of phase equilibria, we were careful to impose a restriction on the validity of the results obtained, owing to our neglect of any effects that might arise from variation of the interfacial areas separating different phases. Furthermore, a phase was defined as a part of a system that was "homogeneous throughout." Such a definition implies that the matter deep in the interior of a phase is subject to exactly the same conditions as the matter at the exterior which forms the surface. This is clearly impossible in any case, since the molecules (or ions) in the interior are surrounded on all sides by the uniform field of force of neighbor molecules (or ions) of the same substance. The molecules at the surface are bounded on one side by neighbors of the same kind but on the other side by an entirely different sort of environment.

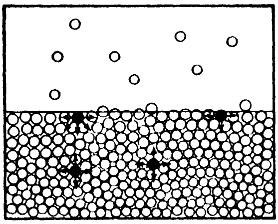


Fig. 16.1. Liquid-vapor interface.

Consider, for example, the surface of a liquid in contact with its vapor, shown in Fig. 16.1. A molecule in the interior of the liquid is in a uniform field of force. A molecule at the surface is subject to a net attraction toward the bulk of the liquid, which is not compensated by an equal attraction from the more highly dispersed vapor molecules. Thus all liquid surfaces, in the absence of other forces, tend to contract to the minimum area. For example, freely suspended volumes of liquid assume a spherical shape, since the sphere has the minimum surface-to-volume ratio.

In order to extend the area of an interface like that in Fig. 16.1, *i.e.*, to bring molecules from the interior into the surface, work must be done against the cohesive forces in the liquid. It follows that the surface portions of the liquid have a higher free energy than the bulk liquid. This extra surface free energy is more usually described by saying that there is a *surface tension*, acting parallel to the surface, which opposes any attempt to extend the interface. A tension is a negative pressure; pressure is a force per unit area, so that surface pressure is a force per unit length. If the surface tension is γ, the work done by the surface in extending its area by an amount $d\sigma$ is $dw = -\gamma\, d\sigma = -dF$, whence

$$dF = \gamma\, d\sigma \tag{16.1}$$

where dF is the change in free energy.

The units of surface tension are evidently dynes per cm in the CGS system. The problems arising in the measurement and interpretation of the surface tension will be taken up later in this chapter. The subject was introduced here at the beginning to illustrate the new type of variable that enters into the description of physicochemical systems as soon as surfaces are explicitly considered. Since the surface of a liquid does not have the same free energy as the bulk liquid, it cannot be said to be in the same thermodynamic state or to be part of the same phase.

When will it be necessary to consider these surface effects? First of all it will obviously be necessary when we wish deliberately to focus our attention on interfacial phenomena rather than bulk properties. Secondly, there will be instances when the interfacial phenomena must be taken into consideration in order to study the system at all. This second case will arise when any considerable fraction of the material in the system exists at or near interfaces.

The degree of subdivision or particle size of a substance is usually the decisive factor determining its surface-to-volume ratio. Extremely porous materials are apparently exceptional cases, but these materials may often be treated as loose aggregates of very small particles. For example, suppose we have a gram of crystalline silica. If for simplicity the crystals, with density ρ, are considered to be small cubes, all of side l, their total surface area will be

$$A = \frac{6l^2}{\rho l^3} = \frac{6}{\rho l}$$

With $\rho = 2.30$, the following results are obtained for the surface area in cm^2 per gram at various particle sizes:

l (cm)	A (cm^2/g)
10^{-1}	26.1
10^{-3}	2,610
10^{-5}	261,000
10^{-6}	2,610,000
10^{-7}	26,100,000

It is evident that the area increases enormously as the particle size decreases. The lower end of the scale, with l below about 10^{-7} cm or 10 Å, corresponds to the dimensions expected for ordinary molecules. From around 10^{-7} to 10^{-4} cm there extends the domain of *colloids*. For particles of colloidal dimensions surface phenomena play a preëminent role, and indeed much of colloidal chemistry is essentially surface chemistry. This entire field is one of extraordinary interest because of its intimate connection with biochemical and physiological processes. The building blocks of living matter, protein molecules, are so large that their dimensions fall within the colloidal realm. From the viewpoint of physical chemistry the living cell is a complex colloidal system.

The great variety of possible colloidal systems may be recalled by reference to Table 16.1 where they are classified according to the kinds of dispersed phase and dispersion medium. We shall be able to discuss only a few of these systems; a fairly comprehensive treatment would require another book at least as large as this one.

TABLE 16.1

CLASSIFICATION OF COLLOIDS

Dispersion Medium	*Dispersed Phase*	*Examples*
Gas	Liquid	Aerosols: fogs, mists
Gas	Solid	Aerosols: smokes
Liquid	Gas	Gas emulsions: foams
Liquid	Liquid	Emulsions
Liquid	Solid	Suspensions: sols and gels
Solid	Gas	Solid foams (*e.g.*, pumice)
Solid	Solid	Solid sols (*e.g.*, colloidal gold in glass)

2. Pressure difference across curved surfaces. Interfaces between two liquids and between a liquid and a vapor are most conveniently studied, because the molecules in fluids are not rigidly fixed in position. They therefore tend to adjust themselves to changes at the interface in such a way as to record automatically the surface tension. This possibility does not arise with liquid-solid or solid-gas interfaces, and measurement of the interfacial tensions in these cases is made by indirect methods.

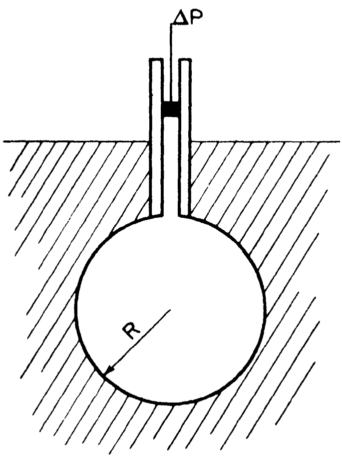


Fig. 16.2. The pressure difference across a curved interface.

As a direct consequence of the existence of a surface tension, it can be shown that across any curved liquid surface there must exist a difference in pressure, the pressure being greater on the concave side than on the convex side.

If a curved surface is displaced parallel to itself to a new position, its area must change if its curvature is to remain the same. Work must be done against the surface tension to effect this change in area.

In Fig. 16.2 is shown a spherical bubble of gas of radius R at the end of a fine capillary tube fitted with a piston. Let the equilibrium pressure inside the bubble be ΔP. It will be assumed that this pressure is entirely due to the surface tension, *i.e.*, the effect of the weight of the liquid will be neglected. Suppose the piston is advanced so as to expand the bubble radius by dR, thereby increasing its surface area $4\pi R^2$ by $8\pi R\, dR$, and its volume $\frac{4}{3}\pi R^3$ by

$4\pi R^2\,dR$. The work done against the surface tension $\gamma\,dA$ is equal to the work done in the expansion at constant pressure ($P\,dV$), so that

$$\gamma(8\pi R\,dR) = (4\pi R^2\,dR)\Delta P$$

and

$$\Delta P = \frac{2\gamma}{R} \tag{16.2}$$

This result applies to liquid-liquid as well as to gas-liquid interfaces. For a more general curved surface with radii of curvature R_1 and R_2 it becomes[1]

$$\Delta P = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \tag{16.3}$$

3. Capillary rise. The rise or fall of liquids in capillary tubes and its application to the measurement of surface tension may now be treated as a direct consequence of the fundamental eq. (16.2). Whether a liquid rises in a glass capillary, like water, or is depressed, like mercury, depends on the relative magnitude of the forces of cohesion between the liquid molecules themselves, and the forces of adhesion between the liquid and the walls of the tube. These forces determine the *contact angle* θ, which the liquid makes with the tube walls (Fig. 16.3). If this angle is less than 90°, the liquid is said to *wet* the surface and a concave meniscus is formed. A contact angle of 90° corresponds to a plane meniscus; a contact angle greater than 90°, to a convex meniscus.

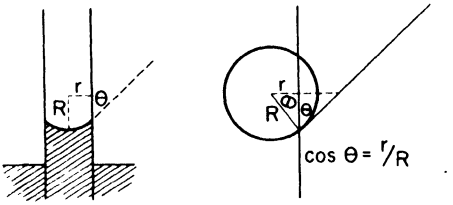


Fig. 16.3. Capillary rise.

The occurrence of a concave meniscus leads to a capillary rise. The pressure under the meniscus is less than that at the plane surface of liquid outside the tube. Liquid rises in the tube until the weight of the liquid column balances the pressure difference. The liquid column acts as a manometer to register the pressure difference across the concave meniscus.

Consider, Fig. 16.3, a cylindrical tube whose radius r is sufficiently small that the surface of the meniscus can be taken as a section of a sphere with radius R. Then, since $\cos\theta = r/R$, from eq. (16.2) $\Delta P = (2\gamma\cos\theta)/r$. If the capillary rise is h, and if ρ and ρ_0 are the densities of the liquid and the surrounding fluid, the weight of the cylindrical liquid column is

---

[1] N. K. Adam, *Physics and Chemistry of Surfaces* (New York: Oxford, 1944, p. 8).

$\pi r^2 gh(\rho - \rho_0)$, or the force per unit area balancing the pressure difference is $gh(\rho - \rho_0)$. Therefore

$$\frac{2\gamma \cos \theta}{r} = gh(\rho - \rho_0), \qquad \gamma = \frac{1}{2} gh(\rho - \rho_0) \frac{1}{\cos \theta} r$$

In many cases the contact angle θ is practically zero, and if the surrounding fluid is a vapor, its density ρ_0 is negligible compared to ρ. These approximations lead to the frequently used formula:

$$\gamma = \tfrac{1}{2}\rho g h r \tag{16.4}$$

4. Maximum bubble pressure. Blowing bubbles provides a second convenient way of measuring surface tensions. Consider a bubble being formed at the end of a small tube immersed in liquid. As one begins to apply pressure, the radius of the bubble is comparatively large. As the bubble grows, the radius at first decreases until it reaches a minimum when the bubble is a hemisphere with a radius equal to that of the small tube. Any further increase in pressure will lead to the loss of the bubble, which will expand and free itself from the tube.

It is clear from eq. (16.2) that the maximum pressure that the bubble can sustain will be that at the position of minimum radius. The applied pressure is balanced by the pressure difference across the curved surface plus a hydrostatic pressure depending on the depth h of the tube outlet under the liquid. Therefore the surface tension is determined from

$$P_{\text{max}} = \frac{2\gamma}{r} + gh(\rho - \rho_0) \tag{16.5}$$

5. The Du Noüy tensiometer. Frequently used for measurements of surface or interfacial tension is the *tensiometer* designed by Lecomte Du Noüy. A platinum ring of radius r is attached to a torsion balance, and the force required to remove the ring from the surface or interface is measured directly. The surface tension acts over the circumference of the ring and there are two sides to the new surface that is formed, so that the applied force $f = 4\pi r\gamma$. A number of correction factors are necessary for precise work.[2]

6. Surface-tension data. Some values for the surface tensions of pure liquids are collected in Table 16.2. Liquids with exceptionally high surface tensions, such as water, are those in which the cohesive forces between the molecules are large, the surface tension being a measure of the work that must be done to bring a molecule from the interior to the surface. We might expect liquids with high surface tension to have high internal pressures, and this relationship is in general confirmed by a comparison of Table 16.2 with Table 14.2.

The surface tensions of solutions may be given a simple qualitative interpretation. Consider, for example, aqueous solutions. Substances that

---

[2] P. Lecomte Du Noüy, *J. Gen. Physiol.*, *1*, 521 (1918); *7*, 403 (1925).

TABLE 16.2
SURFACE TENSION DATA

A. Surface Tensions of Pure Substances at 20°C—Dynes per Cm

Isopentane	13.72	Ethyl iodide	29.9
Nickel carbonyl	14.6	Benzene	28.86
Diethyl ether	17.10	Carbon tetrachloride	26.66
n-Hexane	18.43	Methylene iodide	50.76
Ethyl mercaptan	21.82	Carbon bisulfide	32.33
Ethyl bromide	24.16	Water	72.75

B. Surface Tensions of Liquid Metals and Molten Salts

	°C	γ		°C	γ
Ag	970	800	AgCl	452	125.5
Au	1070	1000	NaF	1010	200
Cu	1130	1100	NaCl	1000	98
Hg	0	470	NaBr	1000	88

markedly lower the surface tension of water are those that, like the fatty acids, contain both a polar hydrophilic group and a nonpolar hydrophobic group. The hydrophilic group, *e.g.*, —COOH in the fatty acids, makes the molecule reasonably soluble if the nonpolar residue is not too predominant. One may expect the hydrocarbon residues in the fatty acids to be extremely uncomfortable[3] in the interior of an aqueous solution, and little work is required to persuade them to come from the interior to the surface. This qualitative picture leads to the conclusion that solutes lowering the surface tension of a liquid tend to accumulate preferentially at the surface. They are said to be *positively adsorbed* at the interface.

On the other hand, solutes such as ionic salts usually increase the surface tension of aqueous solutions above the value for pure water, although these increases are much smaller than the decreases produced by fatty acids and similar compounds. The reason for the observed increases is that the dissolved ions, by virtue of ion-dipole attractions, tend to pull the water molecules into the interior of the solution. Additional work must be done against the electrostatic forces in order to create new surface. It follows that in such solutions the surface layers are poorer in solute than is the bulk solution. The solute is said to be *negatively adsorbed* at the interface.

After the thermodynamic treatment of surfaces has been discussed, it will be possible to give these qualitative conclusions a more quantitative formulation.

---

[3] A way of saying the free energy of the state is high.

The temperature dependence of the surface tension may often be adequately represented by an empirical equation proposed by Ramsay and Shields:

$$\gamma\left(\frac{M}{\rho}\right)^{2/3} = k'(T_c - T - 6) \tag{16.6}$$

Here M is the molecular weight, ρ the density, k' a constant, and T_c the critical temperature of the liquid. Liquids that obey Trouton's rule have values of k' that cluster closely around 2.1.

An alternative representation of the variation of the surface tension is the McLeod equation:

$$\gamma = C(\rho - \rho_0)^4 \tag{16.7}$$

where ρ_0 is the vapor density and C is a constant for each liquid. This equation is the basis of Sugden's *parachor*, a quantity defined by

$$\mathscr{P} = MC^{1/4} = \frac{M\gamma^{1/4}}{\rho - \rho_0} \tag{16.8}$$

The parachor is essentially a molecular volume, modified to eliminate some of the influence of the cohesive forces, which vary from liquid to liquid. The parachor of a molecule can be estimated by adding terms for each of its atoms plus terms for the types of bond (double, single, etc.) that are present.[4]

7. The Kelvin equation. One of the most interesting consequences of surface tension is the fact that the vapor pressure of a liquid is greater when it is in the form of small droplets than when it has a plane surface. This was first deduced by Lord Kelvin. If a liquid distills from a plane surface to a droplet, the droplet must increase in size and therefore in surface area. The increase requires the expenditure of extra work against the surface tension.

Consider a spherical droplet whose radius grows from r to $r + dr$. The increase in surface is from $4\pi r^2$ to $4\pi(r + dr)^2$, which amounts to $8\pi r\, dr$. The corresponding increase in surface free energy is $8\pi\gamma r\, dr$. If dn moles of liquid were distilled from the plane surface whose vapor pressure is P_0 to the droplet whose vapor pressure is P, the free energy change would be given by eq. (3.32) as $dn\, RT \ln P/P_0$. Equating the free energy changes, we have

$$dn\, RT \ln \frac{P}{P_0} = 8\pi\gamma r\, dr$$

But

$$dn = 4\pi r^2\, dr\, \frac{\rho}{M}$$

whence

$$\ln \frac{P}{P_0} = \frac{2M\gamma}{RT\rho r} \tag{16.9}$$

---

[4] For details see: S. Sugden, *The Parachor and Valency* (London: Geo. Rutledge & Sons, Ltd., 1929).

The application of the equation to water droplets is shown in the following calculated pressure ratios:

(Water at 20°C, $P_0 = 17.5$ mm)

r (cm)	10^{-4}	10^{-5}	10^{-6}	10^{-7}
P/P_0	1.001	1.011	1.114	2.95

An equation similar to that of Kelvin can be derived for the solubility of small particles. The procedure should be evident from the connection between vapor pressure and solubility developed in the thermodynamic treatment of solutions in Chapter 6.

The conclusions of the Kelvin equation have been experimentally verified in a number of instances. Thus there can be no doubt that very small droplets of liquid have a considerably higher vapor pressure than bulk liquid, and that very small particles of solid have a considerably greater solubility than the bulk solid. These results lead to the rather curious problem of how new phases can ever arise from old ones.

If, for example, a container filled with water vapor at slightly below the saturation pressure is chilled suddenly, perhaps by adiabatic expansion as in the Wilson cloud chamber, the vapor may become supersaturated with respect to liquid water. It is then in a thermodynamically metastable state, and one may expect condensation to take place immediately. A reasonable molecular picture of condensation would seem to be that two or three molecules of water vapor come together to form a tiny droplet, and that this *nucleus* of condensation then grows by accretion as additional vapor molecules happen to hit it. Now, however, the Kelvin equation indubitably indicates that a tiny droplet like this nucleus, being only a few Ångstroms in diameter, would have a vapor pressure many times that of bulk liquid. As far as tiny nuclei are concerned, the vapor would not be supersaturated at all. Such nuclei should immediately "re-evaporate." This argument, as far as its premises represent reality, would seem to prove that the emergence of a new phase at the expected equilibrium pressure, or even moderately above it, is always a thermodynamic impossibility.

There are two ways of resolving this paradox. In the first place, we know that the Second Law of Thermodynamics is statistical by nature. In any system at equilibrium there are always fluctuations around the equilibrium condition, and if the system contains few molecules, these fluctuations may be relatively large (cf. page 197). For example, the density of a gas is not perfectly uniform throughout its container; in sufficiently small regions the percentage deviation from the average number of molecules may often be considerable. Similarly, there is always a chance that an appropriate fluctuation will lead to the formation of a nucleus of a new phase, even though the tiny nucleus could be called thermodynamically unstable. The chance of such a fluctuation we know indeed to be $e^{-\Delta S/k}$ where ΔS is the deviation of the entropy from the equilibrium value.

It is unlikely, however, that new phases often arise by this fluctuation mechanism and the resultant *spontaneous nucleation.* Calculations show that the chance $e^{-\Delta S/k}$ is usually much too small. It is more likely that tiny solid particles, *e.g.*, dust particles, act as nuclei for further condensation or for crystallization in supersaturated vapors or solutions. Actually, supersaturated vapors seem to be much less finicky than supersaturated solutions about the sort of nuclei that are required. This is because a liquid will condense on almost any surface, but crystallization requires the presence of crystal faces of the proper kind. We are perhaps all familiar with the legendary organic chemist who prepared a compound for the first time, and was unable to bring it to crystallization. A call to a friend brought some seed crystals, and no sooner was the envelope opened than the solution at the other end of the laboratory began to crystallize. Thereafter no difficulty was ever experienced in crystallizing that particular compound: the seeds were in the air.

The phenomena in the change liquid $\rightleftarrows$ vapor are similar. We have all been troubled with the bumping of liquids and have learned to use boiling chips. It has been shown by E. N. Harvey that water carefully freed from all dissolved gases can be heated to 200°C before ebullition takes place, with almost explosive violence.[5]

8. Thermodynamics of surfaces. In Fig. 16.4 are represented two phases, α and β, separated by an interfacial region. The exact position of this region depends on how we choose to draw the boundary planes AA' and BB'. It seems reasonable to place these planes so that the following condition is satisfied: there is no appreciable inhomogeneity in the properties of the bulk phase α up to the surface AA', nor in those of phase β up to the surface BB'. Within the interfacial region the properties of the system vary continuously from purely α- at AA' to purely β- at BB'. Because of the short range of intermolecular forces, the interfacial region will usually be not more than a few molecular diameters in thickness.[6]

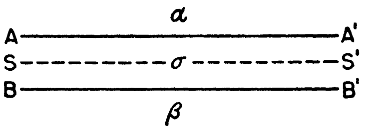


Fig. 16.4. Definition of surface phase.

Any surface SS' drawn within the interfacial region parallel to the surfaces AA' and BB' is called a *surface phase*, and is designated by a symbol σ. A surface phase defined in this way has an area but no thickness. It is a strictly two-dimensional phase. Its area will be denoted by A^σ.

The composition of the surface phase will be described in terms of quantities n_i^σ. We define n_i^σ as the number of moles of component i in the

---

[5] E. N. Harvey *et al., J. Am. Chem. Soc., 67,* 156 (1945).

[6] It should be noted, however, that the attractive forces exerted by an extended surface have a much longer range than those from an isolated molecule. The latter depend on r^{-7}, and the former fall off as r^{-4}. For an extensive survey of the depth of the surface zone see J. C. Henniker, *Rev. Mod. Phys. 21,* 322 (1949).

surface film region, between AA' and BB', minus the number of moles of i that would be within this region if the phases α and β both extended all the way to the surface SS' with unchanged bulk properties. It is evident according to this definition that n_i^σ may be either positive or negative. Now the *surface concentration* c_i^σ, in moles per square centimeter, is defined by

$$c_i^\sigma = \frac{n_i^\sigma}{A^\sigma} \tag{16.10}$$

Other thermodynamic functions, such as surface energy E^σ, surface entropy S^σ, surface free energy F^σ, can be defined by exactly the same method used for the n_i^σ. They are the differences between the energy, entropy, or free energy of the actual interfacial region and the values calculated on the assumption that the phases remain uniform up to the dividing surface.

It is always possible to place the dividing surface SS' so that for one particular component (O) the surface concentration, c_0^σ is zero; *i.e.*, the number of moles of component (O) in the interfacial film between AA' and BB' is exactly what it would be if the bulk phases α and β both remained homogeneous right up to the dividing surface SS'. When the position of the interface is chosen in this way, the surface concentrations c_i^σ of the other components are said to be the concentrations *adsorbed at the interface*. This adsorption can be either positive or negative. In the examples previously considered, solutes dissolved in water, it was found that fatty acids were positively adsorbed at the solution-vapor interface, whereas ionic salts tended to be negatively adsorbed. Now that this concept of *adsorption* has been given a precise definition, it is possible to derive a thermodynamic relation between the extent of adsorption and the change in the surface tension of the solution. This relation is the famous *Gibbs adsorption isotherm.* Its derivation proceeds very similarly to that of the Gibbs-Duhem equation discussed on page 117.

9. The Gibbs adsorption isotherm. We shall consider a system that, for simplicity, consists of two components distributed in two bulk phases with a surface phase σ. Then, in addition to the ordinary state variables describing the bulk phases, new state variables must be introduced to define the state of the surface phase. Our consideration will be restricted to a system at constant temperature and pressure and constant composition of the bulk phases. For the bulk phases alone the differential of the free energy function would be, from eq. (4.27), $dF = -S^\alpha\, dT - S^\beta\, dT + V^\alpha\, dP + V^\beta\, dP + \mu_1\, dn_1^\alpha + \mu_1\, dn_1^\beta + \mu_2\, dn_2^\alpha + \mu_2\, dn_2^\beta$. This entire expression vanishes at constant temperature, pressure, and composition.

When the surface phase is considered we must add the following terms:

$$dF^\sigma = -S^\sigma\, dT + \gamma\, dA^\sigma + \mu_1\, dn_1^\sigma + \mu_2\, dn_2^\sigma$$

At constant temperature this differential of the surface free energy becomes

$$dF^\sigma = \gamma\, dA^\sigma + \mu_1\, dn_1^\sigma + \mu_2\, dn_2^\sigma \tag{16.11}$$

Integrating this expression while holding the intensity factors constant (or using Euler's theorem), we obtain

$$F^{\sigma} = \gamma A^{\sigma} + \mu_1 n_1^{\sigma} + \mu_2 n_2^{\sigma}$$

The complete differential is therefore

$$dF^{\sigma} = \gamma\, dA^{\sigma} + A^{\sigma}\, d\gamma + \mu_1\, dn_1^{\sigma} + n_1^{\sigma}\, d\mu_1 + \mu_2\, dn_2^{\sigma} + n_2^{\sigma}\, d\mu_2$$

Comparison with eq. (16.11) yields

$$A^{\sigma}\, d\gamma = -n_1^{\sigma}\, d\mu_1 - n_2^{\sigma}\, d\mu_2$$

Division by A^{σ} gives

$$d\gamma = -c_1^{\sigma}\, d\mu_1 - c_2^{\sigma}\, d\mu_2 \qquad (16.12)$$

Let us now choose the dividing surface so that the excess of one component (1), which may be called the solvent, vanishes. Then

$$d\gamma = -\Gamma_2\, d\mu_2 \qquad (16.13)$$

where Γ_2 is the concentration of component (2) adsorbed at the interface. Equation (16.13) may be written [from eq. (6.32)]

$$d\gamma = -RT\,\Gamma_2\, d\ln a_2 \qquad (16.14)$$

For an ideal solution, $a_2 = X_2$, the mole fraction, so that

$$d\gamma = -RT\,\Gamma_2\, d\ln X_2$$

or

$$\Gamma_2 = -\frac{1}{RT}\cdot\frac{d\gamma}{d\ln X_2} \qquad (16.15)$$

For a dilute solution, X_2 becomes proportional to c_2, the molar concentration, and

$$\Gamma_2 = -\frac{1}{RT}\cdot\frac{d\gamma}{d\ln c_2} \qquad (16.16)$$

These equations are various forms of the Gibbs adsorption isotherm. The isotherm has been experimentally verified by the ingenious experiments of J. W. McBain at Stanford University. He employed an adaptation of a swiftly moving microtome to slice off the top layer (around 0.05 mm) from a solution and scoop it into a sample tube. The composition of this layer could then be taken to determine Γ_2, and this experimental Γ_2 could be compared with that calculated, via the Gibbs isotherm, from the variation of the surface tension with the concentration of the bulk solution.

The isotherm may also be verified indirectly in a quite remarkable way which will be revealed in a following section, after another technique for studying surface films has been described.

10. Insoluble surface films—the surface balance. As a result of the pioneer work of Fräulein Pockels (1891) and Lord Rayleigh (1899) it was discovered that in some cases sparingly soluble substances would spread over the surface of liquids to form a film exactly one molecule thick. These ***unimolecular films*** may be regarded as essentially two-dimensional states of matter. Experimentally it was first observed that the lowering of the surface tension of water by certain oil films was very slight until a critical amount of oil had spread upon the water surface, whereupon the surface tension fell sharply to a value characteristic of the oil. Rayleigh suggested that the molecules of oil floated freely at the water surface, and as long as any water remained uncovered the surface tension was merely that of pure water. When enough oil was added to form a layer exactly one molecule thick the surface tension decreased abruptly. Pockels observed that such surface films could be made visible by lightly dusting the water surface with talcum powder. The spreading oil film would push the powder particles away, the area of the unpowdered portion providing a measure of the surface covered by the film. She also introduced the valuable technique of cleaning the water surface by sweeping it with a *barrier* which pushed any surface contamination to the end of the tray.

In 1917, Irving Langmuir devised a method for measuring directly the *surface pressure* exerted by a film. The essential features of the instrument used, the film balance, are shown in Fig. 16.5. The so-called *fixed barrier B*, which may be a strip of mica, floats on the surface of the water and is suspended from a torsion wire *W*. At the ends of the floating barrier are attached strips of platinum foil or greased threads, which lie upon the water surface and connect the ends of the barrier to the sides of the trough. These threads prevent leakage of surface film past the float. A movable barrier *A* rests upon the sides of the trough and is in contact with the water surface. A number of the movable barriers are provided for sweeping the surface clean by the Pockels method.

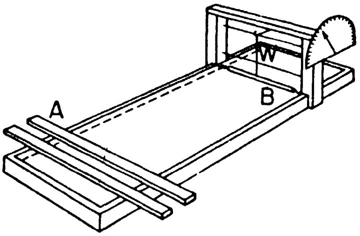


Fig. 16.5. The surface balance.

In a typical experiment, a tiny amount of the insoluble spreading substance is introduced onto the clean water surface. For example, a dilute solution of stearic acid in benzene might be used; the benzene evaporates rapidly, leaving a film of stearic acid. Now the moving barrier is advanced toward the floating barrier. As the surface film is compressed it exerts a surface pressure on the float, pushing it backward. The torsion wire, attached to a calibrated circular scale, is twisted until the float is returned to its original position. The required force divided by the length of the float is the force per unit length or *surface pressure.*

This surface pressure is simply another way of expressing the lowering of the surface tension caused by the surface film. On one side of the float is a clean water surface with tension γ_0, and on the other side a water surface covered to a certain extent with stearic acid molecules, with lowered surface tension γ. The surface pressure f is simply the negative of the change in surface tension, $\gamma - \gamma_0$. Thus, $f = -\Delta\gamma = \gamma_0 - \gamma$.

Langmuir was the first to study the surface-pressure vs. surface-area (f-A) relationships for films of the normal long-chain fatty acids, $CH_3(CH_2)_nCOOH$. A typical f-A isotherm for stearic acid is shown in Fig. 16.6. The surface pressure in dynes per cm is plotted against the available area per molecule of stearic acid, in square Ångstroms. This isotherm is a two-dimensional analogue of a three-dimensional P vs. V isotherm. At large areas the pressure is small and it increases very slowly with decreasing area until a value of about 20.5 Å^2 per molecule is reached. Then the pressure begins to increase rapidly on further compression of the film.

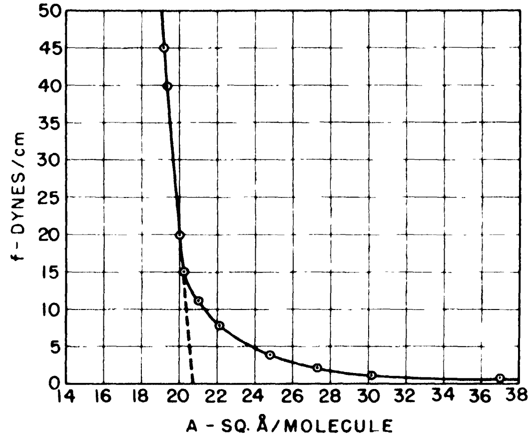


Fig. 16.6. f-A isotherm at 20°C. Stearic acid on distilled water.

It is reasonable to believe that the long chains of stearic acid are highly oriented at the water surface, with their water-loving carboxyl groups buried in the water and their water-hating hydrocarbon chains waving around above the surface. The critical area then corresponds to a tightly packed unimolecular film or *monolayer*, with the stearic acid molecules completely covering the surface. Any further decrease in area can be achieved only by compressing the closely packed film, and as is observed, this requires a considerable surface pressure (just as in the three-dimensional case compression of a solid or liquid is much more difficult than compression of a gas).

The critical area of 20.5 Å^2 may therefore be taken as approximately equal to the cross-sectional area of the hydrocarbon chain. The molecular volume of solid stearic acid is $M/N\rho = 556$ Å^3. The length of the molecule is therefore $556/20.5 = 27.1$ Å, or about 1.50 Å per CH_2 group. This estimate agrees well with the value obtained from X-ray diffraction. The simplicity of the Langmuir method of estimating molecular dimensions is remarkable, and it has had important applications in the study of complex organic compounds such as proteins and sterols.

11. Equations of state of monolayers. The detailed study of various substances in unimolecular films has revealed a great variety in the observed f-A isotherms. Sometimes the films appear to behave like two-dimensional gases, sometimes like two-dimensional liquids or solids. In addition, there are other types of monolayer that seem to have no exact analogues in the three-dimensional world. They can be recognized, however, as definite surface phases by the discontinuities in the f-A diagram which signal their occurrence.

In Fig. 16.7 are a series of f-A isotherms obtained for a number of the fatty acids $C_nH_{2n+1}COOH$ at 25°C. These curves resemble the P-V isotherms for a gas in the neighborhood of the critical temperature. There is a section at low pressures corresponding to the high compressibility of a gas. Then there is an intermediate region where a very small increase in pressure produces a large decrease in volume (the isotherm here does not seem to be absolutely flat and the analogy with the two-phase region in the P-V isotherm is imperfect). Finally there is a rapid rise in the f-A curve corresponding to the compression of a condensed phase. With decreasing molecular weight the quasi-two-phase region becomes less evident, and finally the isotherm appears to be gaseous throughout as in the dotted curve.

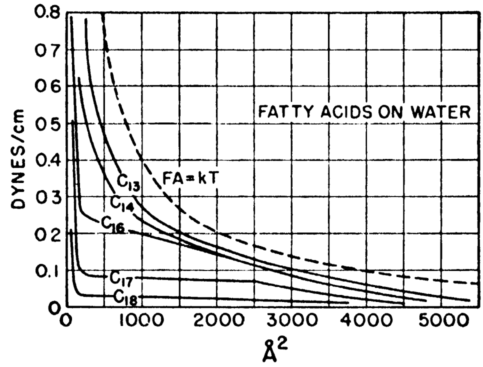


Fig. 16.7. f-A isotherms at low pressures.

If a surface film behaves as an ideal two-dimensional gas, corresponding to the three-dimensional $PV = RT$, we should have[7]

$$fA = kT \qquad (16.17)$$

The area A is usually expressed in Å² per molecule, and f in dynes per cm. The units of k are then (ergs × 10^{-16}) per °C. For example at 300°K, $fA = 1.37 \times 10^{-16} \times 10^{+16} \times 300 = 411$.

Condensed films often follow an equation of state of the form

$$f = b - aA \qquad (16.18)$$

---

[7] This can be proved by working through the derivation on p. 164 for a two-dimensional case. We find $fA = \frac{1}{2}NmC^2 = E_K$ and $E_K = RT$.

where a and b are constants. This equation indicates that the area decreases linearly with increasing surface pressure, *i.e.*, the compressibility of the film is a constant.

Films of the various "liquid" types obey other more complicated equations of state. It is apparent that the ordinary three-dimensional states of aggregation have many counterparts in the two-dimensional world of monolayers.

12. Surface films of soluble substances. As the chain length in the fatty-acid series decreases, the acids become more soluble in water. Finally the solubility becomes so considerable that there is a gradual transition from the formation of practically insoluble surface films to the formation of dilute solutions of the acids in water. The surface tension of pure water is markedly lower by solution of these acids, and accordingly the solute acid is strongly adsorbed at the surface of the solution. This is the situation treated by the Gibbs adsorption isotherm.

As one travels down the homologous series of fatty acids, there is clearly no change in the essential physical situation. There is in each case a lowering of the surface tension, $\gamma_0 - \gamma$, which may be equated to an equivalent surface pressure f. If the surface film is soluble, however, it is not possible to apply the film-balance technique, because the fatty-acid molecules can then bypass the barrier by ducking under it through the solvent.

Experimental measurements by Traube showed that in sufficiently dilute solutions the lowering of the surface tension becomes a linear function of the solute concentration. Thus we may write, with B a constant,

$$\gamma_0 - \gamma = f = Bc_2, \quad \text{or} \quad \frac{-d\gamma}{dc_2} = \frac{df}{dc_2} = B$$

From the Gibbs adsorption isotherm,

$$\Gamma_2 = -\frac{c_2}{RT} \cdot \frac{d\gamma}{dc_2}$$

It follows that

$$\Gamma_2 = \frac{Bc_2}{RT} = \frac{f}{RT}$$

Since the area per molecule A is simply $1/N\Gamma_2$, this expression becomes $fA = kT$. This is exactly the same equation as that obtained with the surface balance for an insoluble unimolecular film of the gaseous type. Surface films formed by spreading insoluble substances and those formed by the positive adsorption of solutes at the surface of a solution are basically alike.

13. Adsorption of gases on solids. We turn our attention next to what at first seems like a distinctly different variety of surface phenomenon. This is the adsorption onto the surface of a solid either of vapor or of components from a liquid solution. The experimental methods used for studying these adsorptions are so different from those employed in surface-tension measurements that the fundamental similarity of the phenomena was obscured for a long time. The adsorption of vapors on solids will be considered first.

Two experimental arrangements for measuring vapor adsorption are illustrated in Fig. 16.8. One is an adsorption balance designed by McBain and Bakr. The *adsorbent* (substance on which the adsorption takes place) is contained in a light platinum bucket suspended by a spiral of quartz fiber. The *adsorbate* (substance that is adsorbed) is at the bottom of the glass tube enclosing the spiral and bucket. The spiral has been calibrated by hanging weights on it, so that any measured elongation, observed with a traveling microscope, corresponds to a known weight. The adsorbate is kept frozen while the tube is evacuated and sealed off. Then it is warmed by a carefully regulated oven surrounding the lower portion of the tube. The temperature of this oven controls the vapor pressure of the adsorbate. The temperature of the adsorbent is controlled by another oven encasing the upper part of the tube. The amount of gas adsorbed is then measured directly by the gain in weight of the adsorbent. The measurements are extended over a range of adsorbent pressures to obtain the adsorption isotherm.

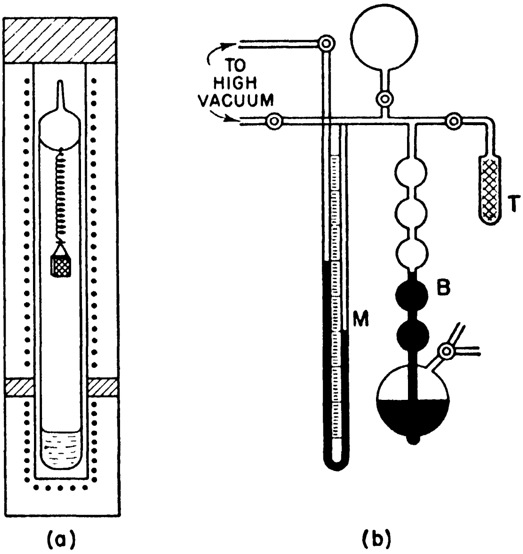


Fig. 16.8. Experimental gas adsorption methods: (a) Gravimetric—McBain balance. (b) Volumetric.

A second experimental arrangement is used in the volumetric method. The adsorbate vapor is contained in a calibrated gas buret (B), and its pressure is measured with the manometer (M). The adsorbent is contained in a thermostated sample tube (T), separated from the adsorbate by a stopcock or cutoff. All the volumes in the apparatus are calibrated. When vapor is admitted to the adsorbent sample, the amount adsorbed can be calculated from the pressure reading after equilibrium is attained. A series of measurements at different pressures determines the adsorption isotherm.

Two typical isotherms are shown in Fig. 16.9. Instead of the pressure, the *relative pressure* P/P_0 is used as a coordinate, where P_0 is the vapor pressure of the liquid adsorbate at the temperature of the isotherm. These isotherms illustrate the two distinct kinds of adsorption behavior that are usually distinguished. The case of nitrogen on silica gel at −196°C is an example of *physical adsorption.* The case of oxygen on charcoal at 100°C is a typical *chemisorption.* There are, as usual, instances in which it is hard to assign the adsorption definitely to one of these types, but in most cases the decision is not difficult.

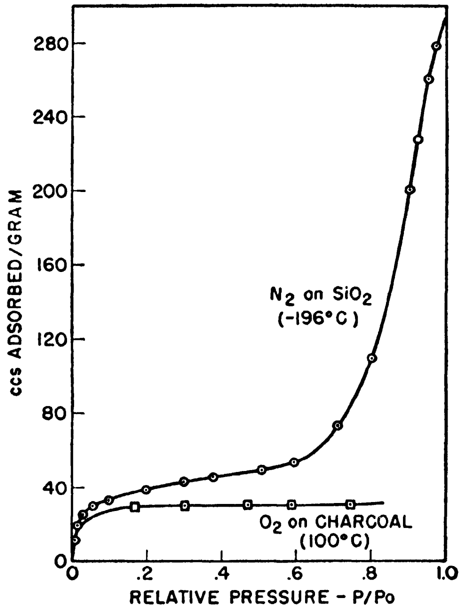


Fig. 16.9. Adsorption isotherms.

Physical adsorption is due to the operation of forces between the solid surface and the adsorbate molecules that are similar to the van der Waals forces between molecules. These forces are undirected and relatively nonspecific. They ultimately lead to the condensation of a vapor into a liquid, when P becomes equal to P_0. The energies of adsorption involved are of the order of a few hundred to a few thousand calories per mole. There will usually be little physical adsorption until the relative pressure P/P_0 reaches an appreciable value (around 0.05). The adsorption increases rapidly at high P/P_0, finally leading to condensation on the surfaces. Even before condensation occurs, for example at relative pressures around 0.8, there may be several superimposed layers of adsorbate on the surface. Physical adsorption is generally quite readily reversible, *i.e.*, on decreasing the pressure the adsorbed gas is desorbed along the same isotherm curve. An exception to this rule is observed when the adsorbent contains many fine pores or capillaries.[8]

In contrast with physical adsorption, chemisorption is the result of much stronger binding forces, comparable with those leading to the formation of chemical compounds. The adsorption may be regarded as the formation of a sort of surface compound. The energies of adsorption range from about 10^4 to 10^5 calories per mole. Chemisorption is seldom reversible. Generally the solid must be heated to a higher temperature and pumped at a high vacuum to remove chemisorbed gas. Sometimes the gas that is desorbed is not the same as that adsorbed; for example, after oxygen is adsorbed on charcoal at 100°C, heating and pumping will cause the desorption of carbon monoxide. On the other hand, hydrogen chemisorbed on nickel, presumably with the formation of surface Ni—H bonds, can be recovered as H_2. Chemisorption is completed when a surface is covered by an adsorbed monolayer, but there is good evidence that physical adsorption may lead to adsorbed layers several molecules thick. Sometimes a physically adsorbed layer may form on top of an underlying chemisorbed layer.

There are cases known in which the same system exemplifies physisorption at one temperature and chemisorption at some higher temperature. Thus nitrogen is physisorbed on iron at −190°C and chemisorbed with the formation of surface iron nitride at 500°C. Chemisorption is of particular importance in contact catalysis, and this field will be discussed in the next chapter as an important aspect of chemical kinetics. Most of the following discussion will be applicable to both physical and chemical adsorption.

14. The Langmuir adsorption isotherm. The first fundamental theory of the adsorption of gases on solids was proposed by Langmuir in 1916. He assumed that the adsorbed molecules could cover a surface until a complete unimolecular layer was formed, after which there was no further adsorption. The Langmuir isotherm may be most easily derived from a kinetic discussion of the condensation and evaporation of gas molecules at the surface. Let θ be the fraction of the surface area that is covered by adsorbed molecules at any time. Then the rate of evaporation of molecules from the surface is proportional to θ, or equal to $k_1\theta$, where k_1 is a constant at constant temperature. This assumption implies that there are no lateral interactions between adsorbed molecules, so that a molecule can evaporate from a well covered surface just as readily as from an almost bare one. The rate of condensation of molecules on the surface is proportional to the area that is not already covered, $1 - \theta$; and to the rate at which molecules strike the surface, which for a given temperature varies directly as the gas pressure. The condensation

---

[8] Just as the vapor pressure of liquids with convex surface (*e.g.*, droplets) is greater than that for plane surfaces, so the vapor pressure of liquids with concave surfaces is less. The change is given by the Kelvin equation. Therefore condensation in capillaries is facilitated, whereas evaporation from capillaries is retarded. When capillary condensation occurs, the adsorption isotherm exhibits hysteresis on desorption.

rate is therefore set equal to $k_2P(1-\theta)$. At equilibrium, the rate of condensation equals the rate of evaporation, so that $k_1\theta = k_2P(1-\theta)$, or

$$\theta = \frac{k_2P}{k_1 + k_2P} = \frac{P}{a+P} \tag{16.19}$$

where $a = k_1/k_2$.

The Langmuir isotherm is shown in the graph in Fig. 16.10. Among the experimental isotherms that appear to be of this type are oxygen on tungsten and nitrogen on mica.

Two limiting cases of the Langmuir isotherm are often of special interest. When the surface is practically bare, *e.g.*, at low pressures, the term k_2P is small compared to k_1, and eq. (16.19) reduces to

$$\theta = \frac{k_2}{k_1}P \tag{16.20}$$

This linear dependence of surface covered on the pressure is evident in the low-pressure region of the isotherm curve. At high pressures, or with particularly strong adsorption at lower pressures, the surface is virtually saturated and increasing the pressure has little effect on the amount of gas adsorbed. This is the flat region of the isotherm. From eq. (16.19) when θ becomes practically unity,

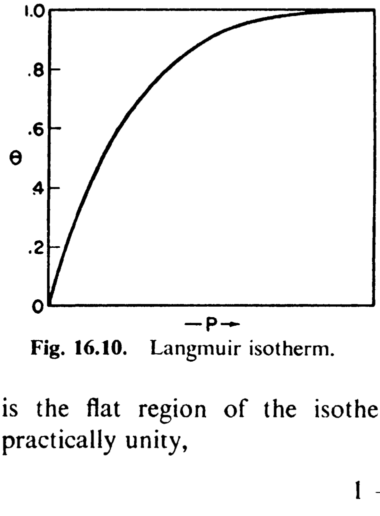


Fig. 16.10. Langmuir isotherm.

$$1 - \theta = \frac{k_1}{k_2P} \tag{16.21}$$

The uncovered surface is inversely proportional to the pressure.

In many instances the experimental isotherms cannot be fitted to a Langmuir-type expression. There is no leveling off in the amount of adsorption at high pressures; instead the typical *S*-shaped isotherm of Fig. 16.9 is obtained. Such curves are especially characteristic of physical adsorption. The Langmuir isotherm fits most cases of chemisorption.

15. Thermodynamics of the adsorption isotherm. A thermodynamic theory of the adsorption isotherm has been developed by G. Jura and W. D. Harkins.[9] It is based on the recognition of the important fact that adsorbed films on solid surfaces (*e.g.*, solid-vapor interfaces) are not essentially different from the films at liquid-vapor interfaces treated by the Gibbs equation (16.14).

When we are dealing with the adsorption of a gas at a solid surface, instead of the activity a of a component in the solution, we can substitute the fugacity of the gas, or as a good approximation simply the pressure. If

---

[9] *J. Am. Chem. Soc., 68,* 1941 (1946).

v is the volume of gas adsorbed per gram of solid, and s is the area of the solid in cm^2 per g (specific area), then v/s is the volume of gas per cm^2 of solid. If V is the molar volume of the gas, v/sV is the number of moles of gas adsorbed per cm^2 of solid surface. But this is exactly Γ_2, so eq. (16.14) may be written, since the differential of surface pressure $df = -d\gamma$,

$$df = \frac{RTv}{sV} \cdot d \ln P \tag{16.22}$$

Now if the two-dimensional equation of state (f-A isotherm) of the adsorbed monolayer is known, it is possible to integrate eq. (16.22) to calculate the ordinary v-P adsorption isotherm for the vapor. Conversely one can use the observed isotherms to determine the two-dimensional equations of state. This treatment brings the adsorption of vapors on solids and the surface tension lowering by films on liquids together into a single comprehensive theory. We shall take as an example the case in which the adsorbed film is of the condensed type, following eq. (16.18).

Since $A = (sV/Nv)$, where N is the Avogadro Number, we have from eq. (16.18)

$$df = -a\,dA = \frac{asV}{Nv^2}\,dv$$

Substituting this in eq. (16.22), we find

$$C\frac{2dv}{v^3} = d \ln P \tag{16.23}$$

where the constant $C = (aV^2s^2/2NRT)$. Integration of eq. (16.23) yields

$$B - \frac{C}{v^2} = \ln P \tag{16.24}$$

Here B is an integration constant.

If the adsorption data are plotted as $1/v^2$ vs $\ln P$, it is found that in many cases linear graphs are obtained. These straight lines indicate that over a considerable pressure range the adsorbed films are of the condensed type.[10] In other cases, different two-dimensional equations of state lead to correspondingly different v-P isotherms. Sometimes phase changes are observed in the adsorption isotherms, the occurrence of which leads to definite breaks and discontinuities in the f-A curves.

16. Adsorption from solution. The adsorption of components from solution onto the surfaces of solid adsorbents, although it has not yet received any satisfactory theoretical treatment, is a phenomenon of great practical importance. Every organic chemist is acquainted with the use of activated charcoal as a decolorizing agent; this material has an extremely high surface area, ranging up to 200 meter^2 per gram. Adsorbents such as diatomaceous

---

[10] The constant C, the negative of the slope of the linear plot, has been shown by Harkins to be simply related to the surface area of the adsorbent s. Thus $s = k_1\sqrt{C}$ where k_1 is a constant for each adsorbate at constant temperature.

earth and kieselguhr are used in refining vegetable oils. Chromatographic adsorption analysis has become one of the most important methods of separating natural products such as amino acids, peptides, and plant pigments.[11] Many of the biochemical reactions catalyzed by enzymes probably occur by virtue of an adsorption from solution onto the enzyme surface.

Adsorption from solution does not in general appear to lead to layers more than one molecule thick. For many cases the experimental data can be fairly well represented by an empirical isotherm proposed by Freundlich in 1909:

$$\frac{x}{m} = k_1 c^{1/n} \tag{16.25}$$

Here x and m are the masses of substance adsorbed and of adsorbent respectively; c is the concentration of the solution when equilibrium is reached; and n is an empirical constant usually greater than unity. This equation implies that if $\log x/m$ is plotted against $\log c$, a straight line will be obtained with slope $1/n$:

$$\log \frac{x}{m} = \log k_1 + \frac{1}{n} \log c \tag{16.26}$$

The Freundlich isotherm is somewhat related to the Langmuir isotherm, eq. (16.19). When the surface is almost covered, the Langmuir isotherm reduces to $x/m = k_1 c^0 = k_1$; when the surface is almost bare, to $x/m = k_1 c^1$. In an intermediate region, it is reasonable to expect that the isotherm could be approximated by raising the concentration to some fractional power, *i.e.*, by eq. (16.25).

17. Ion exchange.[12] Adsorption of electrolytes from solution often occurs as a specific reaction between ions in the solution and localized sites on the adsorbent. The reaction involved is essentially a reversible double decomposition, in which one of the reactants is free to move throughout the solution and the other is held fixed to the solid surface. For example,

$$\text{Na}^+ + {}^+\text{H}—S = \text{H}^+ + \text{Na}^+—S$$

where S denotes the solid surface.

An early example of such a reaction was noted by Aristotle (*c.* 335 B.C.) when he asked: "Why is it that waters near the sea are usually fresh and not salty? Is it because water that has been allowed to filter through sand becomes more drinkable?" Certain sands and zeolites have long been used as water conditioners, exchanging, for example, calcium ions in the water for sodium ions on their surfaces.

The present wide extension of ion-exchange processes is due to the development of synthetic resins with a variety of useful special properties. A typical example may be described. Styrene, $C_6H_5 \cdot CH=CH_2$, is polymerized

---

[11] See Strain, *Chromatographic Adsorption Analysis* (New York: Interscience, 1942).

[12] G. E. Boyd, *Ann. Rev. Phys. Chem.*, *2*, 309 (1951).

with about 10 per cent divinylbenzene to yield a polymer of cross-linked linear chains. This polymer is sulfonated with sulfuric acid or chlorosulfonic acid to introduce into the structure about one SO_3H— group per benzene residue. The resulting resin behaves as a solid strong acid. This material is a good cation exchanger. An anion exchanger can be made by introducing —CH_2NR_3OH groups into the original polymer. In general, the cations with the highest charge and smallest ionic size are most tightly held by the resin. It is most likely that other common adsorbents, such as charcoal or kieselguhr, also owe their effectiveness to an ion-exchange mechanism.

Ion-exchange resins have been applied in chromatographic analysis. A column of adsorbent is percolated with the solution to be separated, and then a suitable solvent is passed through the column. The adsorbed solutes may then occur in distinct bands along the absorption column. One of the most striking successes of this method has been the separation of rare earth cations of both the lanthanide and actinide series.[13]

18. Electrical phenomena at interfaces. Across any interface separating two phases there is in general a difference in electric potential, since the electrical environment of a test charge changes as it is carried from one phase to the other. We have already had occasion to mention this fact in the previous chapter, in the discussion of electrode and liquid-junction potentials.[14]

The potential difference across an interface, since electricity is atomic in nature, may conveniently be pictured as an *electrical double layer*. One phase acquires a net negative charge (excess of electrons), and the other acquires a net positive charge (deficiency of electrons). The first quantitative discussion of this double layer was given in 1879 by Helmholtz, who considered the case of a solid immersed in a solution. He suggested the picture shown in (a), Fig. 16.11, a layer of ions at the solid surface and a rigidly held layer of oppositely charged ions in the solution. The electric potential corresponding to such a charge distribution is also shown. Such double layers are supposed to exist not only at plane surfaces, but also surrounding solid particles suspended in a liquid medium.

The Helmholtz double layer is equivalent to a simple parallel-plate capacitor. If l is the distance separating the oppositely charged plates and ε the dielectric constant of the medium, the capacitance of such a capacitor per square centimeter of interface is $\varepsilon/4\pi l$. If q is the surface charge density (*e.g.*, coulombs per cm^2) the potential difference ΔU across a double layer is

$$\Delta U = \frac{4\pi lq}{\varepsilon} \tag{16.27}$$

---

[13] F. H. Spedding, *Disc. Faraday Soc.*, *7*, 214 (1949); B. H. Ketelle and G. E. Boyd, *J. Am. Chem. Soc.*, *72*, 1862 (1951).

[14] Although the interfacial potential differences are not experimentally measurable, they have been widely used in theoretical discussions, some examples of which are given in the remainder of this chapter.

The Helmholtz model of the double layer is clearly inadequate, since the thermal motions of the liquid molecules could scarcely permit such a rigid array of charges at the interface.[15] Much more reasonable, therefore, is the *diffuse double layer* proposed by Stern in 1924. This is shown in (b), Fig. 16.11. The charge on the solid is rigidly fixed. Adsorbed on top of this there may be a practically immobile layer of oppositely charged molecules of the liquid. Further in the solution there is a diffuse layer of charge, which may have a sign either the same as or opposite from that of the adsorbed layer. Only this diffuse region is free to move, for example under the influence of an applied potential difference. The potential drop ζ in the diffuse layer is called the *zeta potential.*

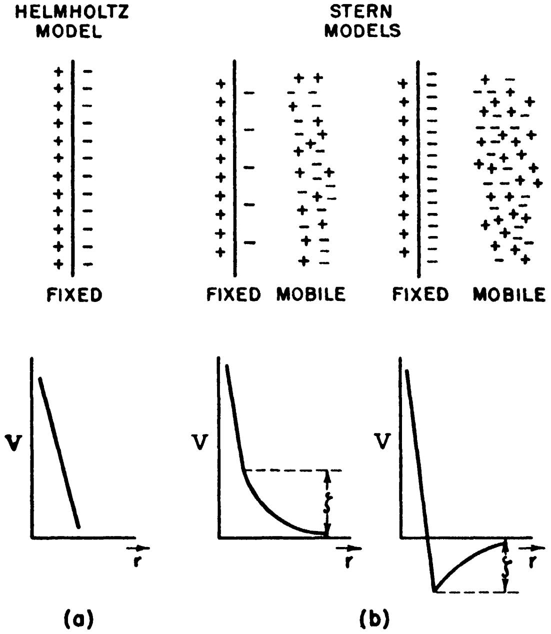


Fig. 16.11. Models for electrical double layers and potential fall in layers.

19. Electrokinetic phenomena. Four interesting effects, all ascribable to the existence of a diffuse mobile double layer at phase interfaces, are grouped under the name of *electrokinetic phenomena.*

First, there is *electroosmosis*, the motion of liquid through a membrane under the influence of an applied electric field. For simplicity a single capillary tube may be considered; typical membranes may be thought of as bundles of such capillaries connected in diverse ways. At the walls of the tube there is a double layer, with zeta potential ζ. If the strength of the applied electric field is $\boldsymbol{E}$, the force acting on a charge q is $\boldsymbol{E}q$.

[15] See page 461 and the discussion of the Debye-Hückel ionic atmosphere.

The treatment of viscosity on page 173 may be consulted for the comparable case in which the force is a mechanical one, *i.e.*, a pressure difference between the ends of the tube. Just as in that case, the force tending to move the liquid is opposed by a frictional resistance equal to $\eta v/l$ where η is the viscosity and v/l the velocity gradient. For steady flow, from eq. (16.27), $\eta v/l = \boldsymbol{E}q = \boldsymbol{E}\varepsilon\zeta/4\pi l$, and

$$v = \frac{\boldsymbol{E}\varepsilon\zeta}{4\pi\eta} \tag{16.28}$$

This gives the linear velocity of flow in terms of the ζ potential and readily obtainable experimental quantities. The volume rate of flow is obtained by multiplying by the cross-sectional area of the capillary tube. It should be noted that for the ζ potential the simple formula for the potential drop in a Helmholtz double layer was used. This is actually a permissible approximation, because if we used a diffuse double layer and integrated over each differential section of its thickness, we should find the potential proportional to l and the velocity gradient proportional to $1/l$, so that the thickness of the double layer would drop out of the calculation in any event.[16]

The converse of electroosmosis is the *streaming potential.* This is the potential difference that arises across a capillary tube or membrane when a stream of liquid is forced through it. The diffuse double layer is swept along by the fluid flow, so that opposite charges are built up at opposite ends of the tube.

Electroosmosis and streaming potential are observed when we are dealing with a fixed solid surface, like the wall of a tube. If the solid surface is that of a colloidal particle, which is itself free to move through the solution, the electrokinetic effects, though arising from the same cause, the existence of a double layer at the interface, appear in a somewhat different guise.

Electrophoresis is the name given to the migration of charged particles in an electric field. It is in fact not really different from the migration of ions, and the particles may be regarded as colloidal electrolytes. Electrophoresis has been of the greatest importance in the study of solutions of proteins. The experimental techniques have been intensively developed by Arne Tiselius and his coworkers at Uppsala, using an apparatus similar to the transport-number cell shown on page 444. Many proteins, as obtained from natural sources such as blood plasma or serum, are really mixtures of several distinct chemical individuals. The behavior of such preparations during electrophoresis provides one of the best ways of separating homogeneous components that can be characterized as pure proteins. The separation depends on the charge carried by the protein molecules, and not on their size.

The protein solution is introduced into one arm of the cell and in the

---

[16] For cylindrical tubes it is not quite correct to use the formula for a parallel-plate capacitor, and the constant 4π is therefore not quite correct.

other arm is placed an appropriate buffer solution. As a current is passed, the more highly charged proteins migrate faster than the less charged proteins, so that finally the solution is separated into a sequence of well defined bands. Since the solutions are transparent, the bands are recorded by an interferometric technique, which gives an extremely sensitive indication of changes in the refractive index.[17]

The fundamental equation governing electrophoresis may be taken to be the same as eq. (16.28), $v = \boldsymbol{E}\epsilon\zeta/4\pi\eta$. Now v is the speed of migration of the colloidal particles, at whose surface there is a double-layer potential ζ. In the case of protein molecules, it is likely that the double layer arises from the ionization of side-chain amino-acid groups (—COOH, NH_2, etc.). Thus the picture is exactly like that used in the Debye-Hückel theory of an ion with its surrounding "atmosphere." The thickness of the double layer corresponds to the thickness of the ionic atmosphere. In other cases, the double layer may be due to adsorption of ions from the solution onto the surface of the colloidal particle. The origin of the charge, however, has little influence on the final effect.

The quartet of electrokinetic phenomena is completed by the *Dorn effect.* This bears the same relation to electrophoresis as streaming potential bears to electroosmosis. It is the potential difference that is set up in a solution when particles are allowed to fall through it.

All of these electrokinetic effects have been interpreted in terms of the zeta potential in an electrical double layer. Unfortunately we have no means of measuring the zeta potential apart from the equations describing the electrokinetic phenomena. Thus the theory seems to lead us around a circle. The circle is not an entirely vicious one, however, because the zeta potentials calculated from measurements of different effects are often quite concordant, and this fact tends to substantiate the underlying model. The calculated ζ potentials range from one or two to 40 to 50 millivolts.

20. The stability of sols. Suspensions in a liquid medium of particles in the colloidal size range are called *sols.* Two kinds of sols are usually distinguished. *Lyophobic*, or solvent-hating, sols are those in which there is little solvation of the colloidal particles. Typical examples are the sols produced by arcing electrodes of platinum, gold, and other metals under water, the ferric oxide sol produced by adding a base to a solution of ferric ions, colloidal sulfur produced by reduction of thiosulfate. *Lyophilic*, or solvent-loving, sols are characterized by strong solvation of the colloidal particles. Examples are protein sols such as gelatin, starch sols and, in some instances, colloidal silica. One of the most striking distinctions between the two types of sol is observed in their viscosities; the viscosity of lyophobic sols is not very different from that of the suspension medium, whereas lyophilic sols have greatly enhanced viscosities, leading in many cases to the formation of *gels* at higher concentrations.

---

[17] See, for example, L. G. Longsworth and D. A. MacInnes, *Chem. Rev., 24,* 271 (1939).

The solvation of colloidal particles helps to account for the stability of the sols. It is clear that the tendency to attain a minimum surface free energy should lead two colliding particles to coalesce into a larger particle with lower surface area. This lower surface area, however, would allow less solvation, and it seems that in the case of the hydrophilic sols this solvation energy more than compensates for the greater surface energy of small particles.

In the case of the lyophobic sols, the solvation energy plays a relatively unimportant role. The reason why these sols do not coagulate is that the particles bear electric charges of the same sign. In Fig. 16.12 is a representation of an arsenious-sulfide sol. The negative charges lead to mutual repulsions, which prevent the particles from approaching each other closely enough to coalesce.

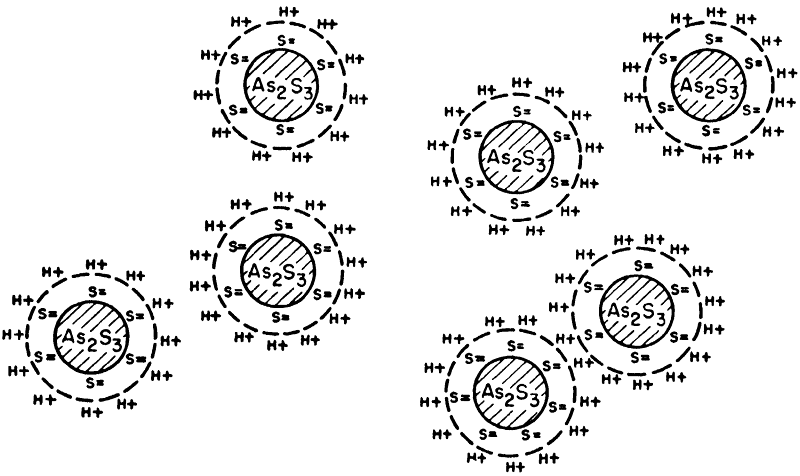


Fig. 16.12. Particles in arsenious-sulfide sol.

The study of the coagulation of sols by added electrolytes reveals another difference between the lyophilic and the lyophobic species. Lyophilic sols are not sensitive to small concentrations of electrolytes, but large concentrations may "salt them out" of solution. The effect seems to be due to a competition for solvent between the electrolyte ions and the colloidal particles. Owing to their superiority in numbers and in intensity of ion-dipole interaction, the ions finally take possession of so much solvent (usually water) that the colloids are forced to retire precipitately from the solution.

By way of contrast, lyophobic sols are commonly coagulated by very small concentrations of added electrolyte. The mechanism is undoubtedly the adsorption of oppositely charged ions at the surface of the colloidal particle. This adsorption neutralizes the electrical double layer and lowers the zeta potential. When ζ has been lowered below a certain critical value, of the order of 10–30 millivolts, coagulation occurs.

In Table 16.3 are summarized the coagulation values for two typical hydrosols, one negatively charged (As_2S_3) and one positively charged (Fe_2O_3). The ion in the electrolyte whose sign is opposite to that of the sol has by far the most important effect on the coagulation. The higher the charge of these ions, the greater is the coagulating power of the electrolyte. Thus Al^{+++} is more effective than K^+ in coagulating the negative As_2S_3 sol. The ion with the same sign as the sol appears to exercise some protective effect. Thus in precipitating the As_2S_3 sol, KCl is more effective than K_2SO_4, presumably because the $SO_4^=$ ion is more protective than the Cl^- ion for a negative sol.

TABLE 16.3

COAGULATION VALUES FOR SOLS*

Negative As_2S_3 Sol		Positive Fe_2O_3 Sol	
Salt	Millimoles per Liter	Salt	Millimoles per Liter
$AlCl_3$	0.093	$K_4Fe(CN)_6$	0.067
$\frac{1}{2}Al_2(SO_4)_3$	0.096	$K_3Fe(CN)_6$	0.096
$BaCl_2$	0.69	K_2SO_4	0.22
$PbCl_2$	0.23	KIO_3	0.90
KCl	50	$KBrO_3$	31
$\frac{1}{2}K_2SO_4$	66	KCl	103

* M. B. Weiser and E. B. Middleton, *J. Phys. Chem.*, *24*, 30 (1920); H. Freundlich, *Z. phys. Chem.*, *73*, 385 (1910).

PROBLEMS

1. How many sodium-ion sites are there per cm^2 of crystal surface in cubic crystallites of sodium chloride? If the crystallites are 1 μ long, how many sites are there per gram?

2. Estimate the height to which a column of water will rise in a glass tube of (a) 1 μ diameter, (b) 10 μ diameter. Assume zero contact angle.

3. What pressure in atmospheres would be necessary to blow capillary water out of a sintered glass filter with a uniform pore width of 0.10 μ?

4. 20 ml of a saturated solution of $PbSO_4$ (0.0040 g per liter) containing radiolead (Th-B) as a tracer to the extent of 1600 counts per minute is shaken with 1.000 g of precipitated $PbSO_4$. The final count in the solution is 450 cpm. If the $PbSO_4$ "molecule" has an area of 18.4 Å^2, calculate the surface area of the $PbSO_4$ in cm^2 per g.

5. From the Kelvin equation for the vapor pressure of small particles, derive an equation for the solubility of small particles. If the bulk solubility of dinitrobenzene in water is 10^{-3} mole per liter, estimate the solubility of crystallites 0.01 μ in diameter.

6. Harkins and Wampler [*J. Am. Chem. Soc.*, *53*, 850 (1931)] obtained the following data for solutions of *n*-butanol in water at 20°C:

Molality, m	0.00329	0.00658	0.01320	0.0264	0.0536	0.1050	0.2110	0.4330
Activity, a . .	0.00328	0.00654	0.01304	0.0258	0.0518	0.0989	0.1928	0.3796
Surf. ten. γ .	72.80	72.26	70.82	68.00	63.14	56.31	48.08	38.87

By means of the Gibbs adsorption isotherm, plot an f-A isotherm from these data. Note that in calculating the surface concentration the number of molecules already present in the surface must be considered in addition to those adsorbed at the interface.

7. An insoluble compound X spreads on water to give a gaseous-type film at low concentrations. When 10^{-7} g of X is added to a 200-cm^2 surface, the surface tension at 25°C is lowered by 0.20 dyne cm^{-1}. Calculate the molecular weight of X.

8. Cassel and Neugebauer [*J. Phys. Chem.*, *40*, 523 (1936)] measured the lowering of the surface tension of mercury by adsorbed xenon at 0°C.

P, mm Xe . . .	69	93	146	227	278
$\gamma_0 - \gamma_1$, dyne cm^{-1} . .	0.80	1.10	1.75	2.75	3.35

Calculate the number of Xe atoms adsorbed per cm^2 at $P = 278$ mm and estimate the fraction of the mercury surface that is then covered by xenon.

9. Calculate the surface pressure f at which the average intermolecular distance in a two-dimensional ideal gas at 0°C is equal to that in a three-dimensional ideal gas at 1 atm and 0°C.

10. How would you plot the Langmuir isotherm in order to obtain a straight line? Apply the linear plot to the data for oxygen on silica at 0°C. [Markham and Benton, *J. Am. Chem. Soc.*, *53*, 497 (1931)]:

p, mm	83.0	142.4	224.3	329.6	405.1	544.1	667.5	760.0
Vol ads, cc at STP/g .	0.169	0.284	0.445	0.646	0.790	1.043	1.270	1.430

11. Derive the v-P adsorption isotherm for the cases in which the surface film f-A equations of state are (a) $fA = kT$, (b) $(f + aA^{-2})A = kT$ (inclusion of a van der Waals type molecular interaction term, a being a constant).

12. The "isosteric" heat of adsorption can be obtained by applying the Clapeyron equation to the variation with temperature of the pressure at which a constant amount of vapor is adsorbed (*i.e.*, the vapor pressure of the surface film at constant amount adsorbed). Calculate ΔH_{ads} and hence ΔF_{ads} and ΔS_{ads} from the following results for N_2 on charcoal:

194°K, P, atm .	1.5	4.6	12.5	66.4
273°K, P, atm .	5.6	35.4	150	694
Cc ads at STP .	0.145	0.894	3.468	12.042

13. The adsorption on charcoal of acetone in aqueous solution was found to be

Acetone conc. mole per liter	0.00234	0.01465	0.04103	0.08862	0.17759	0.26897
Millimoles ads per gram charcoal . . .	0.208	0.618	1.075	1.50	2.08	2.88

Fit these results to a Freundlich isotherm and find the best value for the exponent $1/n$.

14. The motion of a quartz particle 1 μ in diameter in water suspension was followed under a potential gradient of 10 volts per cm, the observed velocity being 3.0×10^{-3} cm per sec. Calculate the zeta potential at the quartz-water interface. Estimate the number of charges carried by the particle.

15. The zeta potential of water against glass is about -0.050 v. Calculate the rate of flow of water by electroosmosis at 25°C through a glass capillary 1 cm long and 1 mm diameter if the potential difference between the ends is 40 v.

REFERENCES

BOOKS

1. Adam, N. K., *The Physics and Chemistry of Surfaces* (New York: Oxford, 1941).
2. Alexander, A. E., and P. Johnson, *Colloid Science* (New York: Oxford, 1949).
3. Boer, J. H. de, *The Dynamical Character of Adsorption* (New York: Oxford, 1953).
4. Burdon, R. S., *Surface Tension* (London: Cambridge, 1948).
5. Freundlich, H., *Capillary Chemistry* (New York: Dutton, 1923).
6. Gregg, S. J., *The Surface Chemistry of Solids* (London: Chapman and Hall, 1951).
7. Harkins, W. D., *The Physical Chemistry of Surface Films* (New York: Reinhold, 1952).
8. Kruyt, H. R. (editor), *Colloid Science* (Amsterdam: Elsevier, 1952).
9. McBain, J. W., *Colloid Science* (Boston: Heath, 1950).
10. Roberts, J. K., *Some Problems in Adsorption* (London: Cambridge, 1939).

ARTICLES

1. Alberty, R. A., *J. Chem. Ed., 25*, 426–33, 619–25 (1948), "Introduction to Electrophoresis."
2. Beams, J. W., *Science in Progress*, vol. II (New Haven: Yale Univ. Press, 1940), 232–64, "The Ultracentrifuge."
3. Langmuir, I., *J. Chem. Soc.*, 511–43 (1940), "Monolayers on Solids."
4. Martin, A. J. P., *Endeavour, 6*, 21–28 (1947), "The Principles of Chromatography."

5. Oster, G., *Chem. Rev.*, *43*, 319–65 (1948), "Applications of Light Scattering to Chemistry."
6. Pauling, L., *Endeavour*, *7*, 43–53 (1948), "Antibodies and Specific Biological Forces."
7. Rideal, E. K., *J. Chem. Soc.*, 423–27 (1945), "Reactions in Monolayers."
8. Snell, C. T., *J. Chem. Ed.*, *24*, 505–11 (1947), "Synthetic Detergents and Surface Activity."
9. Svedberg, T., *Endeavour*, *6*, 89–95 (1947), "The Ultracentrifuge."
10. Tiselius, A., *Endeavour*, *11*, 5–16 (1952), "Some Recent Advances in Chromatography."

CHAPTER 17

Chemical Kinetics

1. The rate of chemical change. The basic questions in physical chemistry are two: where are chemical reactions going, and how fast are they getting there? The first is the problem of equilibrium, or chemical statics; the second is the problem of the rate of attainment of equilibrium, or chemical kinetics.

Chemical kinetics is usually subdivided into the study of homogeneous reactions, those occurring entirely within one phase, and of heterogeneous reactions, those occurring at an interface between phases. Some reactions consisting of a number of steps may begin at a surface, continue in a homogeneous phase, and sometimes terminate on a surface.

Qualitative observations of the velocity of chemical reactions were recorded by early writers on metallurgy, brewing, and alchemy, but the first significant quantitative investigation was that of L. Wilhelmy, in 1850. He studied the inversion of cane sugar (sucrose) in aqueous solutions of acids, following the change with a polarimeter:

$$\underset{}{H_2O} + \underset{\textit{Sucrose}}{C_{12}H_{22}O_{11}} \rightarrow \underset{\textit{Glucose}}{C_6H_{12}O_6} + \underset{\textit{Fructose}}{C_6H_{12}O_6}$$

Wilhelmy found that the rate of decrease in the concentration of sugar c with time t was proportional to the concentration of sugar remaining unconverted. This reaction velocity was written as $-dc/dt = k_1 c$. The constant k_1 is called the *rate constant* or the *specific rate* of the reaction.[1] Its value was found to be proportional to the acid concentration. Since the acid does not appear in the stoichiometric equation for the reaction, it is acting as a catalyst, increasing the reaction rate without being consumed itself.

Wilhelmy integrated the differential equation for the rate, obtaining $\ln c = -k_1 t + \text{constant}$. At $t = 0$, the concentration has its initial value c_0, so that the constant is $\ln c_0$. Therefore, $\ln c = -k_1 t + \ln c_0$, or $c = c_0 e^{-k_1 t}$. This integrated equation was checked by Wilhelmy, and the exponential decrease of concentration with time was closely followed by his data. On the basis of this work, Wilhelmy deserves to be called the founder of chemical kinetics.

The important paper of Guldberg and Waage, which appeared in 1863, has already been described (page 70). It emphasized the dynamic nature of chemical equilibrium, by setting the equilibrium constant equal to the ratio of rate constants, $K = k_f/k_b$.

---

[1] The words "rate," "speed," "velocity" are all synonymous in chemical kinetics, though not so in physical mechanics.

In 1865–1867, A. V. Harcourt and W. Esson[2] studied the reaction between potassium permanganate and oxalic acid. They showed how to calculate rate constants for a reaction in which the velocity is proportional to the product of the concentrations of two reactants. They also discussed the theory of consecutive reactions.

The science of chemical kinetics was now well under way, and to date hundreds of reaction rates have been measured. Yet there is still a great need for accurate experimental data.

2. Experimental methods in kinetics. An experimental determination of reaction velocity requires a good thermostat to maintain the system at constant temperature and a good clock to measure the passage of time. These two requisites are not hard to obtain. It is the pursuit of the third variable, the concentration of reactants or products, that is the source of most difficulties.

A reaction cannot be turned on and off like a stopcock, although a reaction occurring at an elevated temperature can often be virtually stopped by cooling the system. If one takes a sample of the reaction mixture at 2:00 P.M., one would like to know the composition at 2:00 P.M., but few analytical methods are that rapid. It may be 2:05 before the result is obtained, and thus, especially in rapid reactions, it is difficult to determine the concentration c at a definite time t by any sampling technique.

The best method of analysis is therefore one that is practically continuous, and does not require the removal of successive samples from the reaction mixture. Physical properties can be used in this way in appropriate cases. Wilhelmy's use of optical rotation is a case in point. Other physical methods have included:

(1) Absorption spectra and colorimetric analysis;
(2) The measurement of dielectric constant[3];
(3) The measurement of refractive index[4];
(4) Dilatomeric methods, based on the change in volume due to reaction.

One of the most frequently used techniques, applicable to many gas reactions, is to follow the change in pressure. This change can be read almost instantaneously, or it can be recorded automatically. The method would be an ideal one if gas reactions often ran smoothly according to a single stoichiometric equation. Unfortunately, however, many gas reactions are beset by complications and side reactions so that a simple pressure change without concurrent analysis of the reaction products has often led to deceptive results. For example, the decomposition of ethane according to $C_2H_6 \rightarrow C_2H_4 + H_2$ is accompanied by a change in pressure, but actually some methane, CH_4, is included among the products.

---

[2] A. V. Harcourt and W. Esson, *Proc. Roy. Soc.*, *14*, 470 (1865). *Phil. Trans.*, *156*, 193 (1866); *157*, 117 (1867).

[3] T. G. Majury and H. W. Melville, *Proc. Roy. Soc.*, *A 205*, 496 (1951).

[4] N. Grassie and H. W. Melville, *ibid.*, *A 207*, 285 (1951).

There is unlimited scope for experimental ingenuity in the measurement of extremely rapid reactions. A noteworthy example is the work of Johnston and Yost[5] on $2\ NO_2 + O_3 \rightarrow N_2O_5$ under conditions in which reaction is complete within 0.1 sec. A stream of $O_2 + NO_2$ was mixed with a stream of $O_3 + O_2$ in a chamber with tangential jets. After mixing, which was complete within 0.01 sec, a magnetically operated steel gate trapped a portion of the gas mixture. The disappearance of the NO_2, which is brown, was followed by the change of intensity of a beam of transmitted light. The beam was chopped with a rotating sector wheel 300 times per second, and the pulses were allowed to fall on a photomultiplier tube, the output of which was connected to an oscillograph. The pulsations on the oscillograph screen were photographed, the height of each peak giving the NO_2 concentration at intervals of $\frac{1}{300}$ sec.

3. Order of a reaction. The experimental data of chemical kinetics are records of concentrations of reactants and products at various times, the temperature usually being held constant throughout any one run. On the other hand, the theoretical expressions for reaction rates as functions of the concentrations of reactants, and sometimes of products, are differential equations of the general form, $dc_1/dt = f(c_1, c_2 \ldots c_n)$. Here c_1 is the particular product or reactant whose concentration is being followed. Before comparing theory with experiment, it is necessary either to integrate the theoretical rate law, or to differentiate the experimental concentration vs. time curve. The first procedure is usually followed.

The rate laws are of practical importance since they provide concise expressions for the course of the reaction and can be applied in calculating reaction times, yields, and optimum economic conditions. Also, the laws often afford an insight into the *mechanism* by which the reaction proceeds. On the molecular scale the course of a reaction may be complex, and sometimes the form of the empirical rate law will suggest the particular path via which the reaction takes place.

In many instances the rate, which will be written as the decrease in concentration of reactant A, $-dc_A/dt$, is found to depend on the product of concentration terms. For example,

$$\frac{-dc_A}{dt} = k' c_A{}^a \, c_B{}^b \ldots c_N{}^n$$

The *order* of the reaction is defined as the sum of the exponents of the concentration terms in this rate law.

For example, the decomposition of nitrogen pentoxide, $2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$, is found to follow the law, $-dc_{N_2O_5}/dt = k_1 c_{N_2O_5}$. This is therefore a *first-order reaction.*

The decomposition of nitrogen dioxide, $2\ NO_2 \rightarrow 2\ NO + O_2$, follows the law, $-d(NO_2)/dt = k_2(NO_2)^2$. This is a *second-order reaction.* The

---

[5] H. S. Johnston and D. M. Yost, *J. Chem. Phys.*, *17*, 386 (1949).

reaction rate in benzene solution of triethylamine and ethyl bromide, $(C_2H_5)_3N + C_2H_5Br \rightarrow (C_2H_5)_4NBr$, follows the equation, $-d(C_2H_5Br)/dt = k_2(C_2H_5Br)((C_2H_5)_3N)$. This is also a second-order reaction. It is said to be *first-order with respect to* C_2H_5Br, *first-order with respect to* $(C_2H_5)_3N$, and *second-order over-all.*

The decomposition of acetaldehyde, $CH_3CHO \rightarrow CH_4 + CO$, in the gas phase at 450°C fits the rate expression, $-d(CH_3CHO)/dt = k'(CH_3CHO)^{3/2}$. This is a reaction of the three-halves order.

It is to be noted that the order of a reaction need not be a whole number, but may be zero or fractional. It is determined solely by the best fit of a rate equation with the empirical data. Secondly, it is important to realize that there is no necessary connection between the form of the stoichiometric equation for the reaction and the kinetic order. Thus the decompositions of N_2O_5 and of NO_2 have equations of identical form, yet one is a first-order and the other a second-order reaction.

4. Molecularity of a reaction. Many chemical reactions are not kinetically simple; they proceed through a number of steps or stages between initial reactants and final products. Each of the individual steps is called an *elementary reaction.* Complex reactions are made up of a sequence of elementary reactions, each of which proceeds in a single step.

In the earlier literature, the terms "unimolecular," "bimolecular," and "trimolecular" were used to denote reactions of the first, second, and third orders. We now reserve the concept of the *molecularity* of a reaction to indicate the molecular mechanism by which it proceeds. Thus careful studies indicate that the decomposition of hydrogen iodide, $2\,HI \rightarrow H_2 + I_2$, takes place when two HI molecules come together with sufficient kinetic energy to rearrange the chemical bonds from two H—I bonds to an H—H bond and an I—I bond. The elementary process involves two molecules, and this is therefore called a *bimolecular reaction.*

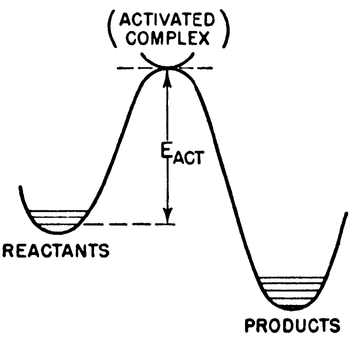


Fig. 17.1. Energy barrier surmounted by system in chemical reaction.

It will be shown later that before a chemical reaction can take place the molecule or molecules involved must be raised to a state of higher potential energy. They are then said to be activated or to form an *activated complex.* This process is shown in schematic form in Fig. 17.1. Reactants and products are both at stable potential energy minima; the activated complex is the state at the top of the potential energy barrier.

In terms of the activated complex, it is possible to give a more exact definition of the molecularity of a reaction. It is equal to the number of molecules of reactants that are used to form the activated complex. In the case of the hydrogen-iodide decomposition, the complex is formed from two HI molecules, and the reaction is *bimolecular*. Clearly the molecularity of a reaction must be a whole number, and in fact it is found to be one, two, or rarely, three.

The experimental rate measurements show that the rate of decomposition of hydrogen iodide is $-dc_{HI}/dt = k_2 c_{HI}^2$. This is therefore a second-order reaction. All bimolecular reactions are second-order, but the converse is not true; there are second-order reactions that are not bimolecular.

A good example of a *unimolecular* reaction is a radioactive decay, *e.g.*, $Ra \rightarrow Rn + \alpha$. Only one atom is involved in each disintegration, and the reaction is unimolecular. It also follows a first-order law, $-dn_{Ra}/dt = k_1 n_{Ra}$, where n_{Ra} is the number of radium atoms present at any time.

The concept of molecularity should be applied only to individual elementary reactions. If a reaction proceeds through several stages, there is little point in talking about its molecularity, since one step may involve two molecules, another three, and so on.

At the risk of repetition: *reaction order* applies to the experimental rate equation; *molecularity* applies to the theoretical mechanism.

5. The reaction-rate constant. The experimental data in a kinetic experiment are values of concentrations at various times. Unless otherwise specified, the concentration unit is moles per liter, and the time is measured in seconds. It is purely a matter of convenience whether the reaction is followed by the decrease in one of the reactants or by the increase in one of the products. These quantities are related by the stoichiometric equation for the reaction.

Consider the decomposition of nitrogen pentoxide, $2\,N_2O_5 \rightarrow 4\,NO_2 + O_2$. Velocity can be expressed in three ways: the rate of disappearance of N_2O_5, $-dc_{N_2O_5}/dt$; the rate of formation of NO_2, $+dc_{NO_2}/dt$; the rate of formation of O_2, $+dc_{O_2}/dt$. Actually, the NO_2 dimerizes to N_2O_4, but the equilibrium for this association is established very rapidly and can easily be taken into acccount, since the equilibrium constant is well known. It is found that the N_2O_5 decomposition follows a first-order law over a range of pressures (10^{-3} to 10 atm) and temperatures (0 to 200°C). This law can be written in three ways:

$$\frac{-dc_{N_2O_5}}{dt} = k_1 c_{N_2O_5}, \quad \frac{+dc_{NO_2}}{dt} = k_1' c_{N_2O_5}, \quad \frac{+dc_{O_2}}{dt} = k_1'' c_{N_2O_5}$$

From the stoichiometry it is evident that $k_1 = \frac{1}{2}k_1' = 2k_1''$. The lesson to be learned is that it is always desirable to state clearly what rate law is being used to express the experimental results. Then the rate constant will have an unambiguous meaning. The choice is arbitrary but it should be explicit.

The units of the rate constant depend on the order of the reaction. For first order, $-dc/dt = k_1 c$, the units of k_1 are moles liter^{-1} sec^{-1} × liter mole^{-1} = sec^{-1}. For second order, $-dc/dt = k_2c^2$, the units of k_2 are moles liter^{-1} sec^{-1} × (liter mole^{-1})^2 = liter mole^{-1} sec^{-1}. In general, for a reaction of the nth order, the dimensions of the constant k^n are (time)$^{-1}$ (concentration)$^{1-n}$.

6. First-order rate equations. The differential rate equation is almost always integrated before it is applied to the experimental data, although occasionally slopes of concentration vs. time curves are taken to determine dc/dt directly.

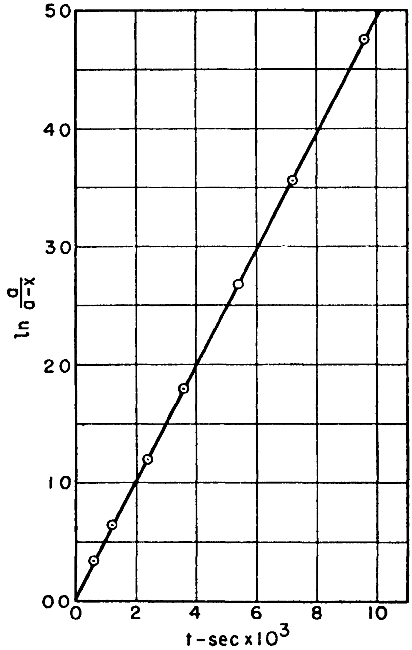


Fig. 17.2. A first-order reaction. The thermal decomposition of nitrogen pentoxide, plotted according to eq. (17.2).

Consider a first-order reaction, $A \rightarrow B + C$. Let the initial concentration of A be a moles per liter. If after a time t, x moles per liter of A have decomposed, the remaining concentration of A is $a - x$, and x moles per liter of B or C have been formed. The rate of formation of B or C is thus dx/dt, and for a first-order reaction this is proportional to the instantaneous concentration of A, so that

$$\frac{dx}{dt} = k_1(a - x) \tag{17.1}$$

Separating the variables and integrating, we obtain

$$-\ln(a - x) = k_1t + \text{const}$$

The usual initial condition is that $x = 0$ at $t = 0$, whence the constant $=$ $-\ln a$, and the integrated equation becomes

$$\ln \frac{a}{a - x} = k_1 t \tag{17.2}$$

or,

$$x = a(1 - e^{-k_1 t})$$

If $\ln (a/a - x)$ is plotted against t, a straight line passing through the origin is obtained, the slope of which is the first-order rate constant k_1.

If eq. (17.1) is integrated between limits x_1 to x_2 and t_1 to t_2, the result is

$$\ln \frac{a - x_1}{a - x_2} = k_1(t_2 - t_1)$$

This interval formula can be used to calculate the rate constant from any pair of concentration measurements.

Applications of these equations to the first-order decomposition of gaseous N_2O_5 are shown in Table 17.1 and Fig. 17.2.[6]

TABLE 17.1
DECOMPOSITION OF NITROGEN PENTOXIDE
(Temperature, 45°C)

Time, t (Seconds)	$P_{N_2O_5}$ (mm)	k (sec^{-1})	Time, t (Seconds)	$P_{N_2O_5}$ (mm)	k (sec^{-1})
0	348.4	—	4200	44	0.000478
600	247	—	4800	33	0.000475
1200	185	0.000481	5400	24	0.000501
1800	140	0.000462	6000	18	0.000451
2400	105	0.000478	7200	10	0.000515
3000	78	0.000493	8400	5	0.000590
3600	58	0.000484	9600	3	0.000467
			∞	0	—

Another test of a first-order reaction is found in its half life τ, the time required to reduce the concentration of A to half its initial value. This concept was discussed on page 215 in connection with radioactive decay. In eq. (17.2) when $x = a/2$, $t = \tau$, and $\tau = (\ln 2)/k_1$. Thus the half life is independent of the initial concentration of reactant. In a first-order reaction, it would take just as long to reduce the reactant concentration from 0.1 mole per liter (m/l) to 0.05 m/l as it would to reduce it from 10 to 5.

7. **Second-order rate equations.** Consider a reaction written as $A + B \rightarrow C + D$. Let the initial concentrations at $t = 0$ be a m/l of A and b m/l of B. After a time t, x m/l of A, and of B, will have reacted, forming x m/l of C and of D. If a second-order rate law is followed,

$$\frac{dx}{dt} = k_2(a - x)(b - x) \tag{17.3}$$

---

[6] F. Daniels, *Chemical Kinetics* (Ithaca: Cornell Univ. Press, 1938), p. 9.

Separating the variables, we have

$$\frac{dx}{(a-x)(b-x)} = k_2\,dt$$

The expression on the left is integrated by breaking it into partial fractions. The integration yields

$$\frac{[\ln(a-x) - \ln(b-x)]}{a-b} = k_2 t + \text{const}$$

When $t = 0$, $x = 0$, and constant $= \ln(a/b)/(a-b)$. Therefore the integrated second-order rate law is

$$\frac{1}{a-b}\ln\frac{b(a-x)}{a(b-x)} = k_2 t \tag{17.4}$$

A reaction found to be second-order is that between ethylene bromide and potassium iodide in 99 per cent methanol, $C_2H_4Br_2 + 3\ KI = C_2H_4 + 2\ KBr + KI_3$. Sealed bulbs containing the reaction mixture were kept in a thermostat. At intervals of two or three minutes a bulb was withdrawn, and its contents were analyzed for iodine by means of the thiosulfate titration. The second-order rate law is $d(I_2)/dt = dx/dt = k_2(C_2H_4Br_2)(KI) = k_2(a-x)(b-3x)$, and the integrated equation is

$$\frac{1}{3a-b}\ln\frac{b(a-x)}{a(b-3x)} = k_2 t$$

Figure 17.3 is a plot of the left side of this equation against time. The excellent linearity confirms the second-order law. The slope of the line is the rate constant, $k_2 = 0.299$ liter mole^{-1} min.$^{-1}$

A special case of the general second-order equation (17.3) arises when the initial concentrations of both reactants are the same, $a = b$. This condition can be purposely arranged in any case, but it will be necessarily true whenever only one reactant is involved in a second-order reaction. An example is the decomposition of gaseous hydrogen iodide, $2\ HI \rightarrow H_2 + I_2$, which follows the rate law, $-d(HI)/dt = k_2(HI)^2$.

In these cases the integrated equation (17.4) cannot be applied, since when $a = b$ it reduces to $k_2 t = 0/0$, which is indeterminate. It is best to return to the differential equation, which becomes $dx/dt = k_2(a-x)^2$. Integration yields

$$1/(a-x) = k_2 t + \text{const}$$

When $t = 0$, $x = 0$, so that const $= 1/a$. The integrated rate law is therefore

$$\frac{x}{a(a-x)} = k_2 t \tag{17.5}$$

The half life of a second-order decomposition is found from eq. (17.5) by setting $x = a/2$ when $t = \tau$, so that $\tau = 1/k_2 a$. The half life varies inversely as the initial concentration. For instance, the partial pressure of decomposing HI would take twice as long to fall from 100 to 50 mm as it would to fall from 200 to 100 mm.

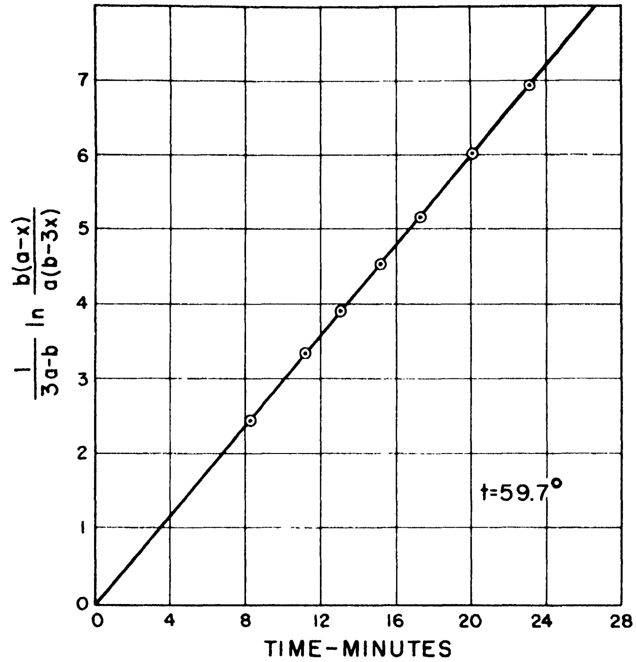


Fig. 17.3. The second-order reaction,
$C_2H_4Br_2 + 3KI \rightarrow C_2H_4 + 2KBr + KI_3$
[From R. T. Dillon, *J. Am. Chem. Soc.*, *54*, 952 (1932).]

8. Third-order rate equation. Third-order reactions are quite rare, and all that have been studied fall into the class:

$$\begin{array}{cccc} 2A & + \; B & \rightarrow \text{products} \\ a-2x & b-x & x \end{array}$$

The differential rate equation is accordingly $dx/dt = k_3(a-2x)^2(b-x)$. This equation can be integrated by breaking it into partial fractions. The result, after we apply the initial condition, $x = 0$ at $t = 0$, is

$$\frac{1}{(2b-a)^2}\left[\frac{(2b-a)2x}{a(a-2x)} + \ln \frac{b(a-2x)}{a(b-x)}\right] = k_3t$$

Examples of gas reactions of the third order, following this rate law, are:

$$2\,NO + O_2 \rightarrow 2\,NO_2$$
$$2\,NO + Br_2 \rightarrow 2\,NOBr$$
$$2\,NO + Cl_2 \rightarrow 2\,NOCl$$

In every case, $-d(NO)/dt = k_3(NO)^2(X_2)$.

9. Opposing reactions. If a reaction is to proceed for some time at a measurable rate, the initial conditions must evidently be fairly remote from the final equilibrium. In many instances the position of equilibrium is so far on the product side, at the temperature and pressure chosen for the experiment, that for all practical purposes one can say that the reaction goes "to completion." This is the case in the N_2O_5 decomposition and the oxidation of iodide ion that have been described. There are other cases in which a considerable concentration of reactants remains when equilibrium is reached. A well known example is the hydrolysis of ethyl acetate in aqueous solution, $CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$. In such instances, as the product concentrations are gradually increased, the velocity of the reverse reaction becomes appreciable. The measured rate of change is thereby decreased, and in order to deduce a rate equation to fit the empirical data, the opposing reaction must be taken into consideration.

The form of the over-all rate equation will be considered for three varieties of such opposed reactions: opposing first orders, opposing second orders, and first vs. second order.

Consider the first species in a reaction $A \rightleftharpoons B$. Let the first-order rate constant in the forward direction be k_1, in the reverse, k_{-1}. Initially at $t = 0$ the concentration of A is a and of B is b. If after a time t, x moles per liter of A have been transformed into B, the concentration of A is $a - x$, and that of B is $b + x$. The differential rate equation is therefore

$$\frac{dx}{dt} = k_1(a - x) - k_{-1}(b + x)$$

or

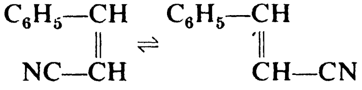
$$\frac{dx}{dt} = (k_1 + k_{-1})(m - x)$$

where $m = (k_1 a - k_{-1} b)/(k_1 + k_{-1})$. Integration yields

$$\ln \frac{m}{m - x} = (k_1 + k_{-1})t \tag{17.6}$$

By Guldberg and Waage's principle, the equilibrium constant $K = k_1/k_{-1}$. Thus equilibrium measurements can be combined with rate data to separate the forward and reverse constants in eq. (17.6).

Such reversible first-order reactions are to be found in some of the intramolecular rearrangements and isomerizations studied by G. B. Kistiakowsky and his co-workers.[7] The cis-trans isomerization of styryl cyanide vapor was followed by the change in the refractive index of the solution obtained on condensation.



$$\begin{array}{c} C_6H_5\text{—}CH \\ \| \\ NC\text{—}CH \end{array} \rightleftharpoons \begin{array}{c} C_6H_5\text{—}CH \\ \| \\ CH\text{—}CN \end{array}$$

Equilibrium at 300°C is at about 80 per cent trans-isomer.

---

[7] Kistiakowsky *et al.*, *J. Am. Chem. Soc.*, *54*, 2208 (1932); *56*, 638 (1934); *57*, 269 (1935); *58*, 2428 (1936).

The case of opposing bimolecular reactions was first treated by Max Bodenstein in his classic study of the combination of hydrogen and iodine.[8] Between 250 and 500°C the reaction $H_2 + I_2 \rightarrow 2\,HI$ can be conveniently studied, but at higher temperatures the equilibrium lies too far on the reactant side. Even in the cited temperature range the reverse reaction must be considered in order to obtain satisfactory rate constants. The concentrations at time t will be denoted as follows:

$$\begin{array}{ccccc} H_2 & + & I_2 & \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} & 2\,HI \\ a - \left(\frac{x}{2}\right) & & b - \left(\frac{x}{2}\right) & & x \end{array}$$

The net rate of formation of HI is

$$\frac{d(\mathrm{HI})}{dt} = \frac{dx}{dt} = k_2\left(a - \frac{x}{2}\right)\left(b - \frac{x}{2}\right) - k_{-2}x^2 \qquad (17.7)$$

When the equilibrium constant $K = k_2/k_{-2}$ is introduced into eq. (17.7) and the equation integrated, the result is

$$k_2 = \frac{2}{mt}\left[\ln\left(\frac{\dfrac{a+b-m}{1-4K} - x}{\dfrac{a+b+m}{1-4K} - x}\right) + \ln\left(\frac{a+b-m}{a+b+m}\right)\right]$$

with $\quad m = \sqrt{(a+b)^2 - 4ab(1-4K)}$

TABLE 17.2

RATE CONSTANTS FOR THE REACTION $H_2 + I_2 \rightleftharpoons 2\,HI$

T(°K)	k_2	k_{-2}	$K = k_2/k_{-2}$
556	1.19×10^{-4}	2.11×10^{-5}	5.64
575	3.53×10^{-4}	7.30×10^{-5}	4.85
629	6.76×10^{-3}	1.81×10^{-4}	3.73
666	3.79×10^{-2}	1.32×10^{-2}	2.87
700	1.72×10^{-1}	6.95×10^{-2}	2.43
781	3.58	1.06×10^{-1}	1.51

Good constants obtained from this rather formidable expression are shown in Table 17.2 for a number of temperatures, together with values of K and k_{-2} from separate experiments.

The third type of opposing reaction, first vs. second order, may be

---

[8] Bodenstein, *Z. physik. Chem.*, *13*, 56 (1894); *22*, 1 (1897); *29*, 295 (1898).

written schematically for the case in which, at $t = 0$, $(B) = (C) = 0$, and $(A) = a$.

$$\begin{array}{ccc} A & \underset{k_2}{\overset{k_1}{\rightleftharpoons}} & B + C \\ a - x & & x \quad x \end{array}$$

The differential equation is $dx/dt = k_1(a - x) - k_2x^2$. The integration yields[9]

$$k_2 = \frac{1}{2mt} \ln \left[\frac{a + x\left(\dfrac{k_2}{k_1} m - \dfrac{1}{2}\right)}{a - x\left(\dfrac{k_2}{k_1} m + \dfrac{1}{2}\right)} \right]$$

with
$$m = \left[\frac{k_1}{k_2} a + \frac{1}{4}\left(\frac{k_1}{k_2}\right)^2\right]^{1/2}$$

These equations would apply to the rate of dissociation of nitrogen tetroxide, $N_2O_4 \rightleftharpoons 2\ NO_2$, but no adequate data are available for this reaction owing to its extreme rapidity. It might have been expected that the reversible dissociation of elementary gases, *e.g.*, $Cl_2 \rightleftharpoons 2\ Cl$, would also follow this law. It is found, however, that two *atoms* usually recombine only in the presence of a third particle or on the wall of the reaction vessel, $Cl + Cl + M \rightarrow Cl_2 + M$. The third particle M is required to take up the excess energy generated in the collision, thereby preventing the atoms from flying apart again.

10. Consecutive reactions. It often happens that the product of one reaction becomes itself the reactant of a following reaction. There may be a series of consecutive steps. Only in the simplest cases has it been possible to obtain solutions to the differential equations of these reaction systems. They are especially important in polymerization and depolymerization processes, and the investigator of chemical kinetics is often blocked here by inadequacies in the available mathematics.

A simple consecutive-reaction scheme that can be treated exactly is one involving only irreversible first-order steps. The general case of n steps has been solved,[10] but only the example of two steps will be discussed. This can be written

$$\begin{array}{ccccc} A & \xrightarrow[k_1]{} & B & \xrightarrow[k_1']{} & C \\ x & & y & & z \end{array}$$

The simultaneous differential equations are

$$-\frac{dx}{dt} = k_1x, \quad -\frac{dy}{dt} = -k_1x + k_1'y, \quad \frac{dz}{dt} = k_1'y$$

---

[9] E. A. Moelwyn-Hughes, *Physical Chemistry* (London: Cambridge, 1947), p. 636.

[10] H. Dostal, *Monatshefte* (Vienna), *70*, 324 (1937). For second-order steps, see P. J. Flory, *J. Am. Chem. Soc.*, *62*, 1057, 1561, 2255 (1940).

The first equation can be integrated directly, giving $-\ln x = k_1 t +$ const. When $t = 0$, let $x = a$, the initial concentration of A. Then const. $= -\ln a$, and $x = ae^{-k_1 t}$. The concentration of A declines exponentially with the time, as in any first-order reaction.

Substitution of the value found for x into the second equation gives

$$\frac{dy}{dt} = -k_1' y + k_1 a e^{-k_1 t}$$

This is a linear differential equation of the first order, whose solution[11] is

$$y = e^{-k_1' t}\left(\frac{k_1 a e^{(k_1' - k_1)t}}{k_1' - k_1} + \text{const}\right)$$

When $t = 0$, $y = 0$, so that const $= -k_1 a/(k_1' - k_1)$.

We now have expressions for x and y. In the reaction scheme followed there is no change in the total number of molecules, since every time an A disappears a B appears, and every time a B disappears a C appears. Thus $x + y + z = a$, and z is calculated to be

$$z = a\left(1 - \frac{k_1' e^{-k_1 t}}{k_1' - k_1} + \frac{k_1 e^{-k_1' t}}{k_1' - k_1}\right) \tag{17.8}$$

In Fig. 17.4, the concentrations x, y, z are plotted as functions of the time, assuming $k_1 = 2k_1'$. The intermediate concentration y rises to a maximum and then falls asymptotically to zero, while the final product rises gradually to a value of a.

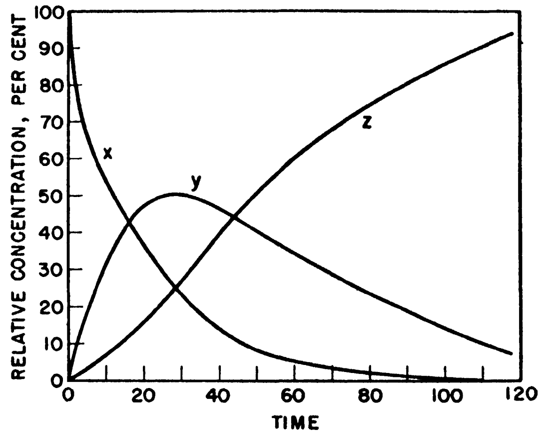


Fig. 17.4. Concentration changes in consecutive first-order reactions.

---

[11] Granville, *Calculus*, p. 380.

Such a reaction sequence was found in the thermal decomposition (pyrolysis) of acetone.[12]

$$(CH_3)_2CO \rightarrow CH_2{=}CO + CH_4$$
$$CH_2{=}CO \rightarrow \tfrac{1}{2}\, C_2H_4 + CO$$

The concentration of the intermediate, ketene, rises to a maximum and then declines during the course of the reaction. Actually, however, the decomposition is more complex than the simple equations would imply.

In dealing with consecutive reactions, the important *bottleneck principle* can sometimes be applied. If one of the steps proceeds much more slowly than any of the others, the over-all reaction velocity will be determined by the speed of this slow step. For instance, in the example above, if $k_1 \ll k_1'$, eq. (17.8) reduces to

$$z = a(1 - e^{-k_1 t})$$

which is identical with eq. (17.2) and includes only the constant of the slow step.

11. Parallel reactions. Sometimes a given substance can react or decompose in more than one way. Then the alternative parallel reactions must be included in analyzing the kinetic data. Consider a schematic reaction,

$$A \left\{ \begin{array}{l} \xrightarrow{k_1} B \\ \xrightarrow{k_1'} C \end{array} \right.$$

In the case of such parallel processes, the most rapid rate determines the predominant path of the over-all reaction. If $k_1 \gg k_1'$, the decomposition of A will yield mostly B. For example, alcohols can be either dehydrated to olefins, or dehydrogenated to aldehydes:

$$C_2H_5OH \left\{ \begin{array}{l} \xrightarrow{k_1} C_2H_4 + H_2O \\ \xrightarrow{k_1'} CH_3CHO + H_2 \end{array} \right.$$

By suitable choice of catalyst and temperature one rate can be made much faster than the other. The product obtained depends upon the relative rates and not upon the equilibrium constants for the two reactions.

12. Determination of the reaction order. In simple reactions of the first or second order, it is not hard to establish the order and evaluate the rate constants. The experimental data are simply inserted into the different integrated rate equations until a constant k is found. The graphical methods leading to linear plots are useful. In more complicated reactions, it is often desirable to adopt other methods for at least a preliminary survey of the kinetics.

The *initial reaction rate* often provides helpful information, for in a sufficiently slow reaction the rate dx/dt can be found with some precision

---

[12] C. A. Winkler and C. N. Hinshelwood, *Proc. Roy. Soc., A 149*, 340 (1935).

before there has been any extensive chemical change. It is then possible to assume that all the reactant concentrations are still effectively constant at their initial values. If $A + B + C \rightarrow$ products, and the initial concentrations are a, b, c, the rate can be written quite generally as

$$\frac{dx}{dt} = k\,(a - x)^{n_1}(b - x)^{n_2}(c - x)^{n_3}$$

If x is very small, the initial rate will be

$$\frac{dx}{dt} = k\,a^{n_1}\,b^{n_2}\,c^{n_3}$$

While we keep b and c constant, the initial concentration of a can be varied, and the resultant change of the initial rate measured. In this way the value of n_1 is estimated. Similarly, by keeping a and c constant while we vary b, a value of n_2 is found; and with a and b constant, variation of c yields n_3.

The initial-rate method is especially useful in those reactions that cannot be trusted to progress to any appreciable extent without becoming involved in labyrinthine complications. If the order of reaction found by using initial rates differs from that found by using the integrated rate equation, it is probable that the products are interacting with the initial reactants.

A frequently useful way of finding the reaction order is the *isolation method*, devised by W. Ostwald. If all the reactants save one, say A, are present initially in high concentrations, their concentrations during the reaction will be relatively much less changed than that of A. In fact, they may be taken to be effectively constant, and the rate equation will have the approximate form:

$$\frac{dx}{dt} = k\,(a - x)^{n_1}\,b^{n_2}\,c^{n_3}\,\ldots = k'\,(a - x)^{n_1}$$

By comparing the data with integrated forms of this equation for various choices of n_1, it is possible to determine the order of the reaction with respect to component A. The orders with respect to B, C, etc., are found in like manner.

The isolation method is often practiced of necessity in reactions in solution if the solvent is one reactant. For example, in the hydrolysis of ethyl acetate, $CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$, the ester concentration is much lower than that of the solvent, water. The reaction follows a rate law that is first order with respect to the ester, the water concentration being effectively constant:

$$\frac{-d(CH_3COOC_2H_5)}{dt} = k_2(CH_3COOC_2H_5)(H_2O) = k_1(CH_3COOC_2H_5)$$

Another way of holding the concentration of a reactant constant is to use a saturated solution with an excess of pure solute phase always present.

An interesting general method of finding the over-all reaction order is based on the half-life times. If all the reactants are taken to have stoichiometric initial concentrations a, the rate law takes the form $dx/dt = k_n(a-x)^n$. Integrating and setting $x = 0$ at $t = 0$, we find

$$k_n t = \frac{1}{n-1}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right]$$

When the time t equals the half life τ, $x = a/2$, so that

$$\tau = \frac{2^{n-1}-1}{a^{n-1}k_n(n-1)}$$

$$\log\tau = (1-n)\log a + \log\left[\frac{2^{n-1}-1}{k_n(n-1)}\right] \qquad (17.9)$$

If log τ is plotted against log a, a straight line should be obtained whose slope is $(1-n)$. In gas reactions the initial pressure can be used instead of the initial concentration.

The half lives determined by A. Farkas[13] for the homogeneous *para-ortho* hydrogen conversion at 923°K are shown in the log-log plot in Fig. 17.5. The slope of the line is -0.52; thus $(1-n) = -0.52$, and $n = 1.52$. The reaction is one of the three-halves order. The reason for this order is that the change $H_2(p) \rightarrow H_2(o)$ proceeds through atomic hydrogen formed by the dissociation $H_2 \rightarrow 2\,H$. Then $H + H_2(p) \rightarrow H_2(o) + H$. The rate is proportional to $(H)(p\text{-}H_2)$. From the dissociation equilibrium $(H) = K^{1/2}(H_2)^{1/2}$, so that the rate is $kK^{1/2}(p\text{-}H_2)^{3/2}$.

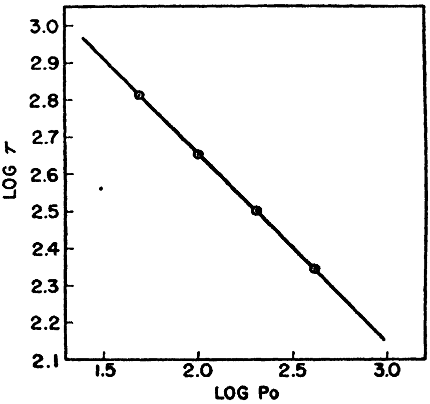


Fig. 17.5. Plot of log half-life vs. log initial pressure for p-o H_2 conversion.

13. Reactions in flow systems. The rate equations that have been discussed all apply to *static systems*, in which the reaction mixture is enclosed in a vessel at constant volume and temperature. We must now consider *flow systems*, in which reactants enter continuously at the inlet of a reaction vessel, while the product mixture is withdrawn at the outlet. We shall describe two examples of flow systems: (a) a reactor in which there is no stirring; (b) a reactor in which complete mixing is effected at all times by vigorous stirring.

Figure 17.6 shows a tubular reactor through which the reaction mixture passes at a volume rate of flow u (*e.g.*, in liters per sec). Let us consider an

---

[13] A. Farkas, *Z. physik. Chem.*, *B 10*, 419 (1930).

element of volume dV sliced out of this tube, and focus attention on one particular component k, which enters this volume element at a concentration c_k and leaves at $c_k - dc_k$. If there is no longitudinal mixing, the net change with time of the number of moles of k within dV (dn_k/dt) will be the sum of two terms, one due to chemical reaction within dV, and the other equal to the excess of k entering dV over that leaving. Thus,

$$\frac{dn_k}{dt} = r_k\,dV - u\,dc_k \tag{17.10}$$

The chemical reaction rate per unit volume is denoted by r_k. The explicit form of r_k is determined by the rate law for the reaction: for a reaction first order with respect to k, $r_k = -k_1c_k$; for second order, $r_k = -k_2c_k^2$, etc.

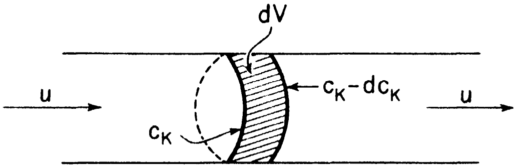


Fig. 17.6. Element of volume in a flow reactor.

After reaction in the flow system has continued for some time, a *steady state* is attained, in which the number of moles of each component in any volume element no longer changes with time, the net flow into the element exactly balancing the reaction within it. Then $dn_k/dt = 0$, and eq. (17.10) becomes

$$r_k\,dV - u\,dc_k = 0 \tag{17.11}$$

After r_k is introduced as a function of c_k, the equation can be integrated. For example, with $r_k = -k_1c_k$,

$$-k_1\frac{dV}{u} = \frac{dc_k}{c_k}$$

The integration is carried out between the inlet and the outlet of the reactor.

$$\frac{-k_1}{u}\int_0^{V_0} dV = \int_{c_{k_1}}^{c_{k_2}} \frac{dc_k}{c_k}$$

$$-k_1\frac{V_0}{u} = \ln\frac{c_{k_2}}{c_{k_1}} \tag{17.12}$$

The total volume of the reactor is V_0, and c_{k_2} and c_{k_1} are the concentrations of k at the outlet and inlet, respectively.

It may be noted that eq. (17.12) reduces to the integrated rate law for a first-order reaction in a static system if the time t is substituted for V_0/u. The quantity V_0/u is called the *contact time* for the reaction; it is the average time that a molecule would take to pass through the reactor. Thus eq. (17.12) allows us to evaluate the rate constant k_1 from a knowledge of the contact time, and of the concentrations of reactant fed to the tube and recovered at the end of the tube. For other reaction orders also, the correct flow reactor equation is obtained by substituting V_0/u for t in the equation for the static system. Many reactions that are too swift for convenient study in a static system can be followed readily in a flow system, in which the contact time is reduced by use of a high flow rate and a small volume.

The derivation of eq. (17.11) tacitly assumed that there was no volume change ΔV as a result of the reaction. Any ΔV would affect the flow rate at constant pressure. In liquid-flow systems, the effects of ΔV are generally negligible, but for gaseous systems the form of the rate equations is considerably modified. A convenient collection of integrated rate laws including such cases is given by Hougen and Watson.[14]

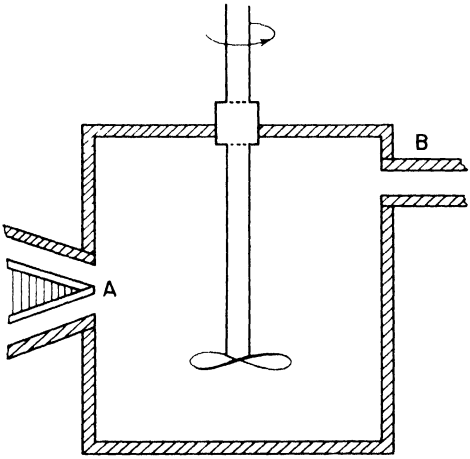


Fig. 17.7. A stirred flow reactor.

An example of a stirred flow reactor[15] is shown in Fig. 17.7. The reactants enter the vessel at A, and stirring at 3000 rpm effects mixing within about a second. The product mixture is removed at B at a rate exactly balancing the feed. After a steady state is attained, the composition of the mixture in the reactor remains unchanged as long as the composition and rate of supply of reactants is unchanged. Equation (17.11) still applies, but in this case $dV = V_0$, the total reactor volume, and $dc_k = c_{k_1} - c_{k_2}$ where c_{k_1} and c_{k_2} are the initial and final concentrations of reactant k. Thus

$$r_k = \frac{u}{V}(c_{k_2} - c_{k_1}) = \frac{-dc_k}{dt}$$

With this method, there is no need to integrate the rate equation. One point

---

[14] O. A. Hougen and K. M. Watson, *Chemical Process Principles* (*Part 3*) (New York: Wiley, 1947), p. 834.

[15] K. G. Denbigh, *Trans. Faraday Soc.*, *40*, 352 (1944); *Disc. Faraday Soc.*, *2*, 263 (1947).

on the rate curve is obtained from each steady-state measurement, and a number of runs with different feed rates and initial concentrations is required to determine the order of the reaction.

An important application of the stirred flow reactor is the study of transient intermediates, the concentration of which in a static system might quickly reach a maximum value, and then fall to zero. An illustration was shown in Fig. 17.4. For example, in the reaction between Fe^{+3} and $Na_2S_2O_3$, a violet color appears, which fades within one or two minutes. In a stirred flow reactor, the conditions can be adjusted so that the color is maintained, and the intermediate responsible, which appears to be $FeS_2O_3^+$, can be studied spectroscopically.

The living cell is in some ways analogous to a continuous flow reaction vessel, in which reactants and products are transferred by diffusion across the cell membrane.

14. Effect of temperature on reaction rate. So far we have been concerned with the problem of finding how the chemical kinetics depends on the concentrations of the various components of the reaction system. This first step is necessary in reducing the raw material of the experimental data to a refined form suitable for theoretical interpretation. The next question is how the constants of the rate equations depend on variables such as temperature and total pressure. The temperature effect has been tremendously useful in providing an insight into the theory of all rate processes.

In 1889, Arrhenius pointed out that since the van't Hoff equation for the temperature coefficient of the equilibrium constant was $d \ln K_c/dT = \Delta E/RT^2$, whereas the mass-action law related the equilibrium constant to a ratio of rate constants, $K_c = k_f/k_b$, a reasonable equation for the variation of rate constant with temperature might be

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \tag{17.13}$$

The quantity E_a is called the *activation energy* of the reaction.

If E_a is not itself temperature dependent, eq. (17.10) yields on integration

$$\ln k = -\frac{E_a}{RT} + \ln A \tag{17.14}$$

where $\ln A$ is the constant of integration. Hence

$$k = Ae^{-E_a/RT} \tag{17.15}$$

A is called the *frequency factor*. This is the famous Arrhenius equation for the rate constant.

From eq. (17.14) it follows that a plot of the logarithm of the rate constant against the reciprocal of the absolute temperature should be a straight line. The validity of the equation is excellently confirmed in this way for a large number of experimental velocity constants. An example from the data of Bodenstein on the $H_2 + I_2 = 2\ HI$ reaction is shown in Fig. 17.8. We shall see later that the Arrhenius equation is only an approximate representation of the temperature dependence of k, but the approximation is usually a very good one.

According to Arrhenius, eq. (17.15) indicates that molecules must acquire a certain critical energy E_a before they can react, the Boltzmann factor $e^{-E_a/RT}$ being the fraction of molecules that manages to obtain the necessary energy. This interpretation is still held to be essentially correct.

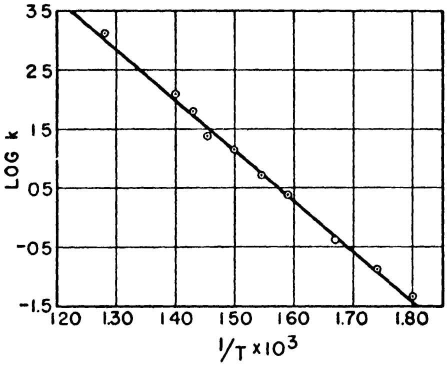


Fig. 17.8. Temperature dependence of rate constant for formation of hydrogen iodide, illustrating applicability of the Arrhenius equation.

By referring back to Fig. 17.1 on page 531, we can obtain a picture of the activation energy as the potential-energy hill that must be climbed to reach the activated state. It is evident also that the heat of reaction Q_v is the difference between the activation energies of forward and backward reactions,

$$\Delta E = Q_v = E_f - E_b \tag{17.16}$$

15. Collision theory of gas reactions. Reaction velocities have been studied in gaseous, liquid, and solid solutions, and at the interfaces between phases. Homogeneous reactions in liquid solutions have undoubtedly been investigated most extensively, because they are of great practical importance and usually require only relatively simple experimental techniques. From a theoretical point of view, however, they suffer from the disadvantage that our understanding of liquids and solutions is inadequate, especially on the molecular scale that is important in chemical changes.

Homogeneous gas reactions, therefore, though harder to follow experimentally, should be more amenable to theoretical elucidation. The statistical theory of gases is well developed and provides an insight into the factors governing the reaction rates.

The first theory of gas reactions postulated that in order for molecules to interact, they must approach each other so closely that they can be said to be in collision. Sometimes a rearrangement of chemical bonds occurs during a collision, forming new molecules from the old ones. The speed of the reaction is equal to the number of collisions per second times the fraction of the collisions that are effective in producing chemical change.

The formula for the number of collisions per second between like molecules in one cc of gas is obtained from eq. (7.16).

$$Z_{11} = \tfrac{1}{2}\sqrt{2}\pi n^2 d^2 \sqrt{\frac{8kT}{\pi m}} = 2n^2 d^2 \sqrt{\frac{\pi kT}{m}} \tag{17.17}$$

Here n is the number of molecules per cc, d is the molecular diameter, and $\sqrt{8kT/\pi m}$ is the average speed of a molecule of mass m. In the case of unlike molecules whose concentrations are n_1 and n_2, the collision frequency becomes

$$Z_{12} = \pi n_1 n_2 d_{12}^2 \sqrt{\frac{8kT}{\pi \mu}} \tag{17.18}$$

Now $d_{12} = (d_1 + d_2)/2$ is the mean molecular diameter and the reduced mass $\mu = m_1 m_2/(m_1 + m_2)$. Note that the factor $\frac{1}{2}$ is not included in the expression for unlike molecules since a collision of the type $B \rightarrow A$ is now distinguishable from $A \rightarrow B$.

Let us calculate Z_{11} for hydrogen-iodide molecules at 700°K and 1 atm pressure. From gas viscosity $d = 4 \times 10^{-8}$ cm. The mass $m = 127.9/6.02 \times 10^{23} = 2.12 \times 10^{-22}$ g; $n = PVN/RT = 1 \times 1 \times 6.02 \times 10^{23}/82.05 \times 700 = 1.05 \times 10^{19}$. Substituting in eq. (17.17), we find $Z_{11} = 1.33 \times 10^{28}$. At a given temperature and pressure the Z_{11} for different molecules hardly ever varies by a factor of more than 50, and for molecules of low molecular weight the variations are much less. (The variable factor is $d^2/m^{1/2}$ and d may run from 2 to 20 Å.)

Now it is obvious that not every collision can lead to reaction; the collision frequency is so extremely large that if such were the case all chemical reactions would be essentially completed in a fraction of a second. The hypothesis is therefore made that only those collisions lead to reaction in which the sum of the energies of the colliding molecules exceeds a certain critical value E[16]. The problem is therefore to calculate the chance that a pair of molecules has an energy greater than E.

The first question that arises is what energy is to be taken into consideration. A complex molecule can acquire energy in various degrees of freedom: translational kinetic energy, rotational kinetic energy, vibrational kinetic and potential energy. Can all of this energy be utilized in effecting the rearrangement of bonds that is called a "chemical reaction"?

The simplest form of the collision theory says that only two degrees of freedom are utilized. These degrees of freedom can best be visualized as the

---

[16] This hypothesis, that if energy is less than E there is never reaction, but if greater than E there is always reaction, is not very reasonable. A reaction probability that is some function of the energy would be more logical.

components of the translation of each molecule along the line of centers at the time of collision. In other words, only the velocity components in the direction of a head-on collision are effective. The chance that two molecules have a relative head-on velocity c, such that $\frac{1}{2}mc^2 = E$, has already been calculated, under a slightly different guise, in Chapter 7. Since the choice of direction is entirely arbitrary, it is simply the distribution law in two dimensions, eq. (7.35):

$$\frac{dn}{n_0} = \left(\frac{m}{kT}\right) e^{-\frac{1}{2}mc^2/kT} c\, dc$$

We wish to transform this expression into the distribution function for the kinetic energy per mole, $E = \frac{1}{2}Nmc^2$. Since $dE = Nmc\, dc$, and $R = Nk$, the result is

$$\frac{dn}{n_0} = \frac{1}{RT} e^{-E/RT} dE$$

This is the chance of a molecule's having an energy between E and $E + dE$ in two degrees of freedom. The chance of its having an energy greater than E is obtained by integrating from E to ∞,

$$\frac{\Delta n}{n_0} = \int_E^\infty \frac{1}{RT} e^{-E/RT} dE = -e^{-E/RT}\Big|_E^\infty = e^{-E/RT}$$

The simple collision theory for a bimolecular reaction therefore gives for the number of molecules reacting per second:

$$\frac{dn}{dt} = \begin{array}{c}\text{number of collisions per sec} \times \text{chance of}\\ \text{collision having energy } E \text{ or greater}\end{array}$$
$$= Z_{12}\, e^{-E/RT}$$

The velocity is usually expressed in moles per liter reacting per second, $dc/dt = k_2c_1c_2$. Since $c = 10^3n/N$, $dc/dt = (10^3/N)\,dn/dt$. The reaction rate is, accordingly,.

$$\frac{dc}{dt} = \frac{10^3}{N}\frac{dn}{dt} = k_2c_1c_2 = k_2\frac{10^6}{N^2}n_1n_2$$

or $$k_2 = \frac{N}{10^3n_1n_2}\cdot\frac{dn}{dt} \quad \text{with} \quad \frac{dn}{dt} = Z_{12}\, e^{-E/RT}$$

Substituting the kinetic-theory expression for Z_{12} from eq. (17.18), we have

$$k_2 = Ae^{-E/RT} = \frac{\pi N d_{12}^2}{10^3}\sqrt{\frac{8kT}{\pi\mu}}\, e^{-E/RT} \tag{17.19}$$

This theoretical expression can be compared with experiment in several ways. It contains three quantities that are not known *a priori*, the rate constant k_2, the collision diameter d_{12}, and the activation energy E. The following comparisons are possible: (1) With a value of E from the Arrhenius equation for the temperature coefficient, and a value of d_{12} from kinetic theory (*e.g.*, viscosity), k_2 can be calculated and compared with experiment. (2) With the experimental k_2 at one temperature and the kinetic-theory d_{12}, a calculated value of E can be compared with the value from the temperature coefficient. (3) With the experimental E and k_2, a d_{12} can be calculated and compared with kinetic-theory or electron-diffraction diameters.

Let us apply method (1) to the HI decomposition. Using the previously cited values for the constants and for d_{12}, we obtain

$$k_2 = \frac{N}{10^3 n^2} Z_{11}\, e^{-E/RT} = \frac{(6.02 \times 10^{23})(1.33 \times 10^{28})}{10^3(1.05 \times 10^{19})^2}\, e^{-E/RT}$$

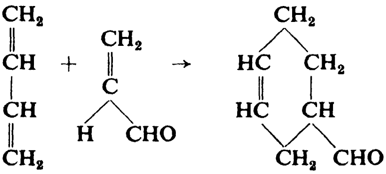
$$= 7.26 \times 10^{10}\, e^{-E/RT}$$

The experimental E is 43,700 cal. Thus at 700°K the calculated rate constant is 2.10×10^{-3} liter mole^{-1} sec^{-1}. The experimental value obtained by Bodenstein was 1.57×10^{-3}. The success of the collision theory in this case is quite remarkable.

Unfortunately, there are few simple second-order gas reactions that can be similarly tested. Table 17.3 contains some of the available data. The calculated frequency factors A are usually around 10^{11} in units of liter mole^{-1} sec^{-1}, so that observed differences in the reaction velocities are caused mainly by activation-energy differences. The experimental A values sometimes deviate considerably from the theoretical.

TABLE 17.3

SECOND-ORDER GAS REACTIONS

Reaction	*Rate Constant (liter sec^{-1} mole^{-1})*
(1) $2\,HI \rightarrow H_2 + I_2$	$2.05 \times 10^9\, T^{1/2}\, e^{-43,700/RT}$
(2) $H_2 + I_2 \rightarrow 2\,HI$	$3.3 \times 10^9\, T^{1/2}\, e^{-38,900/RT}$
(3) $2\,NO_2 \rightarrow 2\,NO + O_2$	$1.31 \times 10^8\, T^{1/2}\, e^{-26,560/RT}$
(4) $2\,NOCl \rightarrow 2\,NO + Cl_2$	$4.3 \times 10^8\, T^{1/2}\, e^{-24,000/RT}$
(5) $CH_3I + HI \rightarrow CH_4 + I_2$	$5.22 \times 10^{10}\, T^{1/2}\, e^{-33,100/RT}$
(6) $C_2H_5I + HI \rightarrow C_2H_6 + I_2$	$1.34 \times 10^{10}\, T^{1/2}\, e^{-29,500/RT}$
(7) 	$1.46 \times 10^6\, e^{-19,700/RT}$
(8) $NO_2 + O_3 \rightarrow NO_3 + O_2$	$5.9 \times 10^{12}\, e^{-7000/RT}$

The collision theory gives a crude physical picture of how bimolecular gas reactions occur which is roughly correct as far as it goes, but factors other than an activation energy and a rigid-sphere collision frequency may influence the rate of reaction. At one time it was popular to rewrite the theoretical equation (17.16) as $k_2 = pAe^{-E/RT}$, where p, which was called the *steric factor*, was supposed to measure the geometrical requirements that must be met if two colliding molecules are to interact. Since there was no independent way to estimate p, it was always possible to assign whatever value was necessary to obtain agreement with experiment. It became simply a measure of the discrepancy between simple collision theory and the experimental results.

16. Collision theory and activation energy. The collision-theory expression for the rate constant contains, in addition to the strongly temperature-dependent $e^{-E/RT}$ term, a mild temperature dependence in the frequency factor. Equation (17.19) can be written $k_2 = a\,T^{1/2}e^{-E/RT}$, so that $d \ln k_2/dT = (E + \frac{1}{2}RT)/RT^2$. Thus the Arrhenius energy of activation is $E_a = E + \frac{1}{2}RT$. It is worth while to make this correction in performing calculations with the theory, but it hardly affects the linear plot of $\ln k$ vs. $1/T$.

There is no reason to assume that the activation energy should be strictly independent of temperature and in careful work a slight temperature dependence has often been noted. The dependence of the heat of reaction, ΔE or ΔH, on temperature is given by Kirchhoff's Equation (page 43) and E_a may behave similarly.

17. First-order reactions and collision theory. The collision theory was developed about the time of World War I by M. Trautz, W. C. McC. Lewis, and others, and as we have seen, it gives a fairly satisfactory account of bimolecular reactions. At the same time a number of gas reactions were being studied that were kinetically of the first order and apparently simple unimolecular decompositions. These reactions seemed to present a paradox: the necessary activation energy must evidently come from the kinetic energy transferred during collisions, yet the reaction velocity did not depend on the collision frequency.

In 1919, a flurry of excitement was caused in the small world of kineticists by the suggestion that the activation of molecules in these unimolecular decompositions was actually effected, not by collisions, but by the absorption of radiation from their environment, especially infrared radiation from the walls of the reaction vessel. This theory was very short-lived since no radiation effects could be demonstrated experimentally, and a better solution of the problem was proposed shortly thereafter. In 1922, F. A. Lindemann (now Lord Cherwell) showed how the collisional mechanism for activation could lead to first-order kinetics.

Consider a molecule A which decomposes according to $A \rightarrow B + C$, with a first-order rate law, $-d(A)/dt = k_1'(A)$. In a vessel full of A, the intermolecular collisions are continually producing molecules with higher than average energy, and indeed sometimes molecules with an energy above some critical value necessary for the *activation* that precedes decomposition. Let us suppose that there is a certain time lag between activation and decomposition; the activated molecule does not immediately fall to pieces, but moves around for a while in its activated state. Sometimes it may meet an energy-poor molecule, and in the ensuing collision it may be robbed of enough energy to be *deactivated.*

The situation can be represented as follows:

$$\begin{tikzcd} A + A \arrow[r, shift left, "k_2"] & A + A^* \arrow[l, shift left, "k_{-2}"] \arrow[d, "k_1"] \\ & B + C \end{tikzcd}$$

Activated molecules are denoted by A^*. The bimolecular rate constant for activation is k_2, for deactivation k_{-2}. The decomposition of an activated molecule is a true unimolecular reaction with rate constant k_1.

The process called *activation* consists essentially in transferring translational kinetic energy into energy stored in internal degrees of freedom, especially vibrational degrees of freedom.[17] The mere fact that a molecule is moving rapidly, *i.e.*, has a high translational kinetic energy, does not make it unstable. In order to cause reaction, the energy must get into the chemical bonds, where high-amplitude vibrations will lead to ruptures, decompositions, and rearrangements. The transfer of energy from translation to vibration can occur only in collisions with other molecules or with the wall. The situation is like that of two rapidly moving automobiles: their kinetic energies will not wreck them unless they happen to collide and the kinetic energy of the whole is transformed into internal energy of the parts.

The point of the Lindemann theory is that there is a lag between the activation of the internal degrees of freedom and the subsequent decomposition. The reason is that a polyatomic molecule can take up collisional energy into a number of its $3n - 6$ vibrational degrees of freedom, and then some time may elapse before this energy flows into the one bond that breaks.

The Lindemann scheme cannot be treated exactly since the differential equations to which it leads are not soluble in closed form. They are

$$\frac{d(A^*)}{dt} = k_2(A)^2 - k_{-2}(A^*)(A) - k_1(A^*)$$

$$\frac{-d(A)}{dt} = k_2(A)^2 - k_{-2}(A^*)(A)$$

$$\frac{d(B)}{dt} = k_1(A^*)$$

An approximation is therefore made that is frequently used in chemical kinetics when the mathematical going becomes too rough. This is the *steady-state approximation.* It is assumed that after the reaction has been under way for a short time, the rate of formation of activated molecules equals their rate of disappearance, so that the net rate of change in (A^*) is zero, $d(A^*)/dt = 0$. In justification of this assumption it can be said that there are not very

[17] Sometimes it is necessary to change the electronic state of a molecule in order to effect the reaction. Such reactions are exceptionally slow if they depend on thermal activation. They are called *nonadiabatic reactions,* an unfortunate name since it has nothing to do with the term *adiabatic* as used in thermodynamics.

many activated molecules present in any event. The value of (A^*) is necessarily small, so that the value of its rate of change must be small, and can usually be set equal to zero without serious error.

With $d(A^*)/dt = 0$, the first equation above becomes $k_2(A)^2 - k_{-2}(A^*)(A) - k_1(A^*) = 0$, and the steady-state concentration of A^* is

$$(A^*) = \frac{k_2(A)^2}{k_{-2}(A) + k_1}$$

The reaction velocity is the rate at which A^* decomposes into B and C, or

$$\frac{d(B)}{dt} = k_1(A^*) = \frac{k_1k_2(A)^2}{k_{-2}(A) + k_1} \tag{17.20}$$

Two special cases now arise.

If the rate of decomposition of (A^*) is much greater than its rate of deactivation, $k_1 \gg k_{-2}(A)$ and the net rate reduces to

$$\frac{d(B)}{dt} = k_2(A)^2$$

This expression is the ordinary second-order law.

On the other hand, if the rate of deactivation of A^* is much greater than its rate of decomposition, $k_{-2}(A) \gg k_1$, and the over-all rate becomes

$$\frac{d(B)}{dt} = \frac{k_1k_2}{k_{-2}}(A) = k_1'(A)$$

It is evident that it is possible to obtain first-order kinetics while preserving a collisional mechanism for activation. This will be the result whenever the activated molecule has so long a lifetime that it is usually deactivated by collision before it has a chance to break into fragments.

Fortunately, there is a fairly critical experimental test of the Lindemann theory. As the pressure in the reacting system is decreased, the rate of deactivation, $k_{-2}(A^*)(A)$, must likewise decrease, and at low enough pressures the condition for first-order kinetics must always fail when $k_{-2}(A)$ is no longer much greater than k_1. The observed first-order rate constant should therefore fall off at low pressures to reach eventually a second-order constant.

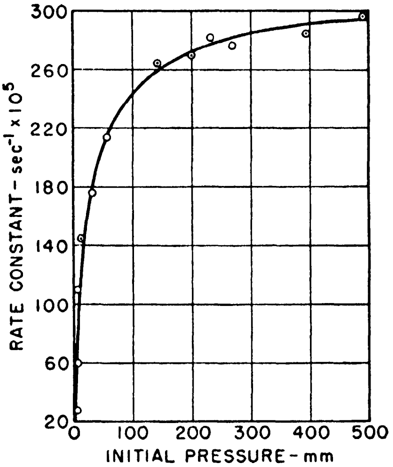


Fig. 17.9. Falling-off of rate constant of azomethane decomposition at low pressures:

$$(CH_3)_2N_2 \rightarrow C_2H_6 + N_2.$$

In Fig. 17.9 are plotted the rate constants obtained by H. C. Ramsperger[18]

---

[18] H. C. Ramsperger, *J. Am. Chem. Soc.*, *49*, 912 (1927).

for the first-order thermal decomposition of azomethane at various initial pressures. In most of the first-order reactions that have been investigated, the rate constant decreases at low pressures (usually 10–100 mm). If the falling rate constant is merely the result of a lowered probability of deactivation, it should be possible to restore the initial rate by adding a sufficient pressure of a completely inert gas. This inert-gas effect has been noted in a number of cases.

The Lindemann theory of unimolecular reactions is very plausible and provides the best explanation for many experiments. Yet some reactions once thought to be simple unimolecular decompositions have been shown to proceed via complex chain mechanisms, which often yield deceptively simple rate laws. This aspect of gas kinetics will be considered a little later in the chapter.

18. Activation in many degrees of freedom. When the first-order rate constant begins to fall at lower pressures, the rate of formation of activated molecules is no longer much greater than their rate of decomposition, and in fact the over-all rate is beginning to be determined by the rate of supply of activated molecules. According to simple collision theory, therefore, the rate at this point should be about $Z_{11}e^{-E/RT}$. When this prediction was compared with experiment in the typical case of the azomethane decomposition, it was found that the reaction was going about 10^8 times faster than was permissible by simple collision theory.

This unfortunate contradiction was soon remedied by C. N. Hinshelwood and G. N. Lewis (independently). The $e^{-E/RT}$ term used to calculate the fraction of activated molecules is based on the condition that the critical energy is acquired in two translational degrees of freedom only. If energy in various internal degrees of freedom also can be transferred in collisions, the probability of a molecule's getting the necessary E is much enhanced. Instead of a simple $e^{-E/RT}$ term, the chance is now[19]

$$P_E = \frac{e^{-E/RT}(E/RT)^{(s/2)-1}}{[(s/2)-1]!} = f_s\, e^{-E/RT}$$

Here s is the number of "square terms" in which the energy can be acquired: translational or rotational energy has one square term per degree of freedom, $\frac{1}{2}mv^2$ or $\frac{1}{2}I\omega^2$; vibrational energy has one for kinetic energy, $\frac{1}{2}mv^2$, and one for potential energy, $\frac{1}{2}\kappa x^2$.

The rate of activation may now be increased by a large factor f_s. For the azomethane case, with $E = 52{,}400$, $T = 563$, the factor $f_s = 10^8$ when $s = 16$. The observed rate of activation can therefore be explained by calling on 16 "square terms" or about 8 vibrational degrees of freedom. Since the molecule contains 10 atoms, there are altogether $3n - 6 = 24$ vibrations. The Lewis-Hinshelwood theory would include a third of these in the activation process.

---

[19] This is a good approximate formula when $E \gg RT$. A derivation is given by Moelwyn-Hughes, *Physical Chemistry*, p. 69.

It has so far proved possible in every case to find a value of s that explains the observed activation rate.[20] Since it may not be easy to transfer energy from translation to vibration and from one vibration to another, the Lewis-Hinshelwood theory would seem to necessitate extremely sticky collisions. Moreover, a clear-cut decision on the validity of the theory is prevented by the possible occurrence of chain reactions in many first-order decompositions. It is now necessary to consider in some detail these chain reactions, which add so many interesting complications to gas kinetics.

19. Chain reactions: formation of hydrogen bromide. After Bodenstein had completed his study of the hydrogen-iodine reaction, he turned to hydrogen-bromine, $H_2 + Br_2 = 2\,HBr$, probably expecting to find another example of bimolecular kinetics. The results[21] were surprisingly different, for the reaction velocity was found to fit the rather complicated expression,

$$\frac{d(\mathrm{HBr})}{dt} = \frac{k(\mathrm{H_2})(\mathrm{Br_2})^{1/2}}{m + (\mathrm{HBr})/(\mathrm{Br_2})}$$

where m and k are constants. Thus the velocity is inhibited by the product, HBr. In the initial stages of the combination, $(HBr)/(Br_2)$ is a small fraction so that $d(HBr)/dt = k'(H_2)(Br_2)^{1/2}$, with an over-all order of 3/2.

There was no interpretation of this curious rate law for thirteen years. Then the problem was solved independently and almost simultaneously by Christiansen, Herzfeld, and Polanyi. They proposed a chain of reactions with the following steps:

Chain initiation	(1)	$Br_2 \xrightarrow{k_1} 2\,Br$
Chain propagation	(2)	$Br + H_2 \xrightarrow{k_2} HBr + H$
	(3)	$H + Br_2 \xrightarrow{k_3} HBr + Br$
Chain inhibition	(4)	$H + HBr \xrightarrow{k_4} H_2 + Br$
Chain breaking	(5)	$2\,Br \xrightarrow{k_5} Br_2$

The reaction is initiated by bromine atoms from the thermal dissociation $Br_2 = 2\,Br$. The chain propagating steps (2) and (3) form two molecules of HBr and regenerate the bromine atom, ready for another cycle. Thus very few bromine atoms are needed to cause an extensive reaction. Step (4) is introduced to account for the observed inhibition by (HBr); since this inhibition is proportional to the ratio $(HBr)/(Br_2)$ it is evident that HBr and Br_2 compete, so that the atom being removed must be H rather than Br.

In order to derive the kinetic law from the chain mechanism, the

---

[20] R. A. Ogg, in *J. Chem. Phys.*, *21*, 2079 (1953), has proposed an interesting chain mechanism for the N_2O_5 case, which previously appeared exceptional.

[21] M. Bodenstein and S. C. Lind, *Z. physik. Chem.*, *57*, 168 (1906).

stationary-state treatment is applied to the reactive atoms, which must be present in low concentrations.

$$\frac{d(\mathrm{Br})}{dt} = 0 = 2k_1(\mathrm{Br_2}) - k_2(\mathrm{Br})(\mathrm{H_2}) + k_3(\mathrm{H})(\mathrm{Br_2}) + k_4(\mathrm{H})(\mathrm{HBr}) - 2k_5(\mathrm{Br})^2$$

$$\frac{d(\mathrm{H})}{dt} = 0 = k_2(\mathrm{Br})(\mathrm{H_2}) - k_3(\mathrm{H})(\mathrm{Br_2}) - k_4(\mathrm{H})(\mathrm{HBr})$$

These two simultaneous equations are solved for the steady-state concentrations of the atoms, giving

$$(\mathrm{Br}) = \left[\frac{k_1}{k_5}(\mathrm{Br_2})\right]^{1/2} \qquad (\mathrm{H}) = k_2\frac{(k_1/k_5)^{1/2}(\mathrm{H_2})(\mathrm{Br_2})^{1/2}}{k_3(\mathrm{Br_2}) + k_4(\mathrm{HBr})}$$

The rate of formation of the product, HBr, is

$$\frac{d(\mathrm{HBr})}{dt} = k_2(\mathrm{Br})(\mathrm{H_2}) + k_3(\mathrm{H})(\mathrm{Br_2}) - k_4(\mathrm{H})(\mathrm{HBr})$$

Introducing the values for (H) and (Br) and rearranging, we find

$$\frac{d(\mathrm{HBr})}{dt} = 2\frac{k_3k_2k_4^{-1}k_1^{1/2}k_5^{-1/2}(\mathrm{H_2})(\mathrm{Br_2})^{1/2}}{k_3k_4^{-1} + (\mathrm{HBr})(\mathrm{Br_2})^{-1}}$$

This agrees exactly with the empirical expression, but now the constants k and m are interpreted as composites of constants for step reactions in the chain. Note that $k_1/k_5 = K$ is the equilibrium constant for the dissociation $\mathrm{Br_2} = 2\ \mathrm{Br}$.

The $\mathrm{H_2} + \mathrm{Cl_2} = 2\ \mathrm{HCl}$ reaction is more difficult to study. It is exceedingly sensitive to light, which starts a chain reaction by photodissociation of chlorine, $\mathrm{Cl_2} + h\nu \rightarrow 2\ \mathrm{Cl}$. The subsequent reaction steps are similar to those with $\mathrm{Br_2}$. The thermal reaction proceeds similarly but it is complicated by wall effects and traces of moisture and oxygen.

Why is the reaction of iodine with hydrogen so different from that of bromine or chlorine? In the iodine case the most rapid mechanism is a

TABLE 17.4

THE HYDROGEN-HALOGEN REACTIONS

APPROXIMATE ACTIVATION ENERGIES OF ELEMENTARY STEPS

	X			
	I	Br	Cl	F
$\mathrm{H_2 + X_2 = 2\ HX}$	40	41	50	>25
$\mathrm{X_2 = 2\ X}$	34	45	60	37
$\mathrm{X + H_2 = HX + H}$	34	>24	8	8
$\mathrm{H + X_2 = HX + X}$	0	1.2	2	4
$\mathrm{H + HX = H_2 + X}$	1.5	<4	6	36

homogeneous bimolecular combination, whereas with bromine the chain mechanism provides a more rapid path. Whenever parallel processes are possible, the most rapid one predominates. Approximate activation energies for the different steps in the $H_2 + X_2 = 2\,HX$ reactions are shown in Table 17.4. The most significant differences are in the $X + H_2 = HX + H$ reaction. In the case of $X = Br$, this has an $E = 24$ kcal, and for $X = I$, $E = 34$ kcal. The higher activation energy effectively prevents the chain-propagation reaction with iodine atoms.

20. Free-radical chains. During the 1920's, a number of organic-molecule decompositions were investigated that seemed to be straightforward unimolecular reactions displaying a marked Lindemann effect at low pressures. It now appears that many of these reactions may actually have complicated chain mechanisms. The clue to their character was found in the transient existence of organic *free radicals.*

In 1900, Moses Gomberg discovered that hexaphenylethane dissociates in solution into two triphenylmethyl radicals,

$$(C_6H_5)_3C—C(C_6H_5)_3 \rightarrow 2\,(C_6H_5)_3C$$

Such compounds with trivalent carbon atoms were at first believed to be chemical anomalies capable of occurring only in complex molecules.

One of the first suggestions that simple radicals might act as chain carriers in chemical reactions was made in 1925 by Hugh S. Taylor.[22] If a mixture of hydrogen and mercury vapor is irradiated with ultraviolet light of $\lambda = 2537$ Å, the mercury atoms are raised to a higher electronic state. They then react with hydrogen molecules, producing hydrogen atoms:

$$Hg(^1S_0) + h\nu(2537\ \text{Å}) \rightarrow Hg(^3P_1)$$
$$Hg(^3P_1) + H_2 \rightarrow HgH + H$$

If ethylene is added to the reaction mixture, there is a rapid reaction to form ethane, butane, and some higher polymeric hydrocarbons. Taylor suggested that the hydrogen atom combined with ethylene, forming a free ethyl radical, C_2H_5, which then started a chain reaction,

$$H + C_2H_4 = C_2H_5$$
$$C_2H_5 + H_2 = C_2H_6 + H, \text{ etc.}$$

In 1929, F. Paneth and W. Hofeditz obtained good evidence that aliphatic free radicals occur in the decomposition of molecules of the metallic alkyls, such as mercury dimethyl and lead tetraethyl. The experiment of Paneth[23] is represented in Fig. 17.10. A current of pure nitrogen at 1–2 mm pressure was saturated with lead tetramethyl vapor by passing over the liquid in *A*. The vapors were next passed through a tube heated at *B* to about 450°C. A lead mirror was deposited on the tube at the heated section, owing to the decomposition of the $Pb(CH_3)_4$. The vapors from the decomposition, after

---

[22] *Trans. Faraday Soc., 21,* 560 (1925).
[23] *Berichte, 62,* 1335 (1929).

flowing down the tube a distance of 10 to 30 cm, were passed over a previously deposited mirror of lead at 100°C. It was observed that this mirror was gradually removed. It appears therefore that the metal alkyl first breaks into free methyl radicals, $Pb(CH_3)_4 \rightarrow Pb + 4\,CH_3$. These are carried along in the stream of nitrogen for a considerable distance before they recombine to stable hydrocarbons. They remove metallic mirrors by reacting with the metal to form volatile alkyls. Thus if the mirror is zinc, $Zn(CH_3)_2$ can be recovered; if antimony, $Sb(CH_3)_3$ is recovered as the mirror is removed.

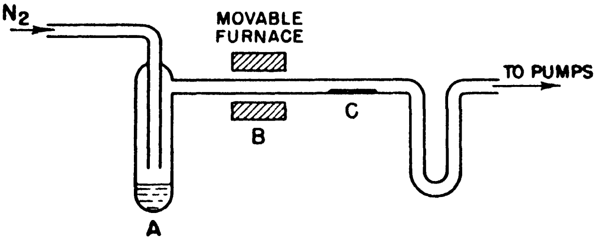


Fig. 17.10. Paneth apparatus for detection of free radicals.

From 1932 to 1934, F. O. Rice and his collaborators[24] showed that the thermal decomposition by the Paneth technique of many organic compounds such as $(CH_3)_2CO$, C_2H_6 and other hydrocarbons, gave products that would remove metal mirrors. They therefore concluded that free radicals were formed in the primary steps of the decomposition of all these molecules.

In 1935 an important theoretical advance was made by Rice and Herzfeld.[25] They showed how free-radical chain mechanisms could be devised that would lead to a simple over-all kinetics. The products from the decompositions were in good agreement with the proposed radical mechanisms. A typical example is the following possible mechanism for the decomposition of acetaldehyde, $CH_3CHO \rightarrow CH_4 + CO$.

$$\text{(1)}\quad CH_3CHO \xrightarrow{k_1} CH_3 + CHO$$

$$\text{(2)}\quad CH_3CHO + CH_3 \xrightarrow{k_2} CH_4 + CO + CH_3$$

$$\text{(3)}\quad 2\,CH_3 \xrightarrow{k_3} C_2H_6$$

One primary split into methyl radicals can result in the decomposition of many CH_3CHO molecules, since the chain carrier, CH_3, is regenerated in step (2). Applying the steady-state treatment to the CH_3 concentration,

$$\frac{d(CH_3)}{dt} = 0 = k_1(CH_3CHO) - k_3(CH_3)^2$$

so that

$$(CH_3) = \left(\frac{k_1}{k_3}\right)^{1/2} (CH_3CHO)^{1/2}$$

---

[24] F. O. Rice, *J. Am. Chem. Soc.*, *53*, 1959 (1931); F. O. Rice, W. R. Johnston, and B. L. Evering, *ibid.*, *54*, 3529 (1932); F. O. Rice and A. L. Glasebrook, *ibid.*, *56*, 2381 (1934).

[25] *J. Am. Chem. Soc.*, *56*, 284 (1934).

The reaction rate based on methane formation is then

$$\frac{d(\mathrm{CH_4})}{dt} = k_2(\mathrm{CH_3})(\mathrm{CH_3CHO}) = k_2\left(\frac{k_1}{k_3}\right)^{1/2}(\mathrm{CH_3CHO})^{3/2}$$

The free-radical scheme predicts an order of 3/2. Actually the experimental data do not permit a clear decision between a 3/2-order reaction and a first-order reaction falling off gradually to second order in accordance with the Lindemann theory.

According to the chain mechanism the empirical rate constant is actually composite: $k_{3/2} = k_2(k_1/k_3)^{1/2}$. The empirical activation energy is therefore related to the activation energies of the elementary reactions by $E_a = E_2 + \frac{1}{2}(E_1 - E_3)$.

The activation energy of the primary split E_1 can be calculated from the heat of reaction, since $Q = E_1 - E_1'$, where E_1' is the E for the reverse reaction. For a radical recombination E_1' is almost zero, so that $Q = E_1$. Thus E_1 can be set equal to the strength of the C—C bond, about 84 kcal. The energy E_2 is about 8 kcal and E_3 is close to 0. Therefore, the predicted $E_a = 8 + \frac{1}{2}(84 - 0) = 50$ kcal. The experimental E_a is 46 kcal.

A primary split into free radicals usually requires a high activation energy whereas E for an elementary decomposition into the final products may be considerably lower. Yet a rapid reaction is possible in spite of the high initial E because of the long chain of steps of low activation energy following the formation of the radicals. Sometimes the scales may be delicately balanced between the two mechanisms, and in certain temperature ranges the radical mechanism and the intramolecular-decomposition mechanism simultaneously occur to appreciable extents. There is good evidence that free-radical chains play an important role in the pyrolyses of hydrocarbons, aldehydes, ethers, ketones, metal alkyls, and many other organic compounds.

The observed first-order rate constants often decline with pressure, but the free-radical theory also has an explanation for this behavior. At low pressures it is easier for radicals to diffuse to the walls of the reaction vessel where they are destroyed by adsorption and recombination. Thus the radical chains are shorter at lower pressures and the rate constant declines.

21. Branching chains—explosive reactions. Most spectacular of chemical reactions are the explosions, which proceed so swiftly that they are completed within a fraction of a second. Special techniques are required to study their kinetics.[26] The theory of chain reactions gives a good interpretation of many of their peculiar features.

The formation of H_2O from H_2 and O_2 when the mixture is heated or reaction is otherwise initiated has been the subject of hundreds of papers, and is still a problem for active research. This reaction displays the upper and lower pressure limits characteristic of many explosions, as shown in

---

[26] See, for example, *Third Symposium on Combustion, Flame, and Explosion Phenomena* (Baltimore: Williams and Wilkins, 1949).

Fig. 17.11. If the pressure of a 2:1 mixture of H_2 and O_2 is kept below the lower line on the diagram, the thermal reaction proceeds slowly. At a temperature of 500°, this lower pressure limit is shown at 1.5 mm, but its value depends on the size of the reaction vessel. If the pressure is raised above this value, the mixture explodes. As the pressure is raised still further, there is a rather unexpected phenomenon. Above a pressure of 50 mm at 500°C there is no longer an explosion, but once again a comparatively slow reaction. This upper explosion limit is strongly temperature-dependent, but it does not vary with size of vessel.

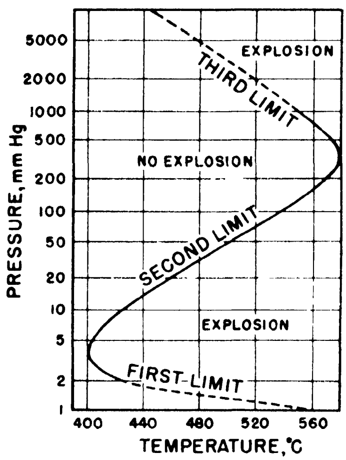


Fig. 17.11. Explosion limits of a stoichiometric hydrogen-oxygen mixture in a spherical KCl-coated vessel of 7.4 cm diameter. (After B. Lewis and G. V. Elbe, *Combustion, Flames, and Explosions of Gases*, Academic Press, 1953, p. 29.)

There are two general reasons for an explosive reaction. If an exothermic reaction is carried out in a confined space, the heat evolved often cannot be dissipated. The temperature therefore increases, so that the reaction is accelerated exponentially, and there is a corresponding rise in the rate of heat production. The reaction velocity increases practically without bound and the result is called a *thermal explosion*.

In other systems the thermal effects are less decisive, and the explosion is due to a different cause, namely, the occurrence of *branched chains* in the reaction mechanism. In the chain reactions discussed so far, each propagating sequence leads to the formation of a molecule of product and the regeneration of the chain carrier. If more than one carrier is produced from the original one, we have a branched chain.

Let us see how the possibility of branching can influence the kinetics of the following schematic chain reaction, in which R represents the reactive chain carrier:

$$A \xrightarrow{k_1} R$$

$$R + A \xrightarrow{k_2} P + \alpha R$$

$$R \xrightarrow{k_3} \text{destruction}$$

In this scheme P is the final product and α is the number of chain carriers formed from one initial R in the chain propagating step. The destruction of chain carriers can occur in two ways. They may diffuse to the walls of the reaction vessel where they become adsorbed and combine in a surface reaction, or they may be destroyed in the gas phase.

If the above scheme is to yield a steady reaction rate, $d(R)/dt$ must be zero.

$$\frac{d(R)}{dt} = 0 = k_1(A)^n - k_2(R)(A) + \alpha k_2(R)(A) - k_3(R)$$

or

$$(R) = \frac{k_1(A)^n}{k_2(A)(1 - \alpha) + k_3}$$

The probability of destruction, proportional to k_3, can be written as the sum of two terms, one k_g for the gas phase reaction, the other k_w for the wall reaction. Then

$$(R) = \frac{k_1(A)^n}{k_2(A)(1 - \alpha) + k_g + k_w} \tag{17.21}$$

In all the cases previously treated α has been unity, so that $(1 - \alpha) = 0$, leaving a radical concentration proportional to the rate of formation over the rate of destruction.

If α is greater than unity, chain branching occurs. In particular, a critical situation arises when α becomes so large that $k_2(A)(\alpha - 1) = k_g + k_w$, for then the denominator becomes zero and the carrier concentration goes to infinity. The reaction rate is proportional to the concentration of the carrier, so that it also increases without bound at this critical condition. The steady-state treatment fails completely, and the reaction goes so rapidly that there is an explosion.

It is now clear why there can be both upper and lower explosion limits. The destruction rate at the wall k_w depends on diffusion of carriers to the wall and this is more rapid at low pressures. Thus when the pressure falls to a point at which chain carriers are being destroyed at the wall as rapidly as they are being produced, an explosive reaction is no longer possible. This lower pressure limit therefore depends on the size and material of the reaction vessel: in a larger vessel fewer radicals reach the wall.

The upper explosion limit is reached when destructive collisions in the gas phase outweigh the chain branching. This upper limit usually increases sharply with temperature, because the chain initiating and propagating steps have an appreciable activation energy, whereas the chain breaking steps, being recombinations of atoms or radicals, need little activation energy. In fact, the presence of a third body is often required to carry off the excess energy generated in the highly exothermic recombination reactions. The velocity above the upper pressure limit often becomes so great that the reaction passes over into a thermal explosion.

For the hydrogen-oxygen reaction a chain scheme somewhat like the following appears to be reasonable:

(1) $H_2 + O_2 \rightarrow HO_2 + H$

(2) $H_2 + HO_2 \rightarrow OH + H_2O$

(3) $OH + H_2 \rightarrow H_2O + H$

(4) $O_2 + H \rightarrow OH + O$
(5) $H_2 + O \rightarrow OH + H$
(6) HO_2 + wall → removal
(7) H + wall → removal
(8) OH + wall → removal

The hydroxyl radical, OH, has been spectroscopically detected in the reaction mixture. Chain branching occurs in steps (4) and (5) since OH, O, and H are all active chain propagators.

22. Trimolecular reactions. The necessity of a third body to carry off the excess energy in atom recombinations is well established. Studies have shown that such reactions as $M + H + H \rightarrow H_2 + M$ and $M + Cl + Cl \rightarrow Cl_2 + M$ are of the third order. The factors that determine the relative efficiencies in promoting recombination of different third bodies M are of great interest in connection with the problem of energy transfer between molecules. In a study of the recombination of iodine and bromine atoms produced by thermal decomposition of the molecules, Rabinowitsch[27] measured the rate constants for the reaction, $X + X + M \rightarrow X_2 + M$: $-d(X)/dt = k_3(X)^2(M)$. The values of k_3 in units of (molecules/cc)$^{-2}$ sec^{-1} × 10^{32} were:

$M =$	He	A	H_2	N_2	O_2	CH_4	CO_2	C_6H_6
$X = Br$	0.76	1.3	2.2	2.5	3.2	3.6	5.4	—
$X = I$	1.8	3.8	4.0	6.6	10.5	12	18	100

It is difficult to calculate the number of "triple collisions" that occur in a gas, but a fairly good estimate should be that the ratio of binary collisions Z_{12} to triple collisions Z_{121} is equal to the ratio of the mean free path to the molecular diameter λ/d. As d is of the order of 10^{-8} cm, and λ at 1 atm pressure is about 10^{-5} cm for most gases, the ratio is about 1000. Rabinowitsch found that this ratio, Z_{12}/Z_{121}, closely paralleled the rate constants of the halogen atom-recombination reactions. In this case at least, the efficiency of the third body seems to depend mainly on the number of triple collisions it undergoes.

Besides three-body recombinations, the only known gas reactions that may be trimolecular are the third-order reactions of nitric oxide mentioned on page 536. Trautz showed that these may actually consist of two bimolecular reactions; for example,

(1) $2\,NO \rightleftharpoons N_2O_2$

(2) $N_2O_2 + O_2 \xrightarrow{k_2} 2\,NO_2$

---

[27] Rabinowitsch, *Trans. Faraday Soc.*, *33*, 283 (1937).

If equilibrium is set up in (1), $K = (N_2O_2)/(NO)^2$. Then, from (2),

$$\frac{d(NO_2)}{dt} = k_2(N_2O_2)(O_2) = k_2K(NO)^2(O_2)$$

The observed third-order constant is $k_3 = k_2K$.

23. The path of a reaction, and the activated complex. With the development of quantum theory and statistical mechanics powerful tools became available for a renewed theoretical attack on chemical kinetics. The simple collision theory can give only qualitative results. It predicts that all bimolecular gas reactions have rate constants around $10^{10}e^{-E/RT}$ liter sec^{-1} $mole^{-1}$, and it is powerless to deal with deviations from this figure. Applied to reactions in solution, the collision theory is even less adequate for there is no unequivocal way of calculating a collision frequency in solution. The newer theories of chemical kinetics dispense with the crude concept of a collision and inquire how the potential energy of the system of nuclei and electrons of the reacting molecules varies as the molecules are brought together.

This is, of course, a problem for quantum mechanics, but it would be hopeless to attempt an exact solution for complicated molecules. It may be recalled that even in calculating stable equilibrium states for molecules, the only success so far achieved has been in the case of H_2, a two-electron problem. On the experimental side, molecular spectra have provided much information about the energy levels and potential-energy diagrams of molecules, and some of these data help to elucidate molecular reactions.

The first successful application of quantum mechanics to a chemical reaction was made in 1931 by Henry Eyring and M. Polanyi.[28] They chose as their subject one of the simplest of all chemical processes, the reaction of a hydrogen atom with a hydrogen molecule.

It is possible to follow this reaction because there are two nuclear-spin isomers of H_2. Pure *para*-H_2 can be made by cooling ordinary equilibrium H_2 (3 *ortho* to 1 *para*) to $-190°C$ in contact with a charcoal catalyst. This *para*-H_2 is then stable unless it is heated to high temperatures or brought into contact with a catalyst after warming. In the presence of hydrogen atoms, the reaction $H + H_2(p) \rightarrow H_2(o) + H$ occurs. This reaction was studied by A. Farkas between 600 and 900°C, the source of H atoms being the thermal dissociation $H_2 = 2\,H$, whose equilibrium is well known. Geib and Harteck[29] followed the reaction between 0 and 100°C, using H atoms produced by passing an electric discharge through H_2. The extent of conversion could be followed by continuous measurement of the thermal conductivity of the gas, which is different for p- and o-H_2 owing to the difference in their specific heats. Both investigations agreed that the activation energy of the reaction is about 7.0 kcal.

---

[28] Eyring and Polanyi, *Z. physik. Chem.*, *B 12*, 279 (1931).

[29] K. H. Geib and P. Harteck, *Z. physik. Chem.*, *Bodenstein Festband*, 849 (1931).

The reaction between hydrogen atoms and hydrogen molecules can also be followed by using deuterium. Then, $D + H - H \rightarrow D - H + H$. The activation energy is 8.5 kcal.

Quantum mechanics treats the reaction as the problem of calculating the potential energy of a system of three hydrogen atoms for all possible distances of separation between the nuclei. It would seem at first that at least six coordinates have to be used: atom (1) could be taken as fixed, and then we could use $x_2y_2z_2$ for atom (2) and $x_3y_3z_3$ for atom (3). Fortunately, preliminary calculations showed that such great detail is not necessary; it is sufficient to calculate the potential energy of the system as one atom, say D, approaches along the line of centers of the molecule H—H. This path will be the most favorable for a reaction to follow, for in this way the approaching atom overlaps the electron cloud of only one of the two other atoms. Only two coordinates are therefore needed: r_2, the distance between the two hydrogen nuclei H_A and H_B, and r_1, the distance of D from H_A.

The reaction then consists in moving the atom D along a straight line through H—H until it reaches an intermediate configuration D—H—H. As the D atom nears the H—H, the H atom on the opposite side gradually stretches away, and finally, if reaction occurs, it departs along the line of centers, leaving as final product D—H + H.

To plot the potential energy E as a function of r_1 and r_2, a three-dimensional diagram is needed, but this plot can be represented by contour lines on a planar map. By appropriately skewing the r_1 and r_2 axes with respect to each other, it is possible to represent the conversion of translational to vibrational energy by the motion of a point (or ball) sliding on the potential-energy surface.[30]

The completed diagram for the system $D + H - H$ is shown in (a), Fig. 17.12. It will repay careful study until the three-dimensional form of the potential energy landscape can be clearly visualized from the map. Even for this simple system, the quantum-mechanical calculations are forced to rely on some rather drastic approximations, but the result is essentially correct.

Consider a cut taken through the map at $r_1 = 4.0$ Å, *i.e.*, at a D—H separation sufficiently large to leave the H—H molecule practically undistorted. The cross section, shown in (b), Fig. 17.12, is then simply the potential energy curve for the H_2 molecule that was described on page 298. The lowest level is the zero point energy of H_2, 6.2 kcal per mole. Higher levels represent vibrational excitation. The plateau at the northeast of the map corresponds to complete dissociation of both hydrogen molecules into H + H + D. In accord with our previous data from the potential-energy curve of H_2, it is 109 kcal high, or 103 kcal above the zero-point energy in H_2.

If one travels along the valley floor, following the dashed line on the

---

[30] S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (New York: McGraw-Hill, 1941), p. 100.

map, the view to right and left looks like the cross section in (b), Fig. 17.12. The elevation, however, gradually rises as one traverses the mountain pass, reaching a height of 14 kcal at the saddle point, whereupon there is a slight

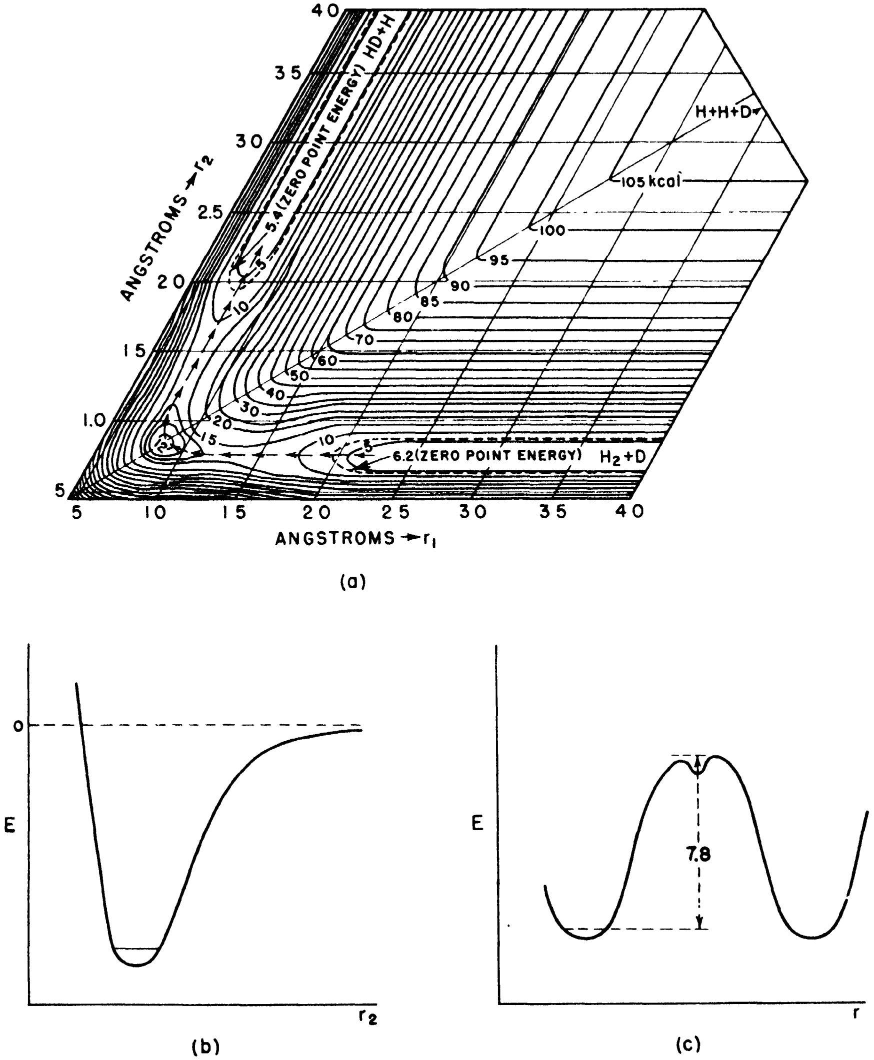


Fig. 17.12. The potential-energy surface for the reaction $D + H_2 = HD + H$. (After H. Eyring.)

dip into a shallow bowl or crater situated at the mid-point of the pass. This depression, where the arrows make a turn on the map, occurs at a configuration D—H—H, with $r_1 = r_2 = 0.95$ Å. This distance is considerably greater than the normal internuclear separation in H_2, which is 0.74 Å.

The configuration at the midpoint of the mountain pass between the two valleys is the *activated complex* for the reaction. When the system reaches this configuration, it can either decompose into DH + H by moving down into the other valley, or return along its original path into D + H_2.

If the potential energy is drawn as a function of distance along the reaction path (dashed line), Fig. 17.12 (c) is obtained. This diagram is almost the same as Fig. 17.1 on page 531, and indeed the little depression at the top of the path is not important to the argument. It is evident that the minimum energy barrier that must be surmounted is 7.8 kcal, and this is the *calculated energy of activation* for the reaction.

The potential-energy surface gives a picture of a chemical reaction from beginning to end. In any reaction there is always a certain configuration at the top of the barrier, the activated complex, which must be reached by the reactants before transformation to products can occur. Only in very simple examples can the potential-energy surface be calculated by quantum mechanics, and then only by means of drastic approximations. The important feature of the new theory, however, is the clear physical picture it gives. The concept of a collision of hard spheres is replaced by that of a smooth and continuous transition from reactants to products.

24. The transition-state theory. The rate of any chemical reaction can be formulated in terms of its activated complex.[31] The rate of reaction is simply the number of activated complexes passing per second over the top of the potential-energy barrier. This rate is equal to the concentration of activated complexes times the average velocity with which a complex moves across to the product side. It makes no difference how these complexes happen to be formed, or how many intermediate stages there may be between reactants and activated complexes. This fact vitiates at one stroke a good deal of popular speculation on mechanisms leading from reactants to complexes.

The calculation of the concentration of activated complexes is greatly simplified if it is assumed that they are in equilibrium with the reactants. This equilibrium can then be treated by means of statistical mechanics. The activated complex is not a state of stable equilibrium since it lies at a maximum and not a minimum of potential energy.[32] Yet more detailed calculations have shown that there is probably little error in treating the equilibrium by ordinary thermodynamic or statistical methods, except perhaps in the case of extremely rapid reactions.

---

[31] The quantitative formulation of reaction rates in terms of activated complexes was first extensively used in the work of H. Eyring [*J. Chem. Phys.*, *3*, 107 (1935); *Chem. Rev.*, *17*, 65 (1935)]. This theory has been applied to a wide variety of "rate processes" besides chemical reactions, such as the flow of liquids, diffusion, dielectric loss, internal friction in high polymers. Other noteworthy contributions to the basic theory were made by M. G. Evans and M. Polanyi [*Trans. Faraday Soc.*, *31*, 875 (1935)], H. Pelzer and E. Wigner [*Z. physik. Chem.*, *B 15*, 445 (1932)].

[32] Strictly speaking the activated state should lie at the maximum in *free energy*. The calculation of this would be even more difficult than the calculation of the potential energy surface.

For example, consider a simple bimolecular reaction:

$$A + B \rightarrow (AB)^{\ddagger} \rightarrow \text{products}$$

If the activated complex $(AB)^{\ddagger}$ is in equilibrium with reactants, the equilibrium constant for the formation of complexes is $K^{\ddagger} = (AB^{\ddagger})/(A)(B)$. The concentration of complexes is $(AB)^{\ddagger} = K^{\ddagger}(A)(B)$.

According to the transition-state theory, the rate of reaction is $-d(A)/dt = (AB)^{\ddagger} \times$ (rate of passage over barrier). The rate of passage over the barrier is equal to the frequency with which the complex flies apart into the products. The complex flies apart when one of its vibrations becomes a translation, and what was formerly one of the bonds holding the complex together becomes simply the line of centers between separating fragments. The frequency ν is equal to ε/h where ε is the average energy of the vibration that leads to decomposition. Since this is by hypothesis a thoroughly excited vibration at the temperature T, it has its classical energy $\varepsilon = kT$, and the corresponding frequency becomes $\nu = kT/h$.

The reaction rate is therefore

$$-\frac{d(A)}{dt} = k_2(A)(B) = K^{\ddagger}(A)(B)\frac{kT}{h}$$

The rate constant is

$$k_2 = \frac{kT}{h}K^{\ddagger} \tag{17.22}$$

This is the general expression given by the transition-state theory for the rate constant of any elementary reaction. To be precise, this expression for k_2 should be multiplied by a factor κ, the *transmission coefficient*, which is the probability that the complex will dissociate into products instead of back into reactants. For most reactions κ is between 0.5 and 1.0.

The activated complex is similar to a normal stable molecule in every respect save one. The sole difference is that one of its vibrational degrees of freedom is missing, having been transformed into the translation along the reaction coordinate that leads to disruption of the complex. Instead of $3n - 6$ vibrations, therefore, a nonlinear complex has $3n - 7$. A linear complex has $3n - 6$ instead of the $3n - 5$ for a linear normal molecule.

The statistical expression for the equilibrium constant $K^{\ddagger}$, from eq. (12.41), is

$$K^{\ddagger} = \frac{f^{\ddagger}}{f_A f_B} e^{-\Delta E_0/RT}$$

Thus

$$k_2 = \frac{kT}{h} \cdot \frac{f^{\ddagger}}{f_A f_B} e^{-\Delta E_0/RT} \tag{17.23}$$

The f's are the partition functions of activated complex and reactants, and ΔE_0 is the difference in the zero-point energies E_0 of reactants and complex, $\Delta E_0 = E_0^{\ddagger} - (E_{0A} + E_{0B} + \ldots)$.

A thermodynamic formulation of eq. (17.22) can also be given by introducing the standard free energy change, $\Delta F_c^{\circ\ddagger} = -RT \ln K_c^{\ddagger}$. Note that this is the difference between the free energy of the activated complex and that of the reactants, when all are in their standard states. In this case the standard state has been taken to be the state of *unit concentration*, because rate constants are usually expressed in terms of concentrations. Since $\Delta F^{\circ\ddagger} = \Delta H^{\circ\ddagger} - T\,\Delta S^{\circ\ddagger}$, eq. (17.22) becomes

$$k_2 = \frac{kT}{h} e^{-\Delta F^{\circ\ddagger}/RT} = \frac{kT}{h} e^{\Delta S^{\circ\ddagger}/R} e^{-\Delta H^{\circ\ddagger}/RT} \tag{17.24}$$

The quantities $\Delta F^{\circ\ddagger}$, $\Delta H^{\circ\ddagger}$, and $\Delta S^{\circ\ddagger}$ are called the *free energy of activation*, the *enthalpy* or *heat of activation*, and the *entropy of activation*.

Now $\Delta H^{\circ\ddagger}$ is almost equivalent to the experimental energy of activation E_a in the Arrhenius equation. Actually $\Delta H^{\circ\ddagger} = \Delta E^{\circ\ddagger} + P\,\Delta V^{\circ\ddagger}$. In *liquid and solid systems* the $P\Delta V$ term is negligible at ordinary pressures, so that from eq. (17.24),

$$\frac{d \ln k_2}{dT} = \frac{E_a}{RT^2} = \frac{\Delta H^{\circ\ddagger} + RT}{RT^2}, \quad \text{and} \quad E_a = \Delta H^{\circ\ddagger} + RT$$

In *ideal gases*, $\Delta H^{\circ\ddagger} = \Delta E^{\circ\ddagger} + P\Delta V^{\circ\ddagger} = \Delta E^{\circ\ddagger} + \Delta n^{\ddagger} RT$. In this case, therefore,

$$\frac{d \ln k_2}{dt} = \frac{E_a}{RT^2} = \frac{\Delta H^{\circ\ddagger} - (\Delta n^{\ddagger} - 1)RT}{RT^2}$$

and

$$E_a = \Delta H^{\circ\ddagger} - (\Delta n^{\ddagger} - 1)RT$$

The term $\Delta n^{\ddagger}$ is the number of moles of complex, always equal to one, minus the number of moles of reactants. In a unimolecular reaction, therefore, $\Delta n^{\ddagger} = 0$; in a bimolecular reaction, $\Delta n^{\ddagger} = -1$, etc. The entropy of activation can therefore readily be calculated from the experimental k and E_a.

25. Collision theory and transition-state theory. Since the activated-complex theory is more comprehensive than the collision theory, the latter should appear as one of its special cases. This can be demonstrated by considering a bimolecular reaction between two *atoms*, A and B:

$$A + B \rightarrow (AB)^{\ddagger} \rightarrow \text{products}$$

The statistical theory expresses the rate constant as

$$k_2 = \frac{kT}{h} \cdot \frac{f_{AB}^{\ddagger}}{f_A f_B} e^{-E_0/RT}$$

The activated complex $(AB)^{\ddagger}$ has five degrees of freedom, three translational and two rotational (the missing vibration has disappeared into the decomposition coordinate). The atoms A and B have translational degrees of freedom only. Using the formulas of Chapter 12, the rate constant, with concentration units of molecules per cc, can be written

$$k_2 = \frac{kT}{h} \cdot \frac{[2\pi(m_A + m_B)kT]^{3/2}h^{-3}\,\dfrac{8\pi^2 IkT}{h^2}\,e^{-E_0/RT}}{(2\pi m_A kT)^{3/2}(2\pi m_B kT)^{3/2}h^{-6}}$$

Note that the mass of the activated complex is $m^{\ddagger} = m_A + m_B$. If $r_A + r_B$ is the internuclear separation, the moment of inertia of the complex is

$$I = \frac{m_A m_B}{m_A + m_B}(r_A + r_B)^2 = \mu(r_A + r_B)^2$$

Introducing this value of I into the expression for k_2,

$$k_2 = 2(r_A + r_B)^2\left(\frac{2\pi kT}{\mu}\right)^{1/2} e^{-E_0/RT}$$

This becomes identical with the collision-theory expression in eq. (17.19) when expressed in the same units.

Thus the transition-state theory reduces to collision theory when the reactants are two atoms, or more generally, whenever all terms due to internal degrees of freedom, except two rotational terms, cancel out between reactants and activated complex. The essential defect of the collision theory is revealed to be its neglect of internal degrees of freedom. It treats the reactant molecules as rigid spheres rather than as pulsating structures of nuclei and electrons. The old steric or probability factor p was a measure of this deficiency. The transition-state theory gives a formally complete account of the effect of internal degrees of freedom, yet we never have adequate details of the dimensions of the activated complex and its vibration frequencies. The best that can be done is to assign approximate values to the partition functions, based on our experience with normal molecules.

The probability of reactions between polyatomic molecules may be lowered because rotational and translational freedoms are lost when the reactants are tied together into the activated complex. This loss of freedom or increase in order is measured also by the entropy of activation, which simply expresses the statistical factors in thermodynamic language.

26. The entropy of activation. The idea of an entropy of activation was developed by Rodebush, La Mer, and others, before the advent of the activated-complex theory, which gave it a precise formulation.

A positive activation entropy $\Delta S^{\ddagger}$ means that the entropy of the complex is greater than the entropy of the reactants. A loosely bound complex has a higher entropy than a tightly bound one. More often there is a decrease in entropy in passing to the activated state.

In bimolecular reactions the complex is formed by association of two individual molecules, and there is a loss of translational and rotational freedom, so that $\Delta S^{\ddagger}$ is negative. In fact, sometimes $\Delta S^{\ddagger}$ is not notably different from ΔS for the complete reaction. This situation is often found in reactions of the type $A + B \rightarrow AB$, and indicates that the activated complex $(AB)^{\ddagger}$ is similar in structure to the product molecule AB.

Formerly such reactions were considered to be very "abnormal" since they had to be assigned very low steric factors. It is now clear that the slow velocity is simply the result of the increase in order, and consequent decrease in entropy, when the complex is formed.

27. Theory of unimolecular reactions. The essential theoretical problem in unimolecular reactions is to extend and refine the Lindemann theory, so that we can interpret the kinetic constants in terms of the molecular structures and vibration frequencies of the reacting molecules. Once a molecule has obtained more than a certain critical amount of internal energy, it is said to be activated. The first part of the problem is to calculate the rate at which a molecule can accumulate this energy. The next question is how long will it take, on the average, for this energy to flow into the bond which is to be broken in the decomposition process. Kassel[33] and others, in 1932, modified the simple equation (17.20) to take into consideration the fact that the lifetime of an activated molecule must depend upon the amount of internal energy that it has acquired in excess of the minimum critical amount required for dissociation. This theory has been greatly extended by N. B. Slater.[34] For the limiting high-pressure rate (first-order rate constant), Slater finds the expression

$$k_1 = \nu e^{-E_0/RT} \tag{17.25}$$

where ν is a weighted root mean square of the frequencies of the normal modes of vibration of the molecule.

$$\nu = \left(\frac{\sum \alpha_i^2 \nu_i^2}{\sum \alpha_i^2}\right)^{1/2}$$

The constants α_i, called *amplitude factors*, can be calculated from the force constants of the vibrations, and the masses of the atoms in the molecule. Confirmation of the general form of eq. (17.25) is provided by the fact that molecular vibration frequencies ν are of the order of 10^{13} sec^{-1}, and the frequency factors of most unimolecular reactions cluster closely about this figure.

The more difficult part of the theory is to calculate the pressure dependence of the rate in the region where the collisional activations are insufficient to maintain a first-order kinetics. Slater has obtained a solution for this problem also, based on a treatment of the vibrating molecule as a collection of classical harmonic oscillators. The results of this theory are most encouraging, but their mathematical form is not very succinct, and we must refer the reader to the original papers for the detailed theoretical equations.

---

[33] L. S. Kassel, *J. Chem. Phys.*, *21*, 1093 (1953). This paper contains references to the earlier work.

[34] N. B. Slater, *Proc. Roy. Soc.*, *A*, *218*, 224 (1953); *Phil. Trans. A*, *246*, 57 (1953).

28. Reactions in solution. It has not been possible to make a complete theoretical analysis of the rates of reactions in liquid solutions, although many special aspects of such reactions are quite well understood. It might seem that collision theory should hardly be applicable at all, since there is no unequivocal way of calculating collision frequencies. It turns out, however, that even the gas-kinetic expressions sometimes give reasonable values for the frequency factors.

First-order reactions, such as the decomposition of N_2O_5, Cl_2O, or CH_2I_2, and the isomerization of pinene, proceed at about the same rate in gas phase and in solution. It appears, therefore, that the rate is the same whether a molecule becomes activated by collision with solvent molecules or by gas-phase collisions with others of its own kind. It is more remarkable that many second-order, presumably bimolecular, reactions have rates close to those predicted from the gas-kinetic collision theory. Some examples are shown in the last column of Table 17.5. The explanation of such an agreement seems to be the following. Any given reactant solute molecule will have to diffuse for some distance through the solution before it meets another reactant molecule. Thus the number of such encounters will be lower than in the gas phase. Having once met, however, the two reactant molecules will remain close to each other for a considerable time, being surrounded by a "cage" of solvent molecules. Thus repeated collisions between the same pair of reactant molecules may occur. The net result is that the effective collision number is not much different from that in the gas phase.

TABLE 17.5

EXAMPLES OF REACTIONS IN SOLUTION

Reaction	Solvent	E_a (kcal)	A (eq. 17.12) liter mole^{-1} sec^{-1}	A_{calc}/A_{obs}
$C_2H_5ONa + CH_3I$	C_2H_5OH	19.5	2.42×10^{11}	0.8
$C_2H_5ONa + C_6H_5CH_2I$	C_2H_5OH	19.9	0.15×10^{11}	14.5
$NH_4CNO \rightarrow (NH_2)_2CO$	H_2O	23.2	42.7×10^{11}	0.1
$CH_2ClCOOH + OH^-$	H_2O	25.9	4.55×10^{11}	0.6
$C_2H_5Br + OH^-$	C_2H_5OH	21.4	4.30×10^{11}	0.9
$(C_2H_5)_3N + C_2H_5Br$	C_6H_6	11.2	2.68×10^{2}	1.9×10^{9}
$CS(NH_2)_2 + CH_3I$	$(CH_3)_2CO$	13.6	3.04×10^{6}	1.2×10^{5}
$C_{12}H_{22}O_{11} + H_2O \rightarrow 2\,C_6H_{12}O_6$ (sucrose)	$H_2O(H^+)$	25.8	1.5×10^{15}	1.9×10^{-4}

There are other cases in which the calculated constant deviates by factors ranging from 10^9 to 10^{-9}. A high frequency factor corresponds to a large positive $\Delta S^{\ddagger}$, and a low frequency factor to a negative $\Delta S^{\ddagger}$. The remarks on the significance of $\Delta S^{\ddagger}$ in gas reactions apply equally well here.

Association reactions may be expected to have low frequency factors owing to the decrease in entropy when the activated complex is formed. An example is the Menschutkin reaction, combination of an alkyl halide with a tertiary amine: $(C_2H_5)_3N + C_2H_5Br \rightarrow (C_2H_5)_4NBr$. Such reactions have values of $\Delta S^{\ddagger}$ from -35 to -50 eu, usually nearly equal to the ΔS for the complete reaction.

A striking example of another kind is found in the rates of denaturation of proteins. Every time we boil an egg, we carry out, among other reactions, the denaturation of egg albumin from a soluble globular protein to an insoluble fibrous protein. A remarkable property of the denaturation reaction is its unusually high temperature coefficient. Atop Pikes Peak, where water boils at 91°C, it would take 12 hours to hardboil an egg (without a pressure cooker). Since about 10 minutes are required at 100°C the corresponding energy of activation is 130 kcal. This is a surprisingly high figure when it is remembered that the usual reaction proceeding at a measurable rate at 100°C has an activation energy of about 15 kcal. From an activation-energy standpoint one might think that it should be impossible to hardboil an egg at all. The reason why the reaction does proceed quite rapidly is that it has the extraordinarily high positive entropy of activation of $+315.7$ eu.

The native protein is a highly organized structure; it is the very antithesis of randomness or disorder. The denaturated protein, by contrast, is disordered and random. In such a change there is a great entropy increase, and apparently the activated complex partakes of a good deal of the disorderliness of the final product. Bound water molecules or ions may be set free on denaturation, also contributing to the increase in entropy. Hence the high $\Delta S^{\ddagger}$ and the possibility of the hardboiled egg.

29. Ionic reactions—salt effects. Electrostatic interactions cause the equilibrium properties of ionic solutions to deviate greatly from ideality. The same causes are responsible for a number of unusual features in the kinetics of reactions between ions. The first effective treatment of these reactions was provided by J. N. Brønsted and N. Bjerrum in their *activity-rate theory*. Proposed in 1922, this is essentially an activated-complex theory applied to charged particles.

Consider a reaction between two ions, A^{z_A} and B^{z_B}, z_A and z_B being the ionic charges. It proceeds through an activated complex, $(AB)^{z_A+z_B}$.

$$A^{z_A} + B^{z_B} \rightarrow (AB)^{z_A+z_B} \rightarrow \text{products}$$

Example: $$S_2O_8^{--} + I^- \rightarrow (S_2O_8{-}I)^{\equiv} \rightarrow 2SO_4^{--} + \tfrac{1}{2}I_2$$

The complex is considered to be in equilibrium with reactants, but since we are dealing with ions, it is necessary to express the equilibrium constant in activities rather than concentrations:

$$K^{\ddagger} = \frac{a^{\ddagger}}{a_A a_B} = \frac{c^{\ddagger}}{c_A c_B} \cdot \frac{\gamma^{\ddagger}}{\gamma_A \gamma_B}$$

The a's and γ's are the activities and activity coefficients. The concentration of activated complexes is $c^{\ddagger} = c_A c_B K^{\ddagger}(\gamma_A \gamma_B)/\gamma^{\ddagger}$.

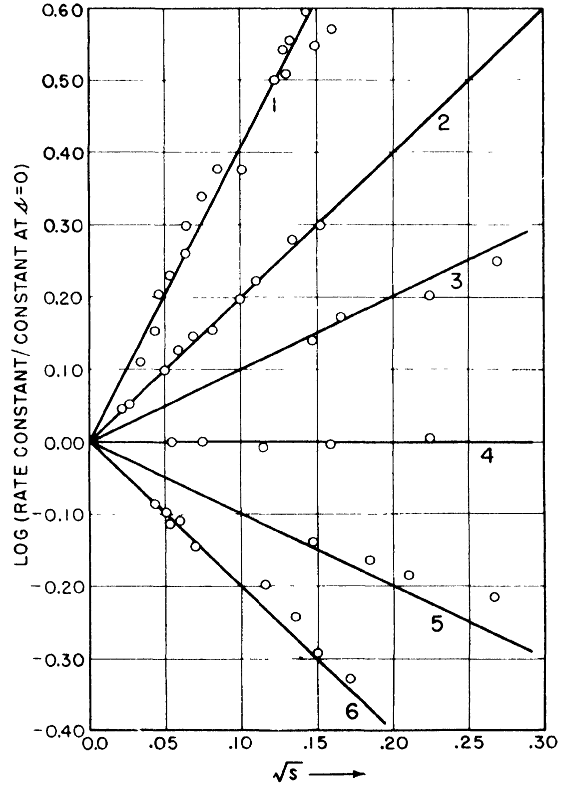


Fig. 17.13. Variations of rates of ionic reactions with the ionic strength. The circles are experimental values: the lines are theoretical, from eq. (17.27).

(1) $2[Co(NH_3)_5Br]^{++} + Hg^{++} + 2H_2O = 2[Co(NH_3)_5H_2O]^{+++} + HgBr_2$
(2) $S_2O_8^{=} + 2I^- = I_2 + 2SO_4^{=}$
(3) $[NO_2NCOOC_2H_5]^- + OH^- = N_2O + CO_3^{=} + C_2H_5OH$
(4) Inversion of cane sugar
(5) $H_2O_2 + 2H^+ + 2Br^- = 2H_2O + Br_2$
(6) $[Co(NH_3)_5Br]^{++} + OH^- = [Co(NH_3)_5OH]^{++} + Br^-$

The reaction rate is $-(dc_A/dt) = k_2 c_A c_B = (kT/h)c^{\ddagger}$. The rate constant is

$$k_2 = \frac{kT}{h} K^{\ddagger} \frac{\gamma_A \gamma_B}{\gamma^{\ddagger}} = \frac{kT}{h} \cdot \frac{\gamma_A \gamma_B}{\gamma^{\ddagger}} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT} \qquad (17.26)$$

In dilute aqueous solution the activity coefficient terms can be estimated from the Debye-Hückel theory. From eq. (15.51), at 25°C in an aqueous solution, $\log_{10} \gamma_i = -0.509\, z_i^2\sqrt{s}$. Taking the $\log_{10}$ of eq. (17.26) and substituting the Debye-Hückel expression, we get

$$\log_{10} k_2 = \log_{10} \frac{kT}{h} K^{\ddagger} + \log_{10} \frac{\gamma_A \gamma_B}{\gamma^{\ddagger}}$$

$$= B + [-0.509\, z_A^2 - 0.509\, z_B^2 + 0.509\, (z_A + z_B)^2]\sqrt{s}$$

$$\log_{10} k_2 = B + 1.018\, z_A z_B \sqrt{s} \tag{17.27}$$

The constant $\log_{10} (kT/h)K^{\ddagger}$ has been written as B.

The Brønsted equation (17.27) predicts that the plot of $\log_{10} k_2$ vs. the square root of the ionic strength should be a straight line. For a water solution at 25°C the slope is nearly equal to $z_A z_B$, the product of the ionic charges. Three special cases can occur:

(1) If z_A and z_B have the same sign, $z_A z_B$ is positive, and the rate constant increases with the ionic strength.

(2) If z_A and z_B have different signs, $z_A z_B$ is negative, and the rate constant decreases with the ionic strength.

(3) If one of the reactants is uncharged, $z_A z_B$ is zero and the rate constant is independent of the ionic strength.

Those theoretical conclusions have been verified in a number of experimental studies. A few examples are illustrated in Fig. 17.13. This change of k_2 with s is called the *primary kinetic salt effect*. It should be noted that the ionic strength s is calculated from $\Sigma\ \frac{1}{2} m_i z_i^2$, and the summation is extended over all the ionic species present in solution, not merely the reactant ions.

Much of the earlier work on ionic reactions is comparatively useless because the salt effect was not understood. It is now often the practice in following the rate of an ionic reaction to add a considerable excess of an inert salt, *e.g.*, NaCl, to the solution, so that the ionic strength is effectively constant throughout the reaction. If pure water is used, the change in ionic strength as the reaction proceeds may lead to erratic velocity constants.

30. Ionic reaction mechanisms. Besides the salt effect discussed by Brønsted, specific interactions between the ions in solution may influence the reaction rates. For reactions between ions of the same charge sign, the salt effect often appears to be governed predominantly by the concentrations and charges of those added ions with a sign opposite to that of the reactant ions.[35]

The mechanism of ionic reactions is often indirectly determined by electrostatic factors, in particular the strong repulsion between ions of the same sign. The reaction $2\ Fe^{+3} + Sn^{+2} = 2\ Fe^{+2} + Sn^{+4}$, for example, occurs rapidly, but the mechanism is probably a series of steps involving the transfer of single electrons between species of opposite charge sign:[36]

$$SnCl_2 + 2\ Cl^- \rightleftharpoons SnCl_4^{--}$$

$$SnCl_4^{--} + Fe^{+3} \rightarrow Fe^{+2} + SnCl_4^-$$

$$SnCl_4^- + Fe^{+3} \rightarrow Fe^{+2} + SnCl_4$$

---

[35] A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, *17*, 1167 (1949).

[36] J. Weiss, *J. Chem. Soc.*, 309 (1944).

Another instance is the over-all reaction,

$$5\ HBr + HBrO_3 = 3\ Br_2 + 3\ H_2O$$

The rate equation is $d(Br_2)/dt = k(H^+)^2(Br^-)(BrO_3^-)$. Note that the rate equation bears no relation to the stoichiometric equation. Owing to electrostatic repulsion, it is unlikely that Br^- and BrO_3^- ions react directly, and the following rate controlling step is suggested by the rate equation:

$$HBr + HBrO_3 \rightarrow HBrO + HBrO_2$$

Rapid secondary reactions yield the final products. Since $(HBr) \sim (H^+)(Br^-)$, and $(HBrO_3) \sim (H^+)(BrO_3^-)$, the observed kinetics is obtained.

31. Catalysis. The word "catalysis" (*Katalyse*) was coined by Berzelius in 1835: "Catalysts are substances which by their mere presence evoke chemical reactions that would not otherwise take place." The Chinese *Tsoo Mei* is more picturesque; it also means "the marriage broker," and so implies a theory of catalytic action. The idea of catalysis extends far back into chemical history. The quest of the alchemist for the philosopher's stone seems like the search of the modern petroleum chemist for the magical catalyst that will convert crude petroleum into high octane fuel. In a fourteenth-century Arabian manuscript, Al Alfani described the "Xerion, aliksir, noble stone, magisterium, that heals the sick, and turns base metals into gold, *without in itself undergoing the least change*." The earliest consciously used catalysts were the ferments or enzymes. "In the seeding and growth of plants, and in the diverse changes of the fluids of the animal body in sickness and in health, a fermentative action takes place" (Marquers, 1778).

Noteworthy was the idea that a mere trace of catalyst suffices to produce great changes, without itself being changed. Its action has been likened to that of a coin inserted in a slot machine that yields valuable products and also returns the coin. In a chemical reaction the catalyst enters at one stage and leaves at another. The essence of catalysis is not the entering but the falling out.

Wilhelm Ostwald was the first to emphasize that the catalyst influences the rate of a chemical reaction but has no effect on the position of equilibrium. His famous definition was: "A catalyst is a substance that changes the velocity of a chemical reaction without itself appearing in the end products." Ostwald showed that a catalyst cannot change the equilibrium position, by a simple argument based on the First Law of Thermodynamics. Consider a gas reaction that proceeds with a change in volume. The gas is confined in a cylinder fitted with a piston; the catalyst is in a small receptacle within the cylinder, and can be alternately exposed and covered. If the equilibrium position were altered by exposing the catalyst, the volume would change, the piston would move up and down, and a perpetual-motion machine would be available.

Since a catalyst can change the rate but not the equilibrium, it follows that a catalyst must accelerate the forward and reverse reactions in the same proportion, since $K = k_f/k_b$. Thus catalysts that accelerate the hydrolysis of esters must also accelerate the esterification of alcohols; dehydrogenation catalysts like nickel and platinum are also good hydrogenation catalysts; enzymes like pepsin and papain that catalyze the splitting of peptides must also catalyze their synthesis from the amino acids.

A distinction is generally made between homogeneous catalysis, the entire reaction occurring in a single phase, and heterogeneous catalysis at phase interfaces. The latter is also called *contact* or *surface catalysis.*

32. Homogeneous catalysis. An example of homogeneous catalysis in the gas phase is the effect of iodine vapor on the decomposition of aldehydes and ethers. The addition of a few per cent of iodine often increases the rate of pyrolysis several hundredfold. The reaction velocity follows the equation,

$$\frac{-d\,(\text{ether})}{dt} = k_2\,(I_2)\,(\text{ether})$$

Dependence of the rate on catalyst concentration is characteristic of homogeneous catalysis. The catalyst acts by providing a path for the decomposition that has a considerably lower activation energy than the uncatalyzed path. In this instance the uncatalyzed pyrolysis has an $E_a = 53$ kcal, whereas with added iodine the E_a drops to 34 kcal.

Most examples of homogeneous catalysis have been studied in liquid solutions. In fact, catalysis in solution is the rule rather than the exception, and it can even be maintained that most reactions in liquid solutions would not proceed at an appreciable rate if catalysts were rigorously excluded. Since the catalysts are usually acids and bases, it is not easy to controvert this hypothesis.

The general formulation of catalysis in solution postulates the formation of an intermediate complex between reactant and catalyst. Suppose the change $A \rightarrow B$ is catalyzed by a substance X, through formation of an intermediate I. Then

$$A + X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I, \qquad I \xrightarrow[k_2]{} B + X$$

Making the steady-state assumption, $d(I)/dt = 0$, we find

$$\frac{d(B)}{dt} = \frac{k_1 k_2 (A)(X)}{k_{-1} + k_2} = k'(A)(X) \tag{17.28}$$

Two limiting cases of eq. (17.28) now arise. If $k_{-1} \gg k_2$, most of the complexes I revert to the initial reactant A, and only a small fraction proceed to the final product B. Then eq. (17.28) becomes $(k_1 k_2/k_{-1})\,(A)(X)$, and the decomposition of the intermediate is the rate-determining step. In a case like this, I is called an *Arrhenius intermediate.*

The other limiting case is $k_2 \gg k_{-1}$. Then the slow step is the rate of formation of intermediate I, and eq. (17.28) reduces to $k_1(A)(X)$. This kind of *I* is called a *van't Hoff intermediate*. In either case, the over-all rate is proportional to the catalyst concentration (X).

The distinction between the two types of intermediate is in most cases difficult or impossible to make experimentally.[37] In any case, the catalysts usually act by lowering the activation energy of the reaction.

The reaction, $2I^- + S_2O_8^= \rightarrow I_2 + 2SO_4^=$, is markedly catalyzed by ferrous or ferric ions. Copper ions have a lesser effect. When Fe^{++} and Cu^{++} ions are both added, their effects are not simply additive; the rate is still more enhanced. This phenomenon is called *promoter action* and is often observed in catalysis. For example, $N/2{,}500{,}000$ Cu^{++} has itself no detectable effect on the velocity, but added to a reaction mixture that already contains $N/32{,}000$ Fe^{++}, it increases the rate by 15 per cent. A possible explanation is that the promoter selectively catalyzes the decomposition of the intermediate formed with the first catalyst, *i.e.*, it increases the constant k_2 in eq. (17.28).

33. Acid-base catalysis. Among the most interesting cases of homogeneous catalysis are reactions catalyzed by acids and bases. This acid-base catalysis is of the utmost importance, governing the rates of a great number of organic reactions, and especially many of the processes of physiological chemistry, for it is likely that many enzymes act as acid-base catalysts.

The earliest studies in this field were those by Kirchhoff in 1812 on the conversion of starch to glucose by the action of dilute acids, and by Thénard in 1818 on the decomposition of hydrogen peroxide in alkaline solutions. The classic investigation of Wilhelmy in 1850 dealt with the rate of inversion of cane sugar by acid catalysts. The hydrolysis of esters, catalyzed by both acids and bases, was extensively studied in the latter half of the nineteenth century. The catalytic activity of an acid in these reactions became one of the accepted measures of "acid strength," being very useful to Arrhenius and Ostwald in the early days of the ionization theory.

In Table 17.6 are some of Ostwald's results on sucrose inversion and methyl-acetate hydrolysis. If we write the acid as HA these reactions are

$$C_{12}H_{22}O_{11} + H_2O + HA \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6 + HA$$
$$CH_3COOCH_3 + H_2O + HA \rightarrow CH_3COOH + CH_3OH + HA$$

The reaction rate may be written $dx/dt = k'(CH_3COOCH_3)(H_2O)(HA)$. Since the water is present in large excess, its concentration is effectively constant. The rate therefore reduces to: $dx/dt = k''(HA)(CH_3COOCH_3)$. Now k'' is called the *catalytic constant*. The values in Table 17.6 are all relative to HCl = 100.

Ostwald and Arrhenius showed that the catalytic constant of an acid is proportional to its equivalent conductivity. They concluded that the nature of the anion was unimportant, and that the only active catalyst was the hydrogen ion, H^+.

---

[37] Cf. G. M. Schwab, H. S. Taylor, and R. Spence, *Catalysis* (New York: Van Nostrand, 1937), p. 68.

TABLE 17.6

OSTWALD'S DATA ON THE CATALYTIC CONSTANTS OF DIFFERENT ACIDS

Acid	Relative Conductivity	k'' (ester)	k'' (sugar)
HCl	100	100	100
HBr	101	98	111
HNO_3	99.6	92	100
H_2SO_4	65.1	73.9	73.2
CCl_3COOH	62.3	68.2	75.4
$CHCl_2COOH$	25.3	23.0	27.1
HCOOH	1.67	1.31	1.53
CH_3COOH	0.424	0.345	0.400

In other reactions it was necessary to consider the effect of the OH^- ion and also the rate of the uncatalyzed reaction. This led to a three-term equation for the observed rate constant, $k = k_0 + k_{H^+}(H^+) + k_{OH^-}(OH^-)$. Since in aqueous solution $K_w = (H^+)(OH^-)$,

$$k = k_0 + k_{H^+}(H^+) + \frac{k_{OH}\,K_w}{(H^+)} \tag{17.29}$$

Since K_w is about 10^{-14}, in 0.1 N acid (OH^-) is 10^{-13}, and in 0.1 N base (OH^-) is 10^{-1}. There is a 10^{12}-fold change in (OH^-) and (H^+) in passing from dilute acid to dilute base. Therefore the (OH^-) catalysis will be negligible in dilute acid and the (H^+) catalysis negligible in dilute base, except in the unusual event that the catalytic constants for H^+ and OH^- differ by as much as 10^{10}. By measurements in acid and basic solutions it is therefore generally possible to evaluate k_{H^+} and k_{OH^-} separately.

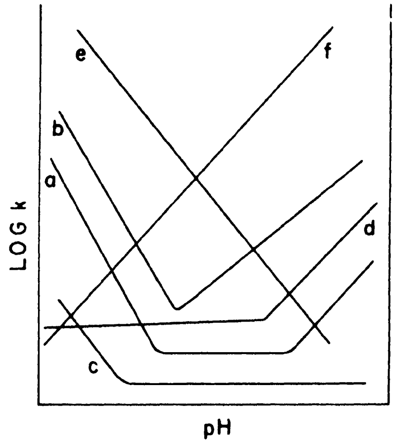


Fig. 17.14. Acid-base catalysis: the influence of pH on rate constants.

If $k_{H^+} = k_{OH^-}$, a minimum in the over-all rate constant occurs at the neutral point. If either k_{H^+} or k_{OH^-} is very low, there is no rise in k on the corresponding side of the neutral point. These and other varieties of rate constant vs. pH curve, arising from different relative values of k_0, k_{H^+}, and k_{OH^-}, are shown in Fig. 17.14.

Examples of each of the different types have been studied experimentally.[38] They include the following:

(a) The mutarotation of glucose

(b) Hydrolysis of amides, γ-lactones, esters; halogenation of acetone

(c) Hydrolysis of alkyl orthoacetates

(d) Hydrolysis of β-lactones, decomposition of nitramide, halogenation of nitroparaffins

(e) Inversion of sugars, hydrolysis of diazoacetic ester, acetals

(f) Depolymerization of diacetone alcohol; decomposition of nitrosoacetonamine

34. General acid-base catalysis. Advances in our understanding of acid-base catalysis have been closely linked with improvements in the theory of electrolytic solutions. The early notion that the conductance ratio, Λ/Λ_0, of a strong electrolyte measures its degree of dissociation has been superseded by the Debye-Hückel idea of complete ionization. In fact, one of the first evidences for the latter viewpoint was the observation of Bjerrum that the catalytic activity of strong acids is proportional to their total concentration in solution rather than to the H^+ concentration as calculated from the Arrhenius theory.

The influence of added salts in the primary kinetic salt effect has already been noted. In addition to this direct dependence of reaction rate on ionic strength, there is an indirect influence important in catalyzed reactions. In solutions of weak acids and bases, added salts, even if they do not possess a common ion, may change the H^+ or OH^- ion concentration through their effect on the activity coefficients. For an acid $HA \rightarrow H^+ + A^-$,

$$K = \frac{a_{H^+}a_{A^-}}{a_{HA}} = \frac{c_{H^+}c_A}{c_{HA}} \cdot \frac{\gamma_{H^+}\gamma_{A^-}}{\gamma_{HA}}$$

Any change in the ionic strength of the solution affects the γ terms and hence the concentration of H^+. Consequently, if the reaction is catalyzed by H^+ or OH^- ions, the reaction rate is dependent on the ionic strength. This is called the *secondary kinetic salt effect.* Unlike the primary effect it does not alter the *rate constant* provided this is calculated from the true H^+ or OH^- concentration.

The broader picture of the nature of acids and bases given by the work of Brønsted and Lowry (page 469) implies that not only H^+ and OH^- but also the undissociated acids and bases should be effective catalysts. The

---

[38] See A. Skrabal, *Z. f. Elektrochem.*, *33*, 322 (1927); R. P. Bell, *Acid-Base Catalysis* (New York: Oxford, 1941).

essential feature of catalysis by an acid is the transfer of a proton from acid to substrate,[39] and catalysis by a base involves the acceptance of a proton by the base. Thus in Brønsted-Lowry nomenclature, the substrate acts as a base in acid catalysis, or as an acid in basic catalysis. In the case of hydrogen ion catalysis in aqueous solution, the acid is really the hydronium ion, OH_3^+.

For example, the hydrolysis of nitramide is susceptible to basic but not to acid catalysis.

$$\begin{aligned} NH_2NO_2 + OH^- &\rightarrow H_2O + NHNO_2^- \\ NHNO_2^- &\rightarrow N_2O + OH^- \end{aligned}$$

Not only the OH^- ion but also other bases can act as catalysts, *e.g.*, the acetate ion:

$$\begin{aligned} NH_2NO_2 + CH_3COO^- &\rightarrow CH_3COOH + NHNO_2^- \\ NHNO_2^- &\rightarrow N_2O + OH^- \\ OH^- + CH_3COOH &\rightarrow H_2O + CH_3COO^- \end{aligned}$$

The reaction rate with different bases B is always $v = k_B(B)(NH_2NO_2)$. Brønsted found that there was a relation between the catalytic constant k_B and the dissociation constant K_B of the base, namely,

$$k_B = CK_B^{\beta} \tag{17.30}$$

or

$$\log k_B = \log C + \beta \log K_B$$

Here C and β are constants for bases of a given charge type. Thus the stronger the base, the higher the catalytic constant.[40]

The nitramide hydrolysis displays *general basic catalysis*. Other reactions provide examples of *general acid catalysis*, with a relation like eq. (17.30) between k_A and K_A. There are also reactions with both general acid and general basic catalysis.

Since a solvent like water can act as either an acid or a base, it is often itself a catalyst. What was formerly believed to be the uncatalyzed reaction, represented by k_0 in eq. (17.29), is in most cases undoubtedly a reaction catalyzed by the solvent acting as acid or base.

35. Heterogeneous reactions. In our description of homogeneous reactions a number of instances have been noted in which the surface of the reaction vessel has a definite influence on the kinetics. Such an effect is very important in establishing the lower pressure limit of an explosive chain reaction. There are many reactions whose velocities are immeasurably slow in homogeneous gaseous or liquid solutions, but which go quite swiftly if a suitable solid surface is available. In fact, in some instances the solid surface can alter the entire course of the reaction.

The earliest instance of this *contact action* or *contact catalysis* was the dehydrogenation of alcohols by metals studied by van Marum in 1796. In

---

[39] Substance whose reaction is being catalyzed.

[40] For polybasic bases, a correction must be made. See R. P. Bell, *op. cit.*, p. 83.

1817, Davy and Döbereiner investigated the glowing of certain metals in a mixture of air and combustible gases; and in 1825, Faraday worked on the catalytic combination of hydrogen and oxygen. These studies laid the experimental foundations of heterogeneous kinetics.

An interesting example was found[41] in the bromination of ethylene: $C_2H_4 + Br_2 = C_2H_4Br_2$. This reaction goes quite readily in a glass vessel at 200°C, and it was at first thought to be an ordinary homogeneous combination, but the rate seemed to be higher in smaller reaction vessels. When the vessel was packed with lengths of glass tubing or with glass beads, the rate was considerably enhanced. This method is frequently used for detecting wall reactions. An increased rate in a packed vessel indicates that a considerable share of the observed reaction is heterogeneous, on the packing and wall, rather than homogeneous, in the gas phase only. A further test was made by coating the inside of the reaction bulb with paraffin wax. This coating inhibited the reaction almost completely.

The decomposition of formic acid illustrates the specificity often displayed by surface reactions. If the acid vapor is passed through a heated glass tube, the reaction is practically one-half dehydration and one-half dehydrogenation.

$$\text{(1)} \qquad HCOOH \rightarrow H_2O + CO$$
$$\text{(2)} \qquad HCOOH \rightarrow H_2 + CO_2$$

If the tube is packed with alumina, Al_2O_3, only reaction (1) occurs; but if it is packed with zinc oxide, ZnO, (2) is the exclusive result. Thus different surfaces can accelerate different parallel paths, and so in effect determine the nature of the products.

It seems evident that the catalytic action of a surface depends on its adsorption of the reactants. Many features of heterogeneous kinetics can be explained by this hypothesis and the application of Langmuir's equation.

A surface reaction can usually be broken into the following elementary steps:

(1) Diffusion of reactants to surface
(2) Adsorption of reactants at surface
(3) Chemical reaction on the surface
(4) Desorption of products from surface
(5) Diffusion of products away from surface

These are consecutive steps and if any one is much slower than all the others, it will become rate-determining.

Steps (1) and (5) are usually rapid. Only with extremely active catalysts might they determine the over-all rate. Diffusion has a $\sqrt{T}$ and chemical reaction has an $e^{-E/RT}$ temperature dependence. Therefore, if a catalytic reaction rate increases only slightly with temperature, it may be diffusion-controlled.

---

[41] R. G. W. Norrish, *J. Chem. Soc.*, 3006 (1923).

Steps (2) and (4) are generally more rapid than step (3), but reactions are known in which they may be the slow stages. Usually, however, the reaction at the surface, step (3), is believed to be rate-determining.

36. Gas reactions at solid surfaces. The Langmuir isotherm (page 515) is based on the gradual coverage of a surface with adsorbed molecules, saturation occurring when the adsorbed layer is uniformly one molecule thick. The isotherm is especially applicable to cases of chemisorption, in which the adsorbed molecules are held to the surface by bonds comparable with those in chemical compounds. This is also the kind of adsorption that can greatly accelerate reaction rates, the chemisorbed layer playing the role of an intermediate compound in catalyzing the reaction. On the other hand, physical or van der Waals adsorption can hardly have more than the slight effect on reaction rates caused by an increased concentration in the adsorbed layer.

The Langmuir isotherm was illustrated in Fig. 16.10 on page 516. It can be roughly divided into three sections: (a) the range of small adsorption or nearly bare surface, where the fractional surface coverage $\theta = bP$; (b) an intermediate region in which approximately $\theta = bP^{1/n}$; (c) the region of almost complete coverage, where effectively $\theta = 1$ over a considerable pressure range. The particular adsorbate gas and adsorbent solid will determine the region of the isotherm useful in a given system. If a gas is strongly adsorbed, the surface may be almost covered even at low pressures; but if a gas is weakly adsorbed, the linear section $\theta = bP$ may extend to quite high pressures.

In a heterogeneous gas reaction, it can usually be assumed that only the adsorbed gas undergoes reaction.[42] If a single reactant is being decomposed at an active surface, three simple special cases can arise. The reaction rate will be proportional to θ, the fraction of surface covered.

(1) Single reactant, weakly adsorbed, $\theta = bP$. Rate: $-dP/dt = k\theta = k\,bP = k'P$. The reaction is first order. Examples of this kind include the decomposition of arsine and phosphine on glass, $AsH_3 \rightarrow As + \frac{3}{2}\,H_2$; hydrogen iodide on platinum, $2\,HI \rightarrow H_2 + I_2$.

(2) Single reactant, moderately adsorbed, $\theta = bP^{1/n}$. Rate: $-dP/dt = k\,b\theta = k\,bP^{1/n} = k'P^{1/n}$. An example is the decomposition of arsine on a surface of metallic arsenic, following the equation $-dP/dt = kP^{0.6}$.

(3) Single reactant, strongly adsorbed, $\theta = 1$. Rate: $-dP/dt = k_0 = k_0P^0$. In such a case the reaction velocity is independent of the pressure. This is called a *zero-order reaction*, a variety of concentration dependence having no parallel in purely homogeneous reactions. The integrated rate equation is $-P = k_0t +$ const or

$$P_0 - P = k_0t \tag{17.31}$$

where P_0 is the initial pressure. When $P = \frac{1}{2}P_0$, $t = \tau$ the half life, so that

---

[42] I. Langmuir, *Trans. Faraday Soc.*, *17*, 621 (1921).

$\tau = \frac{1}{2}(P_0/k_0)$. Examples of zero-order reactions include the decomposition of hydrogen iodide on gold and of ammonia on tungsten. Note that HI on Pt is first order, but HI on Au is zero order. It can be concluded that HI is strongly adsorbed on Au, but only weakly adsorbed on Pt.

Many of these reactions on metal surfaces can be conveniently studied by means of wire filaments sealed into bulbs that can be filled with reactant. The wire can be heated by passage of an electric current and its temperature calculated from the electric resistance. A manometer is attached to the bulb to measure pressure changes.

37. Inhibition by products. So far only adsorption of the reactants has been considered. In other reactions the products are also adsorbed by the solid catalyst, and the competition between reactant and product molecules for the available surface is revealed in the rate equations.

If two adsorbates, A and B, are rivals for the same surface, the kinetic treatment of Langmuir can be applied to the condensation and evaporation of each of them. Corresponding with eq. (16.19), the following result is obtained for θ_A and θ_B, the fractions of area covered by A and B at partial pressures P_A and P_B, with adsorption coefficients b_A and b_B.

$$\theta_A = \frac{b_A P_A}{1 + b_A P_A + b_B P_B}, \quad \theta_B = \frac{b_B P_B}{1 + b_A P_A + b_B P_B} \tag{17.32}$$

The kinetic equations that arise owing to adsorption of two gases can usually be interpreted by these Langmuir isotherms. The following are important special cases:

(1) Reactant A is weakly adsorbed and a product B is strongly adsorbed. Then $b_A P_A \ll b_B P_B \gg 1$. The reaction velocity is still proportional to θ_A, the surface covered with reactant, which in this case, from eq. (17.32), is $\theta_A = b_A P_A / b_B P_B$. Thus, $-dP_A/dt = k'\theta_A = kP_A/P_B$. An example of this behavior is found in the decomposition of ammonia on a platinum filament, $2\,NH_3 \rightarrow N_2 + 3\,H_2$, the rate law being $-dP_{NH_3}/dt = kP_{NH_3}/P_{H_2}$. The product, H_2, is strongly adsorbed and inhibits the reaction.

(2) Both reactant and product are strongly adsorbed. Then $b_A P_A \gg 1 \ll b_B P_B$, and $\theta = b_A P_A/(b_A P_A + b_B P_B)$. In the dehydration of ethanol on a copper catalyst,

$$C_2H_5OH \rightarrow C_2H_4 + H_2O$$

$$\frac{-d(C_2H_5OH)}{dt} = \frac{kP_{C_2H_5OH}}{bP_{C_2H_5OH} + b'P_{H_2O}}$$

Traces of water are strongly adsorbed and severely inhibit the reaction.

38. Two reactants on a surface. From the examples already described, it is simple to extend the Langmuir isotherm treatment to the interaction of two gases. Usually only the results need be cited, since they are readily derived from eq. (17.32).

With two reactants, both weakly adsorbed, the rate is $-dP/dt = k\theta_A\theta_B = k_2 P_A P_B$. This yields a regular second-order kinetics so that such reactions might sometimes be mistaken for homogeneous bimolecular processes. An example is the previously mentioned bromination of ethylene on glass.

An interesting case is that of two reactants, A weakly and B moderately adsorbed. Then,

$$\theta_A = \frac{b_A P_A}{(1 + b_B P_B)}, \qquad \theta_B = \frac{b_B P_B}{(1 + b_B P_B)}$$

$$-\frac{dP}{dt} = k\theta_A\theta_B = \frac{k b_A b_B P_A P_B}{(1 + b_B P_B)^2} = k' \frac{P_A P_B}{(1 + b_B P_B)^2}$$

If P_B is held constant while P_A is varied, the reaction appears to be first-order with respect to A. On the other hand, if P_A is held constant while P_B is varied, the rate first rises with P_B, then passes through a maximum and declines. The maximum occurs at $P_B = 1/b_B$. In physical terms, when the pressure of B becomes too high, B begins to usurp more than its fair share of the surface and ultimately inhibits the rate.

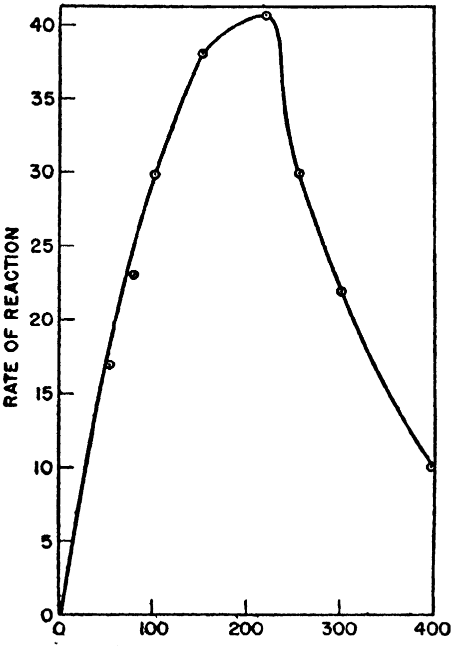


Fig. 17.15. Effect of CO_2 pressure on the water-gas reaction at a platinum surface.

Hinshelwood and Prichard[43] found that the water-gas reaction ($H_2 + CO_2 \rightarrow H_2O + CO$) on a platinum filament at 1000°C conformed to this behavior. Normally this reaction would proceed in both directions, but a

[43] *J. Chem. Soc.*, 806 (1925).

clever expedient rendered it essentially unidirectional. The bulb with the heated filament was completely immersed in a freezing mixture of dry ice and ether, so that as soon as any water vapor formed, it condensed immediately on the walls. Under these conditions and a fixed hydrogen pressure of 100 mm, the results shown in Fig. 17.15 were obtained for the dependence of velocity on the carbon dioxide pressure.

The case of reactant A weakly and B strongly adsorbed obviously leads to $-dP/dt = kP_A/P_B$. Bodenstein found for the oxidation of carbon monoxide on hot quartz, $CO + \frac{1}{2} O_2 \rightarrow CO_2$, $-dP_{CO}/dt = kP_{CO}/P_{O_2}$. The oxygen is strongly adsorbed.

The success of the simple Langmuir isotherms in explaining so many features of heterogeneous gas reactions is indeed one of the most encouraging chapters in chemical kinetics. The phenomena are so diverse and remarkable that they would certainly be completely mystifying without the underlying pattern traced by the theoretical interpretation.

39. Effect of temperature on surface reactions. In all the surface reactions so far discussed it would appear that the slowest step is the actual chemical change occurring in the adsorbed molecules. Neither the rate of adsorption nor the rate of desorption seems to be directly rate-determining, since a satisfactory explanation of the kinetics is given by the Langmuir isotherm, which assumes that the adsorption-desorption equilibrium is established. The observed rate is then determined by the amount of surface covered by reacting molecules and by the specific velocity of the surface reaction. The influence of temperature on the rate therefore must include two factors, the effect on the surface area covered, and the effect on the surface reaction itself.

The plot of $\log k$ vs. $1/T$ is usually linear for a heterogeneous reaction, just as it is in the homogeneous case. From the slope of the straight line an activation energy E_a can be calculated by using the Arrhenius equation. This E_a is called the *apparent activation energy*, since it is usually a composite quantity, including not only the true activation energy of the surface reaction E_t, but also heats of adsorption of reactants and products. The relation between E_a and E_t depends on the particular kinetics followed.

A zero-order reaction is a particularly simple case, since here $\theta = 1$, and as long as the reaction remains zero-order, the fraction of surface covered is independent of temperature, and E_a always equals E_t. The decomposition of HI on gold is a zero-order reaction with $E_a = E_t = 25$ kcal. The homogeneous gas phase decomposition has an $E_a = 44$ kcal. The lowering of the activation energy by 19 kcal is a measure of the marked catalytic effect of the metal surface. An even greater lowering is observed in the zero-order decomposition of ammonia on tungsten with $E_a = 39$ kcal. The homogeneous reaction has an activation energy of over 90 kcal.

If the reactant is weakly adsorbed there are two superimposed temperature effects on the velocity, since the fraction of surface covered is usually strongly temperature-dependent.

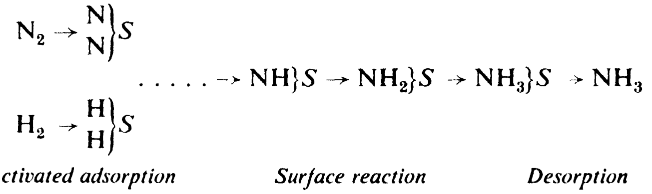
The relation between true and apparent activation energies becomes $E_a = E_t - \lambda$, where λ is the heat of adsorption. The true activation energy of the surface reaction is lowered by an amount equal to the heat of adsorption.[44]

If $-dP/dt = kP_A/P_B$ (reactant A weakly adsorbed, product or second reactant B strongly adsorbed) the relation is $E_a = E_t - \lambda_A + \lambda_B$. For example, Hinshelwood found $E_a = 140$ kcal for the decomposition of ammonia on platinum. Then $E_a = E_t - \lambda_{NH_3} + \lambda_{H_2}$. The heat of adsorption of hydrogen is around 110 kcal. Since the ammonia is weakly adsorbed, λ_{NH_3} is probably only about 5 kcal. Thus $140 = E_t - 5 + 110$, or $E_t = 35$ kcal. On tungsten, the ammonia decomposition is zero order, and $E_a = E_t = 39$ kcal.

40. Activated adsorption. Often the potential-energy barrier that must be surmounted before adsorption can occur is small or negligible, and the adsorption rate is governed by the rate of supply of gas to the bare surface. Sometimes, however, a considerable activation energy, E_{ad}, may be required for adsorption, and its rate, $ae^{-E_{ad}/RT}$, may become slow enough to determine the over-all speed of a surface reaction. Adsorption that requires an appreciable activation energy has been called *activated adsorption*.

The chemisorption of gases on metals usually does not require any appreciable activation energy. The work of J. K. Roberts[45] showed that the adsorption of hydrogen on carefully cleaned metal filaments proceeds rapidly even at about 25°K, to form a tightly held monolayer of adsorbed hydrogen atoms. The heat of adsorption is close to that expected for the formation of covalent metal-hydride bonds. These results were confirmed and extended to other metal-gas systems in the work of O. Beeck with evaporated metal films.[46]

One important exception to this type of behavior has been found in the adsorption of nitrogen on an iron catalyst at about 400°C.[47] This adsorption is a slow activated adsorption and it seems to be the rate determining step in the synthesis of ammonia of these catalysts. If S is the catalyst surface, the reaction can be represented as follows:



$$\begin{array}{l} N_2 \rightarrow \left.\begin{matrix}N\\N\end{matrix}\right\}S \\ \qquad\qquad \ldots\ldots \rightarrow NH\}S \rightarrow NH_2\}S \rightarrow NH_3\}S \rightarrow NH_3 \\ H_2 \rightarrow \left.\begin{matrix}H\\H\end{matrix}\right\}S \end{array}$$

Activated adsorption *Surface reaction* *Desorption*

The adsorption and activation of the hydrogen was ruled out as the slow step because the exchange reaction $H_2 + D_2 \rightleftharpoons 2\ HD$ occurs on the catalyst

---

[44] The reader can easily outline the derivations. See Schwab, Taylor, and Spence, *op. cit.*, p. 236.

[45] J. K. Roberts, *Some Problems in Adsorption* (London: Cambridge, 1939).

[46] O. Beeck, *Discussions Faraday Soc.*, *8*, 118 (1950).

[47] P. H. Emmett and S. Brunauer, *J. Am. Chem. Soc.*, *62*, 1732 (1940).

even at liquid-air temperatures, presumably via the dissociation of H_2 and D_2 into adsorbed atoms. Then it was found that the hydrogens in NH_3 are readily exchanged with deuterium from D_2 on the catalyst at room temperature. This indicates that processes involving N—H bonds are not likely to be rate-determining. The only possible slow step seems to be the activated adsorption of N_2 itself, and this probably governs the speed of the synthetic ammonia reaction. It should be noted that this mechanism is distinctly different from the rate determining reaction *on the surface*, which is the basis of the Langmuir treatment.

41. Poisoning of catalysts. A feature of catalytic action that was noted in the earliest studies and has been ever since a source of sorrow to the chemical manufacturer and of pleasure to the research chemist is the *poisoning* of catalysts by small amounts of foreign substances. Faraday emphasized that platinum used in catalyzing the combination of H_2 and O_2 must be clean and free of grease, and that carbon monoxide must be absent. The highly effective catalytic action of platinum on the oxidation of SO_2 to SO_3 was known early in the nineteenth century, but the process could not be applied practically because the catalyst soon lost all its activity. Not until the reactant gases were obtained in a highly purified state, free of sulfur and arsenic compounds, was it possible to run the reaction for extended periods of time.

Yet, even in industrial catalysis, poisoning is not an unmitigated evil. Sometimes a poison will prevent an undesired reaction. In the dehydrogenation of alcohol to acetaldehyde on nickel, $C_2H_5OH \rightarrow CH_3CHO \rightarrow CH_4 + CO$, the second stage is poisoned by water vapor. In the preparation of acetaldehyde, ordinary 95 per cent alcohol gives a better yield than absolute alcohol. A similar example is the preparation of formaldehyde from methanol with a copper-ceria catalyst, $CH_3OH \rightarrow HCHO \rightarrow CO + H_2$. Traces of chloroform or carbon bisulfide are added to poison the second step.

Sometimes poisoning is highly preferential. A platinum catalyst will hydrogenate either an aromatic ring, like benzene, or an aliphatic ring, like limonene. When poisoned with a little thiophene, the first reaction is eliminated but the second remains.

It is not just a coincidence that catalyst poisons such as CO, H_2S, arsenicals, and the like are also strong physiological poisons. The reason they poison animals is that they inhibit vital biochemical reactions by poisoning the enzymes that catalyze them.

Poison and reactants compete for the available catalyst surface. If the poison wins, the catalyst cannot act. Thus poisons for metallic catalysts are compounds that are strongly adsorbed by the metals. An important question now arises: does the extent of inhibition of the catalyst correspond quantitatively with the fraction of its surface that is seized by the poison? In some cases it does, but cases are also known in which a small amount of poison produces more inhibition than can be explained by a surface-area effect alone.

42. The nature of the catalytic surface. Even the smoothest solid surface is rough on a 10 Å scale. Examination of the cleavage faces of crystals by the most refined optical techniques[48] reveals that they have terrace-like surfaces. Experiments on photoelectric or thermionic emission from metals indicate that the surfaces are a patchwork of areas with different work functions. F. C. Frank[49] has elucidated a mechanism by which crystals often grow from vapor or solution: new atoms or molecules are not deposited on the planar surfaces, but at jogs in the surface associated with *dislocations* in the crystal structure; the resultant surface structure is a miniature replica of the spiral growth pattern of the Babylonian ziggurat. It has been suggested that crystal edges and corners, grain boundaries, and other physical irregularities of the surface may provide *active centers*[50] of unusually high catalytic activity. Adsorption may well be stronger on such special sites, but it must be remembered that strong adsorption is not necessarily conducive to high catalytic activity, and may in fact inhibit the catalysis.

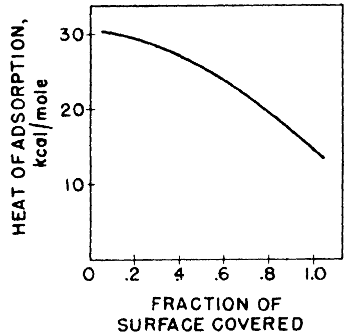


Fig. 17.16. Heat of adsorption at 23°C of hydrogen on evaporated nickel films as a function of surface covered. [From O. Beeck, W. A. Cole, and A. Wheeler, *Disc. Faraday Soc.*, *8*, 314 (1950).]

The heat of adsorption often declines markedly with increasing surface coverage. Typical results are shown in Fig. 17.16. This effect obviously indicates a nonuniform surface. The lack of uniformity, however, may either preëxist in the different adsorption sites, or be caused by the repulsive forces between adsorbed atoms or molecules. Especially if the surface to adsorbate bond is partially ionic, as much recent evidence suggests, the repulsions may become large, markedly lowering the heat of adsorption at higher coverages.

Attempts have been made to correlate catalytic activity with a possible geometrical congruence between catalyst and substrate. An example was the *multiplet hypothesis* of Balandin for the dehydrogenation activity of metal catalysts. For dehydrogenation of cyclohexane to benzene, simultaneous adsorption on six metal atoms arranged in a hexagon was supposedly required. This particular mechanism now appears unlikely, but simultaneous adsorption on two adjacent atoms the proper distance apart may be important in reactions such as the dehydrogenation of paraffins to olefins.

An especially successful explanation of the catalytic mechanism has been made in the case of the cracking of hydrocarbons. The catalysts are silica-alumina mixtures formed by calcining the hydrous oxides. The distribution of the products suggests that the cracking process proceeds through the

---

[48] S. Tolansky, *Multiple Beam Interferometry* (London: Methuen, 1948).
[49] F. C. Frank, *Advances in Physics*, *1* (1952).
[50] H. S. Taylor, *Proc. Roy. Soc.*, *A 108*, 105 (1925).

intermediate formation of carbonium ions.[51] Let us first consider a simple example of a carbonium-ion mechanism, that proposed for the Friedel-Crafts reaction with an $AlCl_3$ catalyst:

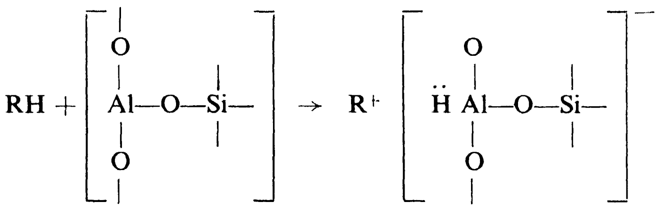
$$(1) \qquad CH_3Cl + AlCl_3 = CH_3^+(AlCl_4)^-$$

$$(2) \qquad CH_3^+ + C_6H_6 = C_6H_5{\cdot}CH_3 + H^+$$

$$(3) \qquad H^+ + (AlCl_4)^- = HCl + AlCl_3$$

The $AlCl_3$ acts as a *Lewis acid*, an acceptor of a pair of electrons. The reaction is thus an example of a generalized acid catalysis in nonaqueous solution.

It has been shown[52] that the solid silica-alumina cracking catalysts also have acidic properties: they react with carbonate solutions to evolve carbon dioxide; they catalyze the inversion of sucrose; they react with and are poisoned by volatile bases such as ammonia and quinoline. The acidic, active centers appear to be sites in which an Al^{+3} ion is surrounded by O^{--} ions tetrahedrally coordinated to Si^{+4} ions. Such a site may act as a strong Lewis acid as follows:



The subsequent cracking reaction is a cleavage of the carbonium ion R^+ at a position one carbon atom away from the C^+.

From the examples that have been given, it is evident that no single theory can account for all the phenomena of contact catalysis. The field has been of great interest to physical chemists because it combines the problems of chemical kinetics with those of the fundamental theory of the solid state. It is also not lacking in industrial applications.

43. Enzyme reactions. The catalysts devised by man have accomplished many noteworthy results in their appointed role as accelerators of chemical reaction rates. Yet their successes appear crude and insignificant when compared with the catalytic activity of the enzymes elaborated by living cells to promote physiological processes.

Consider one example among many, the formation of proteins. This is a synthesis the most skillful organic chemist has been unable to achieve in the laboratory, yet it is carried out rapidly and continuously by living cells. The isotopic tracer experiments of R. Schoenheimer[53] have shown that protein

---

[51] B. S. Greensfelder, H. H. Voge, and G. M. Good, *Ind. Eng. Chem.*, *41*, 2573 (1949).

[52] T. H. Milliken, G. A. Mills, and A. G. Oblad, *Disc. Faraday Soc.*, *8*, 279 (1950).

[53] R. Schoenheimer, *The Dynamic State of Body Constituents* (Cambridge, Mass.: Harvard Univ. Press, 1946).

molecules in the liver tissue of the rat have an average lifetime of only ten days. In addition to this continuous self-replacement, the liver synthesizes glycogen or animal starch from glucose; it manufactures urea which is excreted as the end product of nitrogen metabolism; and it also undertakes to detoxicate any number of unwanted substances, rendering them harmless to the animal organism. This tremendous metabolic activity of the liver is approached, but nowhere equaled, by the chemical activity of other kinds of cells.

H. Büchner was the first to establish, in 1897, that the intact cell was not necessary for many of these catalytic actions, since cell-free filtrates could be prepared containing the *enzymes* in solution. Enzymes are specific, colloidal catalysts. All known enzymes are proteins, so they are necessarily colloids, falling in the range of particle diameter from 10 to 100 $m\mu$. Enzyme catalysis is therefore midway between homogeneous and heterogeneous catalysis, and is sometimes called *microheterogeneous.* A theoretical discussion can be based either on intermediate compound formation between enzyme and substrate molecules in solution, or on adsorption of substrate at the surface of the enzyme.

Enzymes are extremely specific in their catalytic actions. *Urease* will catalyze the hydrolysis of urea, $(NH_2)_2CO$, in dilutions as high as one part of enzyme in ten million of solution, yet it has no detectable effect on the hydrolysis rate of substituted ureas, *e.g.*, methyl urea, $(NH_2)(CH_3NH)CO$. *Pepsin* will catalyze the hydrolysis of the peptide glycyl-L-glutamyl-L-tyrosine, but it is completely ineffective if one of the amino acids has the opposite optical configuration of the D-form, or if the peptide is slightly different, *e.g.*, L-glutamyl-L-tyrosine.

It must be confessed that little is known about the mechanism of enzyme action. Almost all enzymes fall into one of two large classes, the hydrolytic enzymes and the oxidation-reduction enzymes. The enzymes of the first class appear to be complex acid-base catalysts, accelerating ionic reactions, principally the transfer of hydrogen ions. The protein enzymes contain both NH_3^+ and COO^- groups, and therefore act as both acids and bases, and should be very effective in this type of catalysis provided geometrical conditions are satisfied. The oxidation-reduction enzymes catalyze electron transfers, perhaps through intermediate radical formation.

The kinetics of enzyme reactions can often be interpreted successfully by some sort of intermediate complex theory; *e.g.*, that of Michaelis and Menten.[54] The work of Sumner, Northrop, and others in preparing pure crystalline enzymes has now made it possible to measure the absolute rate constants of enzyme reactions. When these data are obtained and successfully interpreted, we shall have made a considerable advance toward an understanding of the physical chemistry of living cells.

---

[54] *Biochem. Zeit.*, *49*, 333 (1913); B. Chance, *J. Biol. Chem.*, *151*, 553 (1943).

PROBLEMS

1. The conversion of acetochloroacetanilide (*A*) into *p*-chloroacetanilide (*B*) was followed by adding KI solution and titrating the iodine liberated with standardized thiosulfate solution. The KI reacts with *A* only.

Time, hr:	0	1	2	3	4	6	8
ml 0.1*N* $S_2O_3^{--}$:	49.3	35.6	25.75	18.5	14.0	7.3	4.6

Calculate the first-order rate constant in sec^{-1}.

2. The inversion of sucrose, $C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$, proceeded as follows at 25°C:

Time, min:	0	30	60	90	130	180
Sucrose inverted, moles per liter:	0	0.1001	0.1946	0.2770	0.3726	0.4676

The initial concentration of sucrose was 1.0023 moles per liter. Calculate the first-order rate constant and the half life of the reaction. Why does this reaction follow a first-order law despite the fact that water enters into the stoichiometric equation? How long would it take to invert 95 per cent of a pound of sugar?

3. The hydrolysis of ethylnitrobenzoate by hydroxyl ions ($NO_2C_6H_4$-$COOC_2H_5 + OH^- = NO_2C_6H_4COOH + C_2H_5OH$) proceeds as follows at 15°C [*J. Chem. Soc.*, 1357 (1936)] when the initial concentrations of both reactants are 0.05 mole per liter.

Time, sec:	120	180	240	330	530	600
% hydrolyzed:	32.95	41.75	48.8	58.05	69.0	70.35

Calculate the second-order rate constant.

4. The reaction $2\ NO + 2\ H_2 = N_2 + 2\ H_2O$ was studied with equimolar quantities of NO and H_2 at various initial pressures:

Initial pressure, mm:	354	340.5	375	288	251	243	202
Half life, τ min:	81	102	95	140	180	176	224

Calculate the over-all order of reaction.

5. The reaction $SO_2Cl_2 = SO_2 + Cl_2$ is a first-order gas reaction with $k_1 = 2.2 \times 10^{-5}$ sec^{-1} at 320°C. What per cent of SO_2Cl_2 is decomposed on heating at 320°C for 90 min?

6. The racemization of an optically active halide in solution is first order with respect to the reactant in each direction and the rate constants are equal. $R_1R_2R_3CX$ (dextro) $\rightleftharpoons$ $R_1R_2R_3CX$ (laevo). If the initial reactant is pure dextro and the rate constant is 1.90×10^{-6} sec^{-1}, find (a) the time to 10 per cent reaction, (b) the per cent reaction after 24 hours.

7. The reaction $C_2H_6 = C_2H_4 + H_2$ follows approximately a 3/2-order law in its initial stages. At 910°K the rate constant is 1.13 sec^{-1} lit$^{1/2}$ mole$^{-1/2}$. Calculate the initial rate, $-d(C_2H_6)/dt$, for an ethane pressure of (a) 100 mm, (b) 300 mm.

8. Find the reaction order and rate constant for $C_6H_5N_2Cl = C_6H_5Cl + N_2$ at 50°C if the initial diazobenzenechloride concentration is 10 g per liter and:

t, min:	6	9	12	14	18	22	24	26	30	∞
N_2 evolved, cc:	19.3	26.0	32.6	36.0	41.3	45.0	46.5	48.4	50.4	58.3

9. Find the rate law of the reaction $3\ HNO_2 = H_2O + 2\ NO + H^+ + NO_3^-$ if the first two of the following steps rapidly attain equilibrium and the third step is slow:

(1) $2\ HNO_2 = NO + NO_2 + H_2O$

(2) $2\ NO_2 = N_2O_4$

(3) $N_2O_4 + H_2O = HNO_2 + H^+ + NO_3^-$

10. Explain the following facts from the standpoint of the adsorption properties of the reactant and product molecules:

(a) The decomposition of NH_3 on W is zero order.

(b) The decomposition of N_2O on Au is first order.

(c) The recombination of H atoms on Au is second order.

(d) The decomposition rate of NH_3 on Pt is proportional to p_{NH_3}/p_{H_2}.

(e) The decomposition rate of NH_3 on Mo is strongly retarded by N_2 but does not approach zero as the surface becomes saturated with N_2.

(f) The rate of $2\ SO_2 + O_2 = 2\ SO_3$ on Pt is $k_1\ (SO_2)/(SO_3)^{1/2}$ when O_2 is in excess.

11. In what proportion of bimolecular collisions does the energy of the "head-on" collision exceed 60 kcal at 300°K, at 600°K, at 1000°K?

12. The following mechanism has been proposed for the thermal decomposition of acetone:

(1) $CH_3COCH_3 \xrightarrow{k_1} CH_3 + CH_3CO$ $E = 84$ kcal

(2) $CH_3CO \xrightarrow{k_2} CH_3 + CO$ $E = 10$ kcal

(3) $CH_3 + CH_3COCH_3 \xrightarrow{k_3} CH_4 + CH_2COCH_3$ $E = 15$ kcal

(4) $CH_2COCH_3 \xrightarrow{k_4} CH_3 + CH_2CO$ $E = 48$ kcal

(5) $CH_3 + CH_2COCH_3 \xrightarrow{k_5} C_2H_5COCH_3$ $E = 5$ kcal

Express the over-all rate in terms of the individual rate constants, taking reaction (1) to be first order. Calculate (a) the over-all energy of activation; (b) the chain length given by the ratio of the chain propagating reaction to the chain stopping reaction. What is the order of the over-all reaction if reaction (1) becomes second order?

13. Triethylamine and methyl iodide are mixed at initial concentrations of 0.02 mole per liter.

Time, sec:	325	1295	1530	1975
% reacted:	31.4	64.9	68.8	73.7

Determine the second-order rate constant. Would you expect the rate to be greater or less if (a) neutral salts were added; (b) the dielectric constant of the solvent were increased? Give reasons.

14. Derive the rate laws for the following competitive reactions:

(1) Dipeptide + enzyme = complex
(2) Complex = dipeptide + enzyme
(3) Complex = enzyme + amino acids

Discuss the design of an experiment to obtain the dissociation constant of the complex from kinetic data.

15. In the polymerization reactions, $A + A = A_2$; $A_2 + A = A_3$; $A_3 + A = A_4 \ldots$, etc., if all the rate constants are identical, the integrated rate equation has the form

$$y = akt\left[\frac{4 + kt}{(2 + kt)^2}\right]$$

Here y is the amount of polymer ($A_2 + A_3 + A_4 + \ldots A_n$), a is the initial amount of reactant A, k is the rate constant, and t is the time. Find the equation for dy/dt, the polymerization rate. What will be the apparent order of reaction during a single run? What will be the order based on the initial rates if the concentration a is varied?

16. A certain reaction is 20 per cent complete in 15 min at 40°C and in 3 min at 60°C. Estimate its activation energy.

17. For the decomposition of N_2O_5,

Temperature, °C:	25	35	45	55	65
$10^5\, k_1$ – sec^{-1}:	1.72	6.65	24.95	75	240

Calculate A and E for the reaction, in the equation $k_1 = Ae^{-E/RT}$. Calculate $\Delta F^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$, for the reaction at 50°C.

18. Consider a reaction subject to acid catalysis that follows the Brønsted relation $k_A = CK^{\alpha}$. Suppose that the reaction is studied in an aqueous solution 0.1 molar in acetic acid and 0.1 molar in sodium acetate. For three hypothetical values 0.1, 0.5, and 1.0 of α, calculate the proportion of the catalysis that would be due to each of the following: H_3O^+, H_2O, CH_3COOH.

19. The rate constant of $2\,N_2O = 2\,N_2 + O_2$ is $4.2 \times 10^9 \exp(-53{,}000/RT)\ \text{sec}^{-1}$. A stream of N_2O is passed through a tube 20 mm in diameter and 20 cm long at a rate of 1 liter per min. At what temperature should the tube be heated in order to have 1.0 per cent O_2 in the exit gas?

20. A sample of nickel foil weighing 5.328 g and having a surface area of 258 cm^2 per g was exposed to pure oxygen at 500°C and 10 cm pressure.

Time, hr:	2	3	4	5	6	7	8	9	10
O_2 uptake, cc at 10 mm, 20°C:	52.4	70.2	85.1	97.9	106.6	118.0	127.7	137.0	146.3

The reaction is $Ni + \frac{1}{2}\,O_2 = NiO$. Fit the data to the parabolic rate law $dy/dt = a/y$ where y is the film thickness, t is the time and a is the rate constant. Calculate a. (NOTE: Integrate the rate equation assuming that at $t = 0, y = y_0$, and cast the integrated equation into a linear form. Then plot the results.)

REFERENCES

BOOKS

1. Amis, E. S., *Kinetics of Chemical Change in Solution* (New York: Macmillan, 1948).
2. Daniels, F., *Chemical Kinetics* (Ithaca: Cornell Univ. Press, 1938).
3. Frost, A. A., and R. G. Pearson, *Kinetics and Mechanism* (New York: Wiley, 1953).
4. Glasstone, S., K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (New York: McGraw-Hill, 1941).
5. Griffith, R. H., *The Mechanism of Contact Catalysis* (New York: Oxford, 1946).
6. Hinshelwood, C. N., *The Kinetics of Chemical Change* (New York: Oxford, 1942).
7. Laidler, K. J., *Chemical Kinetics* (New York: McGraw-Hill, 1950).
8. Moelwyn-Hughes, E. A., *The Kinetics of Reactions in Solution* (New York: Oxford, 1947).
9. Steacie, E. W. R., *Free Radical Mechanisms* (New York: Reinhold, 1946).

ARTICLES

1. Bell, R. P., *J. Chem. Soc.*, 629–34 (1943), "Theory of Reaction Kinetics in Solution."
2. Dainton, F. S., *J. Chem. Soc.*, 1533–1546 (1952), "Atoms and Radicals in Aqueous Media."
3. Eyring, H., *Science in Progress*, vol. IV (New Haven: Yale Univ. Press, 1944), "The Drift toward Equilibrium."
4. Garvin, D., and G. B. Kistiakowsky, *J. Chem. Phys.*, *20*, 105–113 (1952), "The Kinetics of Coordinate Bond Formation."
5. Hinshelwood, C. N., *J. Chem. Soc.*, 694–701 (1947), "Some Observations on Present Day Chemical Kinetics."
6. Laidler, K. J., and S. Glasstone, *J. Chem. Ed.*, *25*, 383–87 (1948), "Rate, Order, and Molecularity in Chemical Kinetics."
7. Michaelis, L., *Science in Progress*, vol. V (New Haven: Yale Univ. Press, 1947), 119–48, "Oxidation and Respiration."
8. Moore, W. J., *J. Electrochem. Soc.*, *100*, 302–313 (1953), "Oxidation of Metals at High Temperatures."
9. Polanyi, M., *Endeavour*, *8*, 3–10 (1949), "Mechanism of Chemical Reactions."
10. Taylor, H. S., *Science in Progress*, vol. V (New Haven: Yale Univ. Press 1947), 91–118, "Contact Catalysis Between Two Wars."

CHAPTER 18

Photochemistry and Radiation Chemistry

1. Radiation and chemical reactions. Thus far our account of chemical kinetics has considered only thermal reactions, those in which the energy needed to climb the hill leading to the activated state comes from the random energies of the reacting molecules and their neighbors. A different way of providing the necessary energy is to bring the reactant molecule into "collision" with quanta of electromagnetic energy (photons); with high-velocity electrons (β rays); or with other corpuscular beams, such as neutrons, protons, or α-particles, obtained either from nuclear reactions or from electric accelerators. The study of reactions caused by any of these methods is the field called *radiation chemistry*. The name arose from the historical fact that the emissions from radioactive elements were called *rays*, α, β, and γ.

The older field called *photochemistry* would logically appear to be a subdivision of radiation chemistry. It is the science of the chemical effects of light, where *light* includes the infrared and ultraviolet, as well as the visible regions of the spectrum, *i.e.*, the range of wavelength from about 1000 to 10,000 Å. The energies of quanta in this range vary from about 1 to 10 ev, or 23 to 230 kcal per mole. These energies are comparable in order of magnitude with the strengths of chemical bonds. Thus, if a molecule absorbs a photon of visible light, definite chemical effects may be expected, yet the collision is still a rather gentle one, and the effects usually follow paths made familiar from spectroscopic studies. In particular, there is almost never enough energy in a single quantum to activate more than one molecule in the primary step.

On the other hand, if a 1,000,000 ev γ-ray photon traverses a medium, thousands of molecules may become activated along its trajectory. As we shall see, these activations often result in ionization of the molecules, whereas in the photochemical region, ionization would be a rare occurrence. Radiations like α, β, γ rays, neutrons, and cyclotron beams, are therefore called *ionizing radiations*. Usually, when we speak of *radiation chemistry* we mean the science of the chemical effects of such highly energetic, ionizing rays. We tend, therefore, to divide the whole subject, on energetic grounds, into *photochemistry* and *radiation chemistry*.

2. Light absorption and quantum yield. Light incident upon a system can be transmitted, refracted and scattered, or absorbed. Grotthuss and Draper, in 1818, first stated the principle that only the absorbed light can produce a chemical change. The fraction of incident light absorbed by a medium is proportional to the thickness of the medium that is traversed. This law was originally stated, in 1729, in a memoir by P. Bouguer, and was later rediscovered by Lambert. It can be expressed as

$$\frac{-dI}{I} = a\,dx \tag{18.1}$$

where I is the intensity of light at a distance x from its entry into the medium, and a is called the *absorption coefficient* or *extinction coefficient.* On integration with the boundary condition $I = I_0$ at $x = 0$, we obtain

$$I = I_0\,e^{-ax} \tag{18.2}$$

In 1852, Beer showed, for many solutions of absorbing compounds in practically transparent solvents, that the coefficient a was proportional to the concentration of solute c. Thus Beer's law is

$$\underline{I = I_0\,e^{-a'cx}} \;\checkmark \tag{18.3}$$

If c is the molar concentration, a' is called the *molar extinction coefficient.* The light absorbed is

$$I_a = I_0 - I = I_0\,(1 - e^{-a'cx})$$

These absorption laws are the bases for various spectrophotometric methods of analysis.[1] They are obeyed strictly only for monochromatic light.

A device that measures the total amount of incident radiation is called an *actinometer.* This measurement, *actinometry,* is a necessary part of any quantitative study of photochemical reactions. Two types of actinometer are commonly used.

One is a *thermopile.* It consists of a number of thermocouples connected in series, with their hot junctions imbedded at a blackened surface which absorbs almost all the incident light and converts it into heat. Calibrated lamps of known energy output are available from the National Bureau of Standards. The emf developed by the thermopile is measured first with the standard lamp and then with the source of radiation of unknown intensity. The reaction vessel is mounted between the thermopile and the light, and the radiation absorbed by the reacting system is measured by the difference between readings with the vessel filled and empty.

Instead of a thermopile, it is possible to employ relative methods of actinometry, which are based on the amount of chemical change produced in previously studied reactions. The *quantum yield* of a photochemical reaction is the number of molecules of reactant consumed or product formed per quantum of light absorbed. One of the most reproducible reactions is the decomposition of oxalic acid *photosensitized* by uranyl salts. The uranyl ion UO_2^{++} absorbs radiation from 2500 to 4500 Å, becoming an excited ion

---

[1] See, for example, the complete account given by M. G. Mellon, *Analytical Absorption Spectroscopy* (New York: Wiley, 1950).

$(UO_2^{++})^*$ which decomposes the oxalic acid. This reaction has a quantum yield of 0.50.

$$UO_2^{++} + h\nu \rightarrow (UO_2^{++})^*$$

$$(UO_2^{++})^* + (COOH)_2 \rightarrow UO_2^{++} + CO_2 + CO + H_2O$$

The oxalic acid concentration is easily followed by titration with permanganate. A quartz vessel filled with the uranyl oxalate mixture can be used exactly like the thermopile, the light absorbed being calculated from the oxalic acid decomposed and the known quantum yield. Another reaction sometimes used as an actinometer is the photochemical hydrolysis of chloroacetic acid, $ClCH_2COOH + H_2O + h\nu \rightarrow CH_2OHCOOH + HCl$. This reaction has a quantum yield of 0.31.

Shortly after the advent of the quantum theory, Einstein applied it to photochemical reactions. He stated the rule that one quantum of absorbed radiation activates one molecule of absorbent, but this activated molecule does not necessarily undergo chemical reaction. The energy $E_E = Nh\nu$, where N is the Avogadro Number, is called *one einstein*. The value of the einstein varies with the wavelength. For visible green light with $\lambda = 6000$ Å, it has a value in kilocalories of

$$E_E = \frac{6.02 \times 10^{23} \times 6.62 \times 10^{-27} \times 3.0 \times 10^{10}}{6 \times 10^3 \times 10^{-8} \times 4.184 \times 10^7 \times 10^3} = 45 \text{ kcal}$$

This is enough energy to break moderately strong bonds, but for C—C bonds and others with strengths higher than 72 kcal it is necessary to use radiation in the ultraviolet region.

3. Primary processes in photochemistry. The results of the absorption of a quantum of radiation were described in some detail in Chapters 10 and 11, in the sections on atomic and molecular spectra.

Absorption by an atom in the line-spectrum region leads to an excited atom; in the region of continuous absorption, to an ion plus an electron.

Absorption by molecules can lead to the different results shown in Fig. 18.1. In (a) the transition is from a stable ground state to a stable excited state. The corresponding spectrum consists of discontinuous bands with a fine structure of closely packed lines. In (b) the transition is to an unstable state that immediately undergoes dissociation. Absorption of a quantum in case (b′) also leads to dissociation, because the energy level reached lies above the binding energy of the excited state. Both (b) and (b′) correspond to continuous absorption spectra, without bands. A third and less usual result is shown in (c). The initial transition is from one stable state to another, but the upper state is "intersected" by the potential-energy surface of an unstable state, and the excited molecule can switch over to this after one or more vibrations. The resultant spectra are quite diffuse but not completely continuous. This phenomenon was named *predissociation* by V. Henri.

It should be noted that all the transitions in Fig. 18.1 are depicted as vertical jumps on the potential-energy diagrams. This picture is in accord with the Franck-Condon principle that electronic transitions occur without influencing the positions of the nuclei.

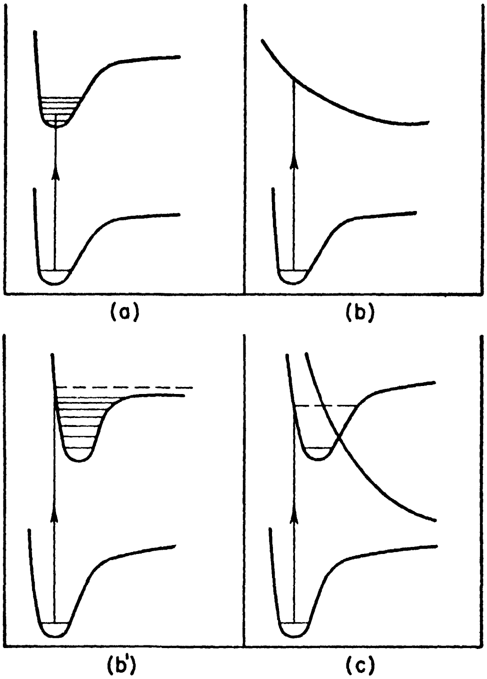


Fig. 18.1. Primary photochemical processes.

4. Secondary processes in photochemistry: fluorescence. If the light absorption lies in the banded region of the spectrum, there are several careers open to the excited molecule formed in the primary step. (1) It may re-emit a quantum of either the same or a different frequency. This emission is called *fluorescence* or *phosphorescence*. (2) It may collide with other molecules and pass on to them some or all of its excitation energy. This energy either can cause reaction in the other molecule, or can be gradually degraded into heat. (3) It may collide with another molecule and react with it. (4) It may spontaneously decompose if the excitation energy reaches a bond that can be broken (predissociation).

Fluorescence is the emission of light which has been absorbed by the molecule. It should not be confused with the *scattering* of light which has not been absorbed, *i.e.*, the *Rayleigh scattering* without change in wavelength, and the *Raman scattering* with change in wavelength. The natural life time of an excited state in a molecule undisturbed by collisions is about 10^{-8} sec. At a pressure of one atmosphere, a molecule experiences about

100 collisions in 10^{-8} sec. As a consequence, excited molecules in most gaseous systems at ordinary pressures usually lose their energies by collision before they have a chance to fluoresce. The fluorescence is said to be *quenched.*

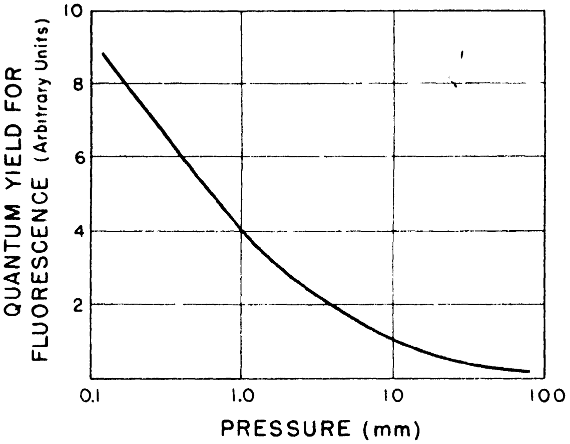


Fig. 18.2. Relative quantum yield for fluorescence of NO_2.

In some such systems, fluorescence can be observed if the pressure is sufficiently reduced. An example is the fluorescence of NO_2 excited by light of wavelength $\lambda = 4000$ Å. In Fig. 18.2 the relative quantum yield for the fluorescence is plotted against the pressure, and the increased quenching at higher pressures is evident. Actually, this case is rather unusual since the life time of the excited state is 10^{-5} sec, instead of about 10^{-8}.

The distinction between *fluorescence* and *phosphorescence* formerly was made on the basis of the duration of the afterglow, a slow decay of luminescence being called *phosphorescence.* Current usage of these terms, however, bases the distinction on a difference in the mechanisms for re-emission

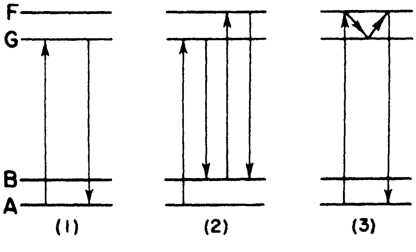


Fig. 18.3. Transitions in fluorescence and phosphorescence. (1) Fluorescence: resonance radiation. (2) Fluorescence (3) Phosphorescence.

of light. In Fig. 18.3 the transitions (1) and (2) indicate the mechanism of fluorescence, absorption of a quantum, followed by re-emission from the excited state reached, either back to the initial state or to a different state.

The re-emission, in exceptional cases, may occur slowly, leading to a long afterglow. The transitions of type (3) indicate the mechanism of phosphorescence. After the initial excitation to the level F, the electron makes a transition to a nearby level G. The level G may be a metastable level, in that the transition from G to lower levels is unlikely owing to low quantum mechanical transition probabilities. Thus, before the molecule can re-emit a quantum of light, it must jump back up to F, and considerable time may elapse before the molecule can acquire from suitable collisions enough energy for this jump. Therefore the afterglow usually has an appreciable duration in phosphorescence because, as we say, the excited molecule has become "trapped in a metastable state."

A kinetic expression for the quenching of fluorescence is obtained by considering the two parallel processes for an excited molecule M^*:

Fluorescence $\quad M^* \xrightarrow{k_1} M + h\nu$

Quenching $\quad M^* + X \xrightarrow{k_2} M + X + \text{kinetic energy}$

The total rate of deactivation is

$$\frac{-d(M^*)}{dt} = k_1(M^*) + k_2(M^*)(X)$$

If the intensity of absorbed light is I_0, and the fluorescent intensity is I, the fraction of excited molecules that fluoresce is

$$\frac{I}{I_0} = \frac{k_1(M^*)}{k_1(M^*) + k_2(M)(X)} = \frac{1}{1 + (k_2/k_1)(X)}$$

If k_1 is known from an independent determination of the life time τ of the excited state in the absence of quencher $X (k_1 = \tau^{-1})$, we can evaluate k_2, the specific rate of the quenching process. It is usual to express the results in terms of a *quenching cross section* σ_Q. This is calculated from eq. (17.18) for the number of binary collisions Z_{12} in a gas. It is the value that must be taken for the cross section $\pi d_{12}^2/4$ in order that the value of k_2 calculated by simple collision theory should exactly equal the experimental value. From eq. (17.19) with $E = 0$, we therefore obtain

$$\sigma_Q = \frac{10^3}{4N}\left(\frac{\pi\mu}{8kT}\right)^{1/2} k_2 \tag{18.4}$$

where k_2 is in the usual units of liter mole^{-1} sec^{-1}.

An example of the results obtained is shown in Table 18.1, which deals with the quenching of mercury resonance radiation ($^3P_1 - {}^1S_0$) by added gases. The great effectiveness of hydrogen and some of the hydrocarbons is due to dissociative reactions like

$$\text{Hg}^* + \text{H}_2 = \text{HgH} + \text{H}, \qquad \text{Hg}^* + \text{RH} = \text{HgH} + \text{R}$$

TABLE 18.1

EFFECTIVE CROSS SECTIONS FOR QUENCHING MERCURY FLUORESCENCE

Gas	$10^{16}\,\sigma_Q$ – cm^2	Gas	$10^{16}\,\sigma_Q$ – cm^2
O_2	13.9	CO_2	2.48
H_2	6.07	PH_3	26.2
CO	4.07	CH_4	0.06
NH_3	2.94	n-C_7H_{16}	24.0

5. Luminescence in solids. The phenomena of excitation followed by re-emission or deactivation are basically the same in solid, liquid, and gaseous systems. In solids, the processes of energy transfer do not, of course, involve collisions, but the degradation of the electronic energy of excitation into the thermal vibrational energy of the crystal provides an analogous mechanism of quenching.

Luminescent solids have been classified as (1) pure, (2) impurity activated. Examples of type (1) are certain inorganic salts such as those of the uranyl ion UO_2^{+2}. Light absorption by these ions is followed by fluorescence both in the crystalline state and in solution, and it is evident that quenching is not efficient. The reason seems to be that electronic excitation occurs in inner orbitals that are effectively shielded from interaction with vibrational levels of neighboring ions or molecules. Another example of a pure luminescent solid is anthracene, which displays a pale violet fluorescence in the purest samples ever obtained. The reason why quenching is inefficient in anthracene can be at least qualitatively understood from the nature of its structure. As shown on page 311 for benzene, the carbon-carbon links in anthracene consist of strong electron-pair σ-bonds in the plane of the rings, and overlapping π-orbitals filled with electrons which are free to move around the ring system. When anthracene absorbs a quantum at about 3700 Å, a π-electron is excited from a filled energy band to an upper empty band. The vibrations of the C—C and C—H bonds in anthracene are closely coupled with the σ-bonds, but are not much influenced by the positions of the π-electrons. Therefore the excitation energy of the π-electrons is not rapidly degraded into thermal vibrational energy, and is instead re-emitted as the violet fluorescence.

If an anthracene crystal contains as little as 0.01 per cent of naphthacene, the characteristic green fluorescence of naphthacene appears and the violet anthracene fluorescence is almost entirely suppressed. When such a crystal is heated, the green fluorescence disappears at the instant of melting, and the violet anthracene fluorescence reappears. The explanation of these remarkable events seems to be the following. When the anthracene crystal absorbs a photon and one of its π-electrons is excited to an upper band, a hole is left behind in the lower band. The hole, being a location of missing negative charge, has an effective positive charge, and hence attracts the electron, somewhat in the way that an H^+ nucleus attracts its planetary electron. Such an association between an excited electron and the hole it has reluctantly left behind is called an *exciton*. Now the exciton hops about through the crystal until it happens to hit a naphthacene molecule, which traps it long enough for the fluorescent emission to take place. Thus, although the photon is almost always absorbed in an anthracene molecule, it is almost always emitted from a naphthacene molecule. The example of naphthacene in anthracene is midway between the pure luminescent crystal and the typical case of impurity activated crystals.

The example of zinc sulfide may be considered as typical of impurity activation. Pure ZnS of stoichiometric composition displays practically no luminescence. If this material is heated at 500–1000°C it dissociates slightly to form ZnS with excess Zn interstitially dissolved: $ZnS(c) \rightarrow Zn_i$ (in ZnS) $+ \frac{1}{2}S_2$. The excess Zn atoms form impurity centers of the type shown in Fig. 13.24 on page 398. When illuminated with light of about 3400 Å, the heat-treated ZnS displays a blue fluorescence and a short-lived phosphorescence. The spectra of the fluorescence and of the phosphorescence are the same, as would be expected from the trap mechanism of phosphorescence shown in Fig. 18.3. The ZnS on illumination also becomes a better conductor of electricity; this phenomenon is called *photoconductivity*.

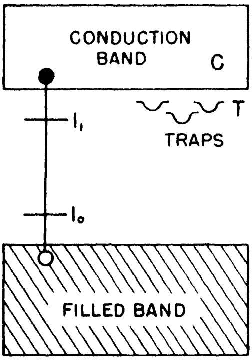


Fig. 18.4. Band model for an impurity-activated phosphor.

An oversimplified model to account for these observations is shown in Fig. 18.4. The levels I_0 and I_1 represent a ground state and an excited state for an impurity center, *e.g.*, an interstitial zinc atom. If a quantum of radiation of sufficient energy is absorbed by the crystal, an electron may be driven from the filled band to the empty conduction band, and a hole is left in the filled band. If the hole and the electron remained associated, the result would be an exciton, similar to that found in anthracene. In pure ZnS, the electron and the positive hole will recombine without the emission of light, the energy being dissipated as heat. The impurity centers, such as excess Zn, provide a mechanism by which the excitation energy can be re-emitted as light. The theoretical interpretation of how they provide this luminescent pathway is still in an unsatisfactory state.

Both pure ZnS and impurity activated ZnS contain "traps" for electrons, metastable levels from which transition to the ground state is forbidden. These traps may be dislocations, grain boundaries, or other impurities in the crystals. Only by thermal excitation back to the conduction band can an electron escape from its trap and eventually emit the phosphorescent radiation. For such a thermal excitation from T to C, the probability p per unit time has the simple form of a first order rate constant, $p = ae^{-E/RT}$, where E is the energy gap between T and C. If n is the number of electrons trapped at any instant, the phosphorescent intensity is proportional to their rate of escape,

$$I = \frac{-dn}{dt} = pn = nae^{-E/RT} \tag{18.5}$$

For a fixed temperature, integration of this equation gives the decay of phosphorescence with time. For the typical example of a thallium activated KCl phosphor, the constants are $a = 3 \times 10^9\ \text{sec}^{-1}$, and $E = 15.5$ kcal per mole.

6. Thermoluminescence. Some phosphors, illuminated while cold, store energy which can later be released as light when they are heated. This phenomenon is called *thermoluminescence.* In a typical experiment, a SrS phosphor was illuminated at room temperature, the light was turned off, and the phosphor was heated at a steady rate of 2.5° per sec. The resulting light emission is shown in Fig. 18.5. It is clear that two distinct trap levels occur, which lead to the two peaks in the thermoluminescent curve.

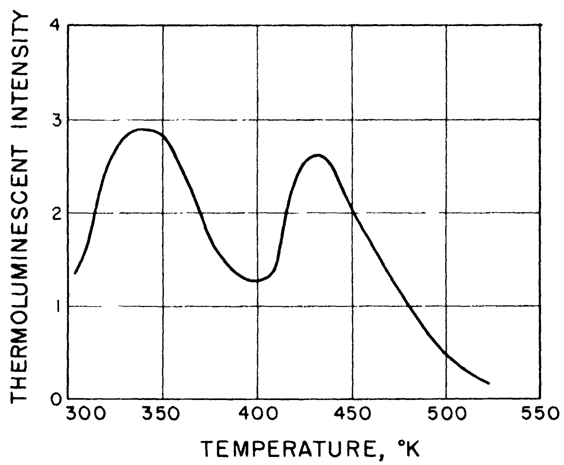


Fig. 18.5. Thermoluminescence of a strontium-sulfide phosphor.

The mathematical analysis of these curves is based on eq. (18.5), which may be written

$$\frac{-dn}{n} = ae^{-E/RT}\, dt$$

For a constant heating rate, $dT = c\, dt$, and

$$\ln \frac{n}{n_0} = -\int_0^T \frac{a}{c}\, e^{-E/RT}\, dT$$

Thus,
$$I = -\frac{dn}{dt} = n_0 a e^{-E/RT} \exp\left(-\int_0^T \frac{a}{c}\, e^{-E/RT}\, dT\right)$$

If the reader cares to take the time to plot this expression for a suitable choice of parameters, he will find that it reproduces an approximately bell-shaped curve like one of those in Fig. 18.5. Thus experiments on thermoluminescence are often used to measure the trap depths E in phosphors.

7. Secondary photochemical processes: initiation of chain reactions. If a molecule is dissociated into fragments as a consequence of absorbing a quantum of radiation, extensive secondary reactions may occur. These are especially likely since the fragments are often atoms or radicals, which are by nature highly reactive. Sometimes, also, the products of the primary fission process are still in excited states, as so-called *hot atoms* or *hot radicals.*

For example, if a mixture of chlorine and hydrogen is exposed to light in the continuous region of the absorption spectrum of chlorine ($\lambda < 4800$ Å) an extremely rapid reaction to hydrogen chloride ensues. The quantum yield Φ is 10^4 to 10^6. Bodenstein was the first to explain the high value of Φ in terms of a long reaction chain. The first step is dissociation of the chlorine molecule,

(1) $Cl_2 + h\nu \rightarrow 2\,Cl$ $\Phi_1 I_a$

This is followed by

(2) $Cl + H_2 \rightarrow HCl + H$ k_2

(3) $H + Cl_2 \rightarrow HCl + Cl$ k_3

(4) $Cl \rightarrow \frac{1}{2}\,Cl_2$ (on wall) k_4

If we set up the steady-state expressions for (Cl) and (H) in the usual way (page 552), we obtain for the rate of HCl production,

$$\begin{aligned}\frac{d(\mathrm{HCl})}{dt} &= k_2(\mathrm{Cl})(\mathrm{H_2}) + k_3(\mathrm{H})(\mathrm{Cl_2}) \\ &= \frac{2k_2\Phi_1 I_a}{k_4}(\mathrm{H_2})\end{aligned}$$

Instead of reaction (4), the chain-ending step might be a gas-phase recombination of chlorine atoms, perhaps with cooperation of a third body M to carry away excess energy.

(5) $Cl + Cl \quad (+M) \rightarrow Cl_2 \quad (+M)$ k_5

In this case, the calculated rate expression would be

$$\frac{d(\mathrm{HCl})}{dt} = k_2(\mathrm{H_2})\left[\frac{\Phi_1 I_a}{k_5}(M)\right]^{1/2}$$

It might be thought that a few simple experiments would suffice to decide whether the rate depends on the first power or on the square root of the light absorbed, and hence to decide the most likely chain-ending mechanism. In fact, however, after dozens of extensive investigations, some questions still remain unanswered. It is likely that reactions (4) and (5) both contribute to the chain ending under most experimental conditions, since in most experiments with pure H_2 and Cl_2 the rate depends on I_a^n, with n somewhere between $\frac{1}{2}$ and 1. The reaction is very sensitive to traces of impurities, especially oxygen, which acts as an inhibitor by removing H atoms: $H + O_2 (+M) \rightarrow HO_2 (+M)$.

In contrast with the high quantum yields of the $H_2 + Cl_2$ reaction are yields in the photochemical decompositions (*photolyses*) of the alkyl iodides. These compounds have a region of continuous absorption in the near ultraviolet, at 2300 to 2500 Å, which leads to a break into free alkyl radicals and iodine atoms,

$$CH_3I + h\nu \rightarrow CH_3 + I$$

The quantum yield of the photolysis is only about 10^{-2}. The reason for the low Φ is that the most likely secondary reaction is a recombination, $CH_3 + I \rightarrow CH_3I$. Only a few radicals react with more alkyl iodide, $CH_3 + CH_3I \rightarrow CH_4 + CH_2I$. The final products are CH_4, CH_2I_2, and I_2. If mercury vapor is added to the system, the quantum yield is much increased. It is evident that the mercury acts by removing iodine atoms, preventing their recombination with alkyl radicals.

A reaction that has received especially careful study is the photolysis of acetone; more than fifty research papers have been devoted to it during the past 25 years.

$$(CH_3)_2CO + h\nu \rightarrow C_2H_6 + CO$$

Small amounts of methane and biacetyl are also formed. Acetone absorbs ultraviolet light, with a banded spectrum from 3300 to 2950 Å merging into a continuous absorption that extends to 2200 Å. Electronic excitation in the carbonyl group is responsible for this absorption, but the C=O bond is strong and energy must flow into the weaker C—C bonds before dissociation can occur.

In an investigation by Farrington Daniels and G. H. Damon,[2] acetone vapor contained in a quartz vessel was irradiated with virtually monochromatic light obtained from a high-pressure mercury-vapor lamp with a quartz monochromator. (This instrument is an adaptation of the spectrograph, designed to isolate and focus a concentrated beam of light having a well defined wavelength.) In a typical experiment, radiation at $\lambda = 3130$ A was used. Measurement with a thermopile gave an absorption rate of 85,200 erg per sec over a period of 23,000 sec. The volume of the vessel was 60.3 cc, the thermostat temperature 56°C, and the pressure increased from 760 to 790.4 mm or $\Delta P = 30.4$ mm.

Apart from minor subsidiary reactions, two moles of product appear for each mole of acetone decomposed. The number of molecules decomposed was therefore

$$n = \frac{30.4}{760} \cdot \frac{273}{329} \cdot \frac{60.3}{22{,}414} \times 6.02 \times 10^{23} = 5.23 \times 10^{19}$$

[2] *J. Am. Chem. Soc.*, *55*, 2363 (1933).

The number of quanta absorbed was

$$q = \frac{85{,}200 \times 23{,}000 \times 3.13 \times 10^{-5}}{6.62 \times 10^{-27} \times 3.0 \times 10^{10}} = 3.08 \times 10^{20}$$

The quantum yield was therefore $\Phi = n/q = 0.17$. It is evident that of the quanta absorbed, less than one in five leads to reaction.

When acetone vapor is irradiated with ultraviolet light there is an intense and beautiful green fluorescence, and it was thought at first that the light that did not cause reaction was emitted in fluorescence. Daniels measured the fluorescent intensity and found that it actually accounted for less than 3 per cent of the light absorbed. Thus about 80 per cent of the radiation absorbed is degraded into heat. It was later shown that the fluorescence was due to biacetyl.

The products from acetone photolysis in a flow system remove lead mirrors, forming $Pb(CH_3)_4$[3]. This result, as well as other evidence, indicates that methyl radicals are formed. The most likely mechanism for the photolysis appears to be[4]

$$\begin{aligned}
(CH_3)_2CO + h\nu &\rightarrow CH_3 + CH_3CO \\
CH_3 + CH_3 &\rightarrow C_2H_6 \\
CH_3CO + CH_3CO &\rightarrow (CH_3CO)_2 \\
CH_3CO &\rightarrow CH_3 + CO \\
CH_3 + CH_3CO &\rightarrow (CH_3)_2CO
\end{aligned}$$

The recombination reaction accounts for the low quantum yield, and, as would be expected, the yield therefore increases as the pressure is lowered.

8. Flash photolysis. The new technique called *flash photolysis* promises to be especially useful in the study of atoms and radicals that have only a short lifetime before reacting.[5] A powerful flash of light, with an energy up to 10^5 joules and a duration of about 10^{-4} sec, is obtained by discharging a bank of capacitors through an inert gas such as argon or krypton. The reactants are in a vessel aligned parallel with the lamp, and at the instant of the flash, an extensive photolysis of the absorbing gas occurs in the reaction vessel. Thus the primary products of photolysis, usually radicals and atoms, are produced in much higher concentrations than in the usual experiment with continuous, relatively low-level illumination. A good method for following the subsequent reactions of the radicals is to make a continuous photographic record of their absorption spectra.

An example of a flash-photolysis investigation is the study by Porter and Wright of the reaction between chlorine and oxygen. A mixture of 10 mm

---

[3] T. G. Pearson, *J. Chem Soc.*, *1934*, 1718; T. G. Pearson and R. H. Purcell, *ibid.*, *1935*, 1151.

[4] A complete discussion of the evidence for the mechanism and a solution of the steady-state rate equation are given by W. Davis, *Chem. Rev.*, *40*, 201 (1947).

[5] R. G. W. Norrish and G. Porter, *Nature*, *164*, 658 (1950); G. Porter, *Proc. Roy. Soc. A 200*, 284 (1950).

Cl_2 and 600 mm O_2 was used in a typical experiment. The flash dissociates almost all the Cl_2 to Cl atoms. In the first second after the flash there is a rapid reaction to form the previously unobserved radical ClO, which is detected by its absorption spectrum.

$$Cl_2 + h\nu \rightarrow 2\,Cl$$
$$2\,Cl + O_2 \rightarrow 2\,ClO$$

The kinetics of the subsequent disappearance of the ClO radicals is now readily followed by a continuous measurement of the intensities of their absorption spectra. The removal of ClO is found to be a second-order reaction, $-d(ClO)/dt = k_2(ClO)^2$, with $k_2 = 4.2 \times 10^7 \exp[(0 \pm 650)/RT]$ liter $mole^{-1}$ sec^{-1}. The constant is uncertain because the molar extinction coefficient of the ClO radicals has not been accurately determined, and the experimental measurements give spectral intensities and not concentrations.

9. Effects of intermittent light. In the flash-photolysis experiment, a high initial concentration is formed of reactive intermediates, which gradually disappear by various reactions during the dark period. In the usual photochemical experiments, a steady intensity of light is used, so that intermediates build up to a steady-state concentration, which is maintained during the course of the run. Let us consider now a situation in which there is a regular sequence of light and dark periods. A convenient way to achieve such an intermittent illumination is to place between the light source and the reaction vessel a rotating circular disk from which sectors have been cut. If four sectors, for example, have angles of $22\frac{1}{2}°$ and are evenly spaced, the light and dark periods in the vessel will be in the ratio 1 : 3, and the flashing rate will be four times the rotation speed of the disk.

The use of the method can be illustrated in terms of a simple schematic reaction mechanism:

(1) $A_2 + h\nu \rightarrow 2A$

(2) $A + B \rightarrow C + A$

(3) $2A \rightarrow$ stable product

The steady-state concentration of the radicals A is $(A) = (\Phi I_a/2k_3)^{1/2}$. If the sector wheel with one-quarter open area is rotated very rapidly (and by "rapidly" we mean with a period much less than the half life for disappearance of radicals A in the dark), the net result is the same as if the intensity of a steady illumination was reduced to one-quarter. Thus the steady-state concentration of A, and hence the rate of reaction, is reduced by a factor of $(\frac{1}{4})^{1/2} = \frac{1}{2}$. On the other hand, suppose that the period of rotation of the sector is long compared to the half life of A. In this case, the concentration of A during each dark period will fall far below the steady-state value. The net result will be the same as if the time of reaction is reduced to one-quarter with the light intensity unchanged. Thus the rate of reaction would be reduced by a factor of $\frac{1}{4}$. In Fig. 18.6, (a) shows how the concentration of radicals varies during the two experiments, and (b) shows how the reaction rate varies with sector speed.

The transition region between reaction rates for slow rotation and those for fast rotation will occur when the sector period is about equal to the half life of the reactive intermediate. Thus the experiments with intermittent illumination provide a method for measuring short half lives of intermediates, which would be difficult to study by other methods. It must be noted, however, that the method cannot be used if the over-all rate is proportional to I_a, the first power of the light intensity.

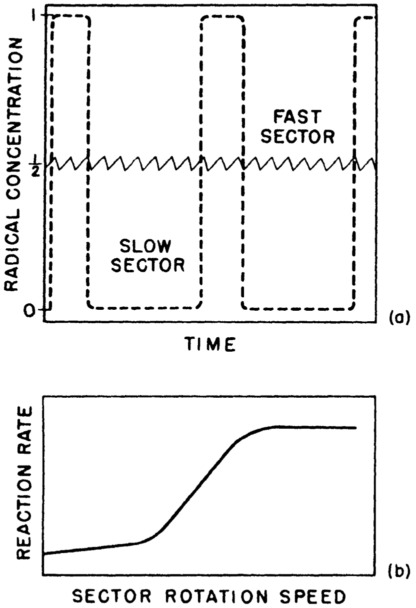


Fig. 18.6. The effect of intermittent light on (a) radical concentration (*b*) reaction rate, for a case in which rate depends on $I_a^{1/2}$.

A typical sector study[6] was that of the photochemical formation of phosgene, which follows a mechanism proposed by Bodenstein:

$$\begin{array}{rl} \mathrm{Cl_2} + h\nu \rightarrow \mathrm{Cl} + \mathrm{Cl} & \Phi I_a \\ \mathrm{Cl} + \mathrm{CO} \rightarrow \mathrm{COCl} & k_2 \\ \mathrm{COCl} \rightarrow \mathrm{Cl} + \mathrm{CO} & k_3 \\ \mathrm{COCl} + \mathrm{Cl_2} \rightarrow \mathrm{COCl_2} + \mathrm{Cl} & k_4 \\ \mathrm{COCl} + \mathrm{Cl} \rightarrow \mathrm{CO} + \mathrm{Cl_2} & k_5 \end{array}$$

---

[6] W. G. Burns and F. S. Dainton, *Trans. Faraday Soc.*, *48*, 39 (1952).

The observed rate law is

$$\frac{d(\mathrm{COCl_2})}{dt} = k'(\Phi I_a)^{1/2}(\mathrm{CO})^{1/2}(\mathrm{Cl_2})$$

From the Bodenstein mechanism, $k' = k_4(k_1k_3/k_2k_5)^{1/2}$. The application of the sector technique made it possible to evaluate each of the rate constants. For example, in liter mole^{-1} sec^{-1},

$$k_4 = 2.5 \times 10^9 \exp(-2960/RT)$$
$$k_5 = 4.0 \times 10^{11} \exp(-830/RT)$$

Reaction (5) goes at almost every collision, with a very small energy barrier. In reaction (4) the activation energy is only 5 per cent of the energy of the Cl—Cl bond that is broken, whereas the frequency factor is only 1 per cent of the collision frequency. The low frequency factor indicates a loss of freedom and decrease in entropy when the activated complex is formed.

In addition to its use in studying intermediates of short life, there is evidence that the principle of intermittent illumination is used by Nature in the ingenious fashion that is typical of her chemical processes. The response of plants to the relative length of day and night is called *photoperiodism.* This phenomenon was first clearly described in 1920, by Garner and Allard of the U.S. Department of Agriculture. Flowering plants may be divided into three classes:

(1) *Long-day plants* flower only when the daily period of illumination is greater than some critical time, *e.g.*, spinach flowers only when the length of day exceeds 13 to 14 hr.

(2) *Short-day plants* flower only when the length of day is less than a critical value; for example, 14 to 14.5 hr for chrysanthemum.

(3) *Day-neutral plants* do not exhibit photoperiodism in their flowering.

Depending on the plant, from 2 to 30 cycles of light and dark are needed to initiate flowering. Even a single flash of light during a dark period may sometimes prevent flowering. The photoperiodic process that controls flowering occurs in the leaves of the plants; in some cases the plant will flower if even one leaf receives the proper light cycle. Although the chemical compounds responsible for initiation or inhibition of flowering are not yet completely known, they appear to act as hormones which build up to a critical concentration in dark periods, and are photochemically destroyed in light periods. Other photoperiodic effects are known in both plants and animals, such as the shedding leaves by deciduous trees, and, possibly, the hibernation of the groundhog.

10. Photosynthesis in green plants. The ultimate source of most of the energy on earth, except nuclear energy, is the radiation received from the sun. This radiation is converted by photosynthesis in green plants into chemical potential energy stored in coal, oil, and carbohydrates. Green plants are reducing agents, converting carbon dioxide and water into fuels. Animals are oxidizing agents, burning the fuels back into water and carbon dioxide. The Second Law of Thermodynamics insists that this vital cycle cannot continue without some outside energy source besides the heat of the environment. The external energy that keeps the cycle spinning comes from the sun's rays. The mechanism of photosynthesis is one of the greatest problems in chemical kinetics.

It has been estimated that during the summer season an average of 1 to 2 cal per cm^2 per min of radiant energy is incident upon green plants in an open field. Of this energy only 2 to 3 per cent is stored in the plant at the end of the summer.

The photosynthetic reaction can be written schematically as

$$(1) \qquad n\,CO_2 + n\,H_2O + \text{light} \rightarrow (CH_2O)_n + n\,O_2$$

The final products are carbohydrates, such as cellulose and starch. The reaction occurs through the mediation of chlorophyll, a magnesium-porphyrin compound. This compound is green since it has two strong absorption bands, one in the red around 6600 Å, the other in the blue around 4250 Å. The maximum intensity of sunlight is in the green region of the spectrum, but most of this green light is not utilized by plants.

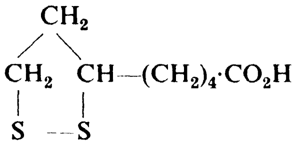
Reaction (1) above for $n = 1$, *i.e.*, one monomer unit incorporated in a carbohydrate, has a $\Delta H = 120$ kcal. Photosynthesis can occur with light of 7000 Å. Since quanta of this red light amount to 38 kcal per mole, at least three or four quanta would be needed to fulfil the energetic requirement for photosynthesis. Under favorable conditions and for short intervals of time, the quantum efficiency of photosynthesis may approach this theoretical limit, reaching perhaps 5 or 6 quanta per CH_2O unit, or a quantum yield Φ of 0.16 to 0.20.

Important information on the photosynthetic mechanism has been obtained from tracer experiments. By means of O–18 it was shown that the evolved oxygen comes entirely from the H_2O, with none from the CO_2. In other words, the H_2O reduces the CO_2.

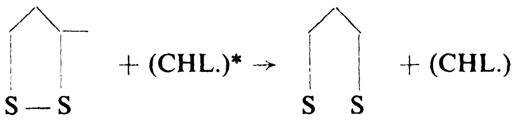
Good progress in elucidating the mechanism of photosynthesis has been made by Melvin Calvin and his co-workers at Berkeley. Their technique has been to supply radioactive (C–14) CO_2 to an aqueous suspension of algae, and to isolate the various radioactive carbon compounds formed after exposure of the suspension to light. Even after 60 sec illumination, about a dozen compounds incorporating C–14 could be detected by an autoradiograph of a paper chromatogram. If the temperature of the algae is lowered to 4°C and they are given only 10 sec illumination, only one product appears on the chromatogram, phosphoglyceric acid, $H_2O_3PO{-}CH_2{-}CHOH{-}C^*O_2H$. This is the earliest intermediate yet identified in the photosynthetic process. Since most of the radioactivity occurs in the carboxyl carbon, the step by which CO_2 is incorporated appears to be a reaction between CO_2

and some two-carbon compound, or some two-carbon group that readily splits off from a larger molecule.

Calvin has also suggested a plausible mechanism for the elementary step that utilizes the light quantum, the so-called *quantum conversion* in photosynthesis. The chloroplasts of the plant contain granules (*grana*) which each contain thousands of molecules of chlorophyll stacked in an almost close packed array. Each packet of molecules acts as a unit in light absorption, so that a quantum absorbed by any one molecule produces an exciton which can move freely throughout the entire granum. Associated with each 1000 chlorophyll molecules is a molecule of 6,8 thioctic acid,



Calvin suggested in 1952 that the conversion of the light quantum occurs when the exciton finds itself next to an adsorbed disulfide,



The dithiyl free radical can then abstract hydrogen from suitable donors, forming the disulfhydryl compound, which can reduce other reducing agents in the cell, and thus lead to the reduction of CO_2.

11. The photographic process. The general features of photography are familiar. A photographic plate is prepared by coating glass or plastic with a film of gelatin in which are suspended small crystals of silver bromide. The AgBr *grains* average 10^{-5} to 10^{-4} cm in diameter, and contain 10^{11} to 10^{12} ion pairs. When the film is exposed to light, a *latent image* is formed, which is believed to consist of submicroscopic specks of silver in some of the grains. The photochemical formation of this latent image is very sensitive to traces of substances, such as silver or silver sulfide, which act as nuclei at which growth of silver can begin in the grains. The latent image is *developed* to a *negative* image by exposure to a mild reducing agent; in this step the grains which contain silver specks are largely reduced to silver. Finally, the negative is *fixed* by dissolving the unreduced silver bromide in sodium thiosulfate.

The problem of outstanding photochemical interest is how the absorbed light forms the latent image. The quantum yield with light of low intensity approaches $\Phi = 1$, *i.e.*, every quantum of light absorbed leads to the formation of one silver atom. The light quanta, however, are absorbed at random over the surface of the AgBr grain, and yet the silver is deposited at relatively few specks within each grain. How is this process accomplished?

The first satisfactory theory was proposed in 1938 by R. W. Gurney and N. F. Mott.[7] There is good evidence that the primary absorption in the AgBr crystal occurs in the Br^- ions as $Br^- + h\nu \rightarrow Br + e$. Light absorption in the ultraviolet region is required to excite an electron from a Br^- ion in an ordinary lattice position. The absorption at longer wavelengths is probably due to Br^- ions at dislocations or other disturbed positions in the structure.

The electron is raised to an empty band in which it can move freely; hence the AgBr becomes photoconducting. The mobile electron moves through the AgBr crystal until it becomes trapped in a pre-existing silver nucleus or in a low-lying energy level of a sensitizer such as Ag_2S. Thus a center of negative charge is produced, attracting Ag^+ ions, which can move through the crystal via interstitial positions. When an Ag^+ ion reaches the negative center it is neutralized, $Ag^+ + e \rightarrow Ag$, and the silver nucleus is thus enlarged. Once a few specks of silver emerge as nuclei, they will catch the photochemically produced electrons, and then grow further by attracting Ag^+ ions.

The Br atom eventually reaches the surface of the AgBr by a process of electron transfer, $Br^- + Br \rightarrow Br + Br^-$. It can then react with constituents of the gelatin. The Br atom is a center of missing negative charge, and it is called a *positive hole*. The Gurney-Mott theory in its original form requires that these positive holes do not recombine with the electrons. As a result of ingenious experiments with thin films of pure AgBr single crystals, J. M. Hedges and J. W. Mitchell[8] have been led to a modification of the theory. They suggest that the function of the sensitizer is to trap the positive holes, preventing their recombination with the electrons. The electrons are then trapped at crystal imperfections, and the silver particles grow there to form the latent image.

It may not be too far-fetched to see a certain similarity between the processes of photography and those of photosynthesis. In both cases a light quantum absorbed in one place can produce a chemical effect some distance away, and in both cases the absorbent is dispersed in small grains in a protein material.

12. Primary processes with high-energy radiation. Table 18.2 summarizes some information about the sources of high-energy radiations. All these radiations produce *ionization* in the matter through which they pass. The Einstein law of photochemical equivalence (page 597) has its counterpart in the principle that the amount of chemical reaction is proportional to the number of ion pairs produced in the reaction medium by an ionizing radiation. The history of this principle goes back to a calculation made by W. H. Bragg in 1907, which indicated that the number of molecules of water decomposed by radon was equal to the number of ions that the same amount of radon would have produced in air. Bragg, however, was evidently not

---

[7] *Proc. Roy. Soc., A 164*, 151 (1938).

[8] *Phil. Mag. 44*, 357 (1953).

TABLE 18.2

RADIATIONS EMPLOYED IN RADIATION CHEMISTRY

Source	Radiation Particle	Typical Maximum Energy, mev
X-ray tube	Photon	0.6
Van de Graaf generator	Electron	6
	Proton	6
Cyclotron	Proton	40
	Deuteron	20
	Alpha	10
	Neutron	40
Betatron	Electron	20
	Photon	
Nuclear reactor (pile)	Photon	Dependent on conditions
	Neutron	
	Fission recoil	
Natural or artificial radioactive isotope	Photon	Dependent on isotope
	Electron	
	Alpha	
	Atom recoil	

impressed by this agreement, which he noted as "a curious parallelism in numbers." In 1908, W. Duane demonstrated that the chemical effects of α-particles were due to the ionization they caused, and in 1910 Marie Curie clearly stated the law of equivalence for α-particles in water. From about 1911 onwards S. C. Lind made use of ion-pair yields in an extensive series of experiments. He found that for some reactions the quantum yield with light and the ion-pair yield with α-particles were nearly identical, but in other cases they might differ by a factor of two or three.

The details of the ionization process depend somewhat on the particle concerned. When an X ray or γ ray interacts with a molecule, the most frequent result is the ejection of an electron by the Compton effect (page 233); *i.e.*, the process is a "collision" between a photon and an electron, in which the electron is driven out of its molecule, and the photon is deflected with altered energy and momentum. The formation of a photoelectron by a process of absorption of the photon, which is the usual event with low-energy quanta, is much less likely at high energies. For example, with 100 kv X rays, only 3 per cent of the electrons are photoelectrons, and 97 per cent are Compton electrons. At 1 mev, almost all the electrons ejected are Comptons, which have an average energy of 440 kv. As a 440 kv electron is slowed to room temperature ($\sim$ 0.02 ev) it ionizes or excites many molecules as it passes near them. One ion pair is produced for about each 30 ev, so that the

440 kv electron produces about 15,000 ion pairs, and two or three times that many excited molecules. The effect of the single ion formed in the first ionization will obviously be negligible compared with that of the numerous secondary ions and excited molecules.

The principal difference between the effects of electrons and those of ions is due to the slower speed of the latter. A proton travels one-fortieth as fast as an electron of the same energy. Thus, for a given path distance, the slowly moving ion produces many more ionizations than the swift electron. For example, per micron of path in water, a 440-kv electron would cause about two ionizations, but a proton of the same energy would cause about 2000 ionizations. The effectiveness in causing ionization simply depends on the length of time that the moving particle remains in the immediate neighborhood of the molecule.

The primary effects of fast neutrons differ somewhat from those of the charged particles, since a neutron can penetrate the electron cloud around an atomic nucleus without electrostatic repulsion. A neutron can thus literally knock the nucleus out of an atom, and usually the nucleus is knocked out so vigorously that some of the electrons are left behind and ionization results. The ejected nuclei may produce further secondary displacements and ionizations. Energetic ions can also knock out nuclei in this way, but they are much less effective than neutrons. For example,[9] in aluminum, a 2-mev neutron will produce about 6000 primary displacements, but a 20-mev proton will produce only about 80. Available sources of radiation are intense enough to produce extensive displacements in solids. For example, in a layer 1 mm deep exposed to a cyclotron beam of 20 mev protons, about 10 per cent of the nuclei would be displaced after an irradiation of 1 coulomb per cm^2. A solid in which the atoms have been displaced in this way is said to be *discomposed.* The phenomena of *discomposition* were first described by E. Wigner during the development of nuclear reactors (piles).

13. Secondary processes in radiation chemistry. As radiation passes through a reaction medium, several excited molecules are formed for each ion formed. The excited molecules are even more important than this fact would indicate, however, since one of the most probable secondary reactions of an ion is its neutralization to yield an excited molecule.[10] If we use a broken arrow to indicate a reaction caused by high-energy radiation, a schematic reaction sequence is as follows.

$$\begin{aligned}
A &\rightsquigarrow A^* \\
A &\rightsquigarrow A^+ + e \\
A^+ + e &\longrightarrow A^* \\
A^* &\longrightarrow \text{break into radicals} \\
A^* &\longrightarrow \text{rearrangement to molecules}
\end{aligned}$$

---

[9] F. Seitz, *Disc. Faraday Soc.*, *5*, 271 (1949).

[10] H. Eyring, J. Hirschfelder, and H. S. Taylor, *J. Chem. Phys.*, *4*, 479, 570 (1936).

It should be noted that any one of these steps may involve reactions more complicated than the simple ones written. For example, the ionization step may occur with a rupture of bonds, as $A \rightsquigarrow B^+ + C + e$. The large number of excited molecules formed in irradiated systems explains the parallelism frequently observed between photochemical and radiochemical reactions.

Examples of many typical reactions are provided by the results observed on irradiation of water. Aqueous systems have been most intensively studied because of their great importance in radiobiology. In pure water, the first steps, regardless of the source of radiation, appear to be

$$H_2O \rightsquigarrow H_2O^+ + e$$
$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$$

The fate of the OH radicals seems to depend on the type of radiation. With slow moving particles (α's) many OH radicals may be produced close together, and a likely subsequent step is radical combination,

$$2\,OH \rightarrow H_2O_2$$

With fast particles (β, γ) the OH radical concentration along the paths is much lower, and removal of radicals by the following sequence appears reasonable:

$$e + H_2O \rightarrow OH + H$$
$$H + H \rightarrow H_2$$
$$H + OH \rightarrow H_2O$$

The dependence of intermediate concentrations on the path of radiation through the system, and the diffusion of intermediates away from the tracks of the radiation particles are typical features of this field of chemical kinetics.

14. Chemical effects of nuclear recoil. When a nucleus emits an α, β, or γ particle, conservation of momentum requires that the product nucleus recoil in a direction opposite to that of the emitted particle. An important effect of such recoil was discovered by Szilard and Chalmers in 1934. They irradiated ethyl iodide ($C_2H_5I^{127}$) with neutrons: $I^{127}(n, \gamma)I^{128}$. The I^{128} is a β emitter of 25 min half life. The ethyl iodide, after irradiation, was shaken with a dilute aqueous solution of ordinary iodine, in which it is not appreciably soluble; much of the radioactive I^{128} was then found in the aqueous layer. Exchange between iodine in ethyl iodide and that in aqueous solution is known to be very slow. It appears, therefore, that the recoil of the iodine nucleus on emission of the γ particle is sufficiently energetic to break the C—I bond in C_2H_5I, thereby converting the iodine into a water-soluble form.

The Szilard-Chalmers effect has since been observed in many n, γ reactions. Besides its intrinsic interest as a new kind of chemical reaction, the effect has practical value in that it provides a method of preparing highly concentrated radioactive elements.

PROBLEMS

1. When propionaldehyde is irradiated at 200 mm and 30°C with light of wavelength 3020 Å, the quantum yield for CO production is found to be 0.54. If the incident light intensity is 15,000 erg per sec, calculate the rate of CO formation. What is the light intensity in einsteins per sec?

2. The photochemical chlorination of chloroform ($CHCl_3 + Cl_2 = HCl + CCl_4$) follows the rate equation $d(CCl_4)/dt = k'I_a^{1/2}(Cl_2)^{1/2}(CHCl_3)$, where I_a is the intensity of light absorbed. Devise a reaction scheme to explain this kinetics.

3. In a study of the quenching of sodium resonance radiation at 200°C, it is found that 1.6 mm of N_2 reduces the fluorescence intensity to 50 per cent of the value in the absence of added gas. If the natural lifetime of the excited Na atom is 10^{-7} sec, calculate the quenching cross section for N_2.

4. Show that when a γ ray of energy E_γ in ev, is ejected from a nucleus of mass m atomic weight units, the recoil kinetic energy of the nucleus in ev is $E_a = 5.33 \times 10^{-10}E_\gamma^2/m$. Calculate the recoil energy of Zn–65 on emission of a 1.1 mev γ ray.

5. Consider a europium-activated $SrSiO_3$ phosphor with a single trap depth of 0.72 ev and $a = 1.5 \times 10^9\ sec^{-1}$. Calculate the time for the luminescent intensity to decay to one-half its initial value at 100°K and at 400°K.

6. A photographic film is exposed for 10^{-3} sec to a 100-watt incandescent light at a distance of 10 meters. If 5 per cent of the power is emitted as visible light to which the film is sensitive, estimate the number of silver atoms that will be produced in a AgBr grain 10 microns in diameter.

REFERENCES

BOOKS

1. Bowen, E. J., *Chemical Aspects of Light* (New York: Oxford, 1946).
2. Garlick, G. F. J., *Luminescent Materials* (New York: Oxford, 1949).
3. James, T. H., and G. C. Higgins, *Fundamentals of Photographic Theory* (New York: Wiley, 1948).
4. Lea, D. E., *Action of Radiation on Living Cells* (London: Cambridge, 1947).
5. Mott, N. F., and R. W. Gurney, *Electronic Processes in Ionic Crystals* (New York: Oxford, 1940).
6. Noyes, W. A., and P. A. Leighton, *The Photochemistry of Gases* (New York: Reinhold, 1941).
7. Rollefson, G. K., and M. Burton, *Photochemistry and the Mechanism of Chemical Reactions* (New York: Prentice-Hall, 1939).

ARTICLES

1. *Annual Reviews of Physical Chemistry.* (Stanford, Cal.: *Ann. Reviews, Inc.*, 1950 to date.) These volumes contain expert reviews of recent progress in photochemistry and radiation chemistry.
2. Allen, A. O., *Disc. Faraday Soc.*, *12*, 79–87 (1952), "Mechanism of Decomposition of Water by Ionizing Radiations."
3. Bowen, E. J., *Quart. Rev.*, *1*, 1–15 (1947), "Fluorescence and Fluorescence Quenching."
4. Bowen, E. J., *Quart. Rev.*, *4*, 236–250 (1950), "Light Absorption and Photochemistry."
5. Burton, M., *J. Chem. Ed.*, *28*, 404–420 (1951), "An Introduction to Radiation Chemistry."
6. Libby, W. F., *J. Am. Chem. Soc.*, *69*, 2523–34 (1947), "Chemistry of Energetic Atoms Produced by Nuclear Reactions."
7. Massey, H. S. W., *Disc. Faraday Soc.*, *12*, 24–33 (1952), "Gaseous Ions and Their Reactions."
8. Maddock, A. G., *Research*, *2*, 556–63 (1949), "Chemical Effects of Nuclear Recoil."

PHYSICAL CONSTANTS AND CONVERSION FACTORS

Physical Constants

Electronic charge	e	$(4.8029 \pm 0.0002) \times 10^{-10}$ esu
Planck constant	h	$(6.6252 \pm 0.0005) \times 10^{-27}$ erg sec
Velocity of light	c	$(299{,}792.9 \pm 0.8)$ km sec^{-1}
Electron rest mass	m	$(9.1085 \pm 0.0006) \times 10^{-28}$ g
Avogadro number	N	$(6.0247 \pm 0.0004) \times 10^{23}$ mole^{-1}
Gas constant per mole	R	$(8.3166 \pm 0.0004) \times 10^{7}$ erg deg^{-1} mole^{-1}
Boltzmann constant	k	$(1.3804 \pm 0.0001) \times 10^{-16}$ erg deg^{-1}
Faraday constant	$\mathscr{F}$	$(96{,}520 \pm 3)$ coulomb mole^{-1}

Conversion Factors

1 bar = 1.000×10^{6} dyne cm^{-2}

1 atm = 1.01325 bar = 1.0332×10^{4} kg m^{-2}

1 erg = 1×10^{-7} joule = 2.3901×10^{-8} defined calorie

1 defined calorie = 4.1840 joule

1 BTU = 1055 joule

1 electron volt = $(1.60207 \pm 0.00007) \times 10^{-12}$ erg = 23.053 kcal mole^{-1}

Wavelength corresponding to 1 ev = $(12{,}397.8 \pm 0.5) \times 10^{-8}$ cm

1 kw = 1.341 hp = 239 cal sec^{-1} = 2545 BTU hr^{-1}

1 coulomb = 3×10^{9} esu

1 weber m^{-2} = 10^{4} gauss = $(3 \times 10^{6})^{-1}$ esu

Name Index

Subject Index