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PRINCIPLES OF CHEMICAL THERMODYNAMICS

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PRINCIPLES OF CHEMICAL THERMODYNAMICS

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PREFACE

It has been the author's experience in the teaching of physical chemistry that one can no longer do justice to the principles of chemical thermodynamics in the conventional introductory physical chemistry course without taking time from much descriptive and theoretical material that does not actually require the use of thermodynamic methods for its interpretation. At the same time, the scope of chemical thermodynamics itself has expanded so greatly during the past twenty-five years that a thorough foundation in this subject is indispensable to the modern chemist, in whatever field of chemistry his efforts may be directed.

This book is intended to serve a course in chemical thermodynamics which may accompany or immediately follow the introductory course in physical chemistry, at either the senior undergraduate or the first-year graduate level. The emphasis throughout is on general principles and their origins, with specific applications to a limited number of fields which are primarily the concern of the chemist. While mathematical formulations are employed freely throughout, no mathematics beyond calculus is required; special mathematical techniques are explained as the need arises. No prior knowledge of thermodynamics is assumed, since this course is designed to replace the ordinary thermodynamics course for chemistry students. The problems given at the end of each chapter constitute an integral part of the presentation. Most of these problems have been selected from the chemical research literature; "answers" may therefore be checked in these cases by consulting the original references. The fact that so many of the problems have been taken from papers appearing within the past few years offers convincing evidence, if such is needed, that chemical thermodynamics is decidedly a living subject. The book has not been planned as a reference source for chemical thermodynamic data, since extensive critical compilations exist elsewhere, notably in the definitive project, "Selected Values of Chemical Thermodynamic Properties," issued by the National Bureau of Standards under the direction of Dr. Frederick D. Rossini.

In keeping with our limited objective, which has been to present the theoretical structure of the science and its applications to chemistry without becoming extensively engaged in side issues of extrathermodynamic origin, certain related matters have not been discussed in detail, particularly where other sources of information are readily available.

Thus, the Debye monatomic heat-capacity formula and the Debye-Hückel limiting law for the activity coefficients of strong electrolytes have been introduced for our present purposes as *ad hoc* results of extra-thermodynamic theoretical investigations. Their origins and the general assumptions underlying their derivations have been briefly indicated, but the reader is referred elsewhere for the actual derivations on the ground that these have little to do with essential thermodynamic theory. Likewise, no discussion except in most general terms has been given of recent theories of nonideal solutions on the ground that, while the tests of such theories rest mainly on thermodynamic data, the theories themselves transcend purely thermodynamic methods of investigation and in a sense constitute a sequel to the material considered to fall within the scope of this book. The Gibbs' surface-concentration theory has not been included for discussion on the ground that, in the author's opinion, much more spectacular progress has been made in this field through applications of Langmuir's oriented monomolecular surface film hypothesis than through quantitative applications of Gibbs' law. With the aid of the references cited throughout the book, it should be possible for the enterprising student to follow up further details of many special applications that may interest him. If time permits, some of these special topics may be explored at greater length in class by means of seminar assignments, a valuable method of instruction at the level indicated.

It has been the author's good fortune to have studied with a great scientist and teacher, Professor Louis P. Hammett. His boldness of enterprise, combined with a passion for accurate knowledge and an impatience with cloudy ideas, has been a source of inspiration through many years. It is a pleasure to acknowledge personal indebtedness to him for advice, criticism, and encouragement in the completion of this work. Any errors are the responsibility of the author, and he will be glad to receive criticism that may improve the book's usefulness.

MARTIN A. PAUL

ENDICOTT, N.Y.
January, 1951

CONTENTS

CHAPTER 1

TEMPERATURE

In all measurements involving heat, and in many other kinds of physical and chemical investigations, the concept of *temperature* is of paramount importance. It is therefore appropriate for us to begin the study of chemical thermodynamics by reviewing how temperature is measured, even though the full theoretical import of the temperature concept can be appreciated only after we have discussed the second law of thermodynamics in Chap. 5.

1-1. Principles of Thermometry. We are endowed by nature with a temperature sense that enables us to distinguish the relative hotness or coldness of objects we touch or are otherwise exposed to (as through thermal radiation). This sense is, however, too crude and limited in range to be directly useful in precise scientific investigations. Therefore various types of *thermometers* have been developed to measure temperature precisely and to extend the range of measurements far beyond that directly accessible to our physiological temperature sense.

The ordinary thermometer is based on some conveniently measured physical property of a standard substance or system, the so-called "thermometric medium," that varies in a single-valued, continuous way as the medium is made hotter. The most familiar type of thermometer is based on the expansion of a liquid, such as mercury, confined within a glass tube. Other types of thermometers are based on the differential expansion of two strips of different metals joined at their extremities, the pressure of a gas confined within a glass or metal tube at fixed volume, the vapor pressure of a liquid, the electric resistance of a metal, the electromotive force set up in a circuit composed of two different metals when their junctions are at different temperatures, the rate of total radiation and also the spectral distribution of the energy radiated by a black body, and certain other thermometric properties that have been found useful in special applications.

In reading a thermometer, we are generally observing directly the temperature of the thermometric medium rather than that of the system to which it is applied. The usefulness of the thermometer for measuring the temperatures of other bodies depends on the following *funda-*

mental thermal principle,[1] which represents a generalization drawn from experience:

Whenever two or more bodies at different temperatures are exposed to each other, whether by direct physical contact, by indirect contact through an intervening material medium, or even at a distance across empty space, they influence each other in the sense that they tend to undergo changes, until ultimately a state of equilibrium has been established from which no further changes take place; such a state of equilibrium is reached only when all the bodies have come to a common temperature.

This fundamental principle is in effect a definition of *temperature equality;* two bodies that have come to equilibrium with each other (by this expression we mean that while they are potentially exposed to each other's influence, no sensible change is taking place in either) must be at the same temperature. The criterion of temperature equality thereby set up is a sufficient, though evidently not a necessary one, for two bodies may be at the same temperature without having come to a state of equilibrium in other respects. The general problem in thermometry, then, is to bring the thermometer to equilibrium with the system whose temperature is to be measured.

Three distinct mechanisms have been recognized whereby temperature equalization may be brought about: thermal conduction, thermal convection, and thermal radiation. A detailed discussion of these mechanisms would involve the concept of heat itself, which we propose to discuss in Chap. 2, as distinguished from that of temperature. The following remarks are therefore intended merely as a brief introductory review.

When temperature equalization takes place directly across the boundary between two bodies, or when it takes place through an intervening material medium that itself undergoes no sensible motion during the process, it is said to take place through *thermal conduction.* The mathematical theory of thermal conduction was established by J. Fourier in his "La Théorie analytique de la chaleur," published in 1822;[2] in this work, Fourier gave the first rational definition of that property of a mate-

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[1] A. G. Worthing and D. Halliday, in their textbook, "Heat," John Wiley & Sons, Inc., New York, 1948, refer to the content of this principle, stated by them, however, in a slightly different form ("two systems in thermal equilibrium with a third are in thermal equilibrium with each other"), as the zeroth law of thermodynamics. The author believes, however, that it is implied by the second law of thermodynamics in its most general form (see Chap. 5). We assume it here temporarily as a starting point, since the second law itself is too abstract to constitute a satisfactory introduction to the subject.

[2] An English translation by A. Freeman of this great classic has been published by G. E. Stechert & Company, New York.

rial substance known as its *thermal conductivity.* The metals have relatively high thermal conductivities, copper and silver being among the best conductors; glass, wood, and many ceramics have relatively low thermal conductivities. There is a general correlation between thermal and electrical conductivities (the Wiedemann-Franz law, discovered in 1853), which has received a satisfactory explanation in terms of the modern electronic theory of atomic structure.

Gases and liquids, in addition to showing thermal conduction, may promote temperature equalization also by means of *thermal convection,* associated with sensible motion of the material fluid substance. When the fluid is unevenly heated by being in contact with a hotter and a colder body, the temperature inhomogeneity set up in the fluid is accompanied in general by an inhomogeneity in its density; under the influence of gravity, therefore, the fluid becomes mechanically unstable, and convection currents are set up that tend to restore mechanical, and with it, thermal equilibrium. The process may be accelerated by means of forced circulation of the fluid (*e.g.*, by means of a pump or a fan). Many of the thermal insulators used in the building industries consist of porous solids entraining relatively large volumes of air; the solid network interferes with convection of the air, and thus reduces its rate of thermal exchange to that characteristic only of its thermal conductivity, which is low in comparison with the ordinary convective conductivity of free air. The net thermal conductivity of the insulator will of course be a mean between the thermal conductivities of the entrained air and of the solid material itself; air at atmospheric pressure is, however, a poorer thermal conductor than most solids (for this reason, cork is a better insulator than solid wood of the same thickness).

Temperature equalization between a hotter and a colder body may proceed even in the absence of any material connection between them by means of *thermal radiation.* This is of course the mechanism by which the sun heats the earth. According to the generally accepted theory of exchanges, first proposed by Pierre Prévost of Geneva in 1792, we believe that *all* bodies are continually emitting radiation, at a rate that increases with temperature, but is independent of the surroundings; the rise or fall of a body's temperature associated with thermal radiation thus represents the net effect of its own radiation and the radiation it receives from the surroundings. In ordinary thermometry, thermal radiation may introduce an important source of error if the thermometer happens to be exposed to radiation from a source at a different temperature outside the system whose temperature is being measured, for the thermometer may then come to an apparently steady state (while it is actually transmitting heat to or from the system) at a temperature some degrees removed from that of the system with which it is in contact. For example, the temperature registered by a meteorological thermometer exposed directly to the sun may be considerably higher than the air temperature as registered by a thermometer standing nearby in the shade. Since thermal radiation, like ordinary light, of which it is a special form, tends to travel in straight lines and is efficiently reflected by a polished metal surface, the thermometer may be protected from radiation, when necessary, by means of a surrounding metal shield, whose own temperature is maintained close to that of the system under investigation. Thermal radiation is a form of electromagnetic radiation in general; the radiation from a body at relatively low temperatures is confined to the infrared region of the spectrum, but as the body's temperature is increased, the region of greatest intensity shifts into the visible range, and the thermal radiation is then perceived in part as ordinary visible light; at still higher temperatures, the region of greatest intensity shifts on into the ultraviolet, but since the total radiation at the same time increases, the intensity of the visible part of the radiation, which then appears as dazzling white light, continues to increase. The laws of thermal radiation have been well established, theoretically and experimentally, and both the total intensity and the "color" or spectral distribution of the thermal radiation from a "black" body, or total radiator, are used independently to measure high temperatures, as we shall see in Sec. 1-7. Thermal radiation provides us with a method for measuring the temperatures of objects at a distance; thus, it is the only direct source of information we have concerning the surface temperatures of the heavenly bodies.

Now, in a general sense, all bodies in the universe are more or less directly exposed to each other, through conduction, convection, radiation, or some combination of these independent mechanisms. Our fundamental thermal principle would therefore imply that they are all influencing each other, undergoing changes that would tend ultimately to equalize their temperatures; strictly construed, thermal equilibrium must be an abstraction never actually realized. Nevertheless, the principle is based on the fact that we recognize and can produce in practice local systems that satisfy it, in the sense that they are relatively self-contained or insulated with respect to thermal changes. Thus, a localized system consisting of a finite number of contiguous material bodies may be so well enclosed by a combination of insulating materials and radiation shields that it comes to an internal state of equilibrium maintained over a period of time long by ordinary laboratory standards of observation, independently of what is going on outside. Changes taking place within a system so insulated are called *adiabatic*. Rapid changes, even when the system is not particularly well insulated, may be effectively adiabatic, if they take place during times short in comparison with the time taken by the system to readjust itself to thermal equilibrium with its surroundings.

Another type of situation that may be realized in practice is for the system to be immersed in a thermostat, a comparatively large body (of air, water, transformer oil, copper, etc.) which serves to screen the system under observation from direct interaction with the world outside. In such a situation, the thermal behavior of the system is determined primarily by its interaction with the thermostat, whose temperature it tends to assume, and only secondarily, or over a long period of time, by the comparatively slow interaction between the thermostat and the external world. The atmosphere of the room, for example, serves ordinarily as a crude kind of thermostat; but thermostats of much higher precision, covering a broad range of working temperatures, and automatically controlled to maintain constant temperatures for weeks at a time without attention, have been developed for specific laboratory and industrial applications. Changes taking place within a system whose temperature is maintained constant are called *isothermal.*

The possibility of measuring temperature at all depends on the possibility of establishing equilibrium between the thermometer and the system under observation rapidly in comparison with the rate at which the properties of the system are undergoing change as it reacts with its environment. The general changes taking place in the system as it approaches ultimate equilibrium in the world at large may, however, be greatly retarded by means of thermal insulation or thermostating. The study of thermally isolated systems and of systems maintained at constant temperature has therefore come to occupy a prominent place in thermodynamic investigation. Following up the same train of thought, the temperature of a system that has not attained a state of internal thermal equilibrium (which would be characterized according to the fundamental thermal principle by uniform temperature throughout all its parts) is in a strict sense undefined. If, however, such a system is explored by means of a thermometer sufficiently sensitive and rapid in response so that it comes to equilibrium with a local element of the system within a time short compared with the rate at which the element is undergoing change as it approaches equilibrium with the rest of the system, then we can measure its instantaneous local temperature, in much the same sense as we measure the temperature of an "isolated" system, which is in reality interacting slowly with its surroundings. In the mathematical theory of thermal conduction, this idea is extended so far as to include the concept of a temperature that may vary continuously from point to point within a material medium as a function of the space coordinates. In chemical thermodynamics, however, we shall be interested primarily in equilibrium states, in which the temperature is uniform throughout the system under investigation.

1-2. Establishment of a Temperature Scale. The thermometer, when used with corrections appropriate to its inherent experimental errors (the nature of which depends on the particular type of thermometer and the manner in which it is applied), thus fundamentally enables us to judge whether two different bodies are at the same temperature, or if they are not, to obtain an objective numerical measure of their relative temperatures. It provides us in general with a sequence of readings of some particular thermometric property, such as the length of a copper bar, the pressure of a gas, the electric resistance of a platinum wire, the emf of a bimetallic circuit, etc., correlated with various degrees of temperature. Before we can assign numerical values to the temperature itself, we must adopt a convention concerning the number that is to represent some standard reproducible difference of temperature. This choice of numerical scale is entirely arbitrary, since only the relative magnitude of one temperature with respect to another, and not the value assigned to any one temperature taken by itself, has physical meaning.

The standard interval on all modern temperature scales is in principle the difference between the *ice point* and the *steam point;* these are the constant temperatures at which ice and steam, respectively, are in equilibrium with water at standard atmospheric pressure (a pressure equal by convention to 1,013,250 dynes/cm^2; this represents the pressure at the base of a mercury column 760 mm in height at the ice point under the influence of standard gravity, $g_0 = 980.665$ cm/sec^2).[1] The difference between the readings of the thermometer (corrected for the various

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[1] Much work has been done at the National Bureau of Standards and elsewhere on the *triple point* of water as a primary fixed thermometric point, in place of the ordinary ice point. While the triple point is somewhat less convenient to set up, requiring the use of a special cell operating at reduced pressure, any uncertainty that may be introduced by the presence of a variable amount of air dissolved in the water at the ice point is eliminated, as well as all reference to the pressure, which at the triple point is fixed by nature (about 4.7 mm Hg). At the Ninth General Conference on Weights and Measures, in October, 1948 (the General Conference is a diplomatic body representing 33 participating nations, established under the terms of an international treaty of 1875, and charged with the power to adopt recommendations concerning standards of weights and measures for international use), a resolution was therefore adopted defining the zero of the centigrade scale as being the temperature 0.0100 deg below that of the triple point of pure water [H. F. Stimson, *Natl. Bur. Standards J. Research,* **42,** 209–217 (1949)]. This change of course has had no immediate practical effect, and will bear anyhow only on work of the highest precision. In order to avoid circumlocution, therefore, we shall continue throughout this chapter to regard zero as identified with the ordinary melting point of ice at atmospheric pressure.

experimental errors) at these two arbitrarily selected fixed points is called the *fundamental interval* of the thermometer. In order to convert readings of the particular thermometric property into temperatures and so to establish a temperature scale, an arbitrary number of degrees is assigned to the temperature difference represented by the fundamental interval, *i.e.*, to the difference between the steam point and the ice point. On the *Celsius* or so-called *centigrade scale* this number is 100°C; on the modern *Fahrenheit scale*, it is 180°F; on the French *Réaumur scale*, it is 80°Ré.

Let A denote this conventional number of degrees assigned between the steam point and the ice point on any of these scales, and let Δ' denote the fundamental interval of some particular thermometer whose readings (of length, pressure, resistance, etc., as the case may be) are represented by the symbol r'; then for any thermometer of the same type a unique temperature scale could be established most simply by means of a linear relation of the form

$$t' - t_0 \equiv \frac{A}{\Delta'}(r' - r'_0) \tag{1-1}$$

where t_0 denotes some standard initial temperature such as the ice point (by convention, 0°C on the Celsius scale, 32°F on the Fahrenheit scale, 0°Ré on the Réaumur scale), at which the instrument reading is r'_0, and t' is the temperature measure *defined* by the new reading r'. In other words, such a temperature measure t' would be defined as increasing in direct proportion to the increase in the thermometric property r', the proportionality constant A/Δ' being merely a conversion factor for converting instrument readings (in centimeters, atmospheres, ohms, etc.) into conventional degrees. Such a temperature scale is in fact set up by the ordinary mercury-in-glass thermometer, whose graduations, constituting actually a linear scale, are marked off on the capillary directly as temperature degrees. A naïve procedure such as this would be entirely adequate for setting up the temperature scale in the absence of other methods of measuring temperature. If, however, one makes measurements with a different type of thermometer, whose readings are represented by r'' and whose fundamental interval is Δ'', then in general the temperature measure t'' given by this second type of thermometer, according to a similar linear equation,

$$t'' - t_0 \equiv \frac{A}{\Delta''}(r'' - r''_0)$$

differs, except at the defined ice point and steam point, from the temperature measure t' given by the first (see Table 1-1). In other words, the electric resistance of a platinum wire does *not* increase *linearly* with the temperature as measured by a mercury-in-glass thermometer, and the coefficient of expansion of mercury in glass is *not* uniform on the temperature scale defined by a constant-volume nitrogen-gas thermometer, etc. Therefore one must in general qualify temperature measurements so obtained, simply by the application of Eq. (1-1), as *mercury-in-glass temperatures* (in high-precision thermometry, even the type of glass must be specified, because different thermometric glasses, having different coefficients of expansion, give slightly different temperature scales), or as *constant-volume hydrogen temperatures*, or as *platinum resistance temperatures*, etc., as the case may be.

TABLE 1-1. APPARENT TEMPERATURES AS REGISTERED BY VARIOUS TYPES OF THERMOMETERS ACCORDING TO EQUATION (1-1)*

Type of thermometer	t_1', °C	t_2', °C
Linear expansion of a copper bar	49.21	206.9
Linear expansion of a silver bar	49.50	203.96
Mercury in Jena 16^{III} glass	50.11	200.29
Platinum resistance	50.36	197.03
Platinum-rhodium thermocouple	46.9	223.4
Copper-constantan thermocouple	48.4	215.6
Constant-volume hydrogen gas	50.003	199.976
Constant-volume helium gas	50.001	199.994
Constant-volume neon gas	50.001	199.997
Constant-volume nitrogen gas	50.010	199.978
Constant-volume air gas	50.013	199.976
Constant-volume argon gas	50.014	199.971
Constant-volume oxygen gas	50.016	199.929
Constant-pressure hydrogen gas	50.004	199.976
Constant-pressure helium gas	50.000	199.999
Constant-pressure neon gas	50.002	199.990
Constant-pressure nitrogen gas	50.032	199.877
Constant-pressure air gas	50.033	199.874
Constant-pressure argon gas	50.034	199.863
Constant-pressure oxygen gas	50.035	199.839

* The values of t_1 and t_2 are the same for all the thermometers (50.000°C and 200.000°C, respectively, on the ideal-gas temperature scale). The results for the gas thermometers, standardized with an initial pressure of 1 m Hg at the ice point, are taken with permission from M. W. Zemansky, "Heat and Thermodynamics," 2d ed., p. 12, McGraw-Hill Book Company, Inc., New York, 1943. The data for the other types of thermometers are computed from information found in Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed.

Now, there is one temperature scale based on the linear equation (1-1) that has greater generality than other scales. One will note in the data of Table 1-1 that if one takes as the thermometric property r' either the pressure at constant volume or the volume at constant pressure for fixed mass of *any gas*, then the temperature t' is found to be *almost* independent of the particular gas. Such deviations as do exist among the different gases (barring those cases in which the gas is known to undergo some kind of chemical change, such as dissociation or association) are entirely the result of deviations from Boyle's law at finite pressures, for if instead of the pressure at constant volume or the volume at constant pressure, one takes the *pressure-volume product* for fixed mass of gas, and at each temperature determines by extrapolation from a series of measurements at different pressures its *limiting value as* $p \rightarrow 0$, then the temperature measure t defined by the linear equation

$$t - t_0 \equiv \frac{A}{\Delta}\left[\lim_{p\rightarrow 0}(pV)_t - \lim_{p\rightarrow 0}(pV)_0\right] \tag{1-2}$$

is entirely independent within experimental error of the particular gas employed. The fundamental interval Δ in Eq. (1-2), which represents the increase in the value of $\lim_{p\rightarrow 0}(pV)$ between the ice point and the steam point, depends of course on the particular gas, as well as on the mass of it contained in the thermometer; but the ratio $\Delta/\lim_{p\rightarrow 0}(pV)_0$, representing the *relative* increase in the value of $\lim_{p\rightarrow 0}(pV)$ between the ice point and the steam point, is a universal constant, whose accepted value according to the most precise experimental measurements is 0.36608 ± 0.00002 (see Table 1-2).

Equation (1-2), which defines the *ideal-gas temperature* t, may therefore be put in the form

$$t - t_0 = \frac{A}{0.36608}\,\frac{\lim_{p\rightarrow 0}(pV)_t}{\lim_{p\rightarrow 0}(pV)_0} - \frac{A}{0.36608}$$

If now we assign to the ice point in place of the arbitrary number represented by t_0 (*e.g.*, $t_0 \equiv 0°\text{C}$ on the Celsius scale), the number $A/0.36608$, then temperature measures on the new scale, which we shall represent by the symbol T, are given by

$$T = \frac{A}{0.36608}\,\frac{\lim_{p\rightarrow 0}(pV)_t}{\lim_{p\rightarrow 0}(pV)_0} \tag{1-3}$$

The number

$$T_0 \equiv \frac{A}{0.36608} \tag{1-4}$$

which represents the ice point on the new or *absolute ideal-gas temperature scale,* thus has the value 273.16 ± 0.01 in terms of centigrade degrees (A = 100°C), or 491.69 ± 0.02 in terms of Fahrenheit degrees (A = 180°F). One of the important practical methods of determining the value of the absolute ice point thus consists of precise measurements of $\lim_{p\to 0}(pV)$ for hydrogen, nitrogen, helium, etc., at the steam point and at the ice point. The extrapolation may be most precisely carried out for gases that deviate least from Boyle's law at those temperatures around atmospheric pressure; for this reason, hydrogen, helium, and nitrogen are better thermometric

TABLE 1-2. RELATIVE INCREASE OF PRESSURE AT CONSTANT VOLUME, OF VOLUME AT CONSTANT PRESSURE, AND OF IDEAL LIMITING pV, BETWEEN THE ICE POINT AND THE STEAM POINT FOR VARIOUS GASES*

Gas	$\left[\dfrac{p_{100} - p_0}{p_0}\right]_{V_0}$	$\left[\dfrac{V_{100} - V_0}{V_0}\right]_{p_0}$	$\dfrac{\lim_{p\to 0}(pV)_{100} - \lim_{p\to 0}(pV)_0}{\lim_{p\to 0}(pV)_0}$
Air	0.36716	0.36711	0.36604
Argon	0.36717	0.36724	0.36604
Carbon dioxide	0.3710	0.37217	0.3665
Carbon monoxide	0.3673	0.3672	0.3663
Ethylene	0.3722	0.3735	0.3665
Helium	0.36613	0.36591	0.36608
Hydrogen	0.36627	0.36603	0.36604
Methane	0.3678	0.3681	0.3662
Neon	0.36628	0.36606	0.36604
Nitrogen	0.36718	0.36709	0.36610
Oxygen	0.36735	0.36746	0.36604

* The value of p_0 in the second and third columns is 1 atm; the data in these columns are taken from the compilation by J. B. M. Coppock, *Phil. Mag.*, (7) **19**, 446–457 (1935). The limiting values in the last column are derived from the following sources:

Air, argon, neon, oxygen: L. Holborn in Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement I, pp. 64–67, 1927.

Carbon dioxide, ethylene: J. B. M. Coppock and R. Whytlaw-Gray, *Proc. Roy. Soc.* (*London*), (A) **143**, 487–505 (1934).

Carbon monoxide: E. P. Bartlett, H. C. Hetherington, H. M. Kvalnes, and T. H. Tremearne, *J. Am. Chem. Soc.*, **52**, 1374–1382 (1930).

Helium: W. Heuse and J. Otto, *Ann. Physik*, (5) **2**, 1012–1030 (1929).

Hydrogen: J. Otto in Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIa, p. 52, 1931.

Methane: H. M. Kvalnes and V. L. Gaddy, *J. Am. Chem. Soc.*, **53**, 394–399 (1931).

Nitrogen: J. Otto, A. Michels, and H. Wouters, *Physik. Z.*, **35**, 97–100 (1934).

The mean, 0.36608 ± 0.00002, represents the result of a critical evaluation of all the data, as given by J. A. Beattie in the symposium, "Temperature. Its Measurement and Control in Science and Industry," pp. 74–88, Reinhold Publishing Corporation, New York, 1941. See also, W. Heuse and J. Otto, *Ann. Physik*, (5) **2**, 1012–1030 (1929); R. T. Birge, *Rev. Modern Phys.*, **13**, 233–239 (1941).

gases than carbon dioxide or ammonia.[1] Temperatures on the absolute scale are related to temperatures on the ordinary scale, having the same number of degrees assigned to the fundamental interval but an arbitrary number t_0 assigned to the ice point itself, through the equation

$$T = t - t_0 + T_0 \tag{1-5}$$

Thus, temperatures on the absolute centigrade or *Kelvin temperature scale*[2] are derived from ordinary centigrade or Celsius temperatures (for which $t_0 \equiv 0°\text{C}$) simply by the addition of 273.16; such temperature measures are designated by the suffix °K; for example, $T_0 = 273.16°\text{K}$. Temperatures on the absolute Fahrenheit or *Rankine temperature scale*[3] are derived from ordinary Fahrenheit temperatures (for which $t_0 \equiv 32°\text{F}$) by the addition of 459.69; such temperature measures, which are occasionally used by chemical and mechanical engineers, are designated by the suffix °R; for example, $T_0 = 491.69°\text{R}$.

Now, according to Avogadro's hypothesis, the value of $\lim\limits_{p \to 0} (p\bar{V})$, where $\bar{V}$ represents the volume per *mole*, is at any given temperature the same for all gases; the accepted value at the ice point is 22.4140 ± 0.0004 liter atm/mole, derived from measurements on oxygen, whose chemical molecular weight has the conventional value 32.0000.[4] The combination of factors

$$R \equiv \frac{1}{T_0} \lim_{p \to 0} (p\bar{V})_0 = \frac{0.36608}{A} \lim_{p \to 0} (p\bar{V})_0 \tag{1-6}$$

occurring in Eq. (1-3) applied to 1 mole of any gas therefore defines a universal constant, known as the *ideal gas constant R*, such that at any temperature

$$\lim_{p \to 0} (p\bar{V})_T = RT \tag{1-7}$$

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[1] The only other method that has been found practicable and sufficiently precise to date is based on the Joule-Thomson effect, to be discussed in Chap. 3. J. R. Roebuck and T. A. Murrell have given the best estimate of $T_0 = 273.17 \pm 0.02°\text{K}$ by this independent method in the symposium "Temperature. Its Measurement and Control in Science and Industry," pp. 60–73, Reinhold Publishing Corporation, New York, 1941; see also J. R. Roebuck, *Phys. Rev.*, **50,** 370–375 (1936).

[2] Named after Sir William Thomson, Lord Kelvin, who derived such a scale in 1852 from the second law of thermodynamics, as we shall see in Chap. 5.

[3] Named after W. J. M. Rankine, nineteenth century British engineer and physicist.

[4] C. S. Cragoe, *J. Research Natl. Bur. Standards*, **26,** 495–536 (1941); see also C. S. Cragoe, in "Temperature. Its Measurement and Control in Science and Industry," pp. 89–126, Reinhold Publishing Corporation, New York, 1941; this value recommended by Cragoe has been adopted by F. D. Rossini and his staff for the critically evaluated compilation, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D. C., Dec. 31, 1947.

This equation is commonly written in the approximate form

$$p\bar{V} = RT \tag{1-8}$$

which may be applied to any gas at pressures sufficiently low so that deviation from Boyle's law does not introduce a significant error; Eq. (1-8) is the familiar *ideal-gas equation of state.* It was not necessary to introduce Avogadro's hypothesis in order to establish the ideal-gas temperature scale, but we have introduced it at this point because the experimental determination of R is so intimately related to the quantities measured in the setting up of the absolute temperature scale. The numerical value of R depends of course on the system of measurement used to represent p and $\bar{V}$, as well as on the number of degrees A assigned to the fundamental interval; thus, $R = 0.0820544 \pm 0.0000034$ liter atm/mole °K; with p and $\bar{V}$ represented in mks units, $R = 8.31439 \pm 0.00034$ joule/mole °K. Other equivalent values may be computed by means of the appropriate conversion factors.[1]

In Chap. 5, we shall find that a temperature scale of even greater generality than the ideal-gas temperature scale can be founded on the second law of thermodynamics. This so-called *thermodynamic temperature scale* is entirely independent of the particular material system used as the thermometer. Its form, however, turns out to be identical with that of the ideal-gas temperature scale, which constitutes therefore an experimental method of measuring temperatures on the thermodynamic scale. We shall accordingly refer to temperatures measured on the ideal-gas temperature scale as *thermodynamic temperatures,* and shall use the symbol t to represent the thermodynamic temperature based on an arbitrarily assigned ice point and fundamental interval (as on the Celsius scale); we shall use the symbol T to represent the *absolute thermodynamic temperature,* based on an ice point defined in relation to the fundamental interval by means of Eq. (1-4), or other equivalent expressions.

Although the adjective "absolute" is customarily applied to the temperature scale given by Eq. (1-3), one should recognize nevertheless that only the relative value of one temperature with respect to another has physical meaning, and not the individual value assigned to any one temperature by itself. A somewhat different method of setting up the "absolute" scale from the one now in use would be to assign instead of an arbitrary number A to the difference between the steam point and the

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[1] Throughout this book, we use the expression *mole* without qualification to mean *gram-mole,* or unit of mass represented by the substance's chemical formula weight in *grams.* In chemical engineering, other chemical units of mass, such as the pound-mole, are also in use; compare O. A. Hougen and K. M. Watson, "Chemical Process Principles," John Wiley & Sons, Inc., New York, 1947.

ice point an arbitrary number T_0 to the absolute ice point itself. This possibility was in fact pointed out in 1854 by J. P. Joule and W. Thomson (Lord Kelvin), *i.e.*, of assigning to T_0 in the equation

$$T \equiv T_0 \frac{\lim\limits_{p\to 0} (pV)_t}{\lim\limits_{p\to 0} (pV)_0} \tag{1-9}$$

a *conventional* numerical value, which in the interest of continuity (though not necessarily in principle) should agree with the best accepted experimental value of T_0 based on the existing scale convention at the time the change should be made; thereafter, any revision made necessary by greater refinement in the measurement of T would go into revision of the interval between the ice point and the steam point, rather than into revision of the value of T_0. Joule and Thomson at the time rejected this method of establishing the absolute temperature scale in favor of the one we use today; but the proposal to assign a permanent conventional value to the absolute ice point has recently been revived by W. F. Giauque,[1] and has received serious consideration by the Advisory Committee on Thermometry of the International Bureau of Weights and Measures, and also by the International Union of Pure and Applied Physics.[2] Giauque's proposal has the advantages that the relation between ordinary temperatures and corresponding "absolute" temperatures would no longer be subject to experimental error, and that in the establishment of "absolute" temperatures directly by means of gas thermometry, the experimental error introduced by the present necessity of measuring $\lim\limits_{p\to 0} (pV)$ at the steam point would be eliminated. It has the disadvantage that in the standardization of other kinds of thermometers, such as platinum resistance thermometers, the steam point would lose its present status as a defined thermometric fixed point, and any experimental error in its establishment (at present thrown into the value of the absolute ice point) would enter the calibration of the thermometer.[3] Of course, no immediate practical effect of such a change in thermometric standards would be noted. For our present purpose, we need only observe further that no

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[1] W. F. Giauque, *Nature*, **143**, 623–626 (1939).

[2] F. G. Brickwedde, *Bull. Am. Phys. Soc.*, **23**, No. 3, 23, (1948) (abstract of a paper presented before the meeting of the American Physical Society in Washington, D.C., April 29 to May 1, 1948). The proposal was put before the Ninth General Conference on Weights and Measures in 1948, and a resolution was adopted recognizing the principle, but deferring the assignment of a definite value to T_0; see Stimson, *op. cit.*, p. 215.

[3] H. T. Wensel, in "Temperature. Its Measurement and Control in Science and Industry," p. 10, Reinhold Publishing Corporation, New York, 1941.

change in our understanding of the essentially comparative nature of the temperature concept is involved, but merely a change in our attitude concerning the most convenient method of realizing the temperature scale in practice.

Having thus briefly reviewed the principles on which the measurement of temperature is based, we shall devote the rest of this chapter to descriptions of several kinds of thermometers used to establish the temperature scale in practice, concluding with a description of the present International Temperature Scale. We shall return to a general discussion of the thermodynamic temperature concept in Chap. 5.

1-3. Liquid-in-glass Thermometers. The earliest known thermometer was invented by Galileo about 1592. It was actually an air thermoscope, consisting of air within a glass bulb, confined over wine in a glass tube leading down into an open cistern or reservoir; as the air expanded or contracted with rising or falling temperature, its volume was indicated by the level of the confining liquid within the connecting tube. A scale was marked on the tube, whose intervals corresponded approximately to one-thousandth the volume of the bulb. Upon the discovery in 1643 of atmospheric pressure and the invention of the mercury barometer by Galileo's former assistant, E. Torricelli, it became evident that the air thermoscope was sensitive to changes in the external pressure of the atmosphere, as well as to temperature changes.

The first hermetically sealed liquid-in-glass thermometer was designed by Grand Duke Ferdinand II of Tuscany, about 1660. It was much like a modern alcohol thermometer, consisting of a glass bulb containing wine or alcohol, sealed to a glass capillary tube, which was sealed off at the opposite end. Thermometers of this type were put to use by scientists at the famous Academica del Cimento, founded by Grand Duke Ferdinand in Florence, and they were long known as Florentine thermometers. Those used for weather observations were commonly standardized by marks placed on the capillary tube denoting the extreme positions reached by the liquid boundary on the hottest day in summer and the coldest day in winter; intermediate temperatures were judged accordingly, on a scale subdividing the interval between these extreme "fixed" points. The Florentine scientists applied the thermometer also to the earliest measurements of human body temperature. Isaac Newton in 1701 used a liquid-in-glass thermometer filled with linseed oil to establish a numerical temperature scale of extended range; using as thermometric fixed points the melting point of packed snow, to which he assigned the number 0, and human body temperature, to which he assigned the number 12, he determined the boiling point of water (34), and the melting points of several metals (*e.g.*, tin 72, bismuth 81, lead 96, etc.); by placing small quantities of these molten metals on a block of heated iron, and observing the time required for each in turn to reach the point of solidification as the block cooled, he was able to establish the well-known cooling law that bears his name.[1]

Mercury thermometers were first introduced about 1724 by Daniel Gabriel Fahrenheit, who made many improvements in the design and reproducibility of liquid-in-glass thermometers. Mercury has several advantages over other available thermometric liquids: it is easily purified, and does not wet clean glass; its low specific heat and high thermal conductivity result in comparatively rapid attainment of equilibrium with its surroundings; it is available in liquid form over quite a wide range of temperatures, from its freezing point at −38.87°C to its normal boiling point at 356.7°C. In ordinary thermometers, the upper part of the capillary may be evacuated before the end is sealed off, so that only mercury vapor is present above the liquid, at its own vapor pressure; but special thermometers are made in which this space is filled with nitrogen gas under pressure, permitting extension of the range up to about 500°C; if the gas were not present, the mercury at high temperatures would tend to distill readily from the lower into the upper part of the capillary. The chief disadvantages of mercury compared with other liquids are its high density, high surface tension, and tendency to stick because of a difference between the contact angles with glass for an advancing and for a retreating interface.

Fahrenheit used his thermometers to establish many thermometric fixed points; he showed, for example, that the variations previously reported in the boiling points of purified liquids were associated with variations in the barometric pressure and that at a given pressure the boiling points were constant and reproducible; he showed also that the freezing point of water was constant and reproducible, once ice crystals had formed; previous observers had been misled by the occurrence of supercooling. By experimenting with so-called freezing mixtures (mixtures of various salts with ice), he discovered reproducible fixed temperatures well below the melting point of ice. His original temperature scale, proposed in 1714, was based on a freezing mixture of ammonium chloride and ice, to which he assigned the number 0 (this was the lowest temperature he was able to produce at that time), and normal human body temperature, to which he first assigned the number 12, but later the number

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[1] Newton's own account of these experiments, originally published anonymously, is given by W. F. Magie, "A Source Book of Physics," pp. 125–128, McGraw-Hill Book Company, Inc., New York, 1935.

96.[1] The latter "fixed" point was clearly unsatisfactory as a primary standard. The modern method of basing the temperature scale on the ice point and steam point as defined standards was proposed in 1742 by Andreas Celsius, astronomer and mathematician at the University of Upsala; Celsius proposed originally to assign the number 0 to the steam point, and the number 100 to the ice point, but at the suggestion of his colleague, M. Strömer, these numbers were later reversed, giving rise to the modern Celsius or centigrade scale. The modern Fahrenheit scale, redefined since Fahrenheit's time, is based on the same two fixed points as the Celsius scale, but the ice point is assigned the number 32°F and the steam point the number 212°F, these numbers corresponding to the approximate temperatures actually found for the two systems on Fahrenheit's original scale. The temperature scale founded by the eighteenth-century physician and zoologist, R. A. de Réaumur, was originally planned so that 1 deg rise should correspond to an increase of one one-thousandth in the volume of the thermometric liquid (an alcohol-water solution); the modern Réaumur scale is, however, based on the arbitrary assignment of 0°Ré to the ice point and 80°Ré to the steam point.

For many years, mercury-in-glass thermometers were the principal instruments available to scientists for the measurement of temperature. The temperature scale was of course established merely by the setting of a linear scale on the capillary tube to subdivide and extend the interval defined by the difference between the ice-point and steam-point readings; modern mercury thermometers are in fact graduated in precisely this way. Aside, however, from the general difficulties that may arise with any kind of thermometer, such as error from exposure to direct thermal radiation, and misleading indications from local temperature inhomogeneities or failure of the system under observation to have reached a state of internal equilibrium, all liquid-in-glass thermometers are subject to a number of specific errors (including deviation from the thermodynamic or ideal-gas temperature scale), the corrections for which are sufficiently large and uncertain so that thermometers of this type are no longer regarded as high-precision instruments. To begin with, there is a parallax error that limits the precision with which the scale may be read, and also an error resulting from sticking of the mercury (other thermo-

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[1] The decimal system of notation was not widely used in Europe until well into the eighteenth century; nonintegral numbers were expressed as rational fractions, *e.g.*, $1\frac{17}{32}$ (this custom is by no means obsolete today, in commercial transactions). All the earlier temperature scales were therefore based on a standard interval between two primary fixed points represented by a number having many integral factors, so that the scale could be conveniently subdivided by means of rational fractions (halves, thirds, quarters, sixths, etc.)

metric liquids that *wet* glass, such as alcohol and toluene, may have comparable drainage errors) which may be reduced by averaging the readings taken with a rising and with a falling thread. Then, among the more important of the specific corrections are the following:[1]

1. *Correction for nonuniformity of the capillary bore.* Since the thermometer bears a linear scale, any variation in the cross-sectional area of the tube results in error. It is difficult to check the cross-sectional area precisely in the finished thermometer, so it is most practical to have the thermometer standardized by a comparison of its readings at temperatures other than the two primary fixed points with those of a standard thermometer of a different type; the National Bureau of Standards will perform this service for a nominal fee, provided that the thermometer satisfies certain specifications with regard to construction; the Bureau also sells standard samples of highly purified chemicals whose melting points have been certified.

2. *Corrections for ice-point shift.* *a.* A temporary depression of the ice-point reading will follow every exposure to a higher temperature, because there is hysteresis in the adjustment of the glass bulb to the "normal" volume; at the ice point itself, it may take several days for the bulb to return to its true equilibrium volume. For this reason, mercury-in-glass temperatures are taken with respect to a variable temporary zero, determined for each reading by immersing the thermometer in an ice bath immediately after the high-temperature exposure; the ice-point reading so obtained, which if the high-temperature exposure was at 100°C may be 0.04 to 0.08°C lower than the reading that would ultimately be obtained if the thermometer were kept for several days at the ice point, is taken to be the temporary zero of the scale, and the high-temperature reading corrected accordingly.

b. There may also be a secular or gradual drift in the ice-point reading of a more permanent nature, resulting from slow changes taking place in the glass; permanent displacement of the ice-point reading can be detected by exposure of the thermometer to the ice-point temperature for several days, in order to overcome the temporary lag.

c. If the thermometer has not been properly annealed, the bulb will undergo permanent contraction when the thermometer is exposed to a high temperature, with the result that the ice-point reading may rise by as much as 20°C on the scale. This should not happen if the thermome-

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[1] Testing of Thermometers, *Natl. Bur. Standards Circ.* C8, (1926); "International Critical Tables," Vol. I, pp. 54–56, McGraw-Hill Book Company, Inc., New York, 1926; J. Busse, Liquid-in-glass Thermometers, in "Temperature. Its Measurement and Control in Science and Industry," pp. 228–255, Reinhold Publishing Corporation, New York, 1941.

ter has been constructed from a good grade of thermometric glass, and been carefully annealed; permanent displacement of the ice-point reading should then not exceed 0.1°C so long as the thermometer is never exposed to temperatures higher than 150°C.

3. *Correction for the mean scale degree.* One must check the fundamental interval of the thermometer periodically (once or twice a year) by a redetermination of the steam-point reading, and correct the entire scale accordingly; changes in the fundamental interval may result from secular changes in the volume of the bulb and the length of the glass scale.

4. *Correction for exposed stem.* Liquid-in-glass thermometers are ordinarily calibrated for total immersion. If the thermometer should be used under conditions such that part of the liquid in the capillary is exposed at a different temperature from that of the system in which the bulb rests, then a correction is necessary to the reading which would have been obtained if the entire stem had been at the same temperature as the bulb. This correction is generally given in the form

$$\delta = \alpha d(t - t_s)$$

where δ is the correction, expressed in scale degrees, α the coefficient of cubical expansion of mercury in glass (0.000158/°C for the typical Jena 16^{III} and Corning normal thermometric glasses), d the number of scale degrees exposed, t the true bulb temperature (the uncorrected reading is generally sufficiently close for this purpose), and t_s the mean temperature of the exposed stem; this latter quantity is difficult to ascertain precisely, because of thermal conduction and radiation; it is usually estimated by means of a second thermometer placed alongside the first, with its bulb near the middle of the exposed stem. For special applications in which the working conditions can be maintained uniform, such as in routine melting-point determinations, partial-immersion thermometers are manufactured, calibrated for a certain depth of immersion (*e.g.*, 75 mm, or 3 in.); if the stem is exposed to air at "normal" laboratory conditions, no stem correction is then necessary, but obviously such thermometers cannot be regarded as high-precision instruments.

5. *Corrections for external and internal pressure.* The bulb of a modern centigrade thermometer has a volume equivalent to about 6000 scale degrees; therefore a change in the volume either of the mercury or of the glass bulb, or the net effect of a change in both, amounting to as much as 0.02 per cent, besides the normal changes with temperature, will result in an apparent difference of 1°C in the temperature readings.

a. External pressure on the bulb will decrease its volume at a rate proportional to its diameter and inversely proportional to the wall thickness. The typical mean effect on a thermometer whose bulb has a diameter within the range 5 to 7 mm is +0.1°C/atm. This effect works in the opposite direction when the thermometer is introduced into an evacuated system.

b. Internal pressure from the weight of the mercury itself tends to enlarge the bulb and at the same time decrease the volume of the mercury, so the coefficient for this effect is about 10 per cent greater than for the external pressure effect. The thermometer is intended to be used normally in a horizontal position; the internal pressure correction applies to readings taken with the thermometer in a vertical or an inclined position, when the readings tend to be too low.

6. *Correction to the thermodynamic scale.* At all temperatures except the defined ice point and steam point, a correction must be applied to the mercury-in-glass temperature, after the thermometer has been corrected for all other experimental errors, in order to reduce the readings to the thermodynamic temperature scale; the coefficient of expansion of mercury in glass is not uniform on this scale. The corrections have been established through fundamental comparison of mercury-in-glass thermometers with gas thermometers, whose readings have been corrected to the ideal-gas state by extrapolation to zero pressure; this comparison was first undertaken by P. Chappuis in 1884, working under the auspices of the newly constituted International Bureau of Weights and Measures. Corrections for several kinds of thermometric glasses are given in Table 1-3.

Liquid-in-glass thermometers for measurements at low temperatures, below the freezing point of mercury, are commonly filled with pentane, alcohol, or toluene. It is customary to calibrate them with respect to a secondary "fundamental" interval, defined by the ice point and the carbon dioxide sublimation point at normal atmospheric pressure, −78.51°C on the thermodynamic temperature scale. The corrections to the thermodynamic temperature scale for a pentane-in-glass thermometer are included in Table 1-3.

1-4. Gas Thermometers. The first true gas thermometer was constructed by Guillaume Amontons in 1702. This thermometer contained air maintained at constant volume by means of a manometer, the pressure being used as a measure of the temperature. Amontons drew the quite modern conclusion that heat represented a form of motion, and estimated the location of the absolute zero point by extrapolating his temperature scale to the point at which the pressure of the gas, at constant volume, would vanish. The skillful experimental work of Joseph Louis Gay-Lussac during the early part of the nineteenth century proved that *all* gases expanded at approximately the same relative rate as the temperature was increased at constant pressure; this work laid the foundations of the universal ideal-gas temperature scale. The researches of H. V.

TABLE 1-3. CORRECTIONS TO THE THERMODYNAMIC TEMPERATURE SCALE FOR LIQUID-IN-GLASS THERMOMETERS*

Mercury-in-glass Corrections, °C

t, °C	*Verre dur* (French hard glass)	Kew glass	Jena 16^{III}	Jena 59^{III}
−39	+0.420			
−20	+0.172	......	+0.16	+0.07
0	0.000	0.00	0.00	0.00
+20	−0.085	0.00	−0.09	−0.04
40	−0.107	+0.01	−0.12	−0.03
60	−0.090	+0.01	−0.10	−0.02
80	−0.050	+0.02	−0.06	0.00
100	0.000	0.00	0.00	0.00
120	+0.06	......	+0.03	−0.05
140	+0.07	......	+0.02	−0.16
160	+0.03	......	−0.02	−0.31
180	−0.04	......	−0.12	−0.52
200	−0.12	......	−0.29	−0.84
300	....	......	−2.7	−4.4
400	....	......	......	−12.6
500	....	......	......	−26.9

Pentane-in-glass Corrections, °C

t, °C	Jena 16^{III}
−180	−21.0
−160	−16.2
−140	−11.6
−120	−7.3
−100	−3.4
−80	−0.2
−78.5	0.0
−60	+2.0
−40	+3.0
−20	+2.4
0	0.0
+20	−4.4

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* "International Critical Tables," Vol. I, pp. 54–56, McGraw-Hill Book Company, Inc., New York, 1926.

Regnault during the middle of the nineteenth century contributed greatly to the precision of gas measurements, and demonstrated the approximate nature of Boyle's law at finite pressures; the idea of extrapolating to zero pressure in order to establish the corrections from real to ideal-gas behavior was conceived by Regnault in 1847, but was first applied experimentally by M. Berthelot in 1898. Modern research on thermometric gases (those gases having the lowest critical temperatures) is being actively pursued, because of its bearing on the determination of the absolute ice point, and on the precise establishment of thermodynamic temperatures in general.[1]

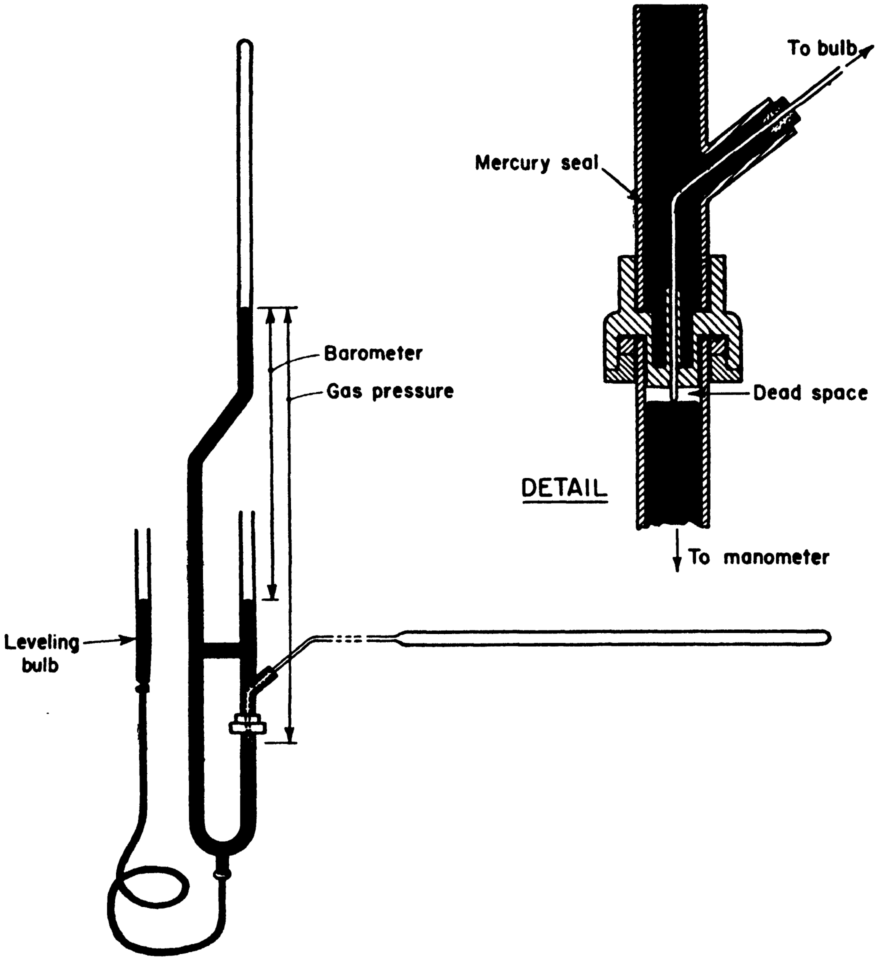

Fig. 1-1. Schematic diagram of constant-volume gas thermometer developed by P. Chappuis at the International Bureau of Weights and Measures.

A close approach to the ideal-gas temperature scale is realized experimentally in the modern constant-volume gas thermometer (Fig. 1-1).

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[1] For reviews, see F. Henning, Temperaturmessung, in "Handbuch der Physik," Vol. IX, Chap. VIII, Springer-Verlag, Berlin, 1926; F. G. Keyes, in "Temperature. Its Measurement and Control in Science and Industry," pp. 45–59, Reinhold Publishing Corporation, New York, 1941; J. A. Beattie, *ibid.*, pp. 74–88; C. S. Cragoe, *ibid.*, pp. 89–126; C. S. Cragoe, *J. Research Natl. Bur. Standards*, **26**, 495–536 (1941).

With hydrogen as the thermometric gas, this thermometer was in fact for many years (1887 to 1927) the standard instrument defining the International Temperature Scale. Because hydrogen leaks through the walls of the bulb at temperatures higher than 500°C, the tendency in recent years has been to replace hydrogen altogether by nitrogen for measurements above room temperature, and because helium has a lower critical point, to replace hydrogen by helium for measurements below room temperature. The gas, ordinarily sufficient in amount to produce a pressure of 1 m Hg at the ice point (the precise correction to the ideal-gas scale obviously depends on the value of this initial pressure), is confined in a platinum-iridium tube about 1 m in length and 36 mm in internal diameter, having a capacity of about 1 liter. It is attached through a platinum capillary tube about 1 m in length to a mercury manometer; the tip of a fine platinum needle projecting just beyond the opening of the connecting capillary tube into the manometer defines a fixed volume of the gas, not counting the bulb's own expansion and contraction with changes in its temperature.

Many corrections which are tedious and difficult to apply are necessary before the temperature can be determined from the pressure readings. These include a "dead space" correction for the gas in the connecting tube and in the small space surrounding the platinum point, correction for change in the volume of the bulb with temperature, and with internal and external pressure, correction for the effects of temperature and pressure on the height of the mercury column, etc. When all these experimental errors have been corrected for, there remains the final correction from the constant volume, $p_0 = 1$ m Hg scale, to the ideal-gas scale; such corrections for several thermometric gases are given in Table 1-4, as determined by F. G. Keyes from a critical analysis of their behavior at various pressures.

With nitrogen gas confined in a platinum-rhodium bulb, temperatures as high as 1600°C have been directly measured by means of gas thermometry. The classic research in this range was conducted by Day and Sosman,[1] who determined the melting point of palladium to be 1549.2 ± 2°C on a constant-volume nitrogen scale; by the use of an ice-point pressure of 350 mm Hg instead of the conventional 1 m Hg, their high-temperature scale became practically identical with the ideal-gas scale, since at the resulting lower pressures, the deviation of nitrogen from Boyle's law was negligible in comparison with other experimental errors. This particular investigation was of the utmost practical and theoretical importance, because it served to verify the thermal radiation laws, which are the only

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[1] A. L. Day and R. B. Sosman, High Temperature Gas Thermometry, *Carnegie Inst. Wash.*, *Pub.* 157, 1911.

means of carrying on the temperature scale beyond this point with satisfactory precision.

At the other end of the temperature scale, the constant-volume helium-gas thermometer may be used without special difficulty down to about 5°K. By means of a special low-pressure helium-gas thermometer, having an ice-point pressure of but 0.20 cm Hg, Keesom and his coworkers succeeded in measuring directly temperatures down to 0.71°K, at which point the vapor pressure of liquid helium is but 0.00036 cm Hg; they used this special gas thermometer to standardize the liquid-helium vapor-pressure thermometer, which is more sensitive and convenient to use in the range below 5°K.[1]

TABLE 1-4. CORRECTIONS OF GAS-THERMOMETER READINGS TO THE THERMODYNAMIC TEMPERATURE SCALE*

t, °C	Corrections, °C			
	Constant volume, p_0 = 1 m Hg			Constant pressure, 1 m Hg
	Hydrogen	Helium	Nitrogen	Nitrogen
−270	....	+0.0364		
−250	+0.0888	+0.0305		
−200	+0.0436	+0.0181		
−150	+0.0230	+0.0101	+0.1879	
−100	+0.0108	+0.0049	+0.0616	
− 50	+0.0037	+0.0017	+0.0174	
0	0.0000	0.0000	0.0000	0.0000
100	0.0000	0.0000	0.0000	0.0000
200	+0.0071	+0.0035	+0.0250	+0.1393
300	....	....	+0.0660	+0.3082
400	....	....	+0.1174	+0.5192
500	....	....	+0.1809	+0.7472
600	....	....	+0.2508	
1000	....	....	+0.5895	

* F. G. Keyes, in "Temperature. Its Measurement and Control in Science and Industry," pp 45–59, Reinhold Publishing Corporation, New York, 1941, with permission.

Gas thermometers are obviously not practicable for ordinary temperature measurements. Their most important function has been the precise establishment on the thermodynamic temperature scale of a number of secondary fixed temperatures, which are used for the standardization of other working thermometers.

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[1] W. H. Keesom, S. Weber, and G. Nørgaard, *Communs. Kamerlingh Onnes Lab. Univ. Leiden* 202b (1929); W. H. Keesom, S. Weber, and G. Schmidt, *ibid.*, 202c (1929); see also, W. H. Keesom, "Helium," Elsevier, Amsterdam, 1942.

1-5. Resistance Thermometers. The electrical resistivity of many metals increases with temperature, and several metals, including platinum and nickel, that undergo no phase transitions or other singularities in behavior over a wide range of temperatures, and that can be obtained in sufficiently pure condition, have been found satisfactory for the construction of resistance thermometers. The first platinum resistance thermometer was constructed by C. William Siemens in 1871, but because of inadequate testing on the part of a special committee of the British Association appointed to report on the new instrument, its further development was retarded for a number of years. It was brought to its present state of perfection mainly through the work of H. L. Callendar, beginning in 1887.[1]

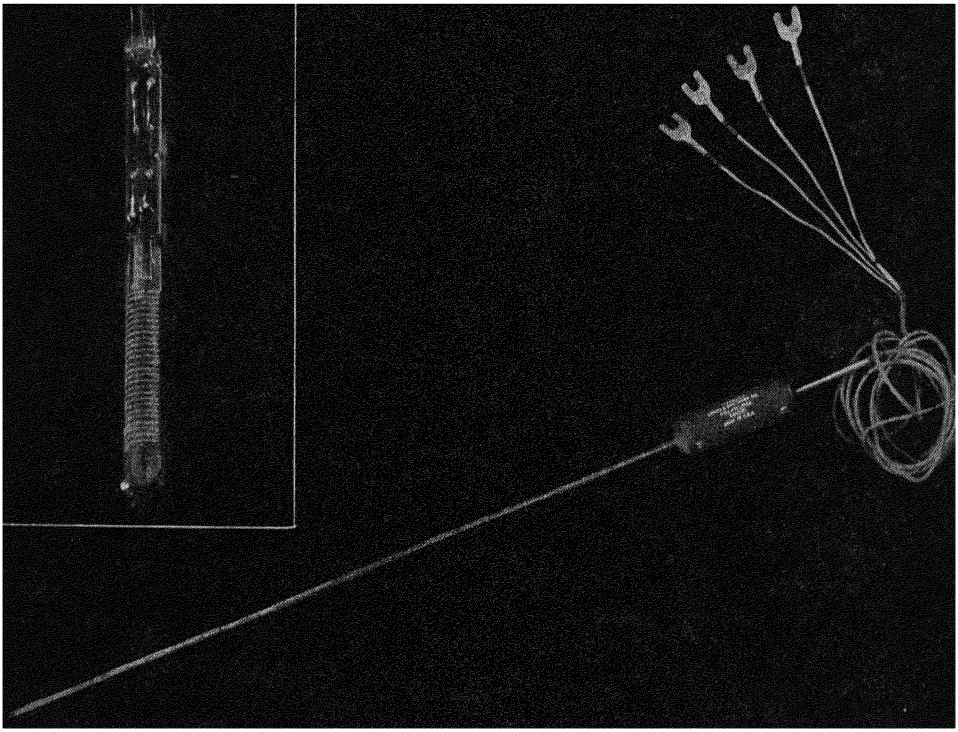

FIG. 1-2. Platinum resistance thermometer of high precision, such as is used to define the International Temperature Scale between −190 and 630.5°C. The thermometer is housed in a glass tube and has four leads for connection to the resistance bridge (see Fig. 1-3). The sensitive element at the tip, a close-up of which is shown in the inset, consists of a coil of fine platinum wire wound on a mica form. The entire assembly is thoroughly aged and adjusted. (*Courtesy of Leeds & Northrup Company, Philadelphia.*)

The coil of a modern platinum resistance thermometer is wound on a

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[1] This work has been described by Callendar's associate, E. H. Griffiths, "Methods of Measuring Temperature," Charles Griffin & Co., Ltd., London, 1925.

mica form from pure platinum wire having a diameter within the limits 0.05 to 0.2 mm and doubled on itself to eliminate induction effects. The purity must be such that the ratio of the resistance at the steam point to the resistance at the ice point is not less than 1.390. The coil is generally made of such a length that the resistance at the ice point is 2.56 ohms for thermometers designed to be used at higher temperatures, or 25.6 ohms for thermometers designed to be used at lower temperatures; the fundamental interval is then 1 ohm or 10 ohms, respectively, but in high-precision thermometry it is always necessary to determine the ice-point and steam-point resistances by direct measurement for each individual thermometer. If the platinum wire has been properly annealed, and if it is never thereafter exposed to temperatures in excess of 1200°C, its resistance at a given temperature will remain stable and reproducible indefinitely.

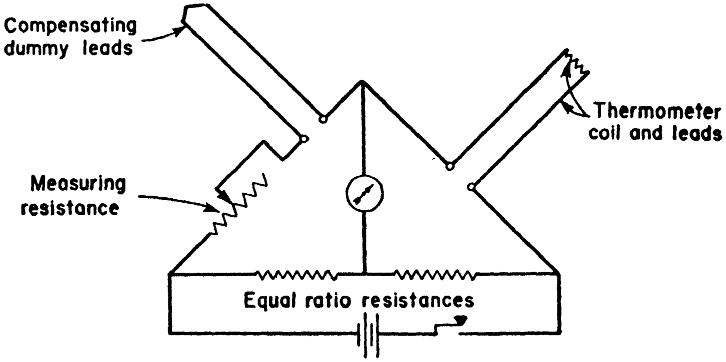

FIG. 1-3. Diagram of thermometer resistance bridge, showing use of compensating leads (details of adjustment for slight inequality of the ratio arm resistances not shown).

Comparatively heavy platinum leads are sealed to the ends of the coil and threaded through a series of mica disks, which serve as insulating supports, and also as baffles to retard air convection currents within the thermometer (Fig. 1-2). Coil and leads are hermetically sealed within a hard-glass or porcelain tube, the entire thermometer being not much larger than an ordinary mercury-in-glass thermometer. The platinum leads end at terminals, to which ordinary copper external leads from the resistance bridge are attached. There are several different methods of eliminating the effect of the lead resistance; one method developed by Callendar consists of including a pair of dummy leads in the thermometer, similar to the coil leads and lying parallel with them throughout their length, but simply joined to each other at the base, just above the coil; the compensating lead system, including a pair of external leads similar to those connected to the coil leads, is put in series with the standard adjustable resistance, in the bridge arm opposite to the one that includes the coil and its lead system (Fig. 1-3). Since resistance-thermometer bridges are always designed with the other two balance arms equal, the measuring resistance thus balances the true coil resistance, the dummy lead resistance canceling out the lead resistance of the coil. The bridge connections must be specially designed so as to keep contact resistances to a minimum, since the changes of resistance that one wishes to measure are quite small by ordinary electrical standards of measurement, of order only 0.01 ohm per 1°C. One of the most convenient and precise resistance bridges designed for this special purpose is that of E. F. Mueller;[1] the Mueller bridge permits one to measure temperatures in the range 0 to 660°C within a precision of ±0.01°C.

Callendar and Griffiths showed that if the platinum is sufficiently pure and properly annealed, the resistance over a temperature range from 0°C to at least 500°C is given accurately by the empirical equation

$$R_t = R_0(1 + At + Bt^2) \tag{1-10}$$

where R_0 denotes the resistance at the ice point and A and B are empirical constants for the individual thermometer. Equation (1-10) is not in a form convenient for calculating the temperature from R_t, even after A and B have been determined; if, however, t' represents the platinum resistance temperature, as defined by the linear equation

$$t' \equiv 100\,\frac{R_t - R_0}{R_{100} - R_0} \tag{1-11}$$

[compare Eq. (1-1)], then one may readily prove by substituting in Eq. (1-10) that

$$t - t' = \delta\left[\left(\frac{t}{100}\right)^2 - \left(\frac{t}{100}\right)\right] \tag{1-12}$$

where δ is a constant for the particular thermometer related to A and B by

$$\delta = -\,\frac{(100)^2B}{A + 100B} \tag{1-13}$$

Therefore, instead of determining A and B, it is more convenient to measure δ directly by observing the value of t' [*i.e.*, from that of R_t by means of Eq. (1-11)] at some third thermometric fixed point. The sulfur point, or normal boiling point of sulfur, 444.600°C on the present International Temperature Scale (see Sec. 1-8), is convenient for this purpose. Once the value of δ has been established by this means, then the correction

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[1] E. F. Mueller, *Natl. Bur. Standards, Tech. News Bull.* **13**, 547–561 (1916); see also, the review by E. F. Mueller in "Temperature. Its Measurement and Control in Science and Industry," pp. 162–179, Reinhold Publishing Corporation, New York, 1941.

from the platinum resistance temperature given by Eq. (1-11) to the International Temperature Scale or to the thermodynamic temperature (conditioned by the value one uses for the sulfur point, concerning which some slight degree of uncertainty has existed) is conveniently made through Eq. (1-12); in applying this equation, the value of t on the right need be known only approximately, since the value of the entire correction is not large; in any event, the equation may be rapidly solved by successive approximations. This procedure was developed originally by Callendar. Later work by Heycock and Neville showed that Eq. (1-12), with the value of δ established by calibration at the sulfur point, is accurate from 0°C to the melting point of copper, 1082°C.[1]

For temperatures below the ice point, the procedure has to be modified, because the quadratic relation (1-10) fails when the temperature range is extended below -40°C. By the addition of another empirically determined constant, in the form

$$R_t = R_0[1 + At + Bt^2 + C(t - 100)t^3] \tag{1-14}$$

satisfactory agreement is obtained down to -190°C; Eq. (1-14) is equivalent to

$$t - t' = \delta\left(\frac{t}{100} - 1\right)\frac{t}{100} + \beta\left(\frac{t}{100} - 1\right)\left(\frac{t}{100}\right)^3 \tag{1-15}$$

where t' and δ have the same significance as before, but β is another constant for the particular thermometer, related to A, B, and C of Eq. (1-14) by

$$\beta = -\frac{(100)^4C}{A + 100B}$$

In applying Eq. (1-15), which was proposed originally by M. S. Van Dusen,[2] one first determines the value of δ for the particular thermometer by calibration at the sulfur point, using Eq. (1-12), which applies from 0°C up; one then determines the value of β in Eq. (1-15), which applies from 0°C down, by calibration at a fourth thermometric fixed point, the oxygen point (normal boiling point of oxygen), -182.970°C, retaining the previously determined value of δ. From the values of δ and β so determined, one may use Eq. (1-15) conveniently to correct platinum

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[1] C. T. Heycock and F. H. Neville, *J. Chem. Soc.*, **67**, 160–199 (1895). See, however, the more recent discussion by B. E. Blaisdell and J. Kaye, in "Temperature. Its Measurement and Control in Science and Industry," pp. 127–140, Reinhold Publishing Corporation, New York, 1941; they recommend a cubic rather than a quadratic empirical relation between R_t and t, for sufficiently high precision even over the range 0 to 660°C.

[2] M. S. Van Dusen, *J. Am. Chem. Soc.*, **47**, 326–332 (1925).

resistance temperatures t' [as given by Eq. (1-11)] to International or thermodynamic temperatures t. Table 1-5 gives typically the value of R_t/R_0 for platinum over a wide range of temperatures, as reported by W. F. Roeser and H. T. Wensel, of the National Bureau of Standards.

Below −190°C, the platinum resistance thermometer becomes rather insensitive for precise temperature measurement; lead resistance thermometers have been found useful down to −259°C, which represents approximately the triple point of hydrogen. No general agreement exists concerning the standardization of resistance thermometers in this range, but a provisional temperature scale between 14 and 83°K, based on several thermometric fixed points established by means of the constant-volume helium thermometer, has been proposed by scientists at the National Bureau of Standards.[1]

TABLE 1-5. PLATINUM RESISTANCE AT VARIOUS TEMPERATURES*

t, °C	R_t/R_0
−200	0.177
−100	0.599
0	(1.000)
+100	1.392
200	1.773
300	2.142
400	2.499
500	2.844
600	3.178
700	3.500
800	3.810
900	4.109
1000	4.396
1100	4.671
1200	4.935
1300	5.187
1400	5.427
1500	5.655

* W. F. Roeser and H. T. Wensel, in "Temperature. Its Measurement and Control in Science and Industry," p. 1312, Reinhold Publishing Corporation, New York, 1941. The specific resistivity of platinum at 0°C is 9.83×10^{-6} ohm cm.

1-6. Thermocouples. If two wires of different metals are joined at their ends, then if the two junctions are at different temperatures, an electromotive force (emf) is developed in the circuit, which can be measured by the introduction of a millivoltmeter or a potentiometer. This effect was discovered by T. J. Seebeck in 1821. Since the emf increases continuously with the difference between the temperatures of the junctions, its value for a particular pair of metals may be used to measure the

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[1] H. J. Hoge and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **22**, 351–373 (1939).

temperature of the one junction relatively to that of the other. In precise measurements, the reference junction is ordinarily maintained at the ice point, while the other exploring junction, the so-called "hot" junction, is inserted in the system whose temperature is being observed. Since a thermocouple junction can be quite small in size, with a correspondingly low heat capacity, thermocouples are convenient to use, and are particularly valuable for following a changing temperature. When there is risk of contamination, the junction is ordinarily protected by a porcelain sheath, which necessarily increases the heat capacity and time lag.

Several different combinations of metals have come into common use. For temperatures below 350°C, the base-metal copper-constantan and iron-constantan thermocouples are satisfactory. Constantan itself is an alloy consisting of 60 per cent copper with 40 per cent nickel, developed originally as a metal having a low temperature coefficient of resistance. The emf of a thermocouple whose junctions are only a few hundred centigrade degrees apart, such as over the range 0 to 350°C when the reference junction is at the ice point, is represented empirically by a rather complex equation of the form

$$E = At - B(1 - e^{-Ct}) \tag{1-16}$$

where A, B, and C are supposedly constant over the given range for the particular pair of metals, but actually vary slightly from one individual thermocouple to another of the same type. In practice, the individual thermocouple is most conveniently standardized by a check of its readings at various fixed temperatures against the values given by standard tables that have been prepared on the basis of Eq. (1-16) from average values of A, B, and C, obtained for a number of samples of the particular metals (see Table 1-6); the deviations from the standard tables are plotted graphically against E as corrections for the individual thermocouple, and since such corrections are usually small, they are recorded with ample precision by this means.[1]

Above 350°C, copper-constantan thermocouples deteriorate rapidly because of air oxidation; iron-constantan thermocouples begin to deteriorate at somewhat higher temperatures, the life of No. 8 gauge wires in air at 760°C being on the average about 1000 hr.[2] The chromel-alumel

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[1] See, for example, W. F. Roeser and H. T. Wensel, *J. Research Natl. Bur. Standards*, **14,** 247–282 (1935); see also their tables in the Appendix to "Temperature. Its Measurement and Control in Science and Industry," Reinhold Publishing Corporation, New York, 1941.

[2] W. F. Roeser, in "Temperature. Its Measurement and Control in Science and Industry," pp. 180–205, Reinhold Publishing Corporation, 1941.

thermocouple is useful up to 1200°C; chromel-P consists of 90 per cent nickel with 10 per cent chromium, while alumel consists of 95 per cent nickel alloyed with 5 per cent aluminum, silicon, and manganese; the life of a No. 8 gauge chromel-alumel thermocouple in air at 1150°C is about 1000 hr.

In high-precision work at elevated temperatures, the most satisfactory thermocouple is the platinum-rhodium thermocouple, first introduced by H. L. Le Châtelier in 1886; this thermocouple serves to define the present International Temperature Scale over the range 630.5 to 1063°C. It consists of a pure platinum wire, coupled with an alloy wire consisting of 90 per cent platinum and 10 per cent rhodium. With the cold junction at the ice point, the emf is related to the temperature of the hot junction over the range 630.5 to 1063°C by means of the empirical equation

$$E = a + bt + ct^2 \tag{1-17}$$

where a, b, and c are constants for the individual thermocouple, whose values vary slightly from one thermocouple to another of the same type. In fundamental work, it is therefore necessary to standardize the individual thermocouple by taking readings at at least three thermometric fixed points established on the International Temperature Scale or on the thermodynamic temperature scale; for this purpose, the freezing points of antimony, silver, and gold are available. Here, too, standard tables of E vs. t have been prepared, based on Eq. (1-17) using average values of a, b, and c obtained from a number of samples of the wires; one conveniently corrects the individual thermocouple therefore by plotting the deviations of its readings from those given by the standard tables, at various standard thermometric fixed points. One may use the platinum-rhodium thermocouple at temperatures up to 1600°C, but in the range above 1063°C, it is necessary that one redetermine the constants in the empirical relationship (1-17); in other words, over the range 1063 to 1600°C, the emf is related to the temperature by

$$E = a' + b't + c't$$

but the constants a', b', c' are different from the constants a, b, c that fit the data over the lower temperature range. The thermocouple must therefore be restandardized by checking its readings at at least three thermometric fixed points in the new temperature range. Table 1-6 includes standard mean values of platinum-rhodium thermocouple readings over an extended range of temperatures.

For approximate temperature measurements, the emf may be measured by means of a millivoltmeter. In fact, industrial thermoelectric pyrometers are manufactured, which consist essentially of millivoltmeters constructed with scales graduated directly in temperature degrees, to be used with a particular type of thermocouple. For precise measurements, however, a potentiometer is essential; Table 1-6 shows, for example, that the platinum-rhodium thermocouple around 900°C has a sensitivity of about 0.011 mv/°C; therefore in order to obtain temperature readings precise to within ±0.1°C, one must be able to measure the emf within ±1 μv. This precision is readily attained by means of a high-precision potentiometer coupled with a sensitive low-resistance galvanometer; special potentiometers have been designed in which the slide-wire is eliminated in favor of fixed resistance coils and a selector switch, and

TABLE 1-6. CORRESPONDING VALUES OF TEMPERATURE AND EMF FOR VARIOUS TYPES OF THERMOCOUPLES

t, °C	$^{90}/_{10}$ Pt-Rh to Pt,* mv	Chromel-P to alumel,† mv	Iron to constantan,‡ mv	Copper to constantan,§ mv
−200	......	−5.75	−8.27	−5.539
−100	......	−3.49	−4.82	−3.349
0	0.000	0.00	0.00	0.000
+100	0.643	+4.10	+5.40	+4.276
200	1.436	8.13	10.99	9.285
300	2.315	12.21	16.56	14.859
400	3.250	16.39	22.07	20.865
500	4.219	20.64	27.58	
600	5.222	24.90	33.27	
700	6.260	29.14	39.30	
800	7.330	33.31	45.72	
900	8.434	37.36	52.29	
1000	9.569	41.31	58.22	
1100	10.736	45.14		
1200	11.924	48.85		
1300	13.120	52.41		
1400	14.312	55.81		
1500	15.498			
1600	16.674			
1700	17.841			

* Platinum-rhodium: W. F. Roeser and H. T. Wensel, *J. Research Natl. Bur. Standards*, **10,** 275–287 (1933).

† Chromel-alumel: W. F. Roeser, A. I. Dahl, and G. J. Gowens, *ibid.* **14,** 239–246 (1935).

‡ Iron-constantan: W. F. Roeser and A. I. Dahl, *ibid.*, **20,** 337–355 (1938).

§ Copper-constantan: L. H. Adams, "International Critical Tables," Vol. I, p. 58, McGraw-Hill Book Company, Inc., New York, 1926.

These tables are given in greater detail by W. F. Roeser and H. T. Wensel in the Appendix to the symposium, "Temperature. Its Measurement and Control in Science and Industry," Reinhold Publishing Corporation, New York, 1941.

other features are introduced to improve the sensitivity and decrease the effects of parasitic emfs.[1]

If one is interested in measuring small temperature differences, without regard to the actual temperature value being measured, the thermocouple is particularly convenient; a sensitive galvanometer may be used directly to measure the thermoelectric current between the two junctions. The thermal sensitivity may be further increased by combining the electrically insulated hot junctions and cold junctions of several thermocouples hooked up in series; such a combination is known as a *thermopile.*

Thermocouples may be used also at low temperatures, but it is necessary of course that they be standardized, preferably through comparison with a standard platinum resistance thermometer or with a helium-gas thermometer. The copper-constantan thermocouple, with the "cold" junction at the ice point, is a quite satisfactory thermometer down to liquid air temperatures (85°K), and with precautions, may be used down as far as 11°K, which is below the triple point of hydrogen.[2]

Among the principal sources of error in thermocouple temperature measurements, aside from the ordinary calibration errors of the electrical measuring instruments, are insulation leaks and stray thermoelectric effects developed in the circuit. The latter effects are attributable to three sources: (1) the Thomson effect, or emf resulting from temperature differences along either wire; (2) the Peltier effect, or emf resulting from temperature differences between bimetallic contacts at other parts of the circuit besides the thermocouple junctions, such as at binding-post connections, switch points, etc.; (3) the Becquerel effect, or emf resulting from strains or inhomogeneities within a single wire.

1-7. Radiation Pyrometers. When a body is at a temperature different from that of the surroundings, it tends to equalize its temperature with that of the surroundings by means of thermal radiation. Unlike thermal conduction and convection, thermal radiation requires no material medium for its transmission; in fact, a material medium between the source and the receiver of the thermal radiation may even absorb or reflect some of the radiation. The thermal energy[3] radiated by a hot body depends not only on its temperature but also on the nature of the radiating surface. G. R. Kirchhoff proved in 1858 that at a given tem-

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[1] See W. P. White, in "Temperature. Its Measurement and Control in Science and Industry," pp. 265–278, Reinhold Publishing Corporation, New York, 1941.

[2] J. G. Aston, in "Temperature. Its Measurement and Control in Science and Industry," pp. 219–227, Reinhold Publishing Corporation, New York, 1941; see also, R. B. Scott, *ibid.*, pp. 206–218.

[3] A precise discussion of the energy concept, and of heat as a form of energy, is given in Chap. 2.

perature, all bodies necessarily have the same ratio of thermal emissive power, or rate of energy radiated per unit of surface area, to absorptive power, or fraction absorbed of the thermal radiation falling on the surface, for radiation of a given wavelength. This ratio is evidently equal to the emissive power of a perfectly black body, for which by definition the absorptive power equals 1 for all wavelengths; a black body or perfect radiator is in other words a body which completely absorbs the thermal radiation falling on it, none being reflected at the surface or transmitted through it. For a black body, therefore, according to Kirchhoff's law, the rate of thermal radiation per unit surface area must be a function of the temperature only, and, conversely, black-body radiation may be used as a measure of the temperature.

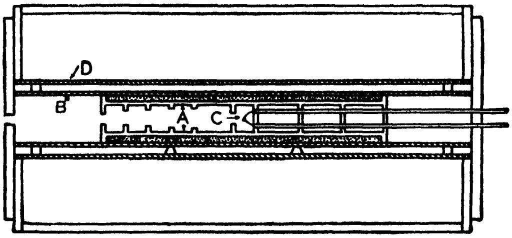

FIG. 1-4. Diagram of a standard experimental black body as designed by W. E. Forsythe. Tubes A, B, and D are of alundum or porcelain. Tube A is wound uniformly with platinum ribbon 2 cm wide and 0.01 mm thick. Tube B is wound with the same kind of ribbon but with a space between windings uniformly increasing on going from the ends toward the center. C is the blackbody. To heat this black-body to the palladium point a current of about 8 to 10 amp at 115 volts is required in the winding of tube A and 5 to 10 amp in the winding of tube B. The space around tube D is packed with some good heat insulator. (*Taken with permission from "Measurement of Radiant Energy," W. E. Forsythe, Ed., McGraw-Hill Book Company, Inc., New York,* 1937.)

We may therefore measure temperature by observing the thermal radiation of a black body in thermal equilibrium with the system under observation. A practical black body may consist of a hollow tube or enclosure having a small viewing aperture and blackened inner walls (see Fig. 1-4); in use, this body is immersed in the system whose temperature is to be measured, and the radiation measuring instrument is sighted on the aperture. Since practically all incident radiation falling on the aperture is absorbed by internal reflections and scattering within the enclosure, the thermal radiation issuing from the aperture is characteristic of that of a black body at the temperature of the enclosure.

Two general types of radiation pyrometers are in use. One type measures the rate of emission of total energy, without regard to its spectral distribution, and is therefore known as a *total-radiation pyrometer.* The other type measures the spectral distribution of the energy radiated, and is known as an *optical pyrometer.*

Total-radiation pyrometers are based on the law

$$\epsilon = \sigma(T^4 - T_s^4) \tag{1-18}$$

where ϵ represents the net rate of transfer of energy per unit area by a black body at absolute thermodynamic temperature T to a black body at absolute thermodynamic temperature T_s. This law was first proposed on the basis of empirical evidence by J. Stefan in 1879 but was later deduced theoretically from thermodynamic reasoning by L. Boltzmann in 1884; the accepted value of the proportionality constant σ, known as Stefan's constant, is $(5.673 \pm 0.004) \times 10^{-5}$ erg/cm^2 sec deg^4.[1] In the total-radiation pyrometer as designed originally by C. Féry in 1904 (see Fig. 1-5), the radiation from the source is focused by means of a concave mirror on the "hot" junction of a thermopile, whose emf is read by means of a voltmeter; a collimating hole admits radiation only from a part of the radiating surface, whose image on the "hot" junction of the thermopile is thus reduced in area as the distance between source and mirror is increased, in direct proportion to the quantity of radiation admitted; therefore, so long as the field defined by the collimator does not take in

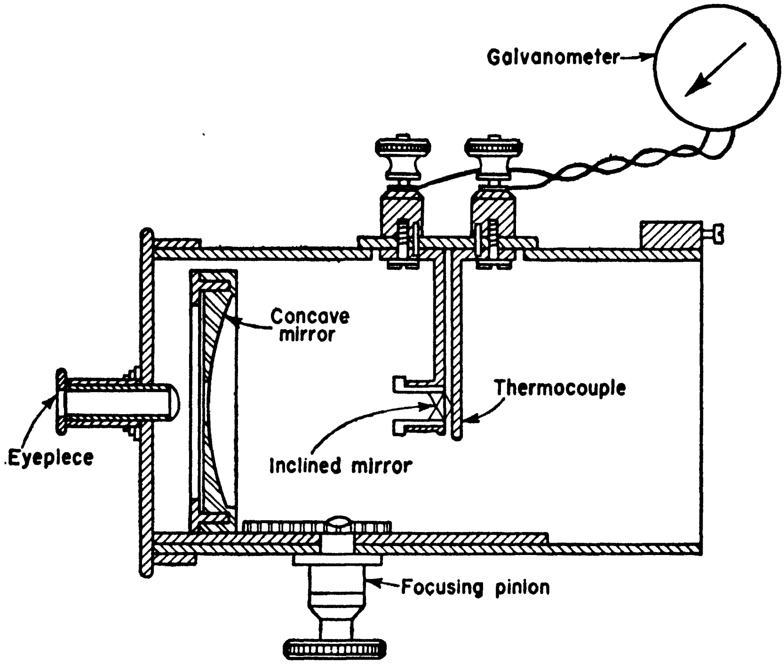

FIG. 1-5. Diagram of a Féry total-radiation pyrometer. (*Taken with permission from A. G. Worthing and D. Halliday, "Heat," John Wiley & Sons, Inc., New York,* 1948.)

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[1] R. T. Birge, *Rev. Modern Phys.*, **13**, 233–239 (1941); this represents a value derived in terms of Planck's constant from the quantum theory of radiation; it is in excellent agreement, however, with the results of direct measurement of total thermal radiation.

more area than that of the source, the intensity of the radiation incident on the thermopile, and hence the readings of the pyrometer, are independent of the distance from the source. Since the emf developed by the thermopile is approximately proportional to the relatively small difference of temperature between its "hot" and "cold" junctions, and since this in turn is approximately proportional to the intensity of the net radiation received by the "hot" junction, the emf is given directly by the relation

$$E = a(T^b - T_s^b)$$

where the constant a includes Stefan's constant and also the particular combination of proportionality factors characteristic of the individual pyrometer; the constant b is close to the theoretical value of 4, but may differ slightly from 4 for the individual pyrometer because the proportionalities between E and the intensity of the net radiation received are not exact, and because of other small thermal corrections. If b were exactly equal to 4, the value of a for the individual pyrometer could be established, and the pyrometer thereby standardized, by means of a reading taken at a single thermometric fixed point, such as the freezing point of gold (1336°K); for temperatures this high, the temperature T_s of the receiver (*i.e.*, the "hot" junction of the thermopile) can be neglected in the equation for the instrument, because of the high power to which both T and T_s are raised. In practice, however, the values of a and b for the individual pyrometer are best determined from a series of readings over a range of temperatures up to the gold point, in comparison with those of a standardized thermometer of a different type, such as the platinum-rhodium thermocouple. For extension of the range to higher temperatures, beyond the range of other types of thermometers, the pyrometer may then be used with a rapidly rotating sectored disk before the collimator; by this means, the intensity of the incident radiation may be cut down by a known fraction of its true value, and correction from the apparent reading to the true temperature made accordingly.

The total-radiation pyrometers used in industry are essentially like that of Fig. 1-5, except that the opening admitting the radiation is usually covered by a protecting plate of glass or quartz. For approximate or comparative purposes, particularly of a control nature, one may dispense with the black body and view the system under investigation directly. One obtains in this way the equivalent black-body temperature, *i.e.*, the temperature at which a black body would show the same intensity of radiation as that actually shown by the system; since ordinary bodies are less efficient radiators than black bodies, the true thermodynamic temperature cannot be lower than the equivalent black-body temperature. One would have to know the absorptive power of the emitting surface in order to estimate the true temperature from the equivalent black-body temperature, but for certain purposes, the equivalent black-body temperature itself may serve as a sufficient indicator.

Optical pyrometers are based practically on Wien's law,

$$J_\lambda = \frac{c_1}{\lambda^5} \exp\left(-\frac{c_2}{\lambda T}\right) \tag{1-19}$$

where $J_\lambda\, d\lambda$ represents the rate of emission of thermal radiation within the wavelength range λ to $\lambda + d\lambda$ per unit area of radiating surface by a black body at the absolute thermodynamic temperature T, and c_1 and c_2 are universal constants independent of T and λ, known, respectively, as the first and second radiation constants. This law was first derived in 1893 by Wilhelm Wien from thermodynamic reasoning based on the classical electromagnetic theory of radiation; it was shown by Max Planck in 1900 to be a special case for sufficiently short wavelengths or sufficiently low temperatures of a more general radiation law,

$$J_\lambda = \frac{c_1}{\lambda^5} \frac{1}{e^{c_2/\lambda T} - 1} \tag{1-20}$$

for whose derivation Planck was compelled to assume a quantum theory of radiation, the first step on the path leading to modern quantum mechanics. Planck's law has been thoroughly verified by experiment; Wien's law is a sufficiently accurate approximation, however, for visible thermal radiation at temperatures up to about 4000°K. If one compares the intensity of black-body radiation at the same wavelength for two different temperatures, T and T°, Eq. (1-19) reduces to

$$\frac{J_\lambda}{J_\lambda^\circ} = \frac{e^{c_2/\lambda T^\circ}}{e^{c_2/\lambda T}}$$

$$\ln \frac{J_\lambda}{J_\lambda^\circ} = \frac{c_2}{\lambda}\left(\frac{1}{T^\circ} - \frac{1}{T}\right) \qquad (e^{c_2/\lambda T} \text{ and } e^{c_2/\lambda T^\circ} \gg 1) \tag{1-21}$$

Planck's generalization of this relation is

$$\frac{J_\lambda}{J_\lambda^\circ} = \frac{e^{c_2/\lambda T^\circ} - 1}{e^{c_2/\lambda T} - 1} \qquad \text{(in general)} \tag{1-22}$$

The value of c_2 used in defining the present International Temperature Scale above 1063°C is 1.438 cm deg.[1] Thus, if in Eq. (1-21), or more generally, in Eq. (1-22), T° represents the gold point, 1336°K, then measurement of the relative intensity $J_\lambda/J_\lambda^\circ$ of monochromatic black-body

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[1] Birge (*ibid.*) gives 1.4385 ± 0.0003 cm deg, as derived by calculation based on Planck's radiation theory from the values of other natural constants; this value is in excellent agreement, however, with the results of direct applications of Planck's law (1-22).

radiation of given wavelength at another temperature compared with that at the gold point serves to measure the other temperature.

The first optical pyrometer was designed by H. L. Le Châtelier in 1892; the object whose temperature was being determined was viewed against the superimposed image of the flame of a standard amyl acetate lamp. The modern disappearing-filament pyrometer, in which the field is viewed against the superimposed image of the filament of an electrically heated incandescent lamp, was introduced by F. L. Morse in 1906. This type of pyrometer is extremely convenient to use; the temperature of the filament is controlled by means of a variable resistance, and the current at which the filament just disappears against the background is measured, a filter being used to ensure approximately monochromatic radiation. When the filament current is too small, the filament stands out dark against the lighter background; when the filament current is too large, the filament stands out bright against the darker background. The pyrometer is standardized either by observations of the current for black-body radiation at several standard thermometric fixed points or by comparison of the readings with those of a standardized thermocouple. Standard radiation sources are commercially available, also, consisting of tungsten ribbon-filament lamps, whose equivalent black-body temperatures have been calibrated as functions of the filament current. For temperatures higher than the freezing point of gold (1336°K), the pyrometer is commonly used in connection with a rotating sectored disk to cut down the incident radiation; thus, if T' represents the apparent temperature reading given by the pyrometer (standardized by means of readings at lower temperatures) when the sector openings constitute an angular aperture of θ radians, then the value of J_λ/J'_λ to be substituted in Eqs. (1-21) or (1-22) will be $2\pi/\theta$, whence from the known wavelength and the value of c_2, one may readily compute the equivalent black-body temperature T of the source.

In another research type of optical pyrometer, described by H. Wanner in 1902, the lamp filament is heated electrically at constant temperature, but the radiation from the filament and the radiation from the source under observation are both plane-polarized by being passed through Nicol prisms so oriented that the two planes of polarization are at right angles to each other; the two fields are then viewed through a Nicol analyzing prism, which is rotated until they appear to be equal in intensity. The setting of the analyzer thus measures the relative intensity from the filament and from the source, and, by substitution in Eqs. (1-21) or (1-22), the temperature of the source (the equivalent black-body temperature if the source is not itself a black body) may be calculated relatively to the established equivalent black-body temperature of the filament; a red filter is generally used to ensure approximately monochromatic radiation. Another similar type of pyrometer makes use actually of a spectrometer to obtain true monochromatic radiation.[1]

If one integrates $J_\lambda \, d\lambda$ from $\lambda = 0$ to $\lambda = \infty$, where J_λ is given approximately by Eq. (1-19), or in general by Eq. (1-20), one of course obtains the Boltzmann total radiation law, Eq. (1-18). An important series of measurements was undertaken by C. E. Mendenhall and W. E. Forsythe in 1914 to intercompare the temperature scales given by the total-radiation pyrometer and by the disappearing-filament optical pyrometer.[2] Over the temperature range between 1750 and 2820°C, the agreement was within experimental error, thus affording excellent confirmation of the theory of thermal radiation in general, and of radiation thermometry in particular. So far as we know, the black-body radiation laws based on Planck's quantum theory are exact, and we may use radiation pyrometers with confidence to extend the temperature scale to indefinitely high temperatures.

1-8. The International Temperature Scale. Everyone recognizes the thermodynamic temperature scale, or its equivalent, the ideal-gas temperature scale, as the fundamental scale to which all temperature measurements should in principle be ultimately referred. In practice, it is expedient to set up a working scale, based on instruments less cumbersome to use than the gas thermometer, and hedged by such conventions that all scientists shall mean the same thing when they report precise temperature measures, and shall not be basing their temperature measures on different conceptions of the best values for such natural constants as the normal boiling point of sulfur, or the second radiation constant. This point of view was originally presented by H. L. Callendar, and ultimately won acceptance in the modern International Temperature Scale, in use since 1927. This scale has been designed to conform as closely as practicable to the thermodynamic temperature scale, in view of the information available at the time of its adoption. In recognition of the fact that no single type of thermometer is satisfactory for measuring temperatures over the entire range that now interests us, the scale is based on a set of thermometric fixed points in addition to the theoretically sufficient ice point and steam point; to each of these fixed points, a temperature has been assigned *by convention,* representing at the time of the scale's adoption the consensus of opinion, as accepted by the General Conference on Weights and Measures, concerning the "best" experimental value on the thermodynamic scale; the number of these defined

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[1] This spectral pyrometer and other types of optical pyrometers are described in detail by Worthing and Halliday, *op. cit.*, pp. 456–466.

[2] C. E. Mendenhall and W. E. Forsythe, *Phys. Rev.*, **4**, 62–70 (1914).

fixed points has been chosen to be sufficient for precise calibration of the standard working thermometers defining the temperature in various parts of the scale, but their values are not to be changed, except as revision is authorized by a future General Conference on Weights and Measures. The present International Temperature Scale (1948) was adopted by the Ninth General Conference in October, 1948, and represents the first revision (all the changes being quite minor in effect) of the scale originally adopted by the Seventh General Conference in 1927.[1]

The standard fixed points, all of which represent phase equilibrium conditions of simple substances, are given in Table 1-7. The oxygen point, the steam point, and the sulfur point are sensitive to variations in the barometric pressure; therefore empirical formulas are given, derived from vapor-pressure data, correcting the temperature for departure of the pressure from the standard value: $p_0 = 1$ atm. The freezing point of antimony is less reproducible than that of the other fixed points, so instead of having an assigned value, the freezing point of the particular sample is determined for the purpose of thermocouple standardization at the higher temperatures by direct measurement with the platinum resistance thermometer, previously standardized in the usual way at the ice point, steam point, and sulfur point. The standard working instruments, and their ranges, are also included in Table 1-7.

Temperatures below the oxygen point have not yet been defined on the International Temperature Scale, because of the uncertainty concerning the values of the fixed points available in that range. This region has, however, become increasingly important because of the practical and theoretical value of thermodynamic measurements extending down to the lowest attainable temperatures. For such purposes, it is desirable that the data extend down at least to the liquid-hydrogen region (normal boiling point, 20.39°K, to the triple point, 13.96°K), and preferably into the liquid-helium region (normal boiling point, 4.22°K). A provisional temperature scale covering the range 14 to 83°K has been described by Hoge and Brickwedde, based on platinum resistance thermometers calibrated fundamentally against the constant-volume helium-gas thermometer; Hoge has also made a survey of possible fixed points that could be used for the standardization of resistance or thermoelectric thermometers in the range below −183°C.[2]

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[1] A translation of the text of the official 1948 report is given by Stimson, *loc. cit.* The original International Temperature Scale (1927) has been described by G. K. Burgess, *J. Research Natl. Bur. Standards*, **1**, 635–642 (1928).

[2] Hoge and Brickwedde, *loc. cit.;* H. J. Hoge, in "Temperature. Its Measurement and Control in Science and Industry," pp. 141–156, Reinhold Publishing Corporation, New York, 1941.

TABLE 1-7. THE INTERNATIONAL TEMPERATURE SCALE (1948)
Standard Fixed Points

Fixed point	Condition	t, °C	Pressure correction, 660–860 mm Hg
Oxygen point	Liquid-vapor equilibrium	−182.970	$t_p = -182.970 + 9.530\left(\frac{p}{p_0} - 1\right) - 3.72\left(\frac{p}{p_0} - 1\right)^2 + 2.2\left(\frac{p}{p_0} - 1\right)^3$
Ice point	Equilibrium, ice and air-saturated water	0	$t_p = 0.010\left(1 - \frac{p}{p_0}\right) - 0.7 \times 10^{-6}h$ (h = depth in mm below surface of water-ice mixture)
Steam point	Liquid-vapor equilibrium	100	$t_p = 100 + 28.012\left(\frac{p}{p_0} - 1\right) - 11.64\left(\frac{p}{p_0} - 1\right)^2 + 7.1\left(\frac{p}{p_0} - 1\right)^3$
Sulfur point	Liquid-vapor equilibrium	444.600	$t_p = 444.6 + 69.010\left(\frac{p}{p_0} - 1\right) - 27.48\left(\frac{p}{p_0} - 1\right)^2 + 19.14\left(\frac{p}{p_0} - 1\right)^3$
Silver point	Solid-liquid equilibrium	960.8	
Gold point	Solid-liquid equilibrium	1063.0	

Standard Measuring Instruments

Range	Instrument	Conditions
Ice point to freezing point of antimony	Platinum resistance thermometer	$R_t = R_0(1 + At + Bt^2)$, where R_0, A, and B are determined by calibration at the ice point, the steam point, and the sulfur point; the platinum should be of such purity that R_{100}/R_0 is greater than 1.3910
Oxygen point to ice point	Platinum resistance thermometer	$R_t = R_0(1 + At + Bt^2 + C(t - 100)t^3)$, where R_0, A and B are determined as above, but the additional constant C is then determined by calibration at the oxygen point
Freezing point of antimony to gold point	Platinum-rhodium thermocouple (platinum vs. 90–10 platinum-rhodium alloy)	$E_t = a + bt + ct^2$, where one junction is maintained at the ice point; a, b, and c are determined by calibration at the antimony point (630.5°C, measured precisely with a standard platinum resistance thermometer), the silver point, and the gold point

TABLE 1-7. THE INTERNATIONAL TEMPERATURE SCALE (1948).—(*Continued*)

Range	Instrument	Conditions
Above gold point...	Optical pyrometer	Planck's law: $$\frac{J_t}{J_{\mathrm{Au}}} = \frac{e^{\frac{c_2}{\lambda(1063+T_0)}} - 1}{e^{\frac{c_2}{\lambda(t+T_0)}} - 1}$$ where J_t/J_{Au} represents ratio of intensities of monochromatic radiation of wavelength λ emitted by a black body at temperature t and at the gold point; T_0 represents the absolute ice point; $c_2 = 1.438$ cm deg

The lowest temperatures of all (below 1°K, and as low as 0.005°K) have been attained by the adiabatic demagnetization method described in Sec. 6-6. The problems of establishing a temperature scale in this region have been described by C. F. Squire.[1]

The highest man-made temperatures are undoubtedly those that have been attained in the explosions of atomic bombs. The surface temperature of the sun, according to radiation pyrometry, is about 6000°K, but considerable uncertainty exists concerning the relationship of the sun's radiation to that of a black body, the only kind of body for which the radiation laws are known precisely. Within a similar limitation, the surface temperatures of the other stars have estimated values ranging between 3500 and 25,000°K. No direct experimental methods exist as yet for determining the interior temperatures of stellar bodies, but studies of atomic energy explosions will no doubt yield pertinent information.

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[1] C. F. Squire, in "Temperature. Its Measurement and Control in Science and Industry," pp. 745–756, Reinhold Publishing Corporation, New York, 1941.

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Problems

1-1. Calculate the value of the gold point on the Fahrenheit and on the Rankine temperature scales.

1-2. List the possible advantages and disadvantages of water and of dibutyl phthalate as thermometric liquids for liquid-in-glass thermometers.

1-3. Calculate the emergent stem correction for a mercury thermometer made of Corning normal glass when the reading is 200.0°C, and the thermometer is immersed to the 0°C mark; assume an average exposed stem temperature of 25°C.

1-4. According to L. Holborn (Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement I, p. 66, 1927) the pV product for hydrogen is represented at moderate pressures by the empirical formulas:

$$\begin{aligned} 0°\text{C}: pV &= 0.99918 + 0.00082094p + 0.0000003745p^2 \\ 100°\text{C}: pV &= 1.36506 + 0.00091400p \end{aligned}$$

where p is represented in meters of mercury and the values of pV are relative to the arbitrary standard, $pV = 1.00000$ at 0°C and $p = 1$ m Hg. Calculate the relative increase in volume, $(V_{100} - V_0)/V_0$, for hydrogen gas at 1 atm (0.76 m Hg) pressure in going from the ice point to the steam point. Calculate also the relative increase in the quantity $\lim\limits_{p \to 0} (pV)$.

1-5. According to Holborn, the pV product for helium, relative to $pV = 1.00000$ at 0°C and 1 m Hg, and with p expressed in meters of mercury is given by the following empirical formulas:

$$\begin{aligned} -183°\text{C}: pV &= 0.32992 + 0.00062286p + 0.000000735p^2 \\ 0°\text{C}: pV &= 0.99930 + 0.00069543p \\ +100°\text{C}: pV &= 1.36518 + 0.00066804p \end{aligned}$$

Calculate the apparent temperature at the oxygen point given by a constant-pressure helium-gas thermometer having a pressure of 1 m Hg. Calculate the ideal-gas temperature at the oxygen point, from the limiting behavior of helium at zero pressure. Calculate by difference the correction to the constant-pressure helium temperature for obtaining the ideal-gas temperature at the boiling point of oxygen.

1-6. A platinum resistance thermometer reading 2.5602 ohms at the ice point and 3.5614 ohms at the steam point (corrected to standard atmospheric pressure) reads 6.7795 ohms at the sulfur point. Calculate the platinum resistance temperature at the sulfur point, and calculate the value of δ in Callendar's equation for this thermometer. What is the temperature on the International Temperature Scale when this thermometer reads 4.5626 ohms?

1-7. What will be the reading of the thermometer of Prob. 1-6 at the equilibrium temperature of condensing steam on a day on which the barometer reads 750.0 mm Hg (corrected to 0°C and standard gravity)?

1-8. The reading of the platinum resistance thermometer of Prob. 1-6 at the oxygen point (corrected to standard atmospheric pressure) is 0.6400 ohm. Calculate the value of β in Van Dusen's equation for this thermometer, and calculate the temperature on the International Temperature Scale when it reads 1.7501 ohms.

1-9. The readings of a platinum-rhodium thermocouple with the reference junction at the ice point are 5.535 mv at the antimony point (established at 630.5°C for the particular sample of antimony by calibration with a standardized platinum resistance thermometer), 9.119 mv at the silver point, and 10.301 mv at the gold point. Calculate the empirical constants a, b, and c in the equation

$$E = a + bt + ct^2$$

and then calculate what value of E may be expected at 1000°C. (Compare with Table 1-6, which corresponds to the data given in this problem.)

1-10. Using a low-resistance lamp-and-scale galvanometer whose microvolt sensitivity is 0.1 μv/mm scale division at 1 m distance from the mirror, what is the approximate difference of temperature between the junctions of a copper-constantan thermocouple (both junctions being around the ice point) that can just be detected by a galvanometer deflection of 1 mm? How many copper-constantan thermocouples must one hook in series so that one could detect by means of this galvanometer a difference of 0.0001°C between the united "hot" and "cold" junctions?

1-11. The solar constant (rate of reception of solar radiation per unit area of the earth's surface normal to the radiation, corrected for atmospheric absorption and reflection) has been estimated by measurement to have the mean value, 1.351×10^6 erg/cm^2 sec. The mean distance to the sun is 149.5×10^6 km, and its radius is 6.96×10^5 km. Calculate the rate at which energy is being radiated per square centimeter of the sun's surface. Calculate therefrom according to the Stefan-Boltzmann law the equivalent black-body temperature at the sun's surface (the temperature of the receiving surface of the earth may be neglected in this calculation, because its fourth power is so much smaller than the fourth power of the sun's surface temperature; verify that this is so).

1-12. Prove that according to Wien's law in the form (1-19), the wavelength corresponding to maximum intensity of black-body radiation at a given temperature always satisfies the formula

$$\lambda_{\max} T = \frac{c_2}{5}$$

where c_2 represents the second radiation constant. Using Birge's recommendation of $c_2 = 1.4385$ cm °K, calculate the value of $\lambda_{\max}$ in angstrom units corresponding to $t = 600$, 800, 1063, and 1600°C. Calculate the value of T when $\lambda_{\max}$ is at the middle of the visible range, 5500 Å.

1-13. The maximum intensity of the sun's radiation occurs at about 4740 Å; using the equation derived in Prob. 1-12, estimate the equivalent black-body temperature of the sun's surface from this independent experimental source, and compare the result with that of Prob. 1-11. (The discrepancy arises from the fact that solar radiation is not true black-body radiation.)

1-14. The spectral emissivity (ratio of the intensity of radiation of given wavelength emitted by the surface to that emitted by a black body at the same temperature) of molten steel is estimated to be 0.37 for radiation at 6500 Å. If the equivalent black-body temperature of a sample of molten steel is 1800°K as measured by an optical pyrometer, what is its true temperature on the International Temperature Scale?

1-15. Tungsten has a spectral emissivity at 6500 Å of 0.44. If a tungsten ribbon is at 2000°K, what will be its apparent temperature, if read with a standardized optical pyrometer?

CHAPTER 2

THE FIRST LAW OF THERMODYNAMICS

Before we are prepared to discuss thermodynamic behavior, we must trace the development of the energy concept, which had its origin in the study of mechanical systems. We shall then take up the origin of the heat concept, and show how J. P. Joule's magnificent experiments during the middle of the nineteenth century effected a fusion between these two apparently diverse concepts, culminating in the great generalization known as the *first law of thermodynamics.*

2-1. Energy. There is a principle of mechanics, apparently first recognized by Gottfried Wilhelm Leibnitz about 1693 on the basis of Galileo's earlier experiments with falling bodies and the pendulum, which states that as an ideal limit for certain types of mechanical systems, their motions are executed in such ways that a certain quantity we call the *total energy,* sum of the *kinetic energy* and the *potential energy,* remains constant with time.[1] This principle of *conservation of energy* in mechanical systems is one of the ways of stating Newton's laws of motion for systems whose forces depend explicitly only on the positions of the moving elements, and not on their velocities or the time; such systems are therefore called *conservative.*

For example, let us consider the motion of a point mass, a body of mass M whose dimensions are sufficiently small in comparison with the distances through which its motion is followed so that its location at any moment can be described adequately by the coordinates of a point; the center of mass of a complex body behaves under certain conditions like a point mass in which is concentrated the entire mass of the body. According to Newton's second law of motion,

$$\mathbf{F} = \frac{d}{d\tau}\left(M\frac{d\mathbf{r}}{d\tau}\right) \tag{2-1}$$

where $\mathbf{F}$ denotes the net force acting on the point mass, and $\mathbf{r}$ denotes its position with respect to an arbitrary origin; $d\mathbf{r}/d\tau \equiv \mathbf{u}$ denotes the velocity. Equation (2-1) is, in general, a three-dimensional vector equation, which includes in compact form the three one-dimensional equations

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[1] Leibnitz's so-called *vis viva* and *vis mortua* were, respectively, twice our modern kinetic and potential energies.

$$F_x = \frac{d}{d\tau}\left(M\frac{dx}{d\tau}\right); \qquad F_y = \frac{d}{d\tau}\left(M\frac{dy}{d\tau}\right); \qquad F_z = \frac{d}{d\tau}\left(M\frac{dz}{d\tau}\right) \tag{2-2}$$

where F_x, F_y, and F_z denote, respectively, the x, y, and z components of the force, and x, y, and z themselves denote the ordinary Cartesian coordinates of the point mass at the time τ. If we take the so-called scalar product of both sides of Eq. (2-1) with the velocity vector $d\mathbf{r}/d\tau$ [this operation is equivalent merely to multiplying each component equation (2-2) by the respective velocity component, and then adding the three resulting equations],

$$\mathbf{F}\cdot\frac{d\mathbf{r}}{d\tau} = \frac{d}{d\tau}\left(M\frac{d\mathbf{r}}{d\tau}\right)\cdot\frac{d\mathbf{r}}{d\tau} = \frac{d}{d\tau}\left[\frac{1}{2}M\left(\frac{d\mathbf{r}}{d\tau}\right)^2\right]$$

and integrate with respect to time between limits τ_0 and τ, then

$$\int_{\tau_0}^{\tau} \mathbf{F}\cdot\frac{d\mathbf{r}}{d\tau}\,d\tau = \frac{1}{2}Mu^2 - \frac{1}{2}Mu_0^2 \tag{2-3}$$

where u represents the magnitude of the velocity (without regard to direction; $u^2 = u_x^2 + u_y^2 + u_z^2$) at the time τ and corresponding location $\mathbf{r}$, while u_0 represents the magnitude of the velocity at the time τ_0 and corresponding location $\mathbf{r}_0$. Now, in general, the integral on the left of Eq. (2-3) is undefined, because the integrand may depend in some way as yet unspecified on the time. In the special case, however, in which $\mathbf{F}$ is an explicit function only of $\mathbf{r}$, varying perhaps implicitly with τ as $\mathbf{r}$ varies with τ, but having always a definite value associated with each value of $\mathbf{r}$, defined without regard to the value of τ, then the integral reduces simply to a line integral in the position variable $\mathbf{r}$, whose value

$$W \equiv \int_{\mathbf{r}_0}^{\mathbf{r}} \mathbf{F}(\mathbf{r})\cdot d\mathbf{r} \equiv \int_{r_0}^{r} F\cos\theta\,dr \tag{2-4}$$

defines the *work* W done by the force on the point mass during its motion from position $\mathbf{r}_0$ to position $\mathbf{r}$; θ in Eq. (2-4) represents the angle between the direction of the force and the direction of the element of displacement, and ($F\cos\theta$) therefore represents the component of the vector force $\mathbf{F}$ along the direction of the path that the point mass is momentarily describing; the value of W may be positive or negative, depending on the sign of $\cos\theta$ during the displacement (*i.e.*, on whether θ is less than or greater than 90°). If furthermore $\mathbf{F}(\mathbf{r})$ satisfies certain necessary conditions of continuity, then the indefinite form of the integral always corresponds to some particular scalar function of $\mathbf{r}$, whose negative is called the *potential energy* of the point mass in the particular force field (*i.e.*, region where $\mathbf{F}$ is defined everywhere as a function of $\mathbf{r}$). The definite integral appearing in Eq. (2-4) may therefore be represented as the algebraic difference between the values of this potential-energy function $V(\mathbf{r})$ at the points $\mathbf{r}_0$ and $\mathbf{r}$, independently of the particular trajectory described by the point mass, in the form

$$\int_{\mathbf{r}_0}^{\mathbf{r}} \mathbf{F}(\mathbf{r}) \cdot d\mathbf{r} \equiv -[V(\mathbf{r}) - V(\mathbf{r}_0)] \tag{2-5}$$

This integral relationship defining the potential-energy function [whose zero point is left arbitrary, depending on the assignment of an integration constant in Eq. (2-5)] may be represented symbolically also by the differential vector equation

$$\mathbf{F} = -\nabla V \tag{2-6}$$

which is shorthand for the three simultaneous one-dimensional equations

$$F_x = -\frac{\partial V}{\partial x}; \qquad F_y = -\frac{\partial V}{\partial y}; \qquad F_z = -\frac{\partial V}{\partial z}$$

In the special case under consideration, therefore, Eq. (2-3) reduces to the form

$$\tfrac{1}{2}Mu^2 + V(\mathbf{r}) = \tfrac{1}{2}Mu_0^2 + V(\mathbf{r}_0) = \epsilon \tag{2-7}$$

The expression $\frac{1}{2}Mu^2$ is called the *kinetic energy* of the point mass. Equation (2-7) thus expresses the fact that motion under the influence of a conservative force (a force whose value everywhere depends only on the spatial coordinates of the point mass) is so executed that the *sum of the kinetic and potential energies remains constant with time*, equal in particular to whatever value it happened to have at the start of the motion ($\tau_0 = 0$). The sum ϵ, called the *total energy* of the point mass, thus appears as an integration constant to a first integral of Newton's second-order differential equations of motion.[1]

A simple example of a potential-energy function is afforded by the motion of a body falling in a vacuum under the influence of gravity; in this case, $V = Mgz$, where z denotes the height above the earth's surface, arbitrarily taken as the zero of potential energy; if one were to take into consideration sufficiently large changes in altitude, one would have to represent the gravity "constant" g as itself a function of z in the force relationship, $F = Mg$, before integrating Eq. (2-5) to find V; but this force is essentially one-dimensional, being directed always toward the center of the earth. Equation (2-7) thus affords an immediate solution of the equation of motion, in the form

$$\tfrac{1}{2}Mu^2 + Mgz = \epsilon$$

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[1] A different but mathematically equivalent first integral, not so useful for our present purpose, is obtained by integrating Eq. (2-1) directly with respect to time; the resulting equation relates impulse to momentum.

where ϵ denotes the sum of the kinetic and potential energies at any stage of the motion; for a body starting from rest at height z_0, for example, the speed acquired at any height z during the free fall is given by

$$\tfrac{1}{2}Mu^2 + Mgz = \epsilon = Mgz_0$$

leading to the familiar relationship

$$u = \sqrt{2g(z_0 - z)}$$

Another example of a potential-energy function is that of a body with charge e under the influence of another body with charge e_0; if r represents the distance between them, then their electrostatic potential energy has the form $V = A(ee_0/Dr)$, where D denotes the dielectric constant of the medium (assumed homogeneous) between the charged bodies and A is a numerical proportionality constant whose value depends on the system of measurement followed; the form of this potential-energy function follows by direct application of Eq. (2-5) to C. A. Coulomb's inverse-square electrostatic force law, taking as the zero of potential energy a state in which the charges are an infinite distance apart.

The concept of conservative forces is readily extended to systems of independent point masses, interconnected point masses in the form of a rigid body or an elastic body, idealized fluid bodies, etc. In each case, the motion is characterized by a constant total energy, which appears as an integration constant when the differential equations of motion are integrated. Different states of motion that may be assumed by the same type of system under different starting conditions are characterized simply by different values of the constant ϵ, which appears therefore as a parameter in the integral equation of motion for the system.

Real mechanical systems, however, are more or less nonconservative. A projectile traveling through air, for example, encounters in addition to the conservative force of gravity a force attributed to air resistance, which increases in a complex manner with the projectile's velocity. In such a case, the potential-energy function in its original sense is undefined, and the method of integrating the differential equations of motion leading to Eq. (2-7) is invalid. It is convenient, however, for us to extend the original interpretation of the potential-energy concept, so that it may be applied to the conservative *component* of the resultant nonconservative force. In the case of the projectile traveling through air, for example, we define its potential energy in the earth's field of gravity exactly as for a projectile traveling in a vacuum, treating the nonconservative force of air resistance, which depends explicitly on the projectile's relative velocity through the air, as an independent component of the resultant force. This procedure supposes that it is legitimate to resolve the net force in such a manner into independently effective components, a supposition justified by general experiments on the compounding of forces. We find then that the total energy, defined as before by the sum of the kinetic and potential energies, instead of being a constant of the motion, decreases with time. It is said to be *dissipated* by the nonconservative force of air resistance. If, for example, the dissipative force has the form $\mathbf{F}_d = -k \dfrac{d\mathbf{r}}{d\tau}$, that is, if it increases in direct proportion to the first power of the velocity (as it actually does in the case of streamlined flow at sufficiently low velocities), then it follows from Eq. (2-3) that

$$-\int_{\tau_0}^{\tau} ku^2\, d\tau = \epsilon - \epsilon_0$$

or

$$\frac{d\epsilon}{d\tau} = -ku^2$$

where for a body moving under the influence of gravity, $\epsilon = \frac{1}{2}Mu^2 + Mgz$. Several distinct types of dissipative processes are recognized besides air resistance: friction in general, viscous resistance to flow of a fluid, electric resistance, the attenuation of a shock wave set up in a material medium, inelastic collisions, etc.

We thus come to regard the mechanical system as possessing a definite *quantity* of energy, which remains constant so long as purely conservative forces are in effect, but may decrease through the action of dissipative forces. We have seen that for conservative forces, the definite integral (2-4) representing the work done by the force $\mathbf{F}$ during the displacement of the moving body from position $\mathbf{r}_0$ to position $\mathbf{r}$ is equal on the one hand to the increase in the kinetic energy [Eq. (2-3)] and on the other to the decrease in the potential energy [Eq. (2-5)], both taken in their algebraic senses with regard to sign. The value of W therefore represents the measure of a quantity of energy in transfer from potential to kinetic form (a negative value of W represents a transfer of energy in the opposite direction). If, in Eq. (2-4), $\mathbf{F}$ is measured in *dynes* and $\mathbf{r}$ in *centimeters*,[1] then the energy represented by W is said to be measured in *ergs* (1 erg $\equiv$ 1 dyne cm $\equiv$ 1 g cm^2/sec^2); if $\mathbf{F}$ is measured in *newtons* and $\mathbf{r}$ in

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[1] Forces themselves are measured fundamentally by the accelerations they produce in standard bodies, according to Eq. (2-1); if in that equation M is measured in *grams* and $(d^2\mathbf{r}/d\tau^2) = d/d\tau(d\mathbf{r}/d\tau)$ in centimeters per second per second, then their product for a given situation will represent by definition the net force acting on the point mass in *dynes;* 1 dyne $\equiv$ 1 g cm/sec^2. If M is measured in *kilograms* and $(d^2\mathbf{r}/d\tau^2)$ in *meters per second per second,* then their product measures the force in *newtons;* 1 newton $\equiv 10^5$ dynes. The ultimate standards of the International Metric System are of course the International Prototype Kilogram, which represents the mass of a certain cylinder of platinum-iridium alloy, and the International Prototype Meter,

meters, then W calculated by Eq. (2-4) is given in *joules* (1 joule $\equiv 10^7$ ergs); it is to be understood that in all relationships such as (2-1), (2-3), (2-4), (2-5), etc., there is implied a numerical proportionality factor on either side of the equation, which may be conveniently set equal to 1 if the units in which the various quantities entering the equation are expressed have been chosen with this end in view; the numerical equality is valid only when consistent units have been employed throughout. In the case of a purely dissipative force or force component, we continue to call W as defined by Eq. (2-4) the work done by the force on the moving body, but in this case, there is no balance between loss of potential energy and gain of kinetic energy; if the force is a purely dissipative one, the total energy decreases, and $-W$ then represents the quantity of energy *dissipated* during the motion of the body from r_0 to r.

The energy concept is readily extended to electrical circuits through direct observation of their properties. In order to maintain an electric current through a given circuit, one must introduce energy in some element of the circuit; this may be accomplished mechanically by means of an electric dynamo or generator, which operates on the principle discovered in 1831 by Michael Faraday that when a metallic conductor moves across a magnetic field an electric current is induced in the circuit of which the conductor happens to form a part. This principle affords a direct means of measuring electrical energy fundamentally in mechanical terms; thus, the ratio of the mechanical work W required in order to turn the dynamo (corrected for purely mechanical dissipative losses, such as through friction and air resistance) to the quantity of electricity q sent through it defines the *electromotive force* of the generating unit,

$$E \equiv \frac{W}{q} \equiv \frac{W}{I\tau} \tag{2-8}$$

where I represents the average current flowing during the time τ. When the dynamo is on open circuit, this emf is equal to the *potential difference*

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which represents the distance at the ice point between two marks engraved on a certain bar of the same alloy. These standards, adopted in 1889, have been preserved in the vaults of the International Bureau of Weights and Measures, near Paris, and the various nations subscribing to the upkeep of the Bureau have certified copies, which serve as national standards. The international standard of time is the Mean Solar Day, representing the interval, averaged throughout the year, between successive transits of the sun across the meridian at the equator; working standards of time are at present maintained by means of pendulum clocks, corrected periodically through astronomical observations. There is a possibility that future time standards may be based on atomic or molecular vibration frequencies; the National Bureau of Standards has announced an experimental clock synchronized to a microwave absorption frequency of the ammonia molecule.

between the terminals, the potential difference between two points of a circuit measuring in general the *net* energy per unit charge expended in transfering electricity from one point to the other. If the generator be connected to an electric motor, then electrical energy may be reconverted to mechanical form as work done by the motor; in an ideal circuit of conductors having no *electric resistance,* energy would in fact be conserved during such a transfer from dynamo to motor. In real conductors, however, some of the energy is always *dissipated* in overcoming electric resistance. According to G. S. Ohm's law, discovered in 1826, if E represents the emf in a circuit through which the current I is flowing, then

$$E = IR \tag{2-9}$$

where R is a property of the circuit called its *electric resistance;* in a circuit consisting of several conductors in series, the circuit resistance is made up of the sum of the separate resistances of the conducting elements. Since according to Eq. (2-8), $EI\tau$ represents the energy introduced into the circuit in electrical form by the generator, therefore if no work is done elsewhere in the circuit, all this energy,

$$\epsilon = EI\tau = I^2R\tau \tag{2-10}$$

is dissipated by the circuit's electric resistance. Some of the energy may be dissipated within the generator through its own internal electric resistance; if the generator's resistance be represented by R_i, and the external circuit resistance by $R_e = R - R_i$, then the quantity of energy $I^2R_i\tau$ is dissipated within the generator and the quantity $EI\tau - I^2R_i\tau = I^2R_e\tau$ in the external circuit. In a simple circuit consisting merely of the generator in series with a metallic conductor doing no work, but dissipating the electrical energy $I^2R_e\tau$, the potential difference E' across the terminals of the generator (and of the external conductor) is thus given by

$$E' = E - \frac{I^2R_i\tau}{I\tau} = E\frac{R_e}{R_e + R_i} \tag{2-11}$$

where E is the emf of the generator, or the potential difference across its terminals when it is running on open circuit ($R_e \rightarrow \infty$).

If, in Eq. (2-8), W is measured in *joules* and q in *coulombs* or I in *amperes* (the latter unit being derived in principle from the metric standards of mass, length, and time by means of A. M. Ampère's law governing the electromagnetic force between two conductors carrying electric currents), then the emf is expressed by definition in *volts; i.e.,* 1 volt coulomb $\equiv$ 1 joule. These are so-called *absolute units.* In practice, however, it has been convenient to measure electrical quantities without immediate reference to their mechanical or absolute significance. This situation has come about because one resistance may be compared with another directly and precisely by means of bridge circuits such as the familiar Wheatstone bridge or the Kelvin bridge, without reference either to other electrical standards or to mechanical standards; likewise, one emf may be compared with another directly and precisely by means of potentiometer circuits, again without reference to other electrical or mechanical standards. For this reason, the various national standardizing laboratories, such as the National Bureau of Standards of the U. S. Department of Commerce, have maintained independent electrical standards of resistance and of emf, based, respectively, on groups of standard wire resistors and on groups of standard galvanic cells of a special type (the Weston normal cell). Until Jan. 1, 1948, the so-called international standard of resistance was based in principle on the international mercury ohm, the resistance of a column of mercury satisfying certain specifications,[1] which had been adopted at the International Conference on Electrical Units and Standards held in London in 1908; but the working standards actually used in this country have been for many years the far more convenient and essentially stable wire resistance coils, which have occasionally been checked against the actual mercury ohm. Likewise, an International Technical Committee meeting in Washington in 1910 adopted the conventional value of 1.01830 international volts as the emf at 20°C of the Weston normal cell; this international standard has been continuously maintained at the National Bureau of Standards (and similarly at other standardizing laboratories) by means of a group of such cells, whose average behavior thus defined the international volt. In 1946, the International Bureau of Weights and Measures, meeting in Paris, after extensive preliminary comparisons of a fundamental nature undertaken by the various national standardizing laboratories, decided that beginning Jan. 1, 1948, all electrical measures would henceforth be expressed in terms of the so-called *absolute units*, derived ultimately from the metric standards (the International Prototype Meter, the International Prototype Kilogram, and the Mean Solar Day) by means of the established electrodynamic laws.[2] The actual physical standards of resistance (wire

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[1] These specifications: mass of 14.4521 g with uniform cross-sectional area (of about 1 mm^2), having a length of 106.300 cm, at the ice point, were intended to reproduce as accurately as possible at the time the "absolute" unit of resistance derived from metric standards by means of Ohm's law, Ampère's law, and Faraday's law of electromagnetic induction; they now have only historical interest.

[2] See H. L. Curtis, Review of Recent Absolute Determinations of the Ohm and the Ampere, *J. Research Natl. Bur. Standards*, **33**, 235–254 (1944); for a description of how the size of a resistance and the size of an electric current are determined fundamentally in mechanical terms, see C. A. Culver, "Theory and Applications of Electricity and Magnetism," pp. 398–401, McGraw-Hill Book Company, Inc., New York, 1947.

coils) and of emf (Weston normal cells) are maintained as heretofore, but in translating the results, the following conversion factors are now to be employed:[1]

1 mean international ohm = 1.00049 (absolute) ohms
1 mean international volt = 1.00034 (absolute) volts

In other words, a resistance coil certified formerly as having a resistance of 1.00000 int ohm is now assigned a resistance of 1.00049 (abs) ohms; likewise, the Weston normal cell is now assigned an emf at 20°C of 1.01865 (abs) volts. The unit of current in this system of measurement, the ampere, is derived through Ohm's law, Eq. (2-9); in other words, if the potential difference E' across the terminals of a conductor is expressed in volts and its resistance R in ohms, then the current given by the equation $I = E'/R$ is expressed directly in amperes.[2]

Now, in every case of "dissipation" of mechanical or electrical energy, some other effect invariably appears, equivalent to one that may be produced by heating. This fact was not plainly recognized until Count Rumford in 1798 conducted the first experiments on the deliberate and controlled conversion of mechanical energy into thermal form. Even then, scientists were slow to grasp the implications, until J. P. Joule during the middle of the nineteenth century conducted his classic investigations of the heating effect produced by an electric current, and the heating effects produced by mechanical means, such as friction and stirring. Let us therefore turn to the development of the concept of heat, up to the time of Joule.

2-2. Heat. We have noted in Sec. 1-1 that when two bodies originally at different temperatures are exposed to each other, through direct con-

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[1] The mean international units to which these conversion factors apply represent the averages of units as maintained at the six national laboratories that participated in this work before the war. The units maintained at the National Bureau of Standards differ slightly from these, so that the conversion factors announced for the adjustment of the values of the standards used in this country are

1 international ohm (U.S.) = 1.000495 (absolute) ohms
1 international volt (U.S.) = 1.00033 (absolute) volts

See Announcement of Changes in Electrical and Photometric Units, *Natl. Bur. Standards Circ.* C459 (1948).

[2] One may measure the quantity of electricity flowing through the circuit directly by means of a chemical coulometer, based on Faraday's law. The silver coulometer is preferred for the most precise work, the quantity of electricity being calculated from the mass of silver deposited at the cathode. The calculation depends on the experimentally established electrochemical conversion factor: 96,485 ± 10 coulombs/g-eq (which depends ultimately on the establishment of the ampere in mechanical terms), and on the atomic weight of silver. See D. A. MacInnes, "The Principles of Electrochemistry," Chap. II, Reinhold Publishing Corporation, New York, 1939.

tact, through common contact with an intervening medium, or even through radiation across empty space, there is a tendency for the hotter body to cool and for the cooler body to warm, until they come ultimately to *thermal equilibrium* at a common temperature. From earliest times, man has imagined that this process takes place through the transfer of *heat* from the hotter to the colder body; *i.e.*, he has called into being a hypothetical agency, heat, to which may be ascribed the responsibility for the change in temperature that a body tends to undergo when under the influence of another body at a different temperature. Following the invention of the thermometer, which provided a precise means of measuring temperature, it became natural to suppose that a given temperature change taking place in a particular material body would correspond to a definite *quantity* of heat. Although the facts are by no means self-evident, careful systematic investigations conducted independently by Brook Taylor about 1725 and by G. W. Richmann about 1748 proved that the quantity of heat, so conceived, given up by a cooling homogeneous body was proportional to its mass and, to a first order of approximation at least, to the number of degrees through which its temperature fell. They found, in effect, that when the mass M_1 of hot water at initial temperature t_1 is mixed with the mass M_2 of cold water at initial temperature t_2 the final equilibrium temperature t is in close agreement with the weighted mean

$$t = \frac{M_1t_1 + M_2t_2}{M_1 + M_2} \tag{2-12}$$

or in other words

$$M_1(t_1 - t) = M_2(t - t_2) \tag{2-13}$$

If we interpret the expression on the left of Eq. (2-13) as a measure of the quantity of heat given up by the hot water, then the expression on the right measures according to the same principle the quantity of heat received by the cold water; or in general, the quantity of heat required to raise the temperature of the mass M from t' to t'' is given by

$$Q = \Gamma M(t'' - t') \tag{2-14}$$

where Γ is a numerical proportionality factor whose value is yet to be determined; an equal quantity of heat is released when the temperature of the same mass falls from t'' to t'.[1] The Taylor-Richmann mixing law

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[1] This fact, too, is not self-evident, but has been confirmed by later experiments in which a given mass of water was heated through a particular temperature interval (1) by electrical means and (2) by thermal interchange with hot water, whose own temperature fell during the process; the quantity of electrical energy required to heat the cold water directly was in exact agreement with the quantity required to

may thus be interpreted in terms of a definite quantity of heat transferred from the hot to the cold water, no net heat being generated or lost during the process. Modern precise calorimetric measurements have shown that Eqs. (2-12) and (2-13) are only approximately correct, and it is necessary to suppose that the "constant" Γ in Eq. (2-14) varies slightly with the particular temperature interval.

If, now, one compares the quantities of heat required to raise the temperatures of equal masses of two *different* homogeneous substances through the same interval of temperature, one finds in general that the two quantities are quite different and bear no obvious relation to each other. Experiments by Joseph Black, about 1760, on the mixing of mercury and other substances with water showed that the general law of mixing has the form

$$\Gamma_1 M_1(t_1 - t) = \Gamma_2 M_2(t - t_2) \tag{2-15}$$

where M_1 and t_1 represent the mass and initial temperature of the one substance, M_2 and t_2 the mass and initial temperature of the other, and t their final equilibrium temperature, but Γ_1 and Γ_2 are characteristic coefficients for the two substances, whose values vary slightly with temperature, but are quite unrelated to each other. This law is supported by all variations of the mixing experiment with respect to the relative masses and the initial temperatures of the bodies mixed. The coefficient Γ of Eq. (2-14), which we may now define by the equation

$$\Gamma \equiv \frac{Q}{M(t'' - t')} \tag{2-16}$$

is in other words a property of the particular homogeneous substance, which we call its *mean specific heat* over the temperature interval t' to t''; the product $M\Gamma$ is known as the *mean heat capacity* over the same temperature interval for the entire body, consisting of mass M of the particular homogeneous substance. While the value of Γ depends on the temperature interval under consideration, we may define a *specific heat, c, at a particular temperature, t′*, by means of the operation

$$c \equiv \frac{1}{M} \lim_{t'' \to t'} \frac{Q}{t'' - t'} \equiv \frac{1}{M}\left(\frac{d'Q}{dt}\right)_{t=t'} \tag{2-17}$$

where Q represents the quantity of heat required to raise the temperature of the mass M of the substance from t' to t''; that is, if one were to plot Q/M vs. t'' as the substance is heated from the initial temperature t' to

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restore the hot water to its original temperature; compare experiments by H. L. Callendar and H. T. Barnes, *Phys. Rev.*, **10**, 202–214 (1900), and experiments by H. L. Callendar, *Trans. Roy. Soc. (London)*, (A)**212**, 1–32 (1912).

various final temperatures t'', then the limiting slope of the resulting curve (which would be a straight line if Γ were strictly independent of t) at the temperature t' would define c precisely at that temperature; the notation d' in the differential coefficient defined by Eq. (2-17) indicates, as we shall explain more fully later, that the value of Q is not altogether defined by the temperature change, but may depend on certain other conditions as well, such as on whether the pressure is maintained constant, or on whether the volume is maintained constant.

We have not as yet assigned a numerical scale to either Q or Γ, which are clearly interrelated. One may establish such a scale by assigning to some standard substance an arbitrary value of Γ for some particular temperature interval; Eq. (2-14) then measures in terms of this convention the quantity of heat received by the standard substance from another source as its temperature is raised through the standard interval. The standard for this purpose has been *water*, to which at constant pressure of 1 atm has been assigned a value of $\Gamma = 1.0000$ between 14.5 and 15.5°C; the value of Q computed accordingly, with water as the recipient of the heat, and with M in Eq. (2-14) represented in *grams*, is then said to be represented in 15° *calories;* with M represented in *kilograms*, the quantity of heat computed according to Eq. (2-14) is said to be represented in 15° *kilogram calories*, or 15° *kilocalories;* $1 \text{ kcal}_{15} \equiv 1000 \text{ cal}_{15}$. In the American and British system of measurement commonly used in engineering, the value of Γ for water at constant pressure of 1 atm is taken to be 1.0000 between 39°F (its temperature of maximum density) and 40°F; with M represented in pounds, Q is then represented according to Eq. (2-14) in *British thermal units;* $1 \text{ Btu} = 252.07 \text{ cal}_{15}$.

The specific heats of other substances relative to that of water at 15°C, including the specific heat of water itself at other temperatures, may be found in principle by the method of mixtures, based on Eq. (2-15). If, for example, one were to adjust M_1 of the substance for given initial temperature t_1, in relation to M_2 of the water so that with $t_2 = 14.5$°C, t were to come out exactly 15.5°C, then since under the circumstances Γ_2 would have the conventional value: $1.0000 \text{ cal}_{15}/\text{g}^\circ\text{C}$, Γ_1 given by Eq. (2-15) would represent directly the mean specific heat of the substance between t_1 and 15.5°C in $\text{cal}_{15}/\text{g}^\circ\text{C}$; the right-hand member of this equation would represent the heat given up by the substance between t_1 and 15.5°C directly in 15° calories, and by plotting Q/M_1 vs. t_1, the slope for any value of t_1 would give exactly the value of c_1, in accordance with Eq. (2-17). In practice, the mean specific heat of water over other temperature intervals has been established, originally through such fundamental measurements, but also by means of Joule's law, to be discussed in Sec. 2-3. Therefore it is not necessary in actual applications of Eq. (2-15) with water as standard calorimetric medium that t and t_2 be restricted, respectively, to 15.5 and 14.5°C; over the range 5 to 90°C, the variation in the specific heat of water turns out in fact to be less than ±0.5 per cent. One will note that the *relative* magnitudes of two different quantities of heat may be established in principle quite independently of the physical properties of water and the temperature scale; thus, if one were to transmit the two quantities of heat to two different masses of water, adjusted (after preliminary exploration) so that starting from the same initial temperature the *same* temperature rise occurred in each, then the two masses would be in direct proportion to the two quantities of heat, quite independently of the particular temperatures involved; all one would need for a thermometer would be a sensitive and reproducible temperature indicator, but the readings could have entirely arbitrary significance; one could use any other homogeneous substance for the calorimetric medium in place of water, subject to limitations based only on convenience and precision.

Black demonstrated also that certain processes, notably phase transitions such as the melting of ice and the condensation of steam, may absorb or liberate heat without significant change in the temperature. He introduced the concept of *latent heat,* to denote the heat absorbed by a system undergoing a change *at constant temperature,* in contrast to "sensible" heat, such as is associated ordinarily with a rise in temperature. Thus, ice in melting to form water at 0°C takes up 79.40 cal_{15}/g; *i.e.*, 1 g of ice originally at 0°C will cool a correspondingly larger mass of water from 15.5°C to final equilibrium temperature of 14.5°C than will 1 g of water originally at 0°C. In a similar sense, water at 100°C in boiling to form steam takes up 539.58 cal_{15}/g, in the sense that 1 g of steam originally at 100°C will warm a correspondingly larger mass of water from 14.5 to 15.5°C in the mixing experiment than will 1 g of water originally at 100°C. The heat absorbed by a solid in melting is known as its *latent heat of fusion;* the heat absorbed by a solid in vaporizing is known as its *latent heat of sublimation;* the heat absorbed by a solid in undergoing transformation to another allotropic solid form is known as the *latent heat of transformation;* the heat absorbed by a liquid in vaporizing is known as the *latent heat of vaporization.* All these latent heats associated with phase transitions are proportional in magnitude to the mass of substance undergoing transformation, and are commonly represented either for 1 gram or for 1 mole; their values depend also on the particular equilibrium temperature at which the transformation is carried out, ordinarily taken to be the normal transition temperature at 1 atm pressure.

2-3. The Mechanical Equivalent of Heat. The experiments on the thermal interchange between bodies initially at different temperatures, including the latent heats of phase transitions, and also the original researches of J. Fourier on thermal conduction, were all consistent with the supposition that heat was conserved during such processes. In fact, there arose during the eighteenth century the concept of heat as an imponderable fluid, which went by the name of *caloric;* to this concept, we owe such expressions as heat "capacity," heat "content," heat "conduction," "flow" of heat, etc. Those who believed in the phlogiston theory of G. E. Stahl went so far as to associate the apparent changes in mass during calcination and combustion with the presumed flow of caloric; but Lavoisier's magnificent demonstration of the role played by oxygen of the air during these changes, and his establishment of conservation of mass as a guiding principle for chemical transformations in general, ruled out the possibility that heat was associated in any way with sensible changes in mass.

Now, the production of heating effects by friction was surely familiar to the eighteenth-century scientists. From it, Francis Bacon long before had concluded that "heat is motion." A similar conclusion was reached by Guillaume Amontons at the opening of the eighteenth century from different evidence, based on his study of the gas thermometer, in quite remarkable anticipation of the kinetic theory of gases. P. S. Epstein has pointed out the extremely interesting fact that physicians prior to and even for several decades after Lavoisier's work on combustion accounted for body heat in terms of a theory initiated by A. Haller, author of a well-known treatise on medicine, that it resulted from friction of the solid particles in blood against the capillaries within the lungs.[1] However, the first scientific study of the production of thermal effects by purely mechanical means was undertaken in 1798 by Sir Benjamin Thompson, Count Rumford.

While supervising the boring of cannon at the arsenal of the Bavarian government in Munich, Rumford's attention was engaged by the considerable "degree of heat" acquired by a brass gun as it was being bored, and the still more intense degree of heat acquired by the metal chips separated from it by the boring tool. According to the prevailing caloric fluid theory of heat, such heat could have appeared only at the expense of a latent heat possibly associated with the separation of the chips; but Rumford convinced himself by measuring the specific heats of the chips and the metal block from which they were separated that no difference existed between their "heat contents." Furthermore, a blunt boring tool, which separated off less metal, was at least as effective in heating the block as a sharper tool. To preclude the possibility that heat could

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[1] P. S. Epstein, "Textbook of Thermodynamics," Chap II, John Wiley & Sons, Inc., New York, 1937.

be entering from the air, Rumford in some of his experiments submerged the entire block and boring tool under water; the effect was undiminished, the water undergoing no apparent change except to acquire the heat developed by the process, as was indicated by a rise in its temperature; in some of these tests, the surrounding water was actually heated to its boiling point, to the intense astonishment of the spectators.[1] The most significant and remarkable fact, clearly recognized by Rumford, was that the source of heat, whatever its nature might be, appeared to be inexhaustible, for through continued motion of the hollowed block against the borer, the heating effect could be prolonged indefinitely.

A further critical experiment was arranged by Humphry Davy in 1799. He caused ice blocks to melt merely by rubbing them against a metal plate; the motion was maintained by means of a clock-driven machine, and the entire apparatus was set up in a vessel evacuated to exclude any material substance that might convey heat. He concluded that the latent heat of fusion could only have been supplied by the frictional motion. Neither Rumford nor Davy, however, left accurate measurements of the quantity of mechanical energy expended in relation to the resulting degree of heating.

During the years 1843 to 1850, J. P. Joule conducted a classic series of measurements concerning the heating effect of an electric current and the production of heating by friction and by stirring. These experiments established beyond any doubt that an exact equivalent of heat could be produced by electrical or mechanical means, the ratio of the electrical or mechanical energy expended to the equivalent quantity of heat (as determined by the rise in temperature produced in a standard body such as water) being invariant. The best modern estimate of the mechanical equivalent of heat is[2]

$$J_{15} = 4.1855 \pm 0.0004 \text{ joule/cal}_{15} \tag{2-18}$$

Joule's own result, $J_{15} = 4.154$ joules/cal$_{15}$ (expressed in modern units) stood for many years as a model of precision.

Electrical methods of heating are in particular so sensitive to control and so precise that they have practically replaced water as the basis for primary calorimetric standardization. The electrical energy thermally "dissipated" by a current flowing through a resistance coil is given by Eq. (2-10), and may be measured in terms of any two of the quantities

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[1] Rumford's account of his experiments, published originally in the *Philosophical Transactions of the Royal Society* (1798), has been included by W. F. Magie in "A Source Book of Physics," pp. 151–161, McGraw-Hill Book Company, Inc., New York, 1935.

[2] R. T. Birge, *Rev. Modern Phys.*, **13**, 233–239 (1941).

E, I, and R, where E is the potential difference, I the current, and R the resistance through the coil; if E is measured in *volts*, I in *amperes*, R in *ohms*, and τ in *seconds*, then the equivalent quantity of heat is given in *joules* by

$$Q = EI\tau = I^2R\tau = \frac{E^2}{R}\tau \tag{2-19}$$

Even when water is actually used as the calorimetric medium to receive the heat being measured, the water equivalent of the calorimeter in modern high-precision measurements is always established fundamentally by measurement of the electrical energy required to heat it through the same temperature increase as was produced by the source of heat under investigation. Evidently, calorimetric measurements based on the electrical standards are quite independent both of the physical properties of water and of the temperature itself; all that is required of the thermometer is that it be sufficiently sensitive to reproduce accurately the initial and final states of the calorimeter, without the need for actual temperature calibration. Specific heat measurements, of course, depend on the temperature scale for their definition.

In recognition of the fact that modern calorimetric measurements are based primarily on electrical standards, rather than on the water calorie, and in order that the existing thermal and thermochemical data need not be subject to revision in the event that a change is made in the most probable value of the mechanical equivalent of the 15° calorie (which depends of course on the physical properties of water), most thermochemists have followed the lead of F. D. Rossini in expressing their results in terms of the *defined* or *thermochemical calorie:*[1]

$$1 \text{ cal} \equiv 4.1840 \text{ joules} \tag{2-20}$$

In other words, one actually measures the electrical equivalent of the heat in joules, and then uses (2-20) as an arbitrary conversion factor to

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[1] E. F. Mueller and F. D. Rossini, *Am. J. Phys.*, **12**, 1–7 (1944); this value has been adopted in "Selected Values of Chemical Thermodynamic Properties," assembled by the National Bureau of Standards staff under the direction of F. D. Rossini since Dec. 31, 1947. Rossini's original proposal was to let 1 cal ≡ 4.1833 int joules, and this value was in general use prior to Jan. 1, 1948. The present value results from the decision to abandon the old international joule from that date in favor of the absolute joule (to which we shall refer simply as the *joule* throughout this book); thermal data expressed in defined calories are unaffected by this change. Some scientists have proposed that we abandon the calorie altogether as a thermal unit, and express all heat measures in joules directly; the thermochemical data in the "International Critical Tables" (1929) were so expressed (in international joules); but by reason of custom and historical associations, the movement has not caught on, and has been more or less superseded for the present by Rossini's proposal.

express the result in conventional heat units. By comparing (2-18) with (2-20), one sees that most recent evidence has made necessary a slight revision in the "absolute" specific heat of water, but this has had no effect on recent thermal and thermochemical data represented in *defined* calories. We shall hereafter use the unqualified term "calorie" and the abbreviation "cal" in reference to the defined or thermochemical calorie given by (2-20); we shall use the term "kilocalorie" and the abbreviation "kcal" in a similar sense to denote a unit one thousand times larger; 1 cal_{15} = 1.00036 ± 0.00010 cal.

2-4. Generalized Conservation of Energy. We have seen that in certain ideal mechanical processes a quantity called the *total energy* stays constant. In real mechanical (and electrical) processes, however, a certain amount of energy is apparently lost, or "dissipated," but invariably some effect is produced equivalent to that of an exactly proportional quantity of heat. At the same time, in purely thermal processes, such as thermal interchange by mixing, heat conduction, radiation, etc., heat itself is conserved.

Joule's law permits us to draw the conclusion that *heat may be regarded as a form of energy.* In this generalized sense, then, *energy is conserved,* both in "dissipative" processes where energy in the restricted purely mechanical sense (kinetic or potential form) disappears, and also in heat engines, where mechanical energy is generated at the expense of heat withdrawn from a high-temperature source. Conservation of mechanical energy in conservative mechanical systems, and conservation of heat in purely thermal processes, become special cases of a more general conservation law that includes *thermodynamic processes,* in which mechanical energy and thermal energy are interchanged. This generalized conception of conservation of energy was recognized and first extensively applied by Hermann Helmholtz in 1847, and is known as the *first law of thermodynamics.*[1]

The firm establishment of the molecular hypothesis on chemical grounds, largely through the influence of S. Cannizzaro in 1860, led to fresh efforts to correlate heat with ordinary mechanical energy of the molecules, an idea that had been in existence for some time, but without concrete evidence. Two rather different though related lines of approach proved to be successful, one the kinetic approach associated with the work of R. J. E. Clausius, Ludwig Boltzmann, and J. Clerk Maxwell, and

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[1] H. Helmholtz, "Über die Erhaltung der Kraft," 1847; this paper was reprinted as No. 1 of W. Ostwald's "Klassiker der exakten Wissenschaften." The principle had been surmised earlier by R. J. Mayer in 1842; Mayer even estimated the value of the mechanical equivalent of heat from the thermal properties of gases, but his argument lacked the experimental foundation later provided by Joule's work.

the other the more general statistical mechanical approach of J. Willard Gibbs. In either theory, heat is differentiated from ordinary mechanical energy (kinetic and potential) only in that the coarseness of our sense perceptions, and of the methods of measurement generally employed in thermodynamic investigation, prevents us from perceiving the perpetual random molecular motion. We perceive readily enough the bulk motion of masses of molecules, but their random motion in an apparently stationary material body is ordinarily perceived only indirectly through the temperature sense. The most striking visible demonstration of the influence of molecular motion is of course the Brownian motion of particles in the colloidal size range. With heat thus conceived as kinetic and potential energy of *random* molecular motion, Joule's law implies that conservation of energy in the thermodynamic sense is simply an extension of the original idea of conservation in the purely mechanical sense; "dissipation" of mechanical energy consists merely of the randomization of energy that had previously been associated with average motion in a particular direction or average location in a particular region. We shall develop this point of view at length in Chap. 10. Formal thermodynamics can be developed, however, without any reference to the underlying structure of material substances, and to this development, it owes its generality. Let us proceed therefore to the formulation of the first law of thermodynamics in mathematical terms.

The truly enormous quantities of energy liberated by the spontaneous decompositions of the radioactive elements, by nuclear fissions, and by exothermic nuclear transformations in general, constitute an apparent exception to the principle of conservation of energy. The origin of this energy has been accounted for, however, on the basis of a conclusion drawn by Albert Einstein in 1905 from his special theory of relativity: the release of energy is associated with an exactly proportional loss of mass, in the ratio $\Delta\epsilon/\Delta M = c^2$, where c represents the invariant speed of light. Thus, the disappearance of 1 g of nuclear mass corresponds to the release of 9×10^{13} joules of energy. Radioactive and other kinds of nuclear transformations are accompanied generally by small but significant changes in mass, which represent the differences between the so-called binding energies of the reactant and product nuclei. For example, the atomic mass of H^1 on the physical atomic-weight scale ($O^{16} = 16.00000$) is 1.00813, while that of He^4 is 4.00389; in the transformation of $4H^1$ to $He^4 + 2\beta^+$, there is thus a net loss of 0.02753 (the mass of the two positrons emitted during the course of this transformation being 2×0.00055 on the atomic-weight scale), which corresponds to 2.474×10^{12} joules for every gram-atom of helium produced. H. A. Bethe and C. von Weizsäcker have shown independently that this prodigious energy, 5 million times the energy released by the ordinary chemical combustion of 4 g-atoms of hydrogen to water in which essentially no mass is lost, is the main source of the sun's energy, being released through a chain reaction involving C^{12}, which is regenerated during each complete cycle. The net changes in mass during ordinary chemical transformations are insignificant by comparison, and cannot be detected by chemical analytical means, as shown, for example, by the classical work of E. W. Morley on the synthesis of water from oxygen and hydrogen, and H. Landolt's series of measurements on several different reactions in sealed vessels, conducted in 1909.

2-5. The Internal Energy. A thermodynamic system may thus exchange energy with its surroundings in two general forms, thermal and nonthermal. Heat, or thermal energy, is energy in transition from one body to another by virtue of a difference between their temperatures; the net flow of heat is invariably in the direction from the hotter to the colder body; this qualification, to which we shall return later, constitutes the basis of the second law of thermodynamics. Work, or nonthermal energy, is energy in transition from one body to another by virtue of a force they exert on each other, in accordance with the fundamental mechanical definition (2-4) and its implications.

Let Q represent the quantity of heat received by the thermodynamic system under investigation and W the quantity of work done by it during some particular interaction with its surroundings; negative values of these quantities will be used to denote, respectively, heat given up by and work done on the system; then $Q - W$ will denote algebraically the net increase in the system's energy, and at the same time, the net decrease in the energy of the surroundings. If the kinetic and potential energies of the system as a whole undergo no change as a consequence, *i.e.*, if no sensible motion is set up in the system, and no sensible change takes place in the positions of any of its parts (such as might affect their potential energies), then any net gain or loss of energy, whether in thermal or nonthermal form, or as a combination of both, must necessarily be recognized by some change in its internal *state*, by which we mean a change in its temperature, or a change in its volume, or a change in the relative amounts of the component parts or in their chemical compositions, etc. If this were not so, then the energy would apparently disappear (or appear) without effect of any kind on the system, contrary to the principle of conservation; *some* change *has* to take place. Therefore it is appropriate for us to define for such a system an *internal energy* U by means of the relation

$$\Delta U \equiv U_2 - U_1 \equiv Q - W \tag{2-21}$$

Any net increase (algebraic) in the kinetic or potential energies of the system, in the ordinary mechanical sense, must in general be subtracted from $Q - W$ in order to leave the net gain in *internal* energy. However, most of the situations encountered in chemical thermodynamics do not in fact involve changes in the system's ordinary mechanical or "external" energy. Such changes, when they are encountered, may in any event be treated by straightforward extension of the principles derived from "static" thermodynamics combined with purely mechanical principles; the hydrodynamic theory of shock waves is a case in point.

Now, while both Q and W depend in general on the particular process by which the given change of state (state 1 to state 2) corresponding to the internal-energy change $U_2 - U_1$ is brought about (one may, for example, change a body of water from 20°C and 1 atm to 40°C and 1 atm either by placing it in contact with a body of hot water, which gives up heat and cools during the process, or by stirring it mechanically as in Joule's experiments), the value of ΔU itself depends by hypothesis only on the initial and final states of the system; if this were not so, then the concept of conservation would be meaningless, for one could proceed to restore the system to its original state by some other method that would require less energy than the energy released during the original change; one would then have two states of the same system indistinguishable in every respect except for a difference of energy, a situation clearly incompatible with the idea of conservation. Energy is conserved only if each distinctive state of the system has its own characteristic energy, so that a fixed quantity of energy is associated with the transition from one particular state to another. We may express this idea in formal mathematical language by asserting that dU in the differential form of Eq. (2-21) for an infinitesimal change in the state

$$dU = d'Q - d'W \tag{2-22}$$

is a *perfect differential* in terms of the variables defining the state (whose precise nature we shall examine in Chap. 3); the notations $d'Q$ and $d'W$ (instead of the conventional dQ and dW) call attention to the fact that these quantities are *not* perfect differentials corresponding to definite functions of the variables defining the state. The integral of dU around any closed path that ultimately restores the system to its original state must vanish:

$$\oint dU = 0 \tag{2-23}$$

Equations (2-22) and (2-23) express, respectively, the equivalence of mechanical and thermal energy, and general conservation of energy for interactions with the environment of a system whose ordinary mechanical energy (in kinetic and potential form) is fixed; together, they constitute the mathematical formulation of the first law of thermodynamics.

A process for which $Q = 0$, that is, one for which no net energy enters or leaves the system in thermal form, is called an *adiabatic* change. For such a process,

$$\Delta U = -W \qquad (Q = 0) \qquad \text{(2-24)}$$

Any work done by a thermally insulated system is therefore at the expense of its internal energy; conversely, net work done on the system by the surroundings in such circumstances is totally conserved in the form of an increase in the internal energy.

A process for which $W = 0$,

$$\Delta U = Q \qquad (W = 0) \qquad \text{(2-25)}$$

represents a purely thermal process; under this condition, heat itself appears to be conserved. In general, W includes a term of the form $\int_{V_1}^{V_2} p\,dV$, which represents mechanical work of expansion against the externally applied pressure p; therefore only if either the volume is fixed or some other compensating change is permitted to take place (such as a volume change always at the same fixed pressure, as we shall see later) will heat appear to be conserved as such.

Internal-energy changes may be measured in either thermal or mechanical energy units, provided that Q and W in Eq. (2-21) are represented in the same way. We shall follow the lead of most American thermochemists in representing internal-energy values in *defined* or *thermochemical calories*, which are based ultimately on mechanical standards and the metric system through Eq. (2-20), although electrical measuring instruments are generally used in the actual standardization of the calorimeters now used to measure Q. The following set of energy conversion factors has been adopted by the National Bureau of Standards as of Dec. 31, 1947, for its compilation, "Selected Values of Chemical Thermodynamic Properties,"[1]

$$\begin{aligned} 1 \text{ cal} &\equiv 4.18400 \text{ joules} = 4.12917 \times 10^{-2} \text{ liter atm} \\ &= 1.16222 \times 10^{-6} \text{ kw hr} = 3.96573 \times 10^{-3} \text{ Btu} \qquad \text{(2-26)} \end{aligned}$$

One will note that no method has been indicated for the establishment of absolute internal-energy values; the first law of thermodynamics states merely the principle of conservation of energy, without comment on the total amount of energy conserved between a given thermodynamic system and its environment, or for that matter in the universe at large. Our internal-energy measurements are therefore confined to energy *differences*

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[1] The *watt* is a unit of *power* or time rate of expenditure or generation of energy; by definition, 1 joule $\equiv$ 1 watt sec; thus, 3.6×10^6 joules = 1 kw hr. The product of potential difference in volts by current in amperes measures the electrical power in watts expended by a given conductor.

between different states of a thermodynamic system, some one of which may for convenience be selected as a reference state, to be assigned an arbitrary energy value.

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Problems

2-1. A pile driver weighing 500 kg is suspended at a height of 10 m from the ground; calculate its potential energy in joules. Calculate its velocity after release as it hits the ground.

2-2. A simple pendulum 3 m long is swinging in an arc making an angle of 10 deg from the vertical on either side. Calculate the difference in potential energy per unit mass of the bob between the highest and lowest points of the path described by its center of mass, and calculate its velocity as it passes through the lowest point.

2-3. A projectile 7.5 cm in diameter, weighing 3 kg, is fired from a gun whose barrel is 200 cm in length. Calculate the pressure required in order to accelerate the projectile to 900 m/sec muzzle velocity, assuming that the powder burns at such a rate as to maintain uniform pressure throughout the projectile's motion within the gun. If the combustion of the powder yields 1000 cal/g, what mass of powder is theoretically required in order to propel the projectile at the given velocity, neglecting heat losses, recoil of the gun, kinetic energy with which the gaseous combustion products escape, etc.?

2-4. Assuming the inverse-square law of universal gravitation, $F = G\dfrac{M_1M_2}{r}$, where G, the universal gravitation constant, has the value 6.670×10^{-8} dyne cm^2/g^2, express the potential energy of a body of mass M_1 as a function of r, its distance from the earth's center, taking the zero of potential energy at infinite distance removed. Comparing the universal force with the ordinary force of gravity M_1g at the earth's surface, where r, the earth's radius, equals 6380 km, calculate the value of M_2, the mass of the earth, using the standard value of $g = 980.665$ cm/sec^2. What vertical velocity must be given to a body at sea level so that its energy will be just sufficient to enable it to escape from the earth (neglecting air resistance)?

2-5. Niagara Falls is 167 ft in height. Calculate the energy in joules potentially available per kilogram of water reaching the falls. If this energy were entirely "dissipated" by the water going over the falls, what difference in temperature would there be between the water at the bottom and the water at the top of the falls? On the average, 20,000 cu ft of water per second (about 7 per cent of the total) is diverted through the hydroelectric power plant on the American side; to how much electric power, in kilowatts, is this theoretically equivalent? Another 36,000 cu ft/sec is diverted on the Canadian side; to how much electric power, in kilowatts, is this equivalent?

2-6. A river carrying on the average 250,000 gal/min of water is to be dammed; how high must the dam be in order to provide 10,000 kw of hydroelectric power?

2-7. A bullet weighing 25 g is fired at 500 m/sec velocity into a lead block ballistic pendulum weighing 10 kg, sufficiently thick to stop it. Calculate the average rise in temperature, before heat losses. The specific heat of lead is 0.0305 cal/g °C around room temperature; the kinetic energy acquired by the pendulum may be neglected.

2-8. A steel slug weighing 25 g is traveling at 500 m/sec. If it were suddenly stopped by a collision, and all its translational kinetic energy "dissipated" in raising the temperature of the slug, what temperature would it attain in the absence of heat losses? (Assume steel to have a mean specific heat of 0.12 cal/g °C, and assume that the slug is originally at 20°C.)

2-9. A pellet of zinc weighing 9.27 g is heated to 400°C and then dropped into a cavity drilled in a copper block weighing 1000.0 g and originally at 0°C; the temperature rise observed in the insulated block is 4.00°C. Taking the specific heat of copper as 0.0919 cal/g °C, calculate the mean specific heat of zinc over the range 4 to 400°C.

2-10. When 100 g of ice at 0°C is mixed in a Dewar flask with 1000 g of water originally at 25°C, what is the final equilibrium temperature, neglecting heat gains or losses from outside?

2-11. Distilled water is to be produced at a rate of 10 kg/hr from a water supply originally at 10°C. The water fed into the still is preheated to an average temperature of 60°C by being passed through the condenser used to condense the steam. If the still is electrically heated, what must be its minimum power rating in order to satisfy this demand, neglecting heat losses through the insulation? What must be the rate of flow of water through the condenser by-passing the still in order to carry off the heat given up by the condensing steam (assuming that the distilled water leaves the condenser at 60°C)?

2-12. A heating coil having a resistance of 200 ohms is connected to the 110-volt line; at what rate does it dissipate energy? How long would it take to heat 1 kg of water 1°C by means of this coil, neglecting heat losses by the water? If one wished to obtain the same heating rate from a 6-volt source, what current and resistance would be required?

2-13. What is the charge on the electron, in coulombs? (Note that the Faraday electrochemical constant represents the quantity of electricity carried by an Avogadro number of electrons.) If a current of 1 amp is flowing through a wire, how many electrons pass through any cross section of the wire per second? Assuming that there is on the average one "free" electron per metal atom, what is the average electron-drift velocity through a No. 14 copper wire (0.0252 cm diameter) in which a current of 1 amp is flowing? What is the drift velocity through a No. 24 copper wire (0.0079 cm diameter) carrying the same current? (Estimate first the number of free electrons per centimeter length of the wire, taking the density of copper as 8.9 g/cm^3.)

2-14. Water at 100°C absorbs 539.77 cal/g of heat in vaporizing at 1 atm pressure; the volume of the saturated steam is 1674 ml/g and of the liquid water, 1.043 ml/g. Calculate the work done per gram of water vaporizing (1 liter atm = 24.2179 cal), and calculate the difference of internal energy between 1 g of steam at 100°C and 1 atm, and 1 g of water at 100°C and 1 atm.

2-15. The mean heat capacity of water over the range 25 to 100°C is 1.000 cal/g °C; over this range, it expands at constant atmospheric pressure by 0.0405 ml/g. Calculate the work of expansion per gram when water is heated from 25 to 100°C at 1 atm, and calculate the difference between the internal energy of water at 100°C and 1 atm, and at 25°C and 1 atm.

2-16. If all the energy released by 1 kg of steam originally at 100°C in cooling at atmospheric pressure to become liquid water at 25°C could be obtained in mechanical form, how high could it lift a 1000-kg load against gravity?

2-17. Calculate the electrostatic potential energy between a Na^+ ion and a Cl^- ion at the equilibrium distance: $r = 2.814 \times 10^{-8}$ cm in the NaCl(c) crystal lattice, taking the zero of potential energy at infinite separation between the particles. (Note that in the potential-energy expression, Ae_1e_2/Dr, the potential energy will be expressed in *ergs* if r is expressed in centimeters, A is set equal to 1, and e_1 and e_2 are then expressed in so-called *electrostatic units;* $D = 1$ in a vacuum, and presumably also in the case under consideration.) Express this energy in calories per mole (*i.e.*, for N_0 isolated ion pairs).

Calculate the mutual electrostatic potential energy per ion pair of two pairs of Na^+ and Cl^- ions arranged as in the actual crystal lattice in alternation at the corners of a square in relation to the electrostatic potential energy of a single pair of ions at the same interionic distance. Calculate likewise the relative electrostatic potential energy per ion pair of four pairs of Na^+ and Cl^- ions arranged as in the actual crystal lattice in alternation at the corners of a cube. (Proceeding in this way, one may calculate the electrostatic potential energy per ion pair of the entire crystal, which for the NaCl type of lattice turns out to have a limiting value of 1.7476 times the energy of an isolated pair of ions at the same interionic distance.)

CHAPTER 3

THERMAL BEHAVIOR OF SIMPLE SYSTEMS

In this chapter, we shall apply the first law of thermodynamics to simple systems consisting of chemical substances undergoing changes that do not affect their compositions. We shall take up its applications to chemical changes in Chap. 4.

3-1. The State of a Thermodynamic System. A thermodynamic system consists of a particular specimen of a recognized material substance, or an interconnected group of different material substances, in which we happen to be interested for the purpose of investigation. We must consider at the outset how we identify the *state* of such a system.

The physical properties of a material substance, those properties such as the density, heat capacity, vapor pressure, etc., determined by operations that do not involve the composition explicitly (though their values may vary with the composition), are of two general types: *extensive* properties whose values are in direct proportion to the mass of the substance under consideration, and *intensive* properties whose values are independent of the mass, and are hence characteristic of the substance rather than of the particular sample of it under consideration. Examples of extensive properties are the volume and the heat capacity; examples of intensive properties are the density, the specific heat, and the specific resistivity. Evidently, one can construct an intensive property of the substance from an extensive property of the sample by dividing the value of the extensive property by the mass of the sample; the adjective "specific" prefixed to the name of the extensive property usually indicates that such a procedure has been followed, as, for example, in the case of specific volume and the case of specific heat.[1] If the substance happens to be a homogeneous chemical substance, having a definite composition and corresponding chemical formula, then it is convenient for the chemist

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[1] This usage is not invariably followed, as for example in specific gravity and specific viscosity, where "specific" means relative to the corresponding value of the property for water, and in specific resistivity; electrical resistance is not strictly an extensive property in the sense here defined, but it varies in direct proportion to the length of the conducting sample and in inverse proportion to its cross-sectional area; one defines the mass-independent specific resistivity in this case by dividing the resistance of the particular sample by its length and multiplying by its cross-sectional area (supposed to be uniform).

to use its *formula weight*, to which we shall assign the symbol $\bar{M}$, as unit of mass. The *molal* volume, the *molal* heat capacity, the *molal* latent heat of vaporization, etc., are thus intensive properties of the substance, in the same sense as the specific volume, the specific heat, the specific latent heat of vaporization, etc. We shall use the noun "mole" and the adjective "molal," with reference to a definite mass of the substance represented by its *formula weight in grams* (the formula in mind being written explicitly where any possible ambiguity may exist), without necessarily implying the existence of physical molecules corresponding to the formula; for example, the molal volume $\bar{V}_{\mathrm{NaCl}}$ will represent the volume of 58.454 g of sodium chloride, although there is no evidence for the existence of NaCl molecules as such in the crystalline or liquid states; likewise, the molal volume $\bar{V}_{\mathrm{CH_3COOH}}$ will represent the volume of 60.052 g of acetic acid, although at least in the vapor state, an appreciable fraction is known to be in the form of dimeric molecules corresponding to the formula $(CH_3COOH)_2$. We shall in general use a bar superscript over the symbol representing an extensive property of the system, in order to represent the corresponding intensive molal property; for example, $\bar{V} = V/n$, where n represents the number of moles, $n = M/\bar{M}$, corresponding to the mass M and volume V; this applies only to homogeneous substances of fixed composition.[1]

Now, it is with the intensive properties that we are primarily concerned when we attempt to define the state of a material substance, because we know from experience that if we examine a larger or a smaller mass of the same substance under the same general set of conditions, all the intensive properties are alike. In fact, experience teaches us that for a *homogeneous substance of fixed composition, i.e.*, a chemical compound or element in a particular one of its allotropic forms, the state is determined in general by the values of *two* independently variable quantities, for example, its temperature and pressure. By this statement, we mean that all its intensive properties assume characteristic values fixed by nature whenever the substance is brought to a given temperature and pressure; on the other hand, unless at least two such independently variable properties are arbitrarily fixed, the values of other intensive properties are without meaning. For example, the density of ammonia gas means nothing

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[1] Chemical engineers express the masses of chemical substances also in *pound-moles*, and other units derived from the United States or British systems of measurement; evidently, 1 pound-mole = 453.5924277 gram-moles, this being the defined ratio of the avoirdupois pound to the gram. We shall use the term *mole* throughout in the sense of *gram-mole*, this being a unit of mass represented by the formula weight in grams; but self-consistent relations may obviously be established in terms of other molal measures of mass.

unless one specifies both the temperature and the pressure to which the density value refers; any other two independently variable properties besides the temperature and the pressure could be used to define the state, because the values of the temperature and the pressure would then be fixed by implication; thus, if one were to specify the density and the coefficient of viscosity of ammonia gas, there would be a unique set of values of the other intensive properties, including the temperature and the pressure, corresponding to the specified values of the density and the viscosity. Generally, however, we find it convenient to regard temperature and pressure as the independent variables on which the state depends, these being the properties most easy to control.

A consequence of this basic concept of the *variance* of a given material system, by which we mean the number of independently variable properties on which its state depends, is the equation of state of a homogeneous substance of fixed composition. Since the variance of such a substance is *two*, the volume, temperature, and pressure for given mass must be so interrelated that the values of any two of these quantities serve to determine the value of the third. This relationship may be expressed formally by the equation

$$f(\bar{V}, T, p) = 0 \tag{3-1}$$

where f represents some function of the three variables, whose exact nature depends on the particular substance, and may be determined in general only through experimental observation. The particular relationship of the general form (3-1) that applies to a given homogeneous substance of fixed composition is known as its *equation of state.* It is usually convenient, though not always so, for us to solve Eq. (3-1) for $\bar{V}$ as an explicit function of T and p,

$$\bar{V} = \bar{V}(T, p) \tag{3-2}$$

Then for a change of state, since the change in $\bar{V}$ is determined entirely by the changes in T and p,

$$d\bar{V} = \left(\frac{d\bar{V}}{dT}\right)_p dT + \left(\frac{d\bar{V}}{dp}\right)_T dp \tag{3-3}$$

The quantities

$$\alpha \equiv \frac{1}{V}\left(\frac{dV}{dT}\right)_p \tag{3-4}$$

$$\beta \equiv -\frac{1}{V}\left(\frac{dV}{dp}\right)_T \tag{3-5}$$

which involve the two differential coefficients appearing in Eq. (3-3), are known, respectively, as the *coefficient of cubical expansion* and the *coeffi-*

cient of compressibility; for solids, the value of $1/\beta$ is known also as *Young's bulk modulus of elasticity.*[1]

Several useful relationships follow from the mathematical properties of Eq. (3-3). Thus, by setting $d\bar{V} = 0$, we may derive an expression for the relation between T and p for a change taking place at constant volume:

$$\left(\frac{dp}{dT}\right)_V = \frac{\alpha}{\beta} \tag{3-6}$$

Furthermore, since $\bar{V}$ is completely determined by the values of T and p, we may apply to Eq. (3-3) Euler's criterion for $d\bar{V}$ to be a perfect differential with respect to variations in T and p:[2]

$$\left[\frac{d}{dp}\left(\frac{d\bar{V}}{dT}\right)_p\right]_T = \left[\frac{d}{dT}\left(\frac{d\bar{V}}{dp}\right)_T\right]_p \tag{3-7}$$

Thus, it follows that

$$\left(\frac{d\alpha}{dp}\right)_T = -\left(\frac{d\beta}{dT}\right)_p \tag{3-8}$$

An example of a simple equation of state is given by the ideal-gas law, $p\bar{V} = RT$, which is applicable approximately to any gas at sufficiently low pressures; the form corresponding to (3-1) is $p\bar{V} - RT = 0$, while the form corresponding to (3-2) is $\bar{V} = RT/p$; one sees that for the ideal gas, $\alpha = 1/T$ and $\beta = 1/p$. The van der Waals equation of state, $(p + a/\bar{V}^2)(\bar{V} - b) - RT = 0$, illustrates a case in which it would be inconvenient to try to express $\bar{V}$ explicitly as a function of T and p in the form (3-2), though the functional relationship implied by Eq. (3-2) of course exists, and Eq. (3-3) is satisfied. For liquids and solids, the state is rather insensitive to variations in the pressure, and in particular, is practically independent of such changes as normally take place in the barometric pressure; the coefficient of compressibility of water at 20°C, for example, is about 4.3×10^{-5}/atm at pressures between 0 and 500 atm, so that one ordinarily does not have to specify the pressure precisely unless one is concerned with pressure variations of at least several atmospheres magnitude. For liquids and solids, the state is considerably more sensitive to variations in the temperature, the coefficient of expan-

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[1] For isotropic solids, like NaCl, the value of α is three times the coefficient of *linear* expansion; for anisotropic crystals, however, the coefficient of linear expansion may have different values for different directions through the crystal.

[2] This criterion is equivalent to the statement that the value of $\partial^2 V/\partial p\, \partial T$ is independent of the order of differentiation, a condition implied by the fact that $\bar{V}$ is completely determined by T and p, without regard to the particular manner in which the state may be varied (see Appendix 1).

sion of water at 1 atm and for temperatures between 20 and 100°C having the average value, 4.8×10^{-4}/deg; in other words, a change of 1°K (or 1°C) in the temperature produces a change in the volume more than ten times greater than that produced by a change of 1 atm in the pressure, within the temperature and pressure ranges noted.

In special circumstances, the state of a homogeneous substance of fixed composition may vary with other quantities besides temperature and pressure as independent variables. If it is a dielectric, then its state in an electric field will vary with the intensity of its polarization, and its properties will therefore not be determined until one has specified the electric field strength, as well as the temperature and pressure. If it is diamagnetic or paramagnetic, then its state in a magnetic field will vary with the intensity of its magnetization, and its properties will therefore depend on the magnetic field strength, as well as on temperature and pressure. If one is interested in light transmission, then one finds that the optical properties depend on the wavelength of the light, as well as on temperature and pressure. Unless such special circumstances are explicitly recognized, however, we shall ordinarily assume that we are dealing with a system in which they are absent; the physical properties will then be completely determined when the temperature and pressure alone are specified.

We have seen in Sec. 2-5 that the internal energy U of a thermodynamic system has to be determined by its state, in the sense that two states indistinguishable in all other respects must necessarily also have identical internal energies. For a homogeneous material substance of fixed composition, the internal energy is therefore one of its physical properties, determined for given mass, along with all the other physical properties, by the values of any two independently variable properties, such as the temperature and the pressure. It is furthermore an extensive property, since experience teaches us that there is no net energy taken in from or released to the surroundings, either in thermal or in nonthermal form, when different samples of the same substance at the same temperature and pressure are combined together; the internal energy of the combined samples must therefore be simply the sum of the internal energies of the separate samples, and hence must increase in direct proportion to the mass.[1] The *specific internal energy*, U/M, must therefore be an *intensive*

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[1] This statement is not entirely accurate when one compares an extremely finely subdivided solid or liquid with the same mass fused into a single unit; one may then find a significant difference in energy associated with the larger surface area of the finely subdivided sample. We shall return to this question in Sec. 6-5, but shall meanwhile assume that surface effects may be ignored in the problems immediately to be considered.

property of such a substance; the *molal internal energy,*

$$\bar{U} \equiv \frac{U}{n} \equiv \frac{U}{M} \bar{M} \tag{3-9}$$

must likewise be an intensive property, and thus may be represented (in the absence of electric fields, magnetic fields, etc.) as a function of temperature and pressure in the general form

$$\bar{U} = \bar{U}(T, p) \tag{3-10}$$

$$d\bar{U} = \left(\frac{d\bar{U}}{dT}\right)_p dT + \left(\frac{d\bar{U}}{dp}\right)_T dp \tag{3-11}$$

The detailed form of (3-10) for a given substance is to be determined by experiment, based on the fundamental relation, Eq. (2-21); *i.e.*, by measuring the net quantity of heat absorbed and the net quantity of work done by the substance as it undergoes changes from one temperature and pressure to another, we may establish empirically how $\bar{U}$ depends on the state; such information characterizes the thermodynamic behavior of the substance within the scope of the first law of thermodynamics. By means of equation-of-state data introduced into Eq. (3-3), we may transform Eq. (3-11) so as to express $\bar{U}$ as a function of $\bar{V}$ and T, or as a function of $\bar{V}$ and p as independent variables, in place of T and p, should this be convenient.

In the case of a homogeneous material substance of *continuously variable composition, i.e.,* a *solution,* the state depends on more independent variables than in the case of a substance whose composition is fixed by nature; in addition to temperature and pressure, one must specify the *composition* as well. In general, a certain minimum *number of components, C,* is required for the complete specification of the composition. For example, in a liquid solution of ethyl alcohol and water, the composition is specified completely by a statement of the proportion in which the *two* substances of fixed compositions, alcohol and water, are present; note that it is not necessary in this case for the proportions of the three different elements present, carbon, hydrogen, and oxygen, to be stated, because in view of the invariant compositions of alcohol and water, not only are these proportions not independently variable, but they are in fact implied completely by the proportion of alcohol to water. The intensive properties of such a solution, *e.g.*, the density, the specific heat, the coefficient of viscosity, etc., are fixed when the values of any *three* independently variable intensive properties, such as the temperature, the pressure, and the percentage of alcohol, are specified; in other words, the variance of this system is *three.* In general, each additional constituent of definite composition whose amount in the solution may be varied by continuous degrees independently of the amounts of the other constituents present increases the variance by one, so that the variance of a solution containing C components is in general $2 + (C - 1)$.

If chemical reactions may take place among the constituents present in a solution, then the number of components necessary in order to specify the composition may be smaller than the number of different chemical species present, because operation of the laws of chemical combination may fix by nature the amounts of certain constituents in relation to the amounts of others; the amounts of the different constituents may then not all be independently variable. Let us reserve the expression *number of components* for reference to the *least number of chemical constituents whose masses in the solution may be independently and continuously varied.* For example, in a gas at 250°C and 1 atm containing PCl_3, Cl_2, and PCl_5, although three different chemical species are present, their relative amounts are not all independently variable, for if the proportion of any two, say that of PCl_3 to Cl_2, is fixed, then the proportion of the third, PCl_5, to either of the other two is also fixed automatically at the given temperature and pressure through equilibrium of the reversible chemical reaction: $PCl_3 + Cl_2 = PCl_5$. Therefore this system has but *two* components defining its state at given temperature and pressure. In fact, if the proportion of PCl_3 to Cl_2 in the mixture happens to be the same as in the compound PCl_5, *i.e.*, if they are present in 1:1 molal proportion, then the number of components becomes only *one*, for in this case the proportion of PCl_3 to Cl_2, which by itself in the general case was sufficient to determine also the proportion of PCl_5 to either, now must remain the same, no matter to what extent chemical combination or the reverse process of dissociation may take place; in other words, only two independent variables, temperature and pressure, are alone sufficient under this condition to fix the state of the system, just as in the case of a single homogeneous substance of fixed composition. One cannot tell from consideration purely of the variance whether PCl_5 in the gaseous state exists as the pure compound or in the form of dissociation products, $PCl_3 + Cl_2$, although of course by introducing the nonthermodynamic idea of comparing the vapor density with that of other gases, *i.e.*, by making use of the ideal-gas law founded on Avogadro's hypothesis, one may readily enough deduce the extent of dissociation. In certain cases, the number of components may depend on the circumstances in which the particular system is placed. A gas at 100°C and 1 atm consisting of H_2, O_2, and H_2O in the absence of a catalyst has *three* components whose masses may be independently varied; at 2000°C, however, where the reversible chemical reaction $2H_2O = 2H_2 + O_2$ establishes equilibrium rapidly among the amounts of the three constituents, the number of components becomes *two*, while if either pure water vapor or a mixture of H_2 and O_2 in 2:1 molal proportion is heated to 2000°C, then the number of components is but *one*. Clearly, a chemical compound such as NaCl counts as but one component, notwithstanding the independent chemical behavior of the ions, Na^+ and Cl^-, of which this compound consists; because of the requirement of electrical neutrality in ordinary chemical systems, the relative amounts of the two ions are not independently variable, but are fixed by nature. One can vary the amount of Cl^- independently of the amount of Na^+ by adding another chloride, such as KCl, but there is then still a necessary interrelation between the total quantity of Cl^- and the total quantity of the two positive ions, Na^+ and K^+; such a combination of NaCl with KCl would thus count as two components toward determining the variance.

In summary, then, the *number of components* in a homogeneous substance of continuously variable composition represents the *least* number of chemical constituents of definite composition whose amounts in the solution may be varied independently of each other. The *variance* of such a substance, representing the number of independently variable intensive properties, is $2 + (C - 1)$, where C represents the number of components. The particular constituents recognized as components is immaterial for our purpose; only their number determines the variance. We may thus represent the internal energy of such a substance as a function of T, p, and the numbers of moles of the various components, n_1, n_2, . . . , n_C formally by means of the equation

$$\begin{aligned} dU = {} & \left(\frac{dU}{dT}\right)_{p,n_1,n_2,\ldots,n_C} dT + \left(\frac{dU}{dp}\right)_{T,n_1,n_2,\ldots,n_C} dp \\ & + \left(\frac{dU}{dn_1}\right)_{T,p,n_2,\ldots,n_C} dn_1 + \left(\frac{dU}{dn_2}\right)_{T,p,n_1,n_3,\ldots,n_C} dn_2 \\ & + \cdots + \left(\frac{dU}{dn_C}\right)_{T,p,n_1,n_2,\ldots,n_{C-1}} dn_C \qquad \text{(3-12)} \end{aligned}$$

where dU satisfies Eq. (2-22). The first two terms on the right represent how U changes with temperature and pressure so long as the composition remains unchanged; these terms must be related to other properties of the solution essentially in the same way as for a chemical substance of naturally fixed composition (such relations will be explored in Sec. 3-2). The remaining terms on the right express formally how U changes with composition at fixed temperature and pressure, relations that must be established empirically for solutions of a particular set of components through measurements in principle of Q and W for such changes of state.

As written, Eq. (3-12), which is a generalization of Eq. (3-11), includes changes such as may result through an increase or decrease in the total mass. Since U is an extensive property of the solution, then if at given temperature and pressure one were to increase the amounts of each component by the same fraction λ so that $dn_1 = \lambda n_1$, $dn_2 = \lambda n_2$, . . . , $dn_C = \lambda n_C$, leaving the composition unchanged, U would increase by the same fraction, $dU = \lambda U$; such a change would correspond in fact merely to taking a larger sample, of mass $M + \lambda M$, at the given temperature, pressure, and composition. Substituting these conditions in Eq. (3-12), one draws the conclusion

$$U = v_1 n_1 + v_2 n_2 + \cdots + v_C n_C \qquad (T, p \text{ const}) \qquad (3\text{-}13)$$

where for short we have introduced the symbols

$$\left.\begin{aligned} v_1 &\equiv \left(\frac{dU}{dn_1}\right)_{T,p,n_2,\ldots,n_C} \\ v_2 &\equiv \left(\frac{dU}{dn_2}\right)_{T,p,n_1,n_3,\ldots,n_C} \\ &\cdots\cdots\cdots\cdots\cdots \\ v_C &\equiv \left(\frac{dU}{dn_C}\right)_{T,p,n_1,n_2,\ldots,n_{C-1}} \end{aligned}\right\} \qquad (3\text{-}14)$$

Thus, the quantities $v_1, v_2, \ldots, v_C$, introduced originally by Eq. (3-12) in a purely formal manner, now acquire the physical interpretation of representing what the respective molal internal energies of the components in the solution *would be* if at given temperature and pressure the total internal energy were to be represented as a sum of terms contributed by the individual components. If Q and W were zero for the process of forming the solution from its components, at uniform temperature and pressure, regardless of composition, then the value of U would necessarily be the same as the sum of the internal energies of the pure components, and $v_1, v_2, \ldots, v_C$ would then be equal, respectively, to the molal internal energies $\bar{U}_1, \bar{U}_2, \ldots, \bar{U}_C$ of the pure components; in general, however, this is not the case, and we shall return to a discussion of the internal energy of solution in Sec. 4-5. The quantities $v_1, v_2 \ldots, v_C$ are themselves intensive properties of the solution, varying with temperature, pressure, and composition; they are known as *differential* or *partial molal internal energies.* Their values are to be determined in principle by experiment, precisely in accordance with the operations represented by Eqs. (3-14); thus, the value of v_i represents the increase in internal energy of the solution (as measured by $Q - W$) per mole of component i added, when that component is added to the solution without sensible change in the temperature, pressure, or composition:

$$v_i = \lim_{\Delta n_i \to 0} \frac{Q - W}{\Delta n_i} \quad (T, p, n_1, \ldots, n_{i-1}, n_{i+1}, \ldots, n_C \text{ const}) \tag{3-15}$$

It is necessary to take the limit for an infinitesimal quantity of the component added, in order to take account of the fact that v_i itself would vary in general with a finite change in the composition. Specification of the values of $v_1, v_2, \ldots, v_C$ as functions of the composition at given temperature and pressure completes the thermodynamic description of a solution within the scope of the first law of thermodynamics, in the same sense that specification of the values of $(dU/dT)_p$ and $(dU/dp)_T$ as functions of temperature and pressure completes the description in the case of a homogeneous substance of fixed composition. Only $(C - 1)$ of the C quantities $v_1, v_2, \ldots, v_C$ need be established independently by measurement, however, because there is then a general mathematical relationship connecting them by virtue of the fact that they are intensive properties, dependent on the composition but not on the total mass of all C components; this relationship, known as the *Gibbs-Duhem equation*,[1] may be derived by differentiation of Eq. (3-13) at constant temperature and pressure in the most general manner with respect to changes in the amounts of the components

$$dU = n_1\,dv_1 + v_1\,dn_1 + n_2\,dv_2 + v_2\,dn_2 + \cdots + n_C\,dv_C + v_C\,dn_C \qquad (T, p \text{ const})$$

and comparison with Eq. (3-12) from which we started; thus

$$n_1\,dv_1 + n_2\,dv_2 + \cdots + n_C\,dv_C = 0 \quad (T, p \text{ const}) \tag{3-16}$$

By integration, one may establish the value of any single v_i from known values of all the others, previously established as functions of the composition; we shall make use of this equation and analogous equations for other thermodynamic properties in Sec. 4-5, and particularly throughout Chap. 7. A precisely similar mathematical treatment may be applied to express the effect of composition on any other extensive property of the solution, such as the volume.

The internal energy of a *heterogeneous* substance consists of the sum of the internal energies of the separate homogeneous parts or phases. In general, the physical mixing of different homogeneous substances that do

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[1] Named after the great American mathematical physicist, J. Willard Gibbs, who derived it in his monumental paper, On the Equilibrium of Heterogeneous Substances, *Trans. Conn. Acad. Arts Sci.*, **3**, 108–248 (1876); **3**, 343–524 (1878), and the French physicist, Pierre Duhem, who developed a similar equation applicable in particular to the partial vapor pressures of solutions, *Compt. rend.*, **102**, 1449–1451 (1886).

not change each other's form or composition is accompanied by no net energy change; and, conversely, we consider that the sorting out of different kinds of substances that can be distinguished at least by visual methods (aided by the ordinary microscope, if necessary) calls for no necessary net expenditure or release of energy, though one may find it convenient to speed the process by screening, centrifuging, flotation, etc. If the grist is so fine, however, that the surface area between the phases must be taken into account, then there may be appreciable surface energy; this energy merges into true solution energy as the grist approaches molecular dimensions. Some of the distinctive properties of colloidal dispersions are associated with the existence of a significant surface energy. We shall discuss the variance of a heterogeneous system later in connection with the general theory of equilibrium to be developed in Chap. 7.

3-2. The Internal Energy as Heat Function at Constant Volume. Let us now turn our attention to the association of the mathematical properties of the internal-energy function implied by Eq. (3-11) with experimental methods of measuring the internal energy in accordance with Eq. (2-21) or its equivalent in differential form, Eq. (2-22); we shall suppose that we are dealing with fixed mass of a homogeneous substance of fixed composition, fixed either by nature as in the case of a chemical element or compound or by agreement as in the establishment of the physical properties of a 25 per cent solution of glycerol in water.

In general, the net work done by a physically stationary thermodynamic system during an infinitesimal change of state may be separated for convenience into a term $p\,dV$ representing mechanical work of expansion against the external pressure p imposed by the environment[1] and a term which we may designate by $d'W'$, representing all work done in a form other than mechanical work of expansion, for example, the work that might be done in electrical form by a change taking place in a galvanic cell; thus

$$d'W = p\,dV + d'W' \tag{3-17}$$

Therefore Eq. (2-22), which defines dU in experimental terms, may be recast in the general form

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[1] The form of this term follows directly from the basic definition, Eq. (2-4); the pressure on a surface of the system represents a force normally directed and equal in magnitude to the pressure multiplied by the surface area on which it acts. If the system expands in such a way that this surface is displaced normally to itself through the distance dr, its area being A, then, according to Eq. (2-4), the element of work done by the system is $pA\,dr$. The product $A\,dr$, however, represents the volume dV generated by the moving boundary; therefore $d'W = p\,dV$, an expression which may be integrated to give the finite amount of work done during a finite expansion, if p is defined at all stages as a function of V.

$$dU = d'Q - p\,dV - d'W' \tag{3-18}$$

Now for most of the situations with which the chemist is concerned, $W' = 0$; a notable exception is the class of electrochemical processes in general, which we shall consider in detail in Chap. 9; but, ordinarily, chemical systems are not constituted to do work except incidentally to a volume change; this is true even of such practical sources of power as the steam engine and the internal-combustion engine.[1] Thus, Eq. (3-18) reduces to

$$dU = d'Q - p\,dV \qquad (W' = 0) \tag{3-19}$$

For a change of state taking place *at constant volume,*

$$\Delta U = Q_v \qquad (W' = 0) \tag{3-20}$$

Under this condition, the quantity of heat absorbed by the system measures directly its increase in internal energy; inasmuch as the value of U depends only on the state of the system, heat itself must therefore be conserved under this condition, and will be released as such in the same amount if the system is restored to its original state. The internal energy U thus serves as a *heat function at constant volume,* in the sense that its value measures the quantity of heat apparently "contained" by the system; one should note that this concept applies only because we have imposed conditions making it impossible for any of the energy to appear in nonthermal form.

Now, the increase in temperature associated with the absorption of heat by a given homogeneous substance measures its *specific heat,* in accordance with the definition (2-17); more generally, for arbitrary mass, the *heat capacity* of the system is defined by

$$C \equiv \frac{d'Q}{dT} \tag{3-21}$$

This definition is incomplete, however, since we have seen that the quantity of heat depends on the conditions under which the temperature change is brought about. But, according to Eq. (3-20), the *heat capacity at constant volume*

$$C_v \equiv \left(\frac{d'Q}{dT}\right)_v = \left(\frac{dU}{dT}\right)_v \qquad (W' = 0) \tag{3-22}$$

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[1] For simplicity, we shall count electrically heated systems in this class; even though the energy expended on such a system comes from the environment originally in electrical form, we may count the energy received into the system as thermal (if our system did not absorb it, it would merely raise the temperature of the heating coil), using Joule's law to compute the equivalent quantity of heat.

must be a definite property of the system, since the change of U depends only on the particular change of state under consideration. The *molal heat capacity at constant volume,* $\bar{C}_v$, represented by

$$\bar{C}_v = \left(\frac{d\bar{U}}{dT}\right)_v \tag{3-23}$$

is in fact an *intensive property of the substance,* determined along with all the other intensive properties by the temperature and pressure. Its value for a given substance cannot be predicted by purely thermodynamic means, but must be determined either empirically by direct measurement, or theoretically on the basis of extrathermodynamic conceptions of molecular structure.

Let us now proceed to expand $\bar{U}$ as a function of temperature and pressure, in accordance with the formal relationship (3-11). For the effect of temperature alone, at constant pressure, from Eq. (3-19),

$$\left(\frac{d\bar{U}}{dT}\right)_p = \left(\frac{d'\bar{Q}}{dT}\right)_p - p\left(\frac{d\bar{V}}{dT}\right)_p \qquad (W' = 0) \tag{3-24}$$

The first term on the right of Eq. (3-24) represents by definition the *molal heat capacity at constant pressure,* $\bar{C}_p$,

$$\bar{C}_p \equiv \left(\frac{d'\bar{Q}}{dT}\right)_p \qquad (W' = 0) \tag{3-25}$$

Since the other terms in Eq. (3-24) are clearly functions only of the state of the system, it follows that $\bar{C}_p$, like $\bar{C}_v$, is an intensive property of the substance, determined by its state. Thus, introducing the notation of Eq. (3-4),

$$\left(\frac{d\bar{U}}{dT}\right)_p = \bar{C}_p - p\bar{V}\alpha \tag{3-26}$$

For the effect of pressure alone, at constant temperature, from Eq. (3-19),

$$\left(\frac{d\bar{U}}{dp}\right)_T = \left(\frac{d'\bar{Q}}{dp}\right)_T - p\left(\frac{d\bar{V}}{dp}\right)_T \qquad (W' = 0) \tag{3-27}$$

The first term on the right of Eq. (3-27) defines an intensive property called the *molal latent heat of pressure variation:*

$$\bar{L}_p \equiv \left(\frac{d'\bar{Q}}{dp}\right)_T \qquad (W' = 0) \tag{3-28}$$

This property is the pressure analogue of the molal heat capacity, representing the quantity of heat absorbed per unit increase in the pressure, when the substance is compressed at constant temperature. Introducing the notation of Eq. (3-5),

$$\left(\frac{d\bar{U}}{dp}\right)_T = \bar{L}_p + p\bar{V}\beta \tag{3-29}$$

Combining Eqs. (3-26) and (3-29),

$$d\bar{U} = (\bar{C}_p - p\bar{V}\alpha)dT + (\bar{L}_p + p\bar{V}\beta)dp \tag{3-30}$$

Equation (3-30) expresses the functional dependence of $\bar{U}$ on T and p in terms of physical properties of the substance all subject to direct experimental measurement.

While $\bar{L}_p$ may be directly measured by means of the operation indicated by Eq. (3-28), the measurement is by no means easy to carry out precisely. We may, however, anticipate a relationship to be derived from the second law of thermodynamics [Eq. (6-8)],

$$\bar{L}_p = -T\bar{V}\alpha \tag{3-31}$$

This enables us to calculate the value of $\bar{L}_p$ from pure equation-of-state data, which are easier to establish at high pressures than direct thermal data; in this relationship, it is necessary that the temperature be represented on the absolute thermodynamic scale; in thermodynamic relationships based purely on the first law of thermodynamics, only temperature differences enter, so that while for the sake of uniformity we have been using T throughout, the ordinary Celsius temperature scale would have been equally satisfactory up to this point. Introducing (3-31) in (3-30),

$$d\bar{U} = (\bar{C}_p - p\bar{V}\alpha)dT + (p\beta - T\alpha)\bar{V}\,dp \tag{3-32}$$

This equation, upon introduction of the required experimental data, enables us to represent $\bar{U}_{T,p}$ at any given temperature T and pressure p, relative to $\bar{U}^\circ_{T_s}$, the internal energy in some standard state defined by temperature T_s and pressure p_0; thus

$$\bar{U}_{T,p} - \bar{U}^\circ_{T_s} = \int_{T_s}^{T} (\bar{C}^\circ_p - p_0\bar{V}\alpha)dT + \int_{p_0}^{p} (p\beta - T\alpha)\bar{V}\,dp \tag{3-33}$$

where the first integral on the right is evaluated at the constant standard pressure p_0, and the second at the constant temperature T; the order of integration is immaterial, according to the first law of thermodynamics, and we could equally well have taken the first integral at the constant pressure p and the second at the constant temperature T_s, using the corresponding thermal and equation-of-state data. As a matter of fact, we seldom make use of Eq. (3-33) in applied chemical thermodynamics, because it is generally much more convenient to represent our thermal data in terms of a modified energy function called the *enthalpy*, whose change is measured directly by the heat absorbed *at constant pressure;* we shall discuss the properties of this function in the section immediately following.

3-3. The Enthalpy as Heat Function at Constant Pressure. Many thermodynamic processes are carried on at the approximately constant pressure of the atmosphere. This is particularly likely to be the case for systems consisting entirely of liquids and solids, where there is usually little advantage to be gained from changing the pressure, unless one is ready to consider really high pressures, in excess of 1000 atm. Even then, one generally finds it more convenient to maintain and measure a uniform pressure rather than a uniform volume, particularly where more than a single homogeneous phase is involved.

For a change of state taking place *at constant pressure,* according to Eq. (3-18),

$$d'Q_p = d(U + pV) + d'W' \tag{3-34}$$

The expression

$$H \equiv U + pV \tag{3-35}$$

defines a useful function of the state of the system (since both U and pV are determined solely by the state), having the fundamental property that for a change of state taking place *at constant pressure,*

$$\begin{aligned} dH &= d'Q_p - d'W' \\ \Delta H &= Q_p \qquad\qquad (W' = 0) \end{aligned} \tag{3-36}$$

More generally, comparing the differential of (3-35) with (3-18),

$$dH = d'Q + V\,dp - d'W' \tag{3-37}$$

The function H, defined by Eq. (3-35), is known as the *enthalpy* of the system; it is of course measured in energy units (*e.g.*, defined calories), just like U.[1] Its change in value for a change of state taking place at a given constant pressure may be established by means of straightforward calorimetry, according to Eq. (3-36); unlike the situation in the measurement of ΔU, it is not necessary for us in the measurement of ΔH to correct the directly measured thermal energy absorbed by the system during the change of state at constant pressure for any volume change that the system may undergo (*i.e.*, for any mechanical work done as a consequence of the volume change). Since the value of H, like the value of U, depends only on the state of the system, heat must necessarily be conserved by

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[1] If p is measured in atm and V in liters, then an expression of the form pV may be expressed in calories through the use of the conversion factor: 1 cal = 0.0412917 liter atm.

the system during changes of state taking place at a uniform fixed pressure, and any heat absorbed during a given change under this condition will be restored as such in the same amount if the system is returned to its original state. Thus, the enthalpy H serves as a *heat function at constant pressure,* in the sense that its value measures the quantity of heat apparently "contained" by the system under that condition; for this reason, H has also been known as the "heat content" and as the "total heat"; these terms have misleading connotations, however, and the neutral synthetic name enthalpy, or merely the symbol H itself without a name, is to be preferred.

For the change of temperature at constant pressure,

$$C_p \equiv \left(\frac{d'Q}{dT}\right)_p = \left(\frac{dH}{dT}\right)_p \qquad (W' = 0) \tag{3-38}$$

where C_p represents the *heat capacity at constant pressure.* The *molal heat capacity at constant pressure,* $\bar{C}_p$, previously defined by Eq. (3-25), thus satisfies the relationship

$$\bar{C}_p = \left(\frac{d\bar{H}}{dT}\right)_p \tag{3-39}$$

and is like $\bar{C}_v$ an intensive property of the substance. A thermodynamic connection between $\bar{C}_p$ and $\bar{C}_v$ at given temperature and pressure follows directly from Eqs. (3-23) and (3-30):

$$\bar{C}_v = \left(\frac{d\bar{U}}{dT}\right)_v = (\bar{C}_p - p\bar{V}\alpha) + (\bar{L}_p + p\bar{V}\beta)\left(\frac{dp}{dT}\right)_v$$

Introducing Eq. (3-6) for $(dp/dT)_v$,

$$\bar{C}_p - \bar{C}_v = -\bar{L}_p\frac{\alpha}{\beta} \tag{3-40}$$

If we substitute for $\bar{L}_p$ the equivalent expression (3-31) based on the second law of thermodynamics, then

$$\bar{C}_p - \bar{C}_v = \frac{T\bar{V}\alpha^2}{\beta} = -T\left(\frac{d\bar{V}}{dT}\right)_p^2\left(\frac{dp}{d\bar{V}}\right)_T \tag{3-41}$$

This relationship permits us to calculate the value of either heat capacity from known values of the other by making use of equation-of-state data; it is particularly useful for the calculation of $\bar{C}_v$ from observed values of $\bar{C}_p$, which is generally the easier to measure; on the other hand, theoretical methods of determining the thermal properties of material substances generally lead directly to the value of $\bar{C}_v$, from which $\bar{C}_p$ may then be calculated by means of Eq. (3-41).

Let us set up the functional dependence of $\bar{H}$ on T and p, for a homogeneous substance of fixed composition,

$$\bar{H} = \bar{H}(T, p) \tag{3-42}$$

$$d\bar{H} = \left(\frac{d\bar{H}}{dT}\right)_p dT + \left(\frac{d\bar{H}}{dp}\right)_T dp \tag{3-43}$$

Because $\bar{H}$ is a function of the state of the system, the value of $d\bar{H}$ for a change in the state of such a substance is completely determined by Eq. (3-43). Now from Eq. (3-37), which represents $d\bar{H}$ in experimental terms according to the first law of thermodynamics,

$$\left(\frac{d\bar{H}}{dp}\right)_T = \left(\frac{d'\bar{Q}}{dp}\right)_T + \bar{V} \qquad (W' = 0)$$

Recalling the definition (3-28),

$$\left(\frac{d\bar{H}}{dp}\right)_T = \bar{L}_p + \bar{V} \tag{3-44}$$

Introducing (3-39) and (3-44) in Eq. (3-43),

$$d\bar{H} = \bar{C}_p\, dT + (\bar{L}_p + \bar{V})dp \tag{3-45}$$

or, substituting for $\bar{L}_p$ its equivalent (3-31) based on the second law of thermodynamics,

$$d\bar{H} = \bar{C}_p\, dT + (1 - \alpha T)\bar{V}\, dp \tag{3-46}$$

This equation enables us to express $\bar{H}_{T,p}$ at any given temperature T and pressure p, relative to $\bar{H}^\circ_{T_s}$, the enthalpy at T_s and p_0, in terms of $\bar{C}^\circ_p$, the heat capacity at the constant standard pressure p_0, and equation-of-state data at the constant temperature T:

$$\bar{H}_{T,p} - \bar{H}^\circ_{T_s} = \int_{T_s}^{T} \bar{C}^\circ_p\, dT + \int_{p_0}^{p} (1 - \alpha T)\bar{V}\, dp \tag{3-47}$$

The value of the first integral on the right of Eq. (3-47) is of course equal to the total quantity of heat absorbed by the substance as it is heated at the constant pressure p_0 from temperature T_s to temperature T (assuming that it undergoes no phase transition in this interval), and could be established directly by straightforward calorimetry; it is customary however to translate the experimental heat measurements in terms of $\bar{C}^\circ_p$ as a function of T, rather than of $\bar{H}^\circ_T$ itself; the data are then in a form independent of the particular reference temperature T_s from which $\Delta\bar{H}$ may be measured, and, furthermore, $\bar{C}^\circ_p$ varies with T much less rapidly than $\bar{H}^\circ_T$ itself.

The absolute value of the enthalpy of a given thermodynamic system in any one state has no assigned meaning, any more than has the absolute value of the internal energy. However, it is possible for us to assign on the basis of the thermochemical principles to be discussed in Chap. 4 relative values $\bar{H}^\circ_{T_s}$ to different chemical substances at the same standard temperature and pressure, representing their standard molal enthalpies with respect to the chemical elements. Equation (3-47) then enables us to extend these so-called *enthalpies of formation* to other temperatures and pressures. Indeed, for those problems in which the composition of the substance under investigation undergoes no change, as in the performance of a steam engine, the relative value of $\bar{H}_{T,p}$ with respect to the standard state value $\bar{H}^\circ_{T_s}$ is all that is required, the value of $\bar{H}^\circ_{T_s}$ itself being left entirely arbitrary. The best choice of a standard reference temperature in principle would be absolute zero on the thermodynamic scale; we shall reserve the symbols $\bar{U}^\circ_0$ and $\bar{H}^\circ_0$ to designate the molal internal energy and enthalpy in such a standard state; however, this choice is not feasible in general because of the lack of sufficient heat-capacity data at low temperatures. The practical standard reference temperature favored at present is 25°C, in line with the recommendations of G. N. Lewis and his associates,[1] but much of the older thermochemical data were obtained with reference to somewhat lower standard temperatures;[2] fortunately, the correction to 25°C is small, and can be made through Eq. (3-47) from knowledge of the value of $\bar{C}^\circ_p$. The standard reference pressure p_0 for solids and liquids is taken to be 1 atm; in the case of gases, because of their uniform behavior in the low-pressure range, as represented by the ideal-gas law, enthalpy values are taken with reference to a hypothetical ideal-gas state at 1 atm at the given temperature, in which the gas would have the same enthalpy as in the limit at zero pressure; that is,

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[1] G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York, 1923. This choice has been adopted by the National Bureau of Standards in its compilations, Selected Values of Properties of Hydrocarbons, *Natl. Bur. Standards Circ.* C461 (1947), and "Selected Values of Chemical Thermodynamic Properties," which has been distributed by the National Bureau of Standards in loose-leaf form quarterly since Dec. 31, 1947.

[2] For this reason, 20°C was adopted in the "International Critical Tables," Vol. V, McGraw-Hill Book Company, Inc., New York, 1927, where incidentally the data are all expressed in terms of international joules; 18°C was adopted by F. R. Bichowski and F. D. Rossini for their compilation, "Thermochemistry of Chemical Substances," Reinhold Publishing Corporation, New York, 1936, following the lead of the great pioneers in the field of thermochemical investigation, Julius Thomsen ("Thermochemische Untersuchungen," J. A. Barth, Leipzig, 1882–1886; "Thermochemistry," English translation by K. A. Burke; Longmans, Green & Co., Inc., New York, 1908) and M. Berthelot ("Thermochimie; données et lois numériques," Gauthier-Villars & Cie., Paris, 1897).

$H^\circ_{T_s}$ is defined by the relationship: $\lim\limits_{p\to 0} \bar{H}_{T_s,p} = \bar{H}^\circ_{T_s}$. The actual values of $\bar{H}_{T_s,p}$ for the gas at other pressures p (including 1 atm as a special case) are related to $\bar{H}^\circ_{T_s}$ through Eq. (3-47), with the limits of integration in the second integral taken to be from 0 to p (note that for an ideal gas the integrand would vanish, since α would equal $1/T$). The effect of pressure on the enthalpy is slight for pressure changes of less than several atmospheres magnitude; for ordinary variations in the barometric pressure, it is altogether negligible.

Phase transitions of a chemical substance of fixed composition ordinarily take place at a constant pressure, determined by the temperature; the so-called *normal* transition temperature corresponds by definition to a fixed pressure of 1 atm. The latent heat of the transition thus measures directly the difference between the enthalpies of the higher temperature and the lower temperature forms at the given equilibrium temperature and pressure. For example,

$$H_2O(c, 0°C, 1\ atm) = H_2O(l, 0°C, 1\ atm); \qquad \Delta H = \bar{L}_{cl} = 1436.3\ cal/mole$$

$$H_2O(l, 100°C, 1\ atm) = H_2O(g, 100°C, 1\ atm); \qquad \Delta H = \bar{L}_{lg} = 9717.5\ cal/mole$$

The symbol $\bar{L}_{cl}$ designates the molal latent heat of fusion (heat absorbed during the transition: crystal → liquid), and the symbol $\bar{L}_{lg}$ the molal latent heat of vaporization (heat absorbed during the transition: liquid → gas). Thus, by applying Eq. (3-47) from the standard state conditions to the transition point, and then adding the enthalpy of the phase transition so measured by the latent heat, one can relate the enthalpies of different phases of the same substance to a common reference state, that, for example, of the phase stable at the reference temperature T_s and 1 atm. The latent heat itself varies with the equilibrium temperature and pressure, which are of course correlated. The molal enthalpy of either phase varies with temperature and pressure according to Eq. (3-46); therefore the difference $\Delta\bar{H}$ between the molal enthalpies of the higher temperature and the lower temperature forms, which equals the molal latent heat of the transition, varies with the equilibrium temperature and pressure according to the equation

$$d\Delta\bar{H} = \Delta\bar{C}_p\, dT + \Delta[(1 - \alpha T)\bar{V}]dp$$

where $\Delta\bar{C}_p$ represents the corresponding difference between the molal heat capacities at constant pressure, and $\Delta[(1 - \alpha T)\bar{V}]$ the corresponding difference between the values of $(1 - \alpha T)\bar{V}$ at constant temperature. Thus, let $\Delta\bar{H}_{T^\circ}$ represent the latent heat at the normal transition temperature, T° at 1 atm; then

$$\Delta\bar{H}_{T,p} = \Delta\bar{H}_{T^\circ} + \int_{T^\circ}^{T} \Delta\bar{C}_p\, dT + \int_{1\text{ atm}}^{p} \Delta[(1 - \alpha T)\bar{V}]dp \qquad (3\text{-}48)$$

where $\Delta\bar{C}_p$ is taken at constant pressure of 1 atm and the second integral is evaluated at the constant temperature T, p representing the equilibrium pressure at that temperature (*e.g.*, the vapor pressure in the case of solid-vapor or liquid-vapor equilibrium). For pressures below 1 atm (*i.e.*, for temperatures below the normal boiling point, in the case of liquid-vapor equilibrium), the pressure integral is practically within experimental error, but for pressures well above atmospheric, this is not necessarily true; one then needs extensive equation-of-state data in order to evaluate this integral. Equation (3-48) is readily generalized for transitions that do not ordinarily exist at 1 atm (such as the vaporization of liquid CO_2); let $\Delta\bar{H}_{T^\circ}$ in that equation represent the latent heat of the transformation at some known equilibrium temperature T° and associated pressure p°, and let $\Delta\bar{C}_p$ stand for the difference between the molal heat capacities of the two phases at the constant pressure p°; then the equation is correct, provided that the range of integration of the second integral extends from p° to p, instead of from 1 atm to p. In few cases, however, does one have sufficient experimental data to apply Eq. (3-48) accurately at pressures much in excess of atmospheric.

3-4. Heat Capacities of Chemical Substances. The effects of pressure on the internal energy and enthalpy of a chemical substance, according to Eqs. (3-32) and (3-46), may be computed purely from equation-of-state data, provided one makes implied use of the second law of thermodynamics through the relation (3-31). The effects of temperature, however, are represented in terms of the thermal property $\bar{C}_p$, whose value cannot be inferred from other nonthermal properties by purely thermodynamic means. This section is devoted to methods of measuring heat capacities, and to certain empirical rules for estimating their values when direct experimental information is wanting.

The relationship between $\bar{C}_p$ and $\bar{C}_v$ has already been derived in Eq. (3-41) in terms of equation-of-state data; therefore the experimental establishment of either of these heat capacities at given temperature and pressure serves, together with nonthermal data for the effects of temperature and pressure on the volume, to determine the other; the direct thermal measurement of $\bar{C}_p$ at the practically constant pressure of the atmosphere is generally far more convenient than that of $\bar{C}_v$. Furthermore, the effect of pressure itself on the value of $\bar{C}_p$ at a given temperature may be readily established in terms of equation-of-state data through the application to Eq. (3-46) of Euler's criterion for $d\bar{H}$ to be a complete or perfect differential in terms of the two independent variables T and p (see Appendix 1):

$$\begin{aligned}\left(\frac{d\bar{C}_p}{dp}\right)_T &= \left[\frac{d}{dT}(1-\alpha T)\bar{V}\right]_p \\ &= -T\bar{V}\left[\alpha^2 + \left(\frac{d\alpha}{dT}\right)_p\right] \\ &= -T\left(\frac{d^2\bar{V}}{dT^2}\right)_p \qquad (3\text{-}49)\end{aligned}$$

Therefore all the purely thermal data one must measure in order to describe the thermal properties of a given homogeneous chemical substance are summarized in an expression for the value of $\bar{C}_p$ at any one fixed pressure, such as 1 atm, as a function of the temperature. If to this information one adds the latent heats of phase transitions, as well as the $\bar{C}_p$ values for the other phases, then one has characterized the thermal behavior of the substance in all its phases. We shall use the symbol $\bar{C}_p^\circ$ for pure liquids and solids to denote the molal heat capacity at constant pressure of 1 atm; we shall use the same symbol for gases to denote $\lim\limits_{p\to 0} \bar{C}_p$, which is equivalent to the actual $\bar{C}_p$ at 1 atm, corrected for deviation from the ideal-gas law by means of Eq. (3-49) integrated from 1 atm to 0.

For solids and liquids at low temperatures up to room temperature, the most convenient method of measuring $\bar{C}_p$ is by means of electrical heating. This method was first applied to solids by W. Gaede in 1902, and was perfected with particular application to low-temperature measurements by Walther Nernst and his associates beginning about 1910. In Nernst's vacuum calorimeter, the substance if it is itself a sufficiently good heat conductor, such as a metal, serves as its own calorimeter; it is shaped to the form of a hollowed block having a plug of the same substance fitted into the hole; a heating coil of platinum wire is wound on the plug, insulated by means of a paraffin coating, and the plug is then inserted into the block. If the substance is either a liquid or a poor heat conductor, it is placed within a hermetically sealed cup of silver or copper, around the outside of which the heating coil is wound; the calorimeter is protected from radiation losses by means of a layer of silver foil covering the heating coil; for measurements down to liquid air temperatures, the cup remains filled with air, but for measurements at lower temperatures, it must be previously filled with hydrogen or helium; the gas is needed in order to equalize the temperature rapidly throughout the vessel by means of its thermal conductivity and convection. The entire calorimeter, whether it consists of the substance itself or of the metal cup and contents, is suspended within a flask having an exit tube through which it may be evacuated. It is brought to the desired initial temperature by immersion of the flask containing the calorimeter and filled initially with air, hydrogen, or helium, depending on the temperature range to be investigated, in a suitable low-temperature bath: ice, liquid air, liquid hydrogen, or liquid helium. It is then insulated from its surroundings by evacuation of the flask to a high vacuum. Electrical energy is measured into the heating coil in successive small amounts, each sufficient to raise the temperature by about 1°C; after each energy input, the resistance of the coil, which may serve as the thermometer (though some investigators prefer to use an independent thermometric resistance coil, separate from the heating coil), is read at short intervals until it becomes steady, showing that thermal equilibrium at the new higher temperature has been established; the ratio of the quantity of energy put in [measured for example by the coil resistance and the potential difference applied to the terminals in accordance with Eq. (2-19)], corrected for losses by the leads and for thermal radiation, to the rise in temperature gives the heat capacity at the mean temperature involved. For poor thermal conductors, the heat capacity of the empty calorimeter cup must be determined by a separate blank run, and the heat capacity of the sample calculated by difference at each mean temperature. F. Lange[1] eliminated the radiation correction by suspending the calorimeter within a brass cylinder inside the evacuated flask, maintained by means of independent electrical heating always at the same temperature as the calorimeter within; equality of temperature was judged by means of a differential thermocouple, with one junction in the calorimeter and the other in the jacket, a method that lends itself conveniently to automatic control over the heating of the jacket; the calorimeter then operates under essentially adiabatic conditions. Detailed descriptions of typical modern adiabatic calorimeters for the measurement of heat capacities at low temperatures have been given by W. F. Giauque and R. Wiebe(University of California), J. G. Aston and C. W. Ziemer (Pennsylvania State College), and H. L. Johnston and E. C. Kerr (Ohio State University), while H. M. Huffman has recently described the entire setup for the undertaking of low-temperature calorimetry, as conducted at the Bartlesville Station of the U.S. Bureau of Mines.[2]

The same type of calorimeter is used to determine the latent heat of fusion, or the latent heat of transformation from one solid phase to another, at low temperatures. The sample is heated electrically from a

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[1] F. Lange, *Z. physik. Chem.*, **110,** 343–362 (1924).

[2] W. F. Giauque and R. Wiebe, *J. Am. Chem. Soc.*, **50,** 106–110 (1928); J. G. Aston and C. W. Ziemer, *ibid.*, **68,** 1405–1406 (1946); H. L. Johnston and E. C. Kerr, *ibid.*, **72,** 4733–4738 (1950); H. M. Huffman, *Chem. Rev.*, **40,** 1–14 (1947).

temperature somewhat below the transition point to a temperature somewhat above it; by plotting the quantity of energy absorbed against the temperature attained, and extrapolating from both directions to the transition point itself, where of course a discontinuity exists, one can determine the quantity of energy absorbed during the change of phase at the transition temperature.

High-temperature heat capacities of solids and liquids are most conveniently measured by the method of mixtures; electrical heating offers theoretical advantages, but these are more than offset by the increasing difficulty at higher temperatures of guarding against radiation and conductive losses. Water itself may be used as the calorimetric medium, but in order to increase the range of measurement and to eliminate the error resulting from the evaporation of water, a copper or aluminum block is commonly used instead. The sample is preheated to the desired initial temperature in a furnace tube mounted above the calorimeter block, in which a cavity has been drilled to receive the sample; the sample is then dropped into the cavity, and the rise in temperature read by means of a group of thermocouples distributed at various points in the block; the calorimeter is standardized by means of electrical heating.[1] This method gives actually the mean heat capacity of the sample between its initial temperature t and its final temperature t_0 (that of the block). The latter temperature may be kept uniform for a series of measurements on the same substance by adjustment of the mass of the sample in relation to the mass of the block as the sample's initial temperature t is varied; if from such a series of measurements one then expresses the mean specific heat, Γ, as a function of t in the empirical form

$$\Gamma = a + b(t - t_0) + c(t - t_0)^2 + \cdots$$

where $(t - t_0)\Gamma$ represents the observed total quantity of heat released per unit mass of sample in cooling from t to t_0, then the instantaneous specific heat c_p at the temperature t is given in terms of the empirical constants $a, b, c, \ldots$ by the formula

$$c_p = \frac{d}{dt}[(t - t_0)\Gamma] = a + 2b(t - t_0) + 3c(t - t_0)^2 + \cdots$$

One could in principle express Q_p/M directly as an empirical function of $(t - t_0)$, and then differentiate with respect to t in order to obtain c_p, but

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[1] For detailed description of this type of calorimeter, see W. P. White, "The Modern Calorimeter," Reinhold Publishing Corporation, New York, 1928. An ice calorimeter for similar purposes has been described by D. C. Ginnings and R. J. Corruccini, *J. Research Natl. Bur. Standards*, **38**, 583–591 (1947); the quantity of ice melted by the sample is measured by the weight of mercury taken into the calorimeter to make up for the volume decrease, the calorimeter being standardized by electrical heating.

in practice the power series for Γ converges more rapidly and is therefore more convenient for computation; the molal heat capacity $\bar{C}_p$ is of course obtained from c_p through multiplication by the substance's formula weight

$$\bar{C}_p = \bar{M}c_p \tag{3-50}$$

The heat capacities of gases are difficult to measure directly because of their low densities at ordinary pressures and the correspondingly large volumes required in order that the quantities of heat involved may be measured with adequate precision. The method of mixtures was used by H. V. Regnault in 1862 to measure $\bar{C}_p$; he circulated the gas through a copper-coil heat interchanger surrounded by water, which served as the calorimetric medium; the gas was preheated to a known temperature, and the mass flowing through the calorimeter was determined by measurement of its volume as it emerged at the temperature of the calorimeter. Holborn and Henning used a similar method, in which the preheated gas was passed through silver tubes packed with silver filings to improve thermal contact with the calorimetric medium, which consisted of paraffin oil; in this way, they succeeded in measuring the heat capacities of gases up to 1400°C.[1] Continuous flow methods have also been used, in which the gas flows at a known uniform rate over an electrically heated wire and the rise in its temperature is measured. The value of $\bar{C}_v$ for hydrogen at low temperatures was measured directly by A. Eucken in a special investigation,[2] using essentially a Nernst vacuum calorimeter consisting of a thin-walled steel vessel containing the gas, with a heating coil wrapped around it; the method is feasible, however, only at low temperatures, where the heat capacity of the metal container has fallen off so that it is not much larger than that of the gas.

Several indirect methods for measuring the heat capacity are based on direct measurement of the ratio

$$\gamma \equiv \frac{\bar{C}_p}{\bar{C}_v} \tag{3-51}$$

This quantity may be measured directly from the temperature change during adiabatic expansion, according to the theory discussed in Sec. 3-5;[3] it may be obtained also from measurements of sound velocity in the gas, which satisfies the well-known Newton relationship

$$u = \sqrt{\gamma \left(\frac{dp}{d\rho}\right)_T} \tag{3-52}$$

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[1] L. Holborn and F. Henning, *Ann. Physik*, **23**, 809–845 (1907).

[2] A. Eucken, *Sitzber. preuss. Akad. Wiss., Physik.-Math. Klasse*, pp. 141–151 (1912).

[3] See J. R. Partington, *Physik Z.*, **14**, 969–973 (1913); *Proc. Roy. Soc. (London)*, (A)**100**, 27–49 (1921).

where p represents the pressure and ρ the density; for an ideal gas, this expression reduces to $u = \sqrt{\frac{RT}{\bar{M}}\gamma}$. By combining the experimentally established value of $\bar{C}_p/\bar{C}_v$ with the value of $\bar{C}_p - \bar{C}_v$ from equation-of-state data according to Eq. (3-41), which for an ideal gas reduces to

$$\bar{C}_p^\circ - \bar{C}_v^\circ = R \qquad \text{(ideal gas)} \qquad (3\text{-}53)$$

one may calculate the value of $\bar{C}_p$.

The purely thermodynamic methods of measuring the heat capacities of gases have been supplemented, however, and in most cases superseded by methods based on statistical molecular theory, the required molecular properties being derived from analyses of their spectra; the spectra give us essentially the various possible energy levels of the given kind of molecule, and the statistical molecular theory, to which we shall give our attention in Chap. 10, provides a general law for the distribution of molecules among energy states. By the introduction of certain generalizations drawn from quantum mechanics, one may apply the statistical method approximately even in the absence of detailed knowledge of the spectrum. It will be useful for us to review briefly at this point some of the generalizations that result from the statistical molecular theory, bearing in mind that such information is essentially extrathermodynamic in origin.

From straightforward kinetic theory, which treats the internal energy of the gas as made up purely of mechanical energy, kinetic and potential, associated with molecular motion, one may show that for an ideal monatomic gas, whose energy at temperatures below the range of electronic excitation must consist entirely of translational kinetic energy, $\bar{C}_v^\circ = \frac{3}{2}R = 2.981$ cal/mole deg. According to Eq. (3-53), then, $\bar{C}_p^\circ = \frac{5}{2}R = 4.968$ cal/mole deg, and $\gamma = 1.667$. These values represent the limiting values for real monatomic gases as $p \rightarrow 0$, the correction to 1 atm pressure being made in accordance with Eq. (3-49); this correction is, however, practically negligible for most of the real monatomic gases, particularly at temperatures above their critical points. Table 3-1 includes the experimentally determined values of γ for several representative monatomic gases, and one sees that the theoretical values are in excellent agreement with the experimental values; the theoretical values of $\bar{C}_p^\circ$ and $\bar{C}_v^\circ$ for these gases are in fact generally more reliable than the experimental, in view of the errors inherent in the experimental methods.

Diatomic gases have, in addition to translational molecular kinetic energy, rotational kinetic energy in two dimensions about the center of gravity (there is none in the third dimension, about the line of centers, because of the comparatively small moment of inertia about this axis), which contributes at ordinary temperatures a term R to the molal heat capacities; there will be, furthermore, a contribution corresponding to vibrational energy, which at sufficiently high temperatures also approaches the value R. The temperature region at which the contribution of vibrational energy to the heat capacity begins to be significant depends in a complex way on the fundamental frequency of vibration, which is a measure of the restoring force between the atoms as they are displaced from their relative equilibrium position; the energy difference between successive vibrational-energy states is proportional to this fundamental vibration frequency (which appears in the infrared absorption spectrum, unless the two atoms happen to be identical), so that if the frequency is high (corresponding to a relatively strong restoring force), then it takes a comparatively high temperature to get appreciable numbers of the molecules into excited vibrational-energy states. For many of the diatomic gases, particularly those involving the smaller atoms, such as N_2, O_2, and CO, the vibrational heat-capacity term is negligible at ordinary room temperature; for I_2 vapor, on the other hand, the vibrational-energy levels are sufficiently closely spaced so that many different states are occupied at ordinary temperatures, giving rise to a practically continuous distribution of molecules with respect to vibrational energy and a contribution to the molal heat capacity correspondingly close to the limiting value R. Thus, we shall expect to find that for diatomic gases, $\bar{C}_p^\circ$ will fall within the range $\frac{7}{2}R$ to $\frac{9}{2}R$, or 6.96 to 8.94 cal/mole deg, with its value increasing through this interval with increasing temperature; molecules consisting of the larger atoms having smaller force constants (ratios of restoring forces to displacements from equilibrium positions) and comparatively low fundamental vibration frequencies will tend to attain the upper limit at lower temperatures than molecules of the smaller atoms having larger force constants and comparatively high fundamental vibration frequencies. The value of γ will fall in the corresponding range, 1.40 to 1.29. Experimental results for several representative diatomic gases are included in Table 3-1; Fig. 3-1 shows how $\bar{C}_p^\circ$ for oxygen gas varies with temperature over the range 200 to 1500°K.

One will note that the change of $\bar{C}_p^\circ$ with temperature for a diatomic gas is entirely the result of the quantization of the vibrational-energy states, which when the average molecular total energy is sufficiently low (as at low temperatures) restricts the accessibility of the higher vibrational-energy states; if the vibrational energy could increase by continuous degrees, as the translational kinetic energy apparently does at ordinary temperatures, then we should expect an equalization on the average of the molecule's energy among all its degrees of freedom; *i.e.*, the mean vibrational kinetic energy, which represents half the mean total vibra-

TABLE 3-1. HEAT CAPACITIES OF GASES

Gas	$\bar{C}_p^\circ$ at 25°C, cal/mole deg	γ Ct t and 1 atm	
		t, °C	γ
A	4.968*	15	1.65†
		−180	1.69†
He	4.968*	18	1.658†
		−183	1.662‡
		−258	1.661‡
Ne	4.968*	0	1.666‡
		−183	1.670‡
		−245	1.667‡
Kr	4.968*	19	1.68
Xe	4.968*	19	1.66
Hg	....	360	1.67
K	....	680–1000	1.69
Na	....	750– 920	1.68
H_2	6.892	0	1.410
		−256	1.661‡
HCl	6.95	100	1.40
HI	6.95	100	1.40
N_2	6.960	0	1.402
CO	6.965	0	1.402
O_2	7.017	0	1.402
NO	7.137	15	1.400
F_2	7.52		
Cl_2	8.06	16	1.35
Br_2	....	20– 350	1.32
ICl	8.46	100	1.31
I_2	8.78	185	1.30
H_2O	8.025	100	1.324
H_2S	8.12	18	1.30
CO_2	8.874	0	1.310
N_2O	9.251	100	1.28
SO_2	9.51	15	1.29
NH_3	8.523	15	1.31
C_2H_2	10.499	15	1.26
CH_4	8.536	0	1.307
CH_3Cl	9.75	16 (0.8 atm)	1.28
CH_2Cl_2	12.28	18 (0.2 atm)	1.22
$CHCl_3$	15.73	100	1.15
CCl_4	19.96	20 (0.1 atm)	1.13
SiH_4	10.24		
SiF_4	18.2		
$SiCl_4$	21.7	14	1.13
C_2H_4	10.41	100	1.18
C_2H_6	12.585	100	1.19
C_3H_8	17.57§	16 (0.5 atm)	1.13

For footnotes, see page 95.

tional energy (the other half being potential energy), would equal the mean translational kinetic energy $\frac{1}{2}RT$ (per mole) in any one of the three spatial dimensions, thus leading to R as the "classical" contribution of any single mode of vibration to the molal heat capacity. Because the vibrational-energy levels are discrete, however, a molecule must acquire a certain minimum increment of energy in order to get out of the lowest into the next from the lowest vibrational state, and at sufficiently low temperatures, few molecules have a chance of acquiring that much extra energy by means of the collisions that distribute the energy of their thermal motion; most of them must therefore stay in the lowest vibrational state until such a temperature has been reached that an appreciable frac-

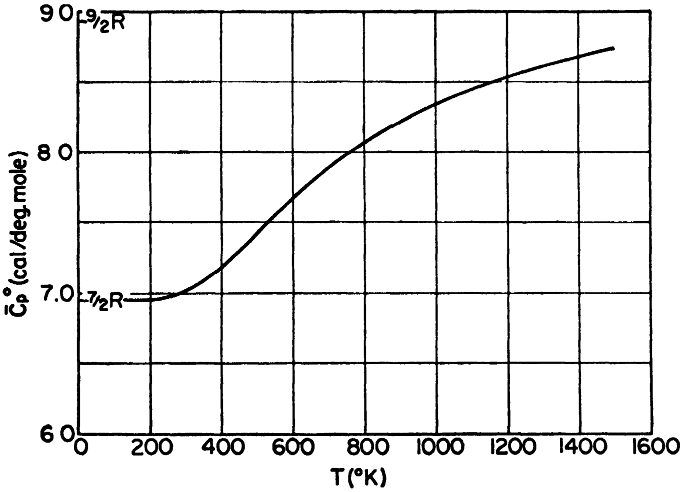

FIG. 3-1. Heat-capacity curve, $\bar{C}_p^\circ$ vs. T, for $O_2(g)$. (*Data from "Selected Values of Chemical Thermodynamic Properties," Series III, National Bureau of Standards, Washington, D.C., March* 31, 1949.)

NOTE: $\bar{C}_p^\circ$ values are taken from "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D.C., 1948, except values for C_2H_2, C_2H_4, C_2H_6, and C_3H_8 which are taken from Selected Values of Properties of Hydrocarbons, *Natl. Bur. Standards Circ.* C461 (1947); these values have been derived by critical evaluation of both calorimetric and spectroscopic sources, and are in general independent of the γ values given in the table. The γ values are taken from the compilation by A. Leduc, in the "International Critical Tables," Vol. V pp. 79–84, McGraw-Hill Book Company, Inc., New York, 1929, except where otherwise noted; most of these values were obtained directly from sound velocity measurements.

[*] Nominal value = $\frac{5}{2}R$; direct calorimetric measurements have been made on argon and helium, but for all the other monatomic gases at temperatures up to several thousand degrees, the theoretical value, $\frac{5}{2}R$, is believed to be precise within experimental error, as shown by the values of the more easily measurable γ. Mercury, potassium, and sodium vapors contain small proportions of diatomic molecules, decreasing with increasing temperature and decreasing pressure.

[†] Limiting value for $p \to 0$, obtained by Scheel and Heuse, as reported by J. R. Partington and W. G. Shilling, "The Specific Heats of Gases," D. Van Nostrand Company, Inc., New York, 1924.

[‡] Limiting value for $p \to 0$, obtained by W. H. Keesom *et al.*, as reported in Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIIc, p. 2323, 1936.

[§] Values for higher gaseous homologues of the alkane series at 25°C increase by approximately 5.760 cal/mole deg per CH_2 group added; the same increment is found in other homologous series, beyond the first few members; see *Natl. Bur. Standards Circ.* C461.

tion of molecules may have sufficient total energy to get into the second and higher vibrational-energy states. Now, the rotational energy is also quantized, but the energy differences between the lower rotational states are generally much smaller than the differences between vibrational states. If, however, one can cool the diatomic gas to sufficiently low temperatures, then the effect of quantization of the rotational energy may make itself felt in a decrease of the heat capacity. This effect is shown strikingly in the case of hydrogen (Fig. 3-2), as discovered by A. Eucken in 1912; here, even at room temperature, $\bar{C}_p^\circ$ is slightly below the lower limit $\frac{7}{2}R$ characteristic of other diatomic gases at temperatures below the range of significant vibrational excitation; but by 60°K, $\bar{C}_p^\circ$ for this gas has fallen to the value of $\frac{5}{2}R$ shown by monatomic gases, and we have the remarkable result that below this temperature, H_2 molecules behave physically like the molecules of a monatomic gas; in other words, the rotational energy in this range is "frozen," in the sense that few of the molecules can acquire sufficient total energy to get into the higher rotational states. One of the noteworthy achievements of quantum mechanics has been the quantitative solution of this problem. Certain diatomic gases whose atoms are identical, including N_2, $Cl^{35}Cl^{35}$, D_2, and particularly H_2 itself, show a further complexity in the rotational contribution to the heat capacity at low temperatures, because of nuclear spin isomerism. Hydro-

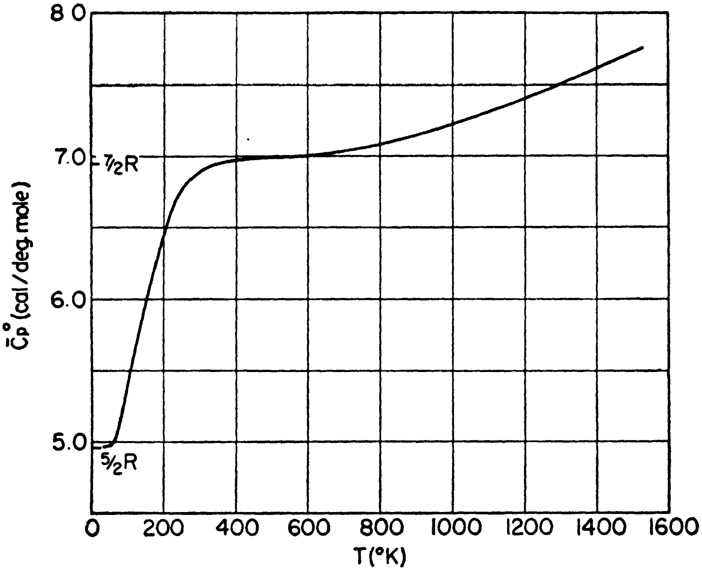

FIG. 3-2. Heat-capacity curve, $\bar{C}_p^\circ$ vs. T, for $H_2(g)$. (*Data from 298°K up from "Selected Values of Chemical Thermodynamic Properties," Series III, National Bureau of Standards, Washington, D.C., March 31, 1949; data below 298°K from work of A. Eucken as reported in "International Critical Tables," Vol. V, p. 82, McGraw-Hill Book Company, Inc., New York,* 1929.)

gen, for example, consists of two isomers, parahydrogen, in which the spins of the two nuclei are paired in opposite directions, and orthohydrogen, in which the spins are in the same direction; these two forms can occupy according to general quantum theory only the even or only the odd rotational-energy levels, respectively; ordinary hydrogen consists of an equilibrium mixture (at ordinary temperatures) of three orthohydrogen molecules to one parahydrogen molecule, but at temperatures of order 60°K, where the molecules tend to get into the lowest or zeroth rotational state, which is an even state, orthohydrogen becomes metastable with respect to transformation into parahydrogen, a change that can be accelerated by adsorption of the gas on activated charcoal; in this way, pure parahydrogen has been prepared, and its contribution to the heat capacity of ordinary hydrogen (the 3:1 orthohydrogen-parahydrogen mixture) established. The entire phenomenon has received a satisfactory theoretical treatment in terms of quantum mechanics.[1]

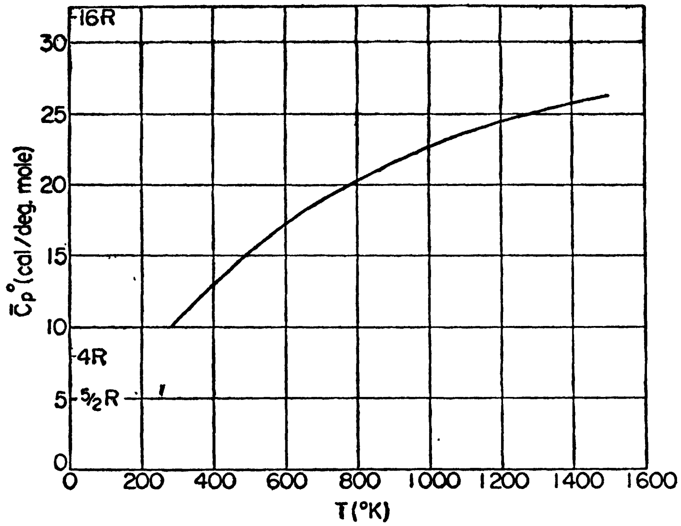

FIG. 3-3. Heat-capacity curve, $\bar{C}_p^\circ$ vs. T, for ethylene $C_2H_4(g)$. (*Data from "Selected Values of Properties of Hydrocarbons," Natl. Bur. Standards Circ.* C461, 1947.)

The molal heat capacities of polyatomic gases are in general larger and increase more rapidly with temperature than the heat capacities of diatomic gases (see Table 3-1 and Fig. 3-3). This is the result of additional fundamental modes of vibration; for nonlinear molecules, there are $(3N - 6)$ such modes of vibration, each potentially capable when fully excited by sufficiently high temperature of contributing R to the heat

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[1] For further details of this remarkable and interesting subject, the reader is referred to A. Farkas, "Orthohydrogen, Parahydrogen and Heavy Hydrogen," Cambridge University Press, New York, 1935.

capacity, where N is the number of atoms in the molecule; the rotational energy also contributes $\frac{3}{2}R$ instead of R to the molal heat capacity of nonlinear molecules at ordinary and high temperatures. In general, the more complex the molecule is, the more likely it is that there will be certain vibrations relatively easily excited; energy may thus be absorbed in increasing the mean molecular vibrational energy in several dimensions, whereas there is vibration possible in but a single dimension in the case of diatomic molecules. From a detailed knowledge of the infrared and Raman spectra, one can establish the rotational-vibrational energy levels, and by the application of the molecular statistical methods to be described in Chap. 10 one can determine the relative molecular population of each level at a given temperature; this information can be used to determine the heat capacity with high precision, though the computation becomes laborious for the more complex types of molecules. Most of the currently accepted heat capacities of gases have been obtained by this means.

The molal heat capacities of crystalline solids show certain regularities first successfully accounted for by a theory proposed by P. Debye.[1] L. Boltzmann had previously attacked this problem by assuming that in a monatomic crystalline solid each atom executed simple harmonic oscillations about its equilibrium position in the crystal lattice, with kinetic and potential energies on the average equal; by supposing that the kinetic energy of this motion had the same mean value as the three-dimensional kinetic energy of translation of gas molecules at the same temperature, $\frac{3}{2}RT$ per mole, he was led to a value of $3RT$ for the internal energy, and hence to $\bar{C}_v^\circ = 3R$. This value, 5.96 cal/mole deg, was in remarkably good agreement with the empirical rule discovered by P. L. Dulong and A. T. Petit in 1819, but like that rule, gave no clue to the well-known exceptions to the rule, such as the heat capacities of carbon and silicon. Further experimental work on the heat capacities of the metallic elements at low temperatures showed that the exceptions to the rule of Dulong and Petit were themselves part of a general pattern, for all the metals show a falling off of the heat capacity as the temperature is lowered sufficiently, diamond and silicon merely showing this effect at much higher temperatures than silver or lead. Albert Einstein in 1907 improved greatly on Boltzmann's treatment by assuming that the vibrational motion of the atoms in the crystal had a common fundamental frequency, but that the energy of the motion was quantized;[2] he adapted to this purpose the formula for the energy levels of a harmonic oscillator that had been found necessary by M. Planck in order to develop a correct theory of thermal radiation; this formula [see Eq. (10-113)] states essentially that the energy

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[1] P. Debye, *Ann. Physik*, **39**, 789–839 (1912).

[2] A. Einstein, *Ann. Physik*, **22**, 180–190 (1907).

of such an oscillator can increase only by integral multiples of the fundamental vibration frequency, which is a fixed property of the particular kind of oscillating system. Einstein was thus able to account for the decrease in $\bar{C}_v^\circ$ with falling temperature in terms of the same principle we now use to account for the change with temperature of the vibrational contribution to the heat capacities of diatomic and polyatomic gases; in fact, the one-dimensional form of Einstein's equation is actually used for this latter purpose, as we shall see in Chap. 10 [Eq. (10-118*b*)], but his equation for the heat capacities of solids left much to be desired in the way of quantitative agreement with experiment, mainly because the atoms of a crystalline solid are not free to oscillate independently of each other.

In Debye's treatment, the internal energy is supposed to consist of quantized energies of vibrations of the crystal as a whole, taken to be a continuous elastic solid; there are then $3N$ (or more precisely, $3N - 6$) fundamental frequencies of vibration, where N represents the number of oscillating units, *i.e.*, the number of atoms in the monatomic crystalline solid body; the number of these fundamental frequencies falling within a given frequency range can be deduced from straightforward mechanical theory of an isotropic elastic medium.[1] The formula that Debye finally obtained by this treatment is

$$\bar{C}_v^\circ = D\left(\frac{\theta}{T}\right) = 9R\left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} \frac{x^4 e^x}{(e^x - 1)^2}\,dx \tag{3-54}$$

where θ is a constant for the given monatomic crystalline solid, called its *characteristic temperature*, whose value may be computed entirely from the elastic constants of the crystal (Poisson's ratio, and the coefficient of compressibility, together with the density), or may be obtained empirically from the observed $\bar{C}_v^\circ$ vs. T relationship (only a single measurement of $\bar{C}_v^\circ$ at some one temperature, preferably near the middle of the range over which it is changing most rapidly with T, is theoretically necessary for the reconstruction of the entire $\bar{C}_v^\circ$ vs. T relation). The definite integral appearing in Eq. (3-54) cannot be represented in terms of familiar analytical functions, but the values of the entire expression define a universal function of θ/T known as the Debye function, $D(\theta/T)$, and have been tabulated through numerical integration (see Appendix 4); the function $(\theta/T)\int_0^{T/\theta} D(\theta/T)d(T/\theta)$, which represents the value of $(\bar{U}_T^\circ - \bar{U}_0^\circ)/T$, has also been tabulated for various numerical values of T/θ, as have the values of certain other thermodynamic functions deter-

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[1] An excellent discussion of Debye's theory is given by J. K. Roberts, "Heat and Thermodynamics," 3d ed., Chap. XXI, Blackie & Son, Ltd., Glasgow, 1940.

mined by $\bar{C}_v^\circ$ by means of the second law of thermodynamics.[1] In Fig. 3-4, the Debye function $D(\theta/T)$ has been plotted against T/θ, and on the graph values of $\bar{C}_v^\circ$ have been plotted for several monatomic regular crystalline solids, with appropriate values of θ assigned; one sees that the agreement with theory in these cases is very good.

Lewis and Gibson[2] pointed out that the Debye equation is a special form of the more general concept that $\bar{C}_v^\circ$ is a universal function of the temperature on a scale T/θ characteristic of each monatomic crystalline substance. Thus, if one plots $\bar{C}_v^\circ$ against log T, one should obtain a family of similar curves for different monatomic crystalline solids, which can be made to coincide by horizontal displacements measuring the relative magnitudes of log θ. The empirical fact that this is so is quite independent of Debye's theory. According to the Debye function, θ represents the value of T at which $\bar{C}_v^\circ$ happens to equal $2.856R$; a similar characteristic temperature may be defined, however, in terms of any other fixed value of $\bar{C}_v^\circ$, and Lewis and Gibson chose to define their θ as the temperature at which $\bar{C}_v^\circ = \frac{3}{2}R$ [about $\frac{1}{4}\theta$ (Debye)], this being about the mid-point of the curve, where $\bar{C}_v^\circ$ is most sensitive to T. Figure

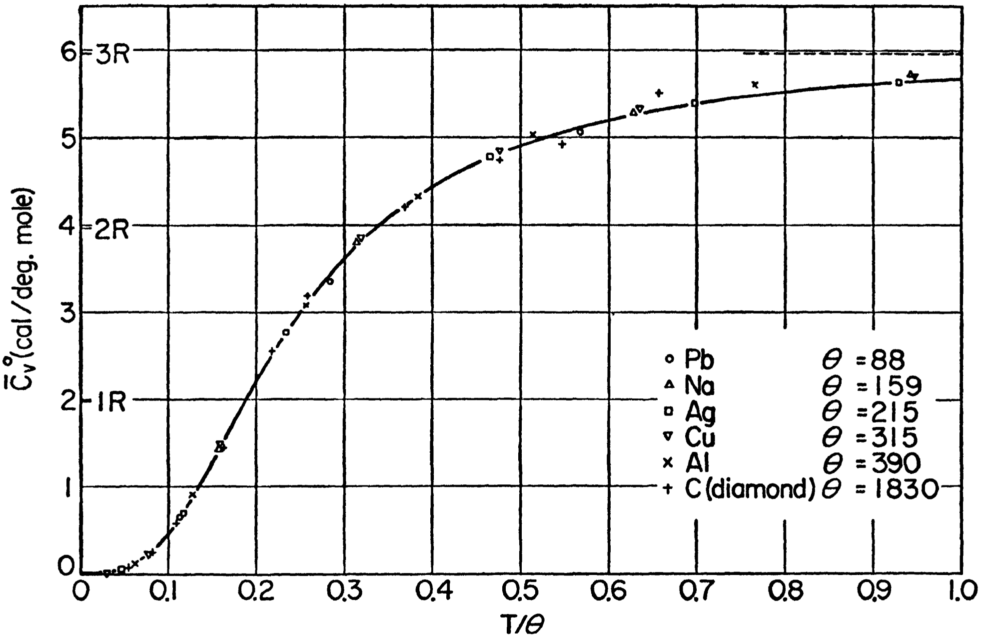

FIG. 3-4. Heat capacities of monatomic crystalline solids. The solid curve represents the Debye function, $D(\theta/T)$, given by Eq. (3-54).

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[1] See Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement I, pp. 705–707 (1927). These values should be multiplied by 1.00076 to allow for revision in the value of R.

[2] G. N. Lewis and G. E. Gibson, *J. Am. Chem. Soc.*, **39**, 2554–2581 (1917).

3-5 shows their standard heat-capacity curve, $\bar{C}_v^\circ$ vs. log (T/θ), plotted with appropriate values of θ for Al, Cu, Pb, and C (diamond); from it, one may construct the entire heat-capacity curve of any regular monatomic crystalline solid from a single accurate measurement of $\bar{C}_v^\circ$ at a temperature not too distant from θ.

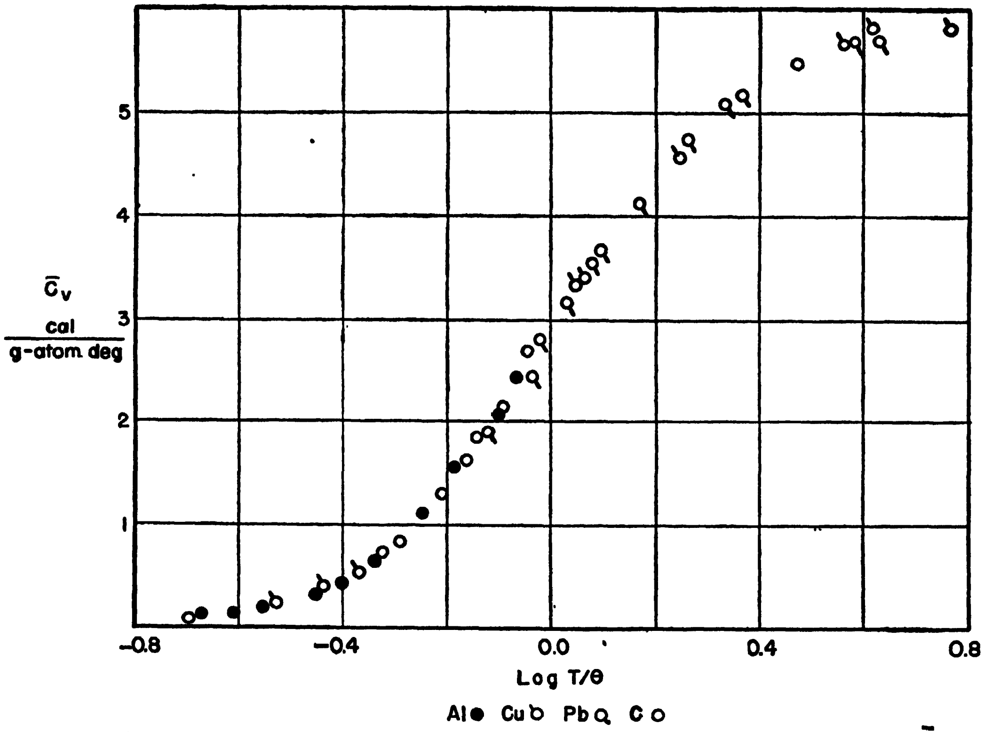

FIG. 3-5. Standard heat-capacity curve for regular monatomic crystalline solids, $\bar{C}_v$ vs. log (T/θ). [*From G. N. Lewis and G. E. Gibson, J. Am. Chem. Soc.*, **39**, 2560 (1917), *with permission.*]

Some of the elements, such as $I_2(c)$, crystallize in molecular lattices, while others, such as graphite, crystallize in lattices showing a certain degree of complexity; to these, the Debye theory in its original form does not apply. On the other hand, many ionic compounds consisting of monatomic ions, such as NaCl and CaF_2, satisfy the Debye theory excellently, with appropriately assigned values of θ, provided that one multiplies $D(\theta/T)$ by a factor to take into account the number of ions represented by the formula, *e.g.*, 2 for NaCl, 3 for CaF_2, etc.

The principal results of Debye's heat-capacity theory may be summarized as follows:

1. $\bar{C}_v$ for crystalline solids consisting of independent monatomic particles arranged in a regular pattern is represented as a universal function of θ/T involving the single parameter θ.

2. In the limit as $T \rightarrow 0$ (in practice, when $T < \theta/12$)

$$\bar{C}_v^\circ = aT^3 \tag{3-55}$$

where for regular monatomic crystals the constant a has the theoretical value $12\pi^4R/5\theta^3$, or $464.57/\theta^3$ in cal/mole deg; but even for many complex crystalline solids that do not satisfy Debye's formula at higher temperatures, it has been found that the law (3-55) is satisfied at sufficiently low temperatures, with a regarded as an empirically determined constant.

3. At sufficiently high temperatures, $\bar{C}_v^\circ$ approaches the theoretical value $3R$, according to the limiting form

$$\bar{C}_v^\circ = 3R\left(1 - \frac{1}{20}\frac{\theta^2}{T^2}\right) \tag{3-56}$$

so that the law of Dulong and Petit is satisfied within 1 per cent when $T > 2.2\theta$; actually, $\bar{C}_v^\circ$ at high temperatures approaching the melting point may increase beyond $3R$, partly because energy begins to be absorbed in electronic excitation, and partly because the Debye picture is oversimplified when one is considering a crystalline solid in which the vibrational motion is so extreme that the crystal is about to lose its stability.

In the calculation of $\bar{C}_p^\circ$ from $\bar{C}_v^\circ$ by means of Eq. (3-41), one does not always have available all the necessary equation-of-state information, particularly at extreme temperatures. For the metals, one may make use of a relation established experimentally and on theoretical grounds by E. Grüneisen in 1908: the ratio of α to $\bar{C}_p^\circ$ is approximately constant with temperature; since furthermore $\bar{V}$ and β vary but slightly with temperature, we may recast Eq. (3-41) in the form

$$\bar{C}_p - \bar{C}_v = A\bar{C}_p^2T \tag{3-57}$$

where $A = \bar{V}\alpha^2/\beta\bar{C}_p^2$ may be evaluated approximately from data obtained at any one temperature; *e.g.*, for silver, $A = 2.3 \times 10^{-5}$ mole/cal from above room temperature down to about −200°C (see also Prob. 3-19, containing data for copper).

Debye's method has been improved and extended to molecular crystals by the work of M. Born and T. von Kármán, and more recently by the work of M. Blackman.[1] Here, account is taken of the interatomic vibrations of the different kinds of atoms with respect to each other, as well as vibrations of the crystal as a whole; Blackman has attempted to take account also of the effect of the discrete structure of the crystal on the

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[1] There is an excellent review of this work by M. Blackman in Reports on Progress in Physics, *Phys. Soc. (London)*, **8**, 11–30 (1941).

motion of individual atoms. Such investigation has led to more or less complex heat-capacity formulas in close agreement with experiment for certain types of crystalline compounds.

In the absence of experimental data, one may roughly estimate the molal heat capacities of the simpler crystalline compounds by assigning independent additive contributions for the various elements present, as shown by H. Kopp and F. C. Neumann. Thus, for estimating $\bar{C}_p^\circ$ over the range 18 to 100°C, one may use the following empirical atomic heat capacities, in cal/mole deg: metals = 6.2; C = 1.8; H = 2.3; B = 2.7; Si = 3.8; O = 4.0; F = 5.0; S = 5.4; P = 5.4; Cl = 5.4; Br = 6.2; I = 6.2. For example, for $CaCO_3$, one estimates a value of

$$6.2 + 1.8 + 3 \times 4.0 = 20.0 \text{ cal/mole deg}$$

whereas the observed value of $\bar{C}_p^\circ$ at 25°C is 19.76 cal/mole deg. It should be emphasized, however, that the additive rule is quite approximate, and not always dependable.

Heat-capacity data for a variety of inorganic substances have been compiled by K. K. Kelley.[1] Kelley has shown that it is possible for one to represent high-temperature molal heat capacities empirically by means of three-constant equations of the form

$$\bar{C}_p^\circ = a + bT + cT^2 \qquad (3\text{-}58)$$

or, even more suitably, of the form

$$C_p^\circ = a' + b'T - c'T^{-2} \qquad (3\text{-}59)$$

Such equations, with empirically determined constants, can be fitted to the experimental heat-capacity data in many cases with a precision of 1 per cent over a range of 1000°K or more (from 273°K up); the range must always be explicitly stated, the equation having no significance outside the stated range. Equation (3-59) has an advantage over Eq. (3-58) in that it integrates giving no power of T higher than the second, when one wishes to represent $\bar{H}_T^\circ$ as a function of T [Eq. (3-47)]. In Kelley's valuable compilations, values of the empirical constants fitting either Eq. (3-58) or Eq. (3-59) to the data are given for all inorganic gases, liquids, and solids for which sufficiently precise and comprehensive high-temperature heat-capacity data were available at the time of publication. Low-temperature heat capacities are reported at various temperatures

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[1] Heat capacities at low temperatures (below 25°C) are given by K. K. Kelley in A Revision of the Entropies of Inorganic Substances—1935, *U.S. Bur. Mines Bull.* 394 (1936); heat capacities at high temperatures (above 0°C) are given in High-temperature Specific-heat Equations for Inorganic Substances, *U.S. Bur. Mines Bull.* 371 (1934); the data are represented in 15° calories.

covering the range from 10 to 298.1°K. This work is being extended by F. D. Rossini and his staff at the National Bureau of Standards as part of the project, "Selected Values of Chemical Thermodynamic Properties." Heat-capacity data for hydrocarbons in particular are to be found in the compilation, Selected Values of Properties of Hydrocarbons, prepared by the National Bureau of Standards in cooperation with the American Petroleum Institute;[1] some of these data have been cast in the form of empirical equations such as (3-58) and (3-59) by H. M. Spencer.[2] Selected heat-capacity data are included in Appendix 3.

3-5. Thermal Behavior of Gases. The thermal behavior of gases shows certain general aspects associated with the universal equation of state

$$p\bar{V} = RT \qquad \text{(ideal gas)} \qquad (3\text{-}60)$$

which all normal gases satisfy in the limit as $p \to 0$, and with regularities in the way in which they deviate from ideal-gas behavior at finite pressures. As we have noted in Sec. 3-1, the equation (3-60) is equivalent to the conditions

$$\alpha = \frac{1}{T}; \qquad \beta = \frac{1}{p} \qquad \text{(ideal gas)} \qquad (3\text{-}61)$$

If we introduce these conditions in Eqs. (3-32) and (3-46), which represent in general how $\bar{U}$ and $\bar{H}$ vary with temperature and pressure, we obtain

$$d\bar{U} = \bar{C}_v^\circ\, dT; \qquad d\bar{H} = \bar{C}_p^\circ\, dT \qquad \text{(ideal gas)} \qquad (3\text{-}62)$$

where $\bar{C}_p^\circ$ and $\bar{C}_v^\circ$ are related as in Equation (3-53) by:

$$\bar{C}_p^\circ - \bar{C}_v^\circ = R \qquad \text{(ideal gas)} \qquad (3\text{-}63)$$

In other words, $\bar{U}$ and $\bar{H}$ for an ideal gas depend only on the temperature, and are independent of the pressure [note that by applying Eq. (3-49) to an ideal gas satisfying Eq. (3-60), we may show that $\bar{C}_p$ would itself be independent of the particular pressure, and by implication through Eq. (3-63), therefore, so would $\bar{C}_v$]. The validity of Eqs. (3-62) depends on Eq. (3-31), which is based on the second law of thermodynamics; they cannot be proved by deduction solely from the first law and the ideal-gas equation of state. Their experimental verification for real gases at such pressures that Eq. (3-60) more or less exactly describes their p-V-T relationships thus constitutes in a sense confirmation of the second law of thermodynamics, which we shall introduce directly in Chap. 5.

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[1] Selected Values of Properties of Hydrocarbons, *Natl. Bur. Standards Circ.* C461 (1947).

[2] H. M. Spencer, *Ind. Eng. Chem.*, **40**, 2152–2154 (1948).

The experimental test of Eqs. (3-62) has been put in several different but equivalent forms. Thus, if one has two vessels connected through a stopcock, and fills one vessel with gas but evacuates the other, then when one opens the stopcock between the vessels, the gas can expand and its pressure fall under conditions such that no work is done on or by the surroundings (so-called *free expansion*); any change in internal energy of the gas under such conditions must necessarily be accompanied either by an equivalent quantity of heat gained from or lost to the surroundings, in accordance with Eq. (2-25), or by a change in the temperature of the gas itself. The first such experiments were conducted by J. L. Gay-Lussac in 1807 on air; he observed that no net temperature change occurred in the gas itself, the momentary initial drop on the high-pressure side being exactly compensated, within experimental error, by an equivalent rise on the other side. This experiment was refined in 1845 by J. P. Joule, who immersed the entire system in water, so that any net heat entering or leaving the gas would be indicated by a corresponding change in the temperature of the water; he could detect no change when air originally at a pressure of 22 atm was allowed to expand freely into the initially evacuated receiver. The method is not particularly sensitive, however, for detecting the small changes in internal energy that we now know do take place.[1]

In 1852, J. P. Joule and William Thomson (Lord Kelvin) devised their famous porous-plug experiment, by means of which the effect of pressure

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[1] A modification of Joule's original experiment was proposed by E. W. Washburn, *J. Research Natl. Bur. Standards*, **9**, 521–528 (1932). He proposed allowing the compressed gas in a bomb to leak out slowly to the pressure of the atmosphere, maintaining the temperature constant by means of electrical heating. Thus if Q represents the quantity of energy received from the heating coil,

$$\begin{aligned} Q &= \int_{p}^{p_s} \left(\frac{dU}{dp}\right)_T dp + W \\ &= \Delta U_T \Big]_{p}^{p_s} + p_s\,\Delta V \qquad (T \text{ const}) \end{aligned}$$

where the second term on the right denotes the work done by the gas against the barometric pressure p_s as its volume increases by ΔV. F. D. Rossini and M. Frandsen *J. Research Natl. Bur. Standards*, **9**, 733–747 (1932), tried the experiment on air, oxygen, and mixtures of CO_2 with oxygen, and found that $(dU/dp)_T$ was practically constant between 0 and 40 atm; thus, for air at 28°C,

$$(dU/dp)_T = (\Delta U/\Delta p)_T = -1.453 \text{ cal/mole atm}$$

and for O_2 at the same temperature, $(dU/dp)_T = -1.556$ cal/mole atm. The method is feasible only if the value of $(dU/dp)_T$ is negative; thus, hydrogen or helium at room temperature would tend to give up energy themselves as the pressure fell. The investigation was undertaken for the purpose of obtaining data for the correction to 1 atm of heats of combustion measured with the oxygen bomb calorimeter.

on the thermal properties of gases can be detected sensitively, even when the deviation from ideal-gas behavior is quite small. In this experiment, a compressed gas maintained at fixed initial pressure p_0 (4.5 atm in the original experiments of Joule and Thomson, but much higher initial pressures have been employed by later investigators) is allowed to flow steadily through a porous plug of cotton, or an ordinary throttle valve, which in effect blocks free expansion but maintains a constant drop in pressure down to the escaping pressure p (1 atm in the original experiments); the temperatures T_0 and T on either side of the plug are measured, at distances back sufficiently far from the plug so that the flow is free of eddies and temperature inhomogeneities; the section of the tube between the two thermometers, including the plug, is packed in insulation to prevent any exchange of heat with the surroundings; the initial temperature T_0 is controlled at will by circulation of the incoming compressed gas through a coiled tube immersed in a water bath or an air bath maintained at the desired temperature. Under the conditions of the experiment, a volume V_0 of gas is forced into the plug at the pressure p_0, while a corresponding volume V comes out on the other side at pressure p; the net work done by the gas in expanding against the throttling reaction of the plug is thus

$$W = pV - p_0V_0$$

Since the expansion is being carried out under adiabatic conditions, this work must be at the expense of the internal energy [Eq. (2-24)],

$$U - U_0 = -W = -pV + p_0V_0 \qquad (Q = 0)$$

Thus

$$U + pV = U_0 + p_0V_0$$

The enthalpy of the gas stays constant as it passes through the plug. Now, the general relation connecting the enthalpy, the temperature, and the pressure is Eq. (3-46); let us define the *differential Joule-Thomson coefficient* μ by means of the expression

$$\mu \equiv \left(\frac{dT}{dp}\right)_H \tag{3-64}$$

Then, according to Eq. (3-46),

$$\mu = \frac{(\alpha T - 1)\bar{V}}{\bar{C}_p} \tag{3-65}$$

By starting with given values of T_0 and p_0 and varying p, the pressure at which the gas escapes on the low-pressure side of the porous plug, one can measure the corresponding value of T, and by plotting T vs. p, establish the isenthalp (curve of constant enthalpy) passing through the point

(T_0, p_0) for fixed mass of gas; the value of μ at given (T, p), which is an intensive property of the substance, is equal to the slope of the isenthalp passing through that point. Figure 3-6 presents isenthalps so constructed for nitrogen, from experimental work of J. R. Roebuck and H. Osterberg; in Fig. 3-7, μ, represented by the slopes of the curves appearing in Fig. 3-6, is plotted against temperature at a series of constant pressures. The integral Joule-Thomson effect represented by the curves in Fig. 3-6 may be put in the form

$$\int_{T_0}^{T} \bar{C}_p \, dT = \int_{p_0}^{p} (\alpha T_0 - 1)\bar{V} \, dp \tag{3-66}$$

where the integral on the left is to be evaluated at the constant pressure p at which the gas emerges from the plug, and the integral on the right at the constant temperature T_0 at which the gas enters the plug; we could equally well have expressed this relation by taking the integral on the left at the constant pressure p_0 and the integral on the right at the constant temperature T, except that T_0 is usually the known controlled temperature in experiments of this kind. The integral on the right is completely determined by the equation of state of the gas, a consequence of our having introduced the second law of thermodynamics implicitly through the relation (3-31); therefore Eq. (3-66), which is the equation for the isenthalp through the point (T_0, p_0), may be solved for T at given p if we know in addition to the equation of state how $\bar{C}_p$ varies with temperature at the constant pressure p. For certain purposes, however, it is useful for us to regard μ itself as a directly measurable property of the gas, which we can determine without knowledge of its equation of state. Typical values for several gases at 1 atm pressure are given in Table 3-2.

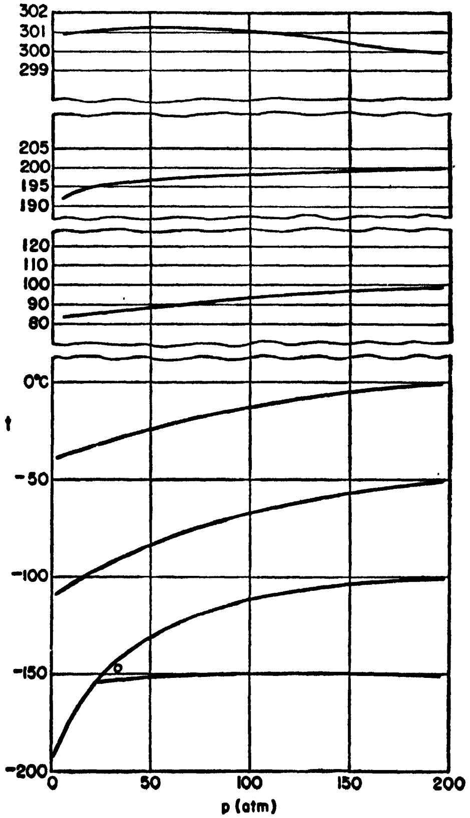

FIG. 3-6. Temperature vs. pressure curves at constant enthalpy for $N_2(g)$ from Joule-Thomson measurements by J. R. Roebuck and H. Osterberg. Circled point represents the critical temperature and pressure.

By introducing Eq. (3-65) in Eq. (3-46), we may readily express the dependence of $\bar{H}$ on the pressure for a real gas in terms of the property μ,

$$d\bar{H} = \bar{C}_p \, dT - \mu \bar{C}_p \, dp \tag{3-67}$$

This relation constitutes the generalization for real gases of the ideal-gas relation (3-62); in other words,

$$\left(\frac{d\bar{H}}{dp}\right)_T = -\mu \bar{C}_p \tag{3-68}$$

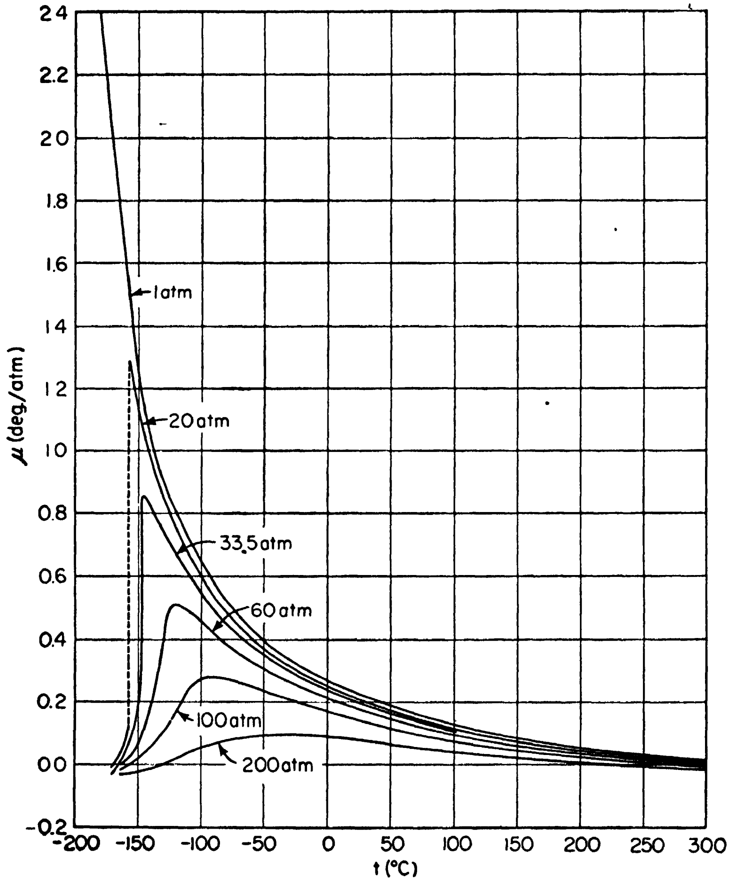

FIG. 3-7. Joule-Thomson coefficient of $N_2(g)$, from data of J. R. Roebuck and H. Osterberg, corrected by Professor Roebuck for a calibration error in the original pressure readings.

Thus, for example, from the data in Table 3-2 and the value of $\bar{C}_p$ for He at 0°C and 1 atm, 5.004 cal/mole deg, given by Roebuck and Murrell, we may infer that at that temperature and pressure, $\bar{H}_T$ is changing with pressure at the rate of $-(-0.0616$ deg/atm$)$ $(5.004$ cal/mole deg$)$ $= +0.3082$ cal/mole atm, and similarly from $\bar{C}_p = 6.909$ cal/mole deg for N_2 at the same temperature and pressure,

$$(d\bar{H}/dp)_T = -(0.2655 \text{ deg/atm})(6.909 \text{ cal/mole deg}) = -1.8343 \text{ cal/mole atm}$$

One sees that experimental establishment of the value of the Joule-Thomson coefficient is indeed an extremely sensitive means of detecting small effects of pressure on the enthalpy, or what is equivalent, slight deviations from ideal-gas behavior.

TABLE 3-2. DIFFERENTIAL JOULE-THOMSON COEFFICIENTS AT 1 ATMOSPHERE PRESSURE*

$$\mu = \left(\frac{dT}{dp}\right)_H$$

Gas	μ, deg/atm	
	At 0°C	At 100°C
Helium	−0.0616	−0.0638
Hydrogen	−0.013	−0.039
Nitrogen	+0.2655	+0.1291
Oxygen	+0.366	+0.193
Argon	+0.43	+0.23
Carbon dioxide	+1.369	+0.729
Ethyl chloride	+5.22	+2.43
Air	+0.2751	+0.1371

* Data for hydrogen, nitrogen, and air, from J. R. Roebuck and T. A. Murrell, in "Temperature. Its Measurement and Control in Science and Industry," pp. 60–73, Reinhold Publishing Corporation, New York, 1941; data for argon are from J. R. Roebuck and H. Osterberg, *Phys. Rev.*, **46**, 785–790 (1934). The other data are from J. R. Roebuck, in "International Critical Tables," Vol. V, pp. 144–146, McGraw-Hill Book Company, Inc., New York, 1929.

The sign of the Joule-Thomson coefficient, which is taken by definition to be positive when the gas cools as its pressure drops, depends on the relative magnitudes of α and $1/T$; if $\alpha > 1/T$, then the coefficient is positive and the gas tends to cool as it expands through the plug, but if $\alpha < 1/T$, then the coefficient is negative and the gas tends to warm as it expands through the plug; for an ideal gas, of course, $\alpha = 1/T$, and $\mu = 0$. For the majority of gases around room temperature and pressure, the value of μ is positive, but for hydrogen it is negative, though it becomes positive at temperatures below −78°C; for helium, likewise,the value of μ is negative at room temperature and pressure, but it becomes positive below −228°C. Further investigation shows that every gas has in fact a characteristic *inversion curve*, or temperature-pressure relationship across which the Joule-Thomson coefficient changes its sign; the inversion curve for nitrogen is shown in Fig. 3-8. One sees that the inversion curve is closed, the value of μ being positive for values of T and p falling within the curve, but negative elsewhere; the entire curve happens to lie below room temperature for hydrogen and for helium. To every pressure below a certain maximum, there corresponds an upper and a lower inversion temperature, of which ordinarily only the upper has any practical importance; below the critical point, the lower branch of the inversion curve belongs to the liquid state, and has actually been followed experimentally for certain condensed gases. The so-called *inversion point* is taken to be the upper inversion temperature in the ideal limit as $p \rightarrow 0$ (practically equal to the upper inversion temperature at $p = 1$ atm).

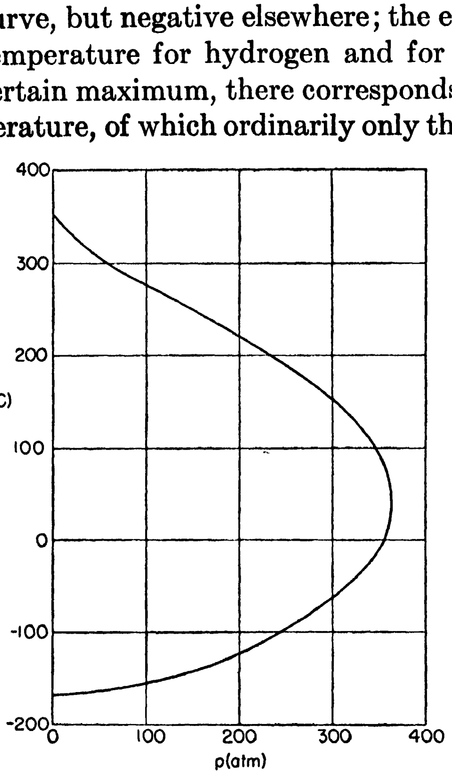

FIG. 3-8. Inversion curve for the Joule-Thomson effect in $N_2(g)$, as established by data of J. R. Roebuck and H. Osterberg.

The inversion of the Joule-Thomson coefficient is clearly related to the interplay between the two opposing van der Waals effects, one the longer range effect of intermolecular attraction, and the other the shorter range effect of the finite molecular volumes.[1] Where the former effect predominates, as at sufficiently low temperatures and molecular concentrations, α will tend to be larger than the ideal-gas value $1/T$; where the latter effect predominates, as at high molecular concentrations, α will tend to be smaller than $1/T$. It is instructive for us to examine a simple equation of state in which an attempt has been made to take these effects into consideration, such as the van der Waals equation itself:

$$\left(p + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT \tag{3-69}$$

Differentiating with respect to $\bar{V}$ at constant pressure,

$$-\frac{2a}{\bar{V}^3}(\bar{V} - b) + \left(p + \frac{a}{\bar{V}^2}\right) = R\left(\frac{dT}{d\bar{V}}\right)_p = \frac{R}{\alpha\bar{V}}$$

Substituting from Eq. (3-69) in the second term on the left, multiplying through by $\bar{V}$, and multiplying numerator and denominator of the right-

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[1] These effects were first proposed by J. D. van der Waals in a paper printed originally in Dutch, "Essay on the Continuity of the Gaseous and Liquid States," Leiden, 1873.

hand term by T,

$$-\frac{2a}{\bar{V}^2}(\bar{V}-b)+\frac{\bar{V}}{(\bar{V}-b)}RT=\frac{RT}{\alpha T}$$

Now, the condition for the inversion curve is that $\alpha T_{\text{inv}} = 1$ [that is, $\mu = 0$ in Eq. (3-65)]; thus, for a van der Waals gas,

$$T_{\text{inv}} = \frac{2a}{bR}\left(\frac{\bar{V}-b}{\bar{V}}\right)^2 \tag{3-70}$$

This equation suggests that for the gas in the low-pressure limit, where $\bar{V} \gg b$, the upper inversion temperature is given by

$$T_{\text{inv}} = \frac{2a}{bR} \qquad (p_{\text{inv}} \rightarrow 0) \tag{3-71}$$

If one substitutes the well-known expressions for a and b in terms of the critical constants, as given by the theory of corresponding states (all tabulations of van der Waals' constants are compiled in this way), one then obtains for the inversion point $T_{\text{inv}} = 27T_c/4$; this expression, while not accurate, is indicative of the order of magnitude of the inversion point; experimentally derived inversion points for several gases are given in Table 3-3.

Another indicative relationship, connecting the inversion point and the Boyle point, may be derived from van der Waals' equation; thus, Eq. (3-69) may be rearranged in the form

$$p\bar{V} = RT + \left(b - \frac{a}{p\bar{V}}\right)p + \frac{ab}{\bar{V}^2}$$

The coefficient of p in the second term on the right of this equation determines essentially how $p\bar{V}$ varies with p for relatively low pressures, the last term not becoming important until higher pressures are reached. Now, the Boyle point is the temperature at which pV remains exactly equal to RT over the low-pressure range; at temperatures below the Boyle point, $p\bar{V}$ tends at first to decrease as p increases from 0 up, while at temperatures above the Boyle point, $p\bar{V}$ tends to increase as p increases from 0 up. Therefore the Boyle point of a van der Waals gas satisfies the condition

$$b - \frac{a}{RT_{\text{Boyle}}} = 0$$

$$T_{\text{Boyle}} = \frac{a}{bR} \tag{3-72}$$

Thus, the inversion point in the zero-pressure limit should equal twice the Boyle point on the absolute thermodynamic scale. This relationship can be regarded only as a rough approximation, as the data included in Table

3-3 show, but one sees in principle how the behavior of the inversion curve for a given gas could be deduced exactly from an accurate equation of state, known in sufficient detail. Since helium, hydrogen, and neon are the only gases whose Boyle points are below room temperature, one can readily perceive why all the other gases have positive Joule-Thomson coefficients from room temperature down to their liquefaction temperatures, at ordinary pressures.

TABLE 3-3. BOYLE POINTS AND INVERSION POINTS OF GASES*
($p = 0$)

Gas	Temperatures, °K		
	T_c	T_{Boyle}	T_{inv}
Helium	5.2	24.1	44.8
Hydrogen	33.2	107.3	195
Nitrogen	126.0	324	621
Air	132.5	347	603
Argon	150.8	410	723

* Values for helium are calculated by F. G. Keyes from precise equation-of-state data ("Temperature. Its Measurement and Control in Science and Industry," p. 59, Reinhold Publishing Corporation, New York, 1941); inversion points for the other gases are given by J. R. Roebuck and H. Osterberg, *J. Am. Chem. Soc.*, **60**, 351 (1938); Boyle points for the other gases are taken from experimental equation-of-state data by L. Holborn and J. Otto, *Z. Physik*, **33**, 1–12 (1925); **38**, 359–67 (1926).

Equation (3-65) constitutes the second of the two practical methods that have been used for the precise determination of the absolute ice point on the ideal-gas or thermodynamic temperature scale, the first being the limiting-density method of M. Berthelot described in Sec. 1-2. The method based on the Joule-Thomson coefficient owes its precision to improvements in the experimental technique of measuring μ developed mainly through the work of J. R. Roebuck and his associates.[1] The procedure is essentially as follows: we may rearrange Eq. (3-65) in the form

$$\mu \bar{C}_p = T\left(\frac{d\bar{V}}{dT}\right)_p - \bar{V}$$

$$\frac{\mu \bar{C}_p}{T^2} = \frac{1}{T}\left(\frac{d\bar{V}}{dT}\right)_p - \frac{\bar{V}}{T^2} = \left[\frac{d}{dT}\left(\frac{\bar{V}}{T}\right)\right]_p$$

Integrating between limits T_0 and T,

$$\frac{\bar{V}}{T} - \frac{\bar{V}_0}{T_0} = \int_T^{T_0} \mu \bar{C}_p \, d\left(\frac{1}{T}\right) \tag{3-73}$$

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[1] J. R. Roebuck, *Proc. Am. Acad. Arts Sci.*, **60**, 535–596 (1925); see also the reviews by J. R. Roebuck and T. A. Murrell, pp. 60-73, and by J. A. Beattie, pp. 74–88, in "Temperature. Its Measurement and Control in Science and Industry," Reinhold Publishing Corporation, New York, 1941.

all terms in this equation referring to a uniform constant pressure. Let this pressure be 1 atm, and let T_0 denote the ice point; then if T represents the steam point, $T = T_0 + 100°\text{K}$ by definition on the absolute centigrade scale, we may write

$$\frac{\bar{V}_{100}}{T_0 + 100\text{ deg}} - \frac{\bar{V}_0}{T_0} = (100\text{ deg})\,\bar{V}_0 \left[\frac{T_0\left(\dfrac{\bar{V}_{100} - \bar{V}_0}{100\text{ deg}\,\bar{V}_0}\right) - 1}{T_0(T_0 + 100\text{ deg})} \right] = I \tag{3-74}$$

where I represents the value of the integral on the right of Eq. (3-73), taken between the steam point and the ice point, to be evaluated directly from experimental values of μ and $\bar{C}_p$ at constant pressure of 1 atm. Since the values of $\bar{V}_{100}$ and $\bar{V}_0$, both at 1 atm, can be measured independently with high precision, Eq. (3-74) may be solved for T_0. This equation is quadratic in T_0, but it may be solved readily by successive approximations in the following manner: let us note that the expression $(\bar{V}_{100} - \bar{V}_0)/100\text{ deg } V_0$ would for an ideal gas exactly define $1/T_0$; its difference from $1/T_0$ for a real gas will therefore be a small number, whose exact value depends on the extent to which the particular gas deviates from ideal behavior at a pressure of 1 atm (see Table 1-2). Let this difference δ be defined by

$$\delta = \frac{\bar{V}_{100} - \bar{V}_0}{(100\text{ deg})\bar{V}_0} - \frac{1}{T_0} \tag{3-75}$$

Upon substitution in Equation (3-74),

$$(100\text{ deg})\bar{V}_0 \frac{\delta}{T_0 + 100\text{ deg}} = I \tag{3-76}$$

Equation (3-76) may now be solved for the small correction δ,

$$\delta = \frac{I}{\bar{V}_0}\left(\frac{T}{100\text{ deg}} + 1\right) \tag{3-77}$$

from experimentally derived values of I and $\bar{V}_0$, even though the value of T_0 in this equation is known only approximately; upon substitution of the value of δ so obtained back in Eq. (3-75), that equation can then be used to compute T_0 precisely; if necessary, successive approximations may be applied between Eqs. (3-75) and (3-77), both of which are themselves exact relations, to obtain the value of T_0 as precisely as is warranted by the precision with which the quantities $\bar{V}_0$, $(\bar{V}_{100} - \bar{V}_0)/\bar{V}_0$, and $\mu\bar{C}_p$ (which determines the value of I) are known. The value of the integral I defined by the right-hand member of Eq. (3-73) apparently also calls for prior knowledge of T_0; one can evaluate this integral graphically, for example, by plotting the value of $\mu\bar{C}_p$ vs. $1/T$, and taking the area under the curve between the abscissas corresponding to the steam point and the ice point; but for this purpose, an approximate knowledge of T_0 is sufficient, because the integral is not a large number, and its value is not sensitive to the precise value assigned to T_0; in any event, the value of I too could be refined by the application of successive approximations, involving the use of Eqs. (3-75) and (3-77). One will note that explicit knowledge of the molecular weight of the gas is not necessary, even though for convenience we have written our equations throughout in terms of molal properties of the gas; for so long as V and C_p refer to the same mass of gas, Eq. (3-73) would stand without regard to the formula weight assigned.

Let us illustrate the computation of T_0 with data obtained by Roebuck and Osterberg for nitrogen.[1] The value of V_0 for this gas at 0°C and 1 atm is 800.0 ml/g, while the value of $(V_{100} - V_0)/V_0$ according to Table 1-2 is 0.36700; the values obtained by Roebuck and Osterberg for μ at 1 atm and temperatures between 0 and 100°C are given in Table 3-4, together with values of C_p, from which Roebuck and Murrell have derived a value of $I = 0.001968$ ml/g deg. Values of $1/T$ based on $T_0 = 273.16$°K are given in the last column of Table 3-4, but one may easily convince oneself that use of the approximate value, $T_0 = 273$°K, would displace the value of I by an insignificant amount. Solving Eq. (3-77) for δ,

TABLE 3-4. JOULE-THOMSON COEFFICIENT AND HEAT CAPACITY OF NITROGEN AT 1 ATMOSPHERE*

t, °C	μ, deg/atm	C_p, cal/g deg	μC_p, ml/g	$1/T$, deg^{-1}
0	0.2655	0.2466	2.703	0.0036608
25	0.2216	0.2467	2.257	0.0033539
50	0.1854	0.2469	1.890	0.0030944
75	0.1555	0.2472	1.587	0.0028722
100	0.1291	0.2476	1.320	0.0026798

* J. R. Roebuck and T. A. Murrell, in "Temperature. Its Measurement and Control in Science and Industry," p. 70, Reinhold Publishing Corporation, New York, 1941.

$$\begin{aligned}\delta &= \frac{0.001968 \text{ ml/g deg}}{800.0 \text{ ml/g}}\left(\frac{273 \text{ deg}}{100 \text{ deg}} + 1\right)\\ &= 0.0000092/\text{deg}\end{aligned}$$

where again, clearly, the precise value assigned to T_0 in this relationship does not have a sensitive effect on the result. Substituting back in

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[1] J. R. Roebuck and H. Osterberg, *Phys. Rev.*, **48**, 450–457 (1935); see also, Roebuck and Murrell, *op. cit.*, p. 70.

Eq. (3-75),

$$\begin{aligned}\frac{1}{T_0} &= 0.0036700/\text{deg} - 0.0000092/\text{deg}\\ &= 0.0036608/\text{deg}\\ T_0 &= 273.16°\text{K}\end{aligned}$$

This method utilizes entirely experimental data obtained at 1 atm pressure, and eliminates the uncertainty introduced in Berthelot's method by the extrapolation to zero pressure; similar data have been reported by Roebuck for helium and for air.[1]

The Joule-Thomson cooling effect has been of practical value in the liquefaction of gases. Thus, in the Linde process for liquefying air, described by C. Linde in 1895, regenerative cooling based on the Joule-Thomson effect is used to take the gas from room temperature down ultimately below its critical temperature (132.6°K); in other words, part of the expanded air, cooled by expanding through the throttle valve, is used to precool the compressed air as it passes from the compressor to the throttle valve. Heat interchange between the incoming gas from the compressor, which is first cooled to −20°C by means of an ice-brine freezing mixture, and the gas issuing from the throttle is effected by circulation of the gas through a system of concentric tubes; since the Joule-Thomson cooling becomes more effective as the temperature is lowered, the recycling of part of the cooled gas through a second-stage compressor and throttle valve provides sufficient cooling to liquefy it after the machine has run through a few preliminary cooling cycles. The Joule-Thomson cooling in a single stage is rather small, about 25 deg for air at an initial temperature of −20°C, expanding from 100 atm to 1 atm, but regenerative cooling permits the effect to become cumulative. Hydrogen must first be cooled below its upper inversion point, −78°C, in some other manner before further cooling by means of the Joule-Thomson effect can be obtained; above that temperature, the gas warms on expanding through the throttle valve. By precooling hydrogen with liquid air, James Dewar was able to take advantage of the Joule-Thomson effect to cool the gas below its critical point, using the Linde method, and he succeeded in liquefying hydrogen for the first time in 1898. Helium, the most difficult gas to liquefy, was first liquefied by H. Kamerlingh Onnes in 1908, using essentially the same method; he became convinced from a study of the equation of state of helium at liquid hydrogen temperatures (14 to 33°K) that its inversion point lay above the normal boiling point of hydrogen (20.39°K), and therefore he precooled the compressed helium by means of liquid hydrogen before permitting it to flow through the throttle valve.

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[1] J. R. Roebuck, *Phys. Rev.*, **50**, 370–375 (1936).

The drop in temperature during a single stage of cooling by the Joule-Thomson effect is given by Eq. (3-66), where p the final pressure is ordinarily taken to be 1 atm; under this condition, for given initial temperature T_0, the greatest degree of cooling is obtained for that particular initial pressure p_0 making the term on the right a maximum (where one should bear in mind that the integral comprising this term is to be evaluated at the constant temperature T_0). If we set up the condition for this term to be a maximum by differentiating with respect to p and setting the result (which is simply the integrand itself) equal to zero, we find on comparing with (3-65) that this condition is equivalent to starting with such a pressure that μ at the given temperature T_0 is equal to zero; in other words, the most effective initial pressure is the inversion pressure at the given initial temperature; a higher initial pressure than this will actually result in a lesser degree of cooling, because a higher pressure puts the gas in a region in which μ is initially negative. The same condition applies of course to any particular final pressure, whether it be 1 atm or some other fixed pressure: the greatest degree of cooling consistent with the given initial temperature T_0 and final pressure p is always obtained when the gas has been compressed to the inversion pressure corresponding to the temperature T_0. For air at −20°C, this pressure is about 200 atm.

The cooling of a gas by means of the Joule-Thomson effect, while technically simple to carry out, is a rather inefficient process, since none of the work that the compressed gas is potentially capable of delivering is realized. The temperature can be lowered more efficiently by permitting the gas to expand under adiabatic conditions against a piston, thereby delivering back part of the mechanical energy that went into its compression. While the Joule-Thomson effect depends on deviation of the gas from ideal behavior, adiabatic expansion against a piston offering mechanical resistance can be used effectively to cool a gas whose behavior is practically ideal; much lower operating pressures are required than for Joule-Thomson cooling. The principles, which are of general interest, may be illustrated with reference to an ideal gas. Let us consider first what happens as the gas is initially compressed, at essentially constant temperature; under this condition, most of the energy spent on the gas in compressing it flows off to the surroundings in the form of heat (if the gas were insulated instead, its temperature would rise). Thus, in general, for *isothermal changes* taking place in a *real gas*, according to Eq. (3-32),

$$(d\bar{U})_T = (p\beta - T\alpha)\bar{V}\,dp = d'\bar{Q} - p\,d\bar{V} \quad (T \text{ const}) \qquad (3\text{-}78)$$

But we have seen that for an *ideal gas* satisfying the equation of state (3-60), $\bar{U}$ is a function of T only [Eq. (3-62)]; this is a consequence of the ideal-gas equation of state combined with the second law of thermodynamics, and is demonstrated independently by the original Joule experiment on gases at moderate pressures, within the range in which they satisfy approximately the ideal-gas law. Hence, for an ideal gas,

$$(d'\bar{Q})_T = (d'\bar{W})_T = p\,d\bar{V} = RT\frac{d\bar{V}}{\bar{V}} \qquad \text{(ideal gas)}$$

$$\bar{Q}_T = \bar{W}_T = RT\ln\frac{\bar{V}_2}{\bar{V}_1} \qquad \text{(ideal gas)} \qquad (3\text{-}79)$$

$$= RT\ln\frac{p_1}{p_2} \qquad \text{(ideal gas)} \qquad (3\text{-}80)$$

where p_1 and $\bar{V}_1$ denote the initial pressure and volume, and p_2 and $\bar{V}_2$ denote the final pressure and volume. We have assumed here that the gas is expanding or contracting against an external pressure at all times equal to its own equilibrium pressure at the instantaneous volume and temperature, as given by the ideal-gas equation $p = RT/\bar{V}$. Equations (3-79) and (3-80) therefore really provide upper limits (in the algebraic sense) to the work that can be done by the ideal gas, and to the equivalent quantity of heat that can be absorbed from the surroundings. For isothermal changes taking place in a real gas, we must replace Eqs. (3-79) and (3-80) by the general relations

$$\left.\begin{aligned} \bar{W}_T &= \int_{\bar{V}_1}^{\bar{V}_2} p\,d\bar{V} \\ \bar{Q}_T &= \int_{\bar{V}_1}^{\bar{V}_2} p\,d\bar{V} + \int_{p_1}^{p_2} (p\beta - T\alpha)\bar{V}\,dp \end{aligned}\right\} \qquad (3\text{-}81)$$

which are derived from Eq. (3-78), where again, the upper limits to the values of $\bar{W}_T$ and $\bar{Q}_T$ for a change between given initial and final states are obtained if one introduces actual equation-of-state data in Eqs. (3-81); but for an *ideal* gas, *all* the work done by the gas during expansion at constant temperature is at the expense of an exactly equal quantity of heat taken in from the surroundings, and, likewise, *all* the work done on the gas during compression at constant temperature passes on as thermal energy to the surroundings.

On the other hand, for *adiabatic changes* taking place in a *real gas*, according to Eq. (3-32),

$$d\bar{U} = (\bar{C}_p - p\bar{V}\alpha)dT + (p\beta - T\alpha)\bar{V}\,dp = -p\,d\bar{V} \qquad (Q = 0) \qquad (3\text{-}82)$$

Now, for an *ideal gas*, the middle member of Eq. (3-82) reduces to $\bar{C}_v^\circ\,dT$ [Eq. (3-62)]; thus

$$d'\bar{W} = p\,d\bar{V} = RT\frac{d\bar{V}}{\bar{V}} = -\bar{C}_v^\circ\,dT \qquad \text{(ideal gas; } Q = 0)$$

$$\bar{W} = \int_{T_2}^{T_1} \bar{C}_v^\circ\,dT \qquad \text{(ideal gas; } Q = 0) \qquad (3\text{-}83)$$

where

$$\int_{T_2}^{T_1} \bar{C}_v^\circ \, d \ln T = R \ln \frac{\bar{V}_2}{\bar{V}_1} \qquad \text{(ideal gas; } Q = 0\text{)}$$

Let us assume that $\bar{C}_v^\circ$ is sensibly constant with T; this is not necessarily true for an ideal gas, but it may be approximately true over a temperature range that is not too large, particularly for the simpler gases whose vibrational energy terms do not contribute greatly to the heat capacity at ordinary temperatures. This last equation then reduces approximately to

$$\bar{C}_v^\circ \ln \left(\frac{T_1}{T_2}\right) = R \ln \left(\frac{\bar{V}_2}{\bar{V}_1}\right) \qquad \text{(ideal gas; } Q = 0\text{)}$$

Bearing in mind that for an ideal gas, according to Eq. (3-63),

$$\frac{R}{\bar{C}_v^\circ} = \frac{(\bar{C}_p^\circ - \bar{C}_v^\circ)}{\bar{C}_v^\circ} = \gamma - 1,$$

we obtain the following equivalent conditions for adiabatic expansion or compression:

$$\frac{T_2}{T_1} = \left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{\gamma-1} \qquad \text{(ideal gas; } Q = 0\text{)} \qquad (3\text{-}84)$$

$$= \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}} \qquad \text{(ideal gas; } Q = 0\text{)} \qquad (3\text{-}85)$$

$$\frac{p_2}{p_1} = \left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{\gamma} \qquad \text{(ideal gas; } Q = 0\text{)} \qquad (3\text{-}86)$$

The work done by the gas during adiabatic expansion is entirely at the expense of its internal energy, and hence if the gas is ideal, its temperature must necessarily fall. The maximum work of expansion consistent with given initial and final states, given by Eq. (3-83), is obtained if the pressure on the piston against which the gas works is at all stages equal to the equilibrium pressure of the gas, $p = RT/\bar{V}$, consistent with its instantaneous temperature and volume; practically, of course, the work actually obtained will be less than the maximum, since the pressure on the piston has to be kept somewhat smaller than the equilibrium gas pressure in order that the gas shall overcome friction and expand at a finite rate. The upper limit to the adiabatic work (3-83) may also be expressed in the equivalent form

$$\bar{W} = \int_{\bar{V}_1}^{\bar{V}_2} p \, d\bar{V} = p_1 \bar{V}_1^\gamma \int_{\bar{V}_1}^{\bar{V}_2} \frac{d\bar{V}}{\bar{V}^\gamma}$$

$$= \frac{p_1 \bar{V}_1^\gamma}{\gamma - 1} \left[\frac{1}{\bar{V}_1^{\gamma-1}} - \frac{1}{\bar{V}_2^{\gamma-1}} \right] \qquad \text{(ideal gas; } Q = 0\text{)} \qquad (3\text{-}87)$$

Thus, for air ($\gamma = 1.4$) initially at 10 atm and $-20°\text{C}$, adiabatic expansion to 1 atm may ideally lower the temperature, according to Eq. (3-85), to

$$\begin{aligned} T_2 &= 253°\text{K}\left(\frac{1\text{ atm}}{10\text{ atm}}\right)^{0.286} \\ &= 253°\text{K}\ (0.517) \\ &= 131°\text{K} \end{aligned}$$

whereas Joule-Thomson expansion through a porous plug at an initial pressure of 100 atm and an initial temperature of $-20°\text{C}$ would lower its temperature at 1 atm only to about $-45°\text{C}$ (228°K) in a single stage. In using essentially isothermal compression, followed by adiabatic expansion against a piston offering mechanical resistance (*e.g.*, by means of a reciprocating engine), to liquefy the gases having low critical temperatures, one of the major difficulties consists of finding suitable low-temperature lubricants for the pistons; ordinary lubricating oils congeal at liquid-air temperatures. This difficulty was overcome in the case of air by G. Claude, who in 1909 designed a liquefier in which petroleum ether was used as the lubricant in the adiabatic expansion cylinder. For liquefying hydrogen or helium by the adiabatic expansion principle, P. Kapitza designed a machine in which a small clearance is left between the cylinder and the piston of the insulated expansion chamber, so that a small quantity of the gas itself escaping through the clearance serves as the lubricant.[1] By this means, helium may be cooled directly from ordinary temperatures down below its inversion point, without the use of liquid hydrogen; precooling with liquid air or liquid nitrogen increases the efficiency comparatively cheaply, but even this is not essential; the final compression, below the inversion point, is followed by Joule-Thomson expansion, which results in liquefaction of the helium. Regenerative cooling is used in both Claude's and Kapitza's adiabatic expansion engines, part of the cold expanded gas being diverted to precool the incoming compressed gas.

To describe adiabatic relations between the temperature and the pressure of a real gas, it is more convenient to use the enthalpy function rather than the internal-energy function, as was done in setting up Eq. (3-82). Thus, from (3-37) and (3-46),

$$d\bar{H} = \bar{C}_p\,dT + (1 - \alpha T)\bar{V}\,dp = \bar{V}\,dp \qquad (Q = 0;\ W' = 0)$$

This relation is thermodynamically exact, and is entirely equivalent to (3-82); it follows that,

$$\left(\frac{dT}{dp}\right)_{Q=0} = \frac{\alpha T\bar{V}}{\bar{C}_p} = -\frac{\bar{L}_p}{\bar{C}_p} \qquad (Q = 0) \qquad (3\text{-}88)$$

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[1] P. Kapitza, *Proc. Roy. Soc.* (*London*), (A)**147**, 189–211 (1934); *Nature*, **133**, 708–709 (1934).

Before this equation can be integrated, one must be able to separate the variables T and p, since in general both $\bar{C}_p$ and $\alpha\bar{V}$ $[=(d\bar{V}/dT)_p]$ depend on both T and p. Thus, it may be possible from an accurate equation of state or from direct experimental information for one to represent $\bar{C}_p$ as a function of T averaged over the approximate pressure range in question and $\alpha\bar{V}$ or $\bar{L}_p$ as a function of p averaged over the approximate temperature range in question. One will then be able to integrate Eq. (3-88) to obtain a good second approximation to the exact relationship between T and p during an adiabatic change with p equal throughout to the instantaneous equilibrium pressure of the gas; the first approximation is given by the ideal-gas relationship (3-85).

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Problems

3-1. The linear expansion of a silver bar between −253 and 101°C is represented from work of W. H. Keesom and A. F. J. Jansen (Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIb, p. 1158, 1931) by the empirical equation

$$l_t = l_0[1 + (17.79066t + 0.0034641t^2 + 0.000059343t^3 + 0.0000003575t^4) \times 10^{-6}]$$

where l_t is the length at the Celsius temperature t, and l_0 the length at 0°C. Express the coefficient of *cubical* expansion α of silver as a function of temperature. [Note that $\alpha = 3\,\frac{1}{l}\left(\frac{dl}{dt}\right)_p$; in computing the value of this expression, one may use l_0 in place of l, the true length at the particular temperature t, with negligible error over the temperature range in question.] Calculate therefrom the value of α at −200, −100, 0, and 100°C.

3-2. The coefficient of cubical expansion of CCl_4 at 20°C and 1 atm is 1.236×10^{-3}/deg, and the coefficient of compressibility at 20°C has the mean value 91.6×10^{-6}/atm between 0 and 100 atm. Estimate the change in volume (neglecting changes in the coefficients themselves) when 200 liters of CCl_4 originally at 20°C and 1 atm is (*a*) heated to 30°C and 1 atm and (*b*) compressed to 50 atm at 20°C. If the CCl_4 completely fills a sealed drum at 20°C and 1 atm, at what temperature will the pressure within the drum reach 50 atm, assuming that the drum itself undergoes no significant change in volume? The density of CCl_4 being 1.595 g/ml at 20°C and 1 atm, estimate the change in molal enthalpy when CCl_4 is compressed at 20°C from 1 to 100 atm.

3-3. The following data, taken from work of P. W. Bridgman (Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Vol. II, p. 1226, 1923), give the volume of methanol, relative to $V = 1.0000$ at 0°C and 1 kg/cm²:

t p	20°C	50°C	80°C
1 kg/cm²............	1.0238	1.0610	1.1005
500 kg/cm²............	0.9823	1.0096	1.0416
1000 kg/cm²............	0.9530	0.9763	1.0023

Calculate the mean coefficient of expansion between 20 and 50°C, and between 50 and 80°C, at each of the three pressures; calculate also the mean coefficient of compressibility between 1 and 500 kg/cm², and between 500 and 1000 kg/cm², at each of the three temperatures.

3-4. Equation-of-state data for gases are commonly presented in the form of pV at various temperatures and pressures, relative to its value at some arbitrary temperature and pressure, *e.g.*, 0°C and 1 atm, or 0°C and 1 m Hg; this form is convenient because pV varies relatively slowly with p, whereas V itself varies relatively rapidly. Prove that $\alpha = \frac{1}{pV}\left[\frac{d(pV)}{dt}\right]_p$ and $\beta = \frac{1}{p} - \frac{1}{pV}\left[\frac{d(pV)}{dp}\right]_T$.

3-5. The following data have been taken for CO from work of E. P. Bartlett, H. C. Hetherington, H. M. Kvalnes, and T. H. Tremearne [*J. Am. Chem. Soc.*, **52,** 1374–1382 (1930)]:

t p atm	pV (pV = 1.0000 at 0°C and 1 atm)					
	−50°C	−25°C	0°C	25°C	50°C	100°C
0	0.8173	0.9089	1.0004	1.0920	1.1837	1.3668
1	0.8162	0.9082	1.0000	1.0918	1.1836	1.3671
25	0.7903	0.8938	0.9894	1.0866	1.1822	1.3752
50	0.7622	0.8768	0.9796	1.0831	1.1826	1.3837
75	0.7388	0.8632	0.9740	1.0832	1.1882	1.3946
100	0.7264	0.8592	0.9745	1.0864	1.1955	1.4062

(*a*) Calculate the coefficient of expansion at 0°C and 1 atm, and at 0°C and 50 atm. (It is sufficiently precise in this case to take the mean coefficients between −25 and +25°C, since the differential coefficients are changing so slowly with temperature.)

(*b*) Calculate the coefficient of compressibility at 25 atm and −50°C, and at 25 atm and +50°C. (Note that at the latter temperature and pressure, $[d(pV)/dp]_T$ is sensibly equal to 0.)

(*c*) Demonstrate that $\Delta\alpha/\Delta p$ at 0°C between 1 and 50 atm approximately equals $-(\Delta\beta/\Delta t)$ at 25 atm between −50 and +50°C. (The relation would become exact if one were to take limits as Δp and Δt became infinitesimally small about a common point, *e.g.*, at 25 atm and 0°C.)

3-6. An equation of state proposed by M. Berthelot has the form

$$p\bar{V} = RT\left[1 + \frac{9}{128}\frac{pT_c}{p_cT}\left(1 - 6\frac{T_c^2}{T^2}\right)\right]$$

where T_c and p_c represent, respectively, the critical temperature and pressure. Prove that for a gas satisfying this equation

$$\left(\frac{d\bar{V}}{dT}\right)_p = \frac{R}{p}\left[1 + \frac{108}{128}\frac{p}{p_c}\frac{T_c^3}{T^3}\right] \quad \text{and} \quad \left(\frac{d\bar{V}}{dp}\right)_T = -\frac{RT}{p^2}$$

Show that Eq. (3-7) applies.

NOTE: Berthelot's equation has the advantage over van der Waals' equation in that it can be solved conveniently for $\bar{V}$ as an explicit function of p and T; it fails, however, to reproduce the minimum in the $p\bar{V}$ vs. p isothermals at temperatures below the Boyle point, which evidently is assigned the empirical value $T_{\text{Boyle}} = \sqrt{6}\,T_c$. Its usefulness is therefore confined to moderately low pressure, where it affords a reasonably good second approximation to real gas behavior, beyond the first approximation afforded by the ideal-gas law itself.

3-7. State the variance and number of components in each of the following homogeneous systems:

(*a*) Aqueous H_2SO_4 solution.

(*b*) A gas mixture of SO_3, SO_2, and O_2, in arbitrary initial proportions, heated to 350°C and 1 atm.

(*c*) A gas mixture of NO_2 and N_2O_4.

(*d*) An aqueous solution of NaCl and KNO_3 in arbitrary proportions.

(*e*) An aqueous solution containing NaCl and KNO_3 in equimolal proportion.

(*f*) A gas mixture of N_2, O_2, and NO at 25°C and 1 atm, of unspecified composition.

(*g*) NH_3 heated to 1000°C and 1 atm (where it is practically completely dissociated into nitrogen and hydrogen).

(*h*) An alloy (solid solution) of Au and Ag.

(*i*) Pure crystalline $CuSO_4{\cdot}5H_2O$.

(*j*) Saturated aqueous $CuSO_4$ solution. (Note that the condition of saturation fixes the composition at whatever temperature and pressure is specified).

3-8. Calculate the mechanical work of expansion when 1 mole of liquid water is heated at constant pressure of 1 atm from 25°C to 100°C; its specific volume is 1.0029 ml/g at 25°C and 1.0434 ml/g at 100°C, both at 1 atm. What is the value of $\bar{H}°$ for water at 100°C, relative to its value at 25°C? $\bar{C}_p^0 = 18.03$ cal/mole deg, constant within 0.5 per cent over the temperature range in question.

3-9. Calculate the mechanical work of expansion when 1 mole of $NH_3(g)$ is heated at constant pressure of 1 atm from 25°C to 100°C; assume the ideal-gas law. What is the value of $\bar{H}$ at 100°C and 1 atm, relative to its value at 25°C and 1 atm? (Use the empirical equation for $\bar{C}_p$ given in Appendix 3.)

3-10. Calculate the value of $\bar{L}_p$ for $H_2O(l)$ at 25°C and 1 atm according to Eq. (3-31); its coefficient of expansion at that temperature and pressure has the value 2.58×10^{-4}/deg, and its density has the value 0.99707 g/ml. Calculate therefrom the heat absorbed (taken in the algebraic sense) when 1 mole of $H_2O(l)$ is compressed at 25°C from 1 atm to 100 atm ($\bar{L}_p$ does not vary sensibly with pressure over that small a range). If this quantity of heat were applied to change the temperature of the water itself (as in adiabatic compression), instead of being transmitted to the surroundings, what would be the corresponding rise in temperature? (The effect of pressure on the heat capacity of liquid water may be neglected in this computation.)

3-11. Calculate the value of $\bar{C}_p - \bar{C}_v$ for water at 25°C and 1 atm, using Eq. (3-41) and the data given in the preceding problem; the value of β for water at the given temperature and pressure is 43×10^{-6}/atm.

3-12. Using the results of Prob. 3-6, show that for a gas satisfying Berthelot's equation of state, $\bar{C}_p - \bar{C}_v = R\left(1 + \frac{108}{128}\frac{p}{p_c}\frac{T_c^3}{T^3}\right)^2$. Estimate according to this equation the per cent deviation (with proper sign) of $\bar{C}_p - \bar{C}_v$ from R for NH_3(g) at 25°C and 1 atm; at 25°C and 2 atm; for N_2(g) at 25°C and 1 atm.

3-13. Using Eq. (3-46) and Prob. 3-6, show that for a Berthelot gas,

$$\left(\frac{d\bar{H}}{dp}\right)_T = \frac{9}{128}\frac{RT_c}{p_c}\left(1 - 18\frac{T_c^2}{T^2}\right).$$

Estimate from this equation the change in enthalpy when 1 mole of CO_2(g) is compressed at 25°C from 1 to 50 atm. Estimate also the difference between the ideal-gas enthalpy $\bar{H}_T^\circ$ (at $p \rightarrow 0$) and the actual enthalpy $\bar{H}_{T,1\text{ atm}}$ at 1 atm for CO_2(g) at 25°C; carry out the same calculation for N_2(g) at 25°C, for He(g) at 25°C, and for H_2O(g) at 100°C.

3-14. Calculate the molal enthalpy of He(g) at 1200°K and 1 atm, relative to its value at 298.16°K and 1 atm; the value of $\bar{C}_p$ may be taken to be sensibly constant, and equal to 4.97 cal/mole deg.

3-15. Show by integration that for a homogeneous substance whose heat capacity can be represented with sufficient precision by an empirical equation in the form (3-59) proposed by Kelley:

$$\bar{H}_{T_2} - \bar{H}_{T_1} = (T_2 - T_1)\left(a' + b'\frac{T_1 + T_2}{2} - \frac{c'}{T_1T_2}\right) \qquad (p \text{ const})$$

Using the empirical heat-capacity equations given in Appendix 3, calculate the molal enthalpies of O_2(g), CO(g) and CO_2(g) at 1200°K and 1 atm, relative to their values at 298.16°K and 1 atm.

3-16. The heat capacity $\bar{C}_p^\circ$ for *n*-butane in the ideal-gas state has the following values at various temperatures [*Natl. Bur. Standards Circ.* C461, Selected Values of Properties of Hydrocarbons, from work of K. S. Pitzer]:

T, °K	C_p°, cal/mole deg
300	23.77
400	29.80
500	35.54
600	40.42
700	44.61
800	48.23
900	51.42
1000	54.20

Using the values at 300, 600, and 900°K, calculate suitable values of a', b', and c' in the empirical heat-capacity equation (3-59), and then test the equation at 500 and 1000°K. (Note that a somewhat better fit may be obtained by application of the method of least squares to determine the empirical coefficients from all the data given.) Calculate $\bar{H}_T^\circ$ at 1000°K relative to its value at 298.16°K, using your empirical heat-capacity equation (note Prob. 3-15); compare with the value of 28,935 cal/mole reported for this quantity in *Natl. Bur. Standards Circ.* 461.

3-17. When ZnO(c) at 1 atm is cooled from 700 to 0°C, it gives up 8132 cal/mole, and when it is cooled from 1300 to 0°C, it gives up 16,010 cal/mole, according to work of W. P. White and A. L. Day recorded by K. K. Kelley (*U.S. Bur. Mines Bull.* 371). From low-temperature work, the molal heat capacity at 0°C has the value 9.35 cal/mole deg. Express $\bar{C}_p^\circ$ as a function of T in the form (3-59), and calculate therefrom the value of $\bar{C}_p^\circ$ at 1000°K.

NOTE: If $\bar{C}_p^\circ$ can be represented with satisfactory precision by means of an equation of form (3-59), then the *mean* molal heat capacity between temperatures T_0 (*e.g.*, 273.16°K in the present instance) and T is given according to the formula in Prob. 3-15 by

$$\overline{(\bar{C}_p^\circ)}_{T_0,T} = a' + b'\frac{T + T_0}{2} - \frac{c'}{T_0 T} = \frac{\bar{H}_T - \bar{H}_{T_0}}{T - T_0} \tag{1}$$

Therefore if in addition to two mean heat-capacity values, to be computed from directly measured $\bar{H}_T - \bar{H}_{T_0}$ values, we have the instantaneous $\bar{C}_p^\circ$ value at the temperature T_0, which is to correspond to the empirical formula

$$(\bar{C}_p^\circ)_{T_0} = a' + b'T_0 - \frac{c'}{T_0^2} \tag{2}$$

then we have sufficient data to calculate a', b', and c' in a convenient form; thus

$$\overline{(\bar{C}_p^\circ)}_{T_0,T} - (\bar{C}_p^\circ)_{T_0} = b'\frac{(T - T_0)}{2} - \frac{c'}{T_0}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

$$\frac{\overline{(\bar{C}_p^\circ)}_{T_0,T} - (\bar{C}_p^\circ)_{T_0}}{(T - T_0)} = \frac{b'}{2} + \frac{c'}{T_0^2 T} \tag{3}$$

By setting up the two experimental values of the expression on the left of Eq. (3) at two different temperatures T, one can readily eliminate b' between the resulting simultaneous equations by subtraction, and solve first for c'; the value of b' directly follows from either set of experimental data in (3), and the value of a' can then be computed from the experimental value of $(\bar{C}_p^\circ)_{T_0}$ according to (2).

3-18. Carry out a similar computation to that of Prob. 3-17 for Fe_2O_3(c); K. K. Kelley (*U.S. Bur. Mines Bull.* 371) reports molal enthalpies relative to 0°C of 12,000 cal/mole at 400°C and 23,180 cal/mole at 700°C (from original calorimetric work of W. A. Roth and W. W. Bertram) and a value of $\bar{C}_p^\circ$ at 0°C of 23.42 cal/mole deg. Using the formula derived in Prob. 3-15, calculate the value of $\bar{H}_T - \bar{H}_{273.16}$ at $T = 1073.16$°K, and compare with the experimental value, 27,060 cal/mole.

3-19. The following data are given for copper by A. Eucken in "Handbuch der Experimental Physik," Vol. VIII, p. 211, 1929:

t, °C	α, deg^{-1}	β, atm^{-1}	$\bar{C}_p^\circ$, cal/mole deg
−190	27.0×10^{-6}	0.71×10^{-6}	3.18
+ 20	49.2×10^{-6}	0.76×10^{-6}	5.84
500	60.0×10^{-6}	0.91×10^{-6}	6.57
1000	72.0×10^{-6}	1.06×10^{-6}	7.30

Test the constancy of $(\alpha/\bar{C}_p^\circ)^2/\beta$, as called for by Grüneisen's law; and from the density at 20°C of 8.92 g/ml, calculate the value of A (mole/cal) in Eq. (3-57).

3-20. The molal heat capacity at constant atmospheric pressure of copper, critically evaluated from several experimental sources by K. K. Kelley (*U.S. Bur. Mines Bull.* 434), is as follows:

T, °K	$\bar{C}_p^\circ$, cal/mole deg
25	0.24
50	1.50
100	3.86
150	4.91
200	5.42
298.16	5.86

Calculate at each temperature the value of $\bar{C}_v$, using Eq. (3-57) and the value of A found in Prob. 3-19. From the corresponding value of θ/T given by the Debye function $D(\theta/T)$ in Appendix 4, compute the value of θ at each of the temperatures given.

3-21. The molal heat capacity of silver, as measured by A. Eucken, K. Clusius, and H. Woitinek (reported in Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIIc, p. 2230, 1936), has the following values:

T, °K	$\bar{C}_p^\circ$, cal/mole deg
11.43	0.072
13.74	0.127
20.20	0.398
28.56	1.028
43.48	2.333
55.88	3.199
74.56	4.066
124.20	5.165
205.30	5.754

At 20°C, the value of $\bar{C}_p^\circ$ is 6.05 cal/mole deg, $\alpha = 56.7 \times 10^{-6}$/deg, $\beta = 0.98 \times 10^{-6}$/atm, $\rho = 10.5$ g/ml. Assuming Grüneisen's law, leading to Eq. (3-57), show that

$$\bar{C}_p^\circ - \bar{C}_v = (2.3 \times 10^{-5} \text{ mole/cal})(\bar{C}_p^\circ)^2 T$$

Calculate at each of the temperatures given the value of $\bar{C}_v$, and by looking up the corresponding value of θ/T for the Debye function, calculate a value of θ for each reading.

Measurements of $\bar{C}_p^\circ$ for silver below liquid-hydrogen temperatures have been made by W. H. Keesom and J. A. Kok, who used liquid helium to precool the samples; their data, as reported in Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIIc, p. 2230, 1936, are as follows (selected values):

T, °K	$\bar{C}_p^\circ$, cal/mole deg
1.671	0.0004149
2.535	0.001088
3.452	0.002161
4.020	0.003046
4.920	0.005013

Using your value of θ deduced from the higher temperature measurements, calculate the theoretical value of $\bar{C}_p^\circ$ according to the Debye limiting law (3-55) at each of these temperatures, and compare with the experimental values; note that at these low temperatures the difference between $\bar{C}_p^\circ$ and $\bar{C}_v$ is negligible. Test the limiting law (3-55) at the three lowest temperatures given in the preceding table (data of Eucken, Clusius, and Woitinek).

3-22. Prove that for a substance whose heat capacity below the temperature T' satisfies the Debye T^3 law (3-55), whether or not it satisfies the Debye theory at higher temperatures, the enthalpy at temperature T' relative to the enthalpy at 0°K (neglecting the difference between $\bar{C}_p^\circ$ and $\bar{C}_v$ at the low temperatures necessarily involved) has the value

$$\bar{H}_{T'}^\circ - \bar{H}_0^\circ = \tfrac{1}{4}(\bar{C}_p^\circ)_{T'}T'$$

Calculate the quantity of heat one would have to remove in order to cool 10 g of copper from 25 to 0°K, using the heat-capacity data given in Prob. 3-20.

3-23. The heat capacity of KCl has been measured at low temperatures by W. H. Keesom and C. W. Clark [*Physica*, **2**, 698–706 (1935)], with the following results:

T, °K	$\bar{C}_p^\circ$, cal/mole deg
2.345	0.000936
2.71	0.001612
3.52	0.00338
4.29	0.00554
5.14	0.01010
6.73	0.01902
7.89	0.0390
9.23	0.0620
10.06	0.0838
13.01	0.214
14.73	0.310
17.09	0.458

By plotting log $\bar{C}_p^\circ$ vs. log T (using logarithmic graph paper) test the Debye T^3 law for this substance.

The heat capacity of KCl has been measured at intermediate temperatures by J. C. Southard and R. A. Nelson [*J. Am. Chem. Soc.*, **55**, 4865–4869 (1933)], with the following results (selected):

T, °K	$\bar{C}_p^\circ$, cal/mole °K
16.69	0.427
21.21	0.842
32.41	2.360
44.25	4.189
69.92	7.365
89.28	8.844
116.47	10.03
158.02	11.06
205.23	11.64
246.41	11.98
273.34	12.15
284.68	12.25

From the four lowest values, calculate a mean value of θ corresponding to Debye's function (note that in principle $\bar{C}_v = 2D(\theta/T)$ for this substance); around 0°C, $\alpha = 1.0 \times 10^{-4}$/deg, $\beta = 5.3 \times 10^{-6}$/atm, and $\rho = 1.99$ g/ml; determine the correction $\bar{C}_p^\circ - \bar{C}_v$ according to the form (3-57), assuming Grüneisen's law, and calculate the theoretical value of $\bar{C}_p^\circ$ at each of the higher temperatures according to Debye's law, using the mean θ value deduced from the low-temperature data. Compare with the experimental values.

3-24. The heat capacity of NH_3(c) and NH_3(l) at 1 atm has been measured at low and intermediate temperatures by R. Overstreet and W. F. Giauque [*J. Am. Chem. Soc.*, **59**, 254–259 (1937)], with the following smoothed results:

T, °K	$\bar{C}_p^\circ$, cal/mole deg	T, °K	$\bar{C}_p^\circ$, cal/mole deg	T, °K	$\bar{C}_p^\circ$, cal/mole deg
15	0.175	100	6.246	200(l)	17.58
20	0.368	110	6.877	210	17.75
30	1.033	120	7.497	220	17.90
40	1.841	130	8.102	230	18.03
50	2.663	140	8.699	240	18.12
60	3.474	150	9.272		
70	4.232	160	9.846		
80	4.954	170	10.42		
90	5.612	180	11.03		
		190	11.71		

(*a*) Plot $\bar{C}_p^\circ$ vs. T, and by graphical integration, determine the difference in enthalpy for NH_3(c) between 15°K and its melting point, 195.42°K.

(*b*) Estimate according to the equation in Prob. 3-22 the difference in enthalpy for NH_3(c) between 0°K and 15°K, assuming the T^3 law. Combining with the result of part (*a*), calculate the value of $\bar{H}_T^\circ - \bar{H}_0^\circ$ for NH_3(c) at its melting point.

(*c*) By graphical integration, determine the increase in enthalpy for NH_3(l) between the freezing point, 195.42°K, and the normal boiling point, 239.74°K. Taking the heat of fusion as 1351.6 cal/mole at 195.42°K, and the heat of vaporization as 5581 cal/mole at 239.74°K, calculate the value of $\bar{H}_T$ for NH_3(g) at 239.74°K and 1 atm, relative to $\bar{H}_0^\circ$ for NH_3(c) at 0°K and 1 atm.

(*d*) Using Berthelot's equation of state (Prob. 3-13), calculate the difference between $\bar{H}_{1\,\text{atm}}$ and $\bar{H}^\circ$ for NH_3(g) at 239.74°K.

(*e*) The value of $\bar{C}_p$ for NH_3(g) accepted by Kelley is 8.36 cal/mole deg at 239.74°K and 1 atm, and 8.49 cal/mole deg at 298.16°K and 1 atm. Assuming a linear increase of $\bar{C}_p$ with temperature, calculate the increase in $\bar{H}_T$ for NH_3(g) between its normal boiling point and 298.16°K, and determine the value of $\bar{H}_T$ for NH_3(g) at 298.16°K and 1 atm, relative to $\bar{H}_0^\circ$ of NH_3(c).

3-25. Show that for a gas satisfying Berthelot's equation of state,

$$\left(\frac{d\bar{C}_p}{dp}\right)_T = \frac{324}{128}\frac{RT_c^3}{p_cT^3}.$$

Use this equation to calculate the value of $\bar{C}_p$ for methane at 25°C and 1 atm, the ideal-gas value $\bar{C}_p^\circ$ (corresponding to $p = 0$) being 8.536 cal/mole deg as derived from spectroscopic data (*Natl. Bur. Standards Circ.* C461). Perform the same calculation for NH_3(g), whose $\bar{C}_p^\circ$ value at 25°C is 8.523 cal/mole deg.

G. Waddington and D. R. Douslin [*J. Am. Chem. Soc.*, **69**, 2275–2279 (1947)] give for the heat capacity of *n*-hexane (g) at 365.15°K:

p, mm Hg	$\bar{C}_p$, cal/mole deg
235.7	40.440
479.4	40.685
760.0	40.950

Calculate the value of $\bar{C}_p^\circ$ by extrapolation, and compare with the result of applying Berthelot's equation of state to the data for 1 atm (look up the necessary critical constants).

3-26. By applying Euler's criterion for $d\bar{H}$ to be a perfect differential in terms of the independent variables T and p in Eq. (3-67), prove that

$$\left(\frac{d\bar{C}_p}{dp}\right)_T = -\left[\frac{d(\mu\bar{C}_p)}{dT}\right]_p$$

The following Joule-Thomson coefficients have been determined experimentally for methane by R. A. Budenholzer, B. H. Sage, and W. N. Lacey [*Ind. Eng. Chem.*, **31**, 369–374 (1939)]; the values given represent the limits at zero pressure from measurements at higher pressures, and are practically equal to the values at 1 atm; the ideal-gas $\bar{C}_p^\circ$ values are quoted by them by interpolation from spectroscopic calculations by R. D. Vold [*J. Am. Chem. Soc.*, **57**, 1192–1195 (1935)]:

t, °C	CH_4(g) at $p = 0$	
	μ, deg/atm	$\bar{C}_p^\circ$, cal/mole deg
21.11	0.405	8.511
37.78	0.359	8.668
54.44	0.318	8.837
71.11	0.283	9.022
87.78	0.253	9.227
104.44	0.227	9.439

Calculate the value of $(d\bar{C}_p/dp)_T$ for methane at 25°C and at 100°C, in the limit as $p \rightarrow 0$ (plot $\mu\bar{C}_p^\circ$ vs. t, and take the slopes at the appropriate values of t), and determine therefrom the corrections: $\bar{C}_p - \bar{C}_p^\circ$ at both temperatures for calculating the real value of $\bar{C}_p$ at 1 atm from the ideal-gas value $\bar{C}_p^\circ$. Note that this method is thermodynamically exact, and the calculations are approximate only in so far as one treats differential coefficients as ratios of finite differences; measurement of the Joule-Thomson coefficient provides essentially the same information as would be given by the actual equation of state. Compare the result at 25°C with that obtained in Prob. 3-25, where of course we were using a hypothetical equation of state that has no theoretical foundation.

3-27. Apply the equation derived in Prob. 3-26 to nitrogen at 25°C and 1 atm, using the data given in Table 3-4; plot $\mu\bar{C}_p$ vs. t, and take the slope of the resulting curve at 25°C, to determine $(d\bar{C}_p/dp)_T$ at 25°C and 1 atm.

3-28. Show that for a gas satisfying Berthelot's equation of state (Prob. 3-6)

$$\mu = -\frac{9}{128}\frac{RT_c}{p_c\bar{C}_p}\left(1 - 18\frac{T_c^2}{T^2}\right)$$

and show also that Eq. (3-66) for the integral Joule-Thomson effect assumes the form

$$\int_{T_0}^{T}\bar{C}_p\,dT = \frac{9}{128}\frac{RT_c}{p_c}\left[1 - 18\left(\frac{T_c}{T_0}\right)^2\right](p_0 - p)$$

Use the former of these approximate empirical equations to estimate the value of μ for nitrogen at 0°C and 1 atm, at 0°C and 100 atm, and at −150°C and 1 atm; the values of $\bar{C}_p$ under these conditions are, respectively, 6.909, 8.242, and 6.940 cal/mole deg, according to J. R. Roebuck and H. Osterberg [*Phys. Rev.*, **48,** 450–457 (1935)]. The experimentally observed values of μ under the three conditions are, respectively, 0.2655, 0.1715, and 1.265 deg/atm, according to the data of Roebuck and Osterberg (corrected for error in their original pressure readings). Note that the only effect of pressure on the value of μ according to Berthelot's equation of state comes about through its effect on the value of $\bar{C}_p$, which in turn is given by the equation derived in Prob. 3-25.

Use the integral equation to estimate the drop in temperature when nitrogen at 0°C and 100 atm is allowed to expand through an insulated throttle valve to 1 atm pressure; the value of $\bar{C}_p$ at 1 atm may be taken as constant and equal to 6.91 cal/mole deg over the temperature range in question.

3-29. The velocity of sound has been measured in hydrogen at 1 atm pressure and various temperatures by R. E. Cornish and E. D. Eastman [*J. Am. Chem. Soc.*, **50,** 627–652 (1928)], with the following results, corrected for the confining effect of the tube in which sound resonance was set up:

T, °K	u, cm/sec
372.52	146,630
369.40	146,110
333.31	138,930
308.96	133,770
294.27	130,710
269.02	125,150
238.23	118,170
203.63	109,900
182.41	104,630
165.58	100,160
145.64	94,715
135.71	92,000
81.12	73,800

(*a*) Assuming that hydrogen can be treated as an ideal gas at 1 atm over the temperature range in question, calculate the value of γ at each temperature, and demonstrate that the rotational energy of these diatomic molecules apparently becomes "frozen" at the lower temperatures. (One must of course express the value of R in the ideal-gas sound-velocity formula in cgs units, if u is so expressed.)

(*b*) Show that for a gas satisfying Berthelot's equation of state, Eq. (3-52) assumes the form

$$u = \sqrt{\frac{RT}{\bar{M}}}\,\gamma\left[1 + \frac{9}{128}\frac{pT_c}{p_cT}\left(1 - 6\frac{T_c^2}{T^2}\right)\right]$$

NOTE: $(dp/d\rho)_T = -(\bar{V}^2/\bar{M})(dp/d\bar{V})_T$, since $\rho = \bar{M}/\bar{V}$; apply the result for $(dp/d\bar{V})_T$ derived in Prob. 3-6.

Show that for hydrogen at 372.52°K, introduction of Berthelot's equation of state is equivalent to reducing u by the factor 1/1.00047 before applying the ideal-gas relation $u_{\text{ideal}} = \sqrt{\frac{RT}{\bar{M}}\gamma}$. Calculate the value of γ at that temperature accordingly, using a calculating machine if one is available, or five-place logarithms, in order to obtain five significant figures in the result.

(*c*) Using the formula of Prob. 3-12 derived from Berthelot's equation of state, show that for hydrogen at 372.52°K and 1 atm, $\bar{C}_p - \bar{C}_v = 1.00005R$, within the degree of approximation afforded by Berthelot's equation. Combining this result with the value of $\bar{C}_p/\bar{C}_v$ derived in the preceding section, calculate precise values of $\bar{C}_p$ and $\bar{C}_v$ at the given temperature and pressure. (For the introduction of actual equation-of-state data for hydrogen instead of the Berthelot approximation, consult the original paper of Cornish and Eastman.)

3-30. To what theoretical pressure must helium be compressed at an initial temperature of 0°C so that on doing work of adiabatic expansion, its temperature may fall to the inversion point, 44.8°K, at 1 atm? (Assume the ideal-gas relation.) What must the initial pressure be if the compressed gas is cooled initially to −20°C by means of an ice-brine cooling mixture? What must it be if the compressed gas is precooled to −77°C with solid CO_2? What must it be if the compressed gas is precooled to −190°C with liquid air?

3-31. What temperature will air ($\gamma = 1.4$) originally at 20°C ideally attain if it is suddenly compressed to one-fifth its original volume, so rapidly that no heat is at first lost to the surroundings? What compression ratio will raise the temperature of air adiabatically from 80°C to 1000°C? (Note that these effects are encountered in internal-combustion engines, during the stage preliminary to ignition of the fuel.)

3-32. Starting with 1 mole of nitrogen at 0°C and 1 atm, how much work must be done, at least, in order to compress it to half its original volume under adiabatic conditions? How much work must be done, at least, in order to compress it to half its original volume at constant temperature of 0°C? What final temperature is theoretically attained in the adiabatic compression?

3-33. The equation of state proposed by H. L. Callendar for steam has the form

$$p(\bar{V} - b) = RT - \frac{Ap}{T^c}$$

where b has physical significance similar to that of b in van der Waals' equation and is assigned the value 0.018 liter/mole characteristic of the liquid state at ordinary temperatures and pressures, A is an empirical constant representing the effect of intermolecular attraction, and $c = \bar{C}_v^\circ/R$. For temperatures and pressures not exceeding the critical values (647.2°K and 218.17 atm), the value of c may be taken as constant and equal approximately to $^{10}/_{3}$; the value of A, determined empirically, is about 2.0×10^8 liter deg^c/mole. Calculate $(d\bar{V}/dT)_p$ in terms of Callendar's constants, and show that the enthalpy function for steam has the form

$$d\bar{H} = \bar{C}_p\,dT - \left[\frac{(c+1)A}{T^c} - b\right]dp$$

Show that the enthalpy $\bar{H}_{T,p}$ at temperature T and pressure p relative to $\bar{H}^\circ_{T_s}$, the enthalpy at temperature T_s and zero pressure, is therefore given by

$$\bar{H}_{T,p} - \bar{H}^\circ_{T_s} = (c+1)R(T - T_s) - \left[\frac{(c+1)A}{T^c} - b\right]p$$

Use this equation, with the given values of A, b, and c, to calculate the difference in enthalpy between steam at 360°C and 50 atm and steam at 100°C and 1 atm.

Taking $\bar{C}^\circ_p$ for $H_2O(l)$ as practically constant and equal to 18.0 cal/mole deg between 0 and 100°C, and taking the latent heat of vaporization at 100°C as 9717 cal/mole, what is the molal enthalpy of steam at 360°C and 50 atm relative to that of liquid water at 0°C and 1 atm?

NOTE: Since the enthalpy difference between liquid water at 0°C and 1 atm and at 0°C and 50 atm is practically negligible, the quantity just calculated represents the net heat required in order to transform water at constant pressure of 50 atm from 0°C to steam at 360°C; it does *not* equal the net heat that would be absorbed if the water were first heated at constant pressure of 1 atm to 360°C and then compressed.

3-34. In measuring the heat of fusion of ethyl chloride, J. Gordon and W. F. Giauque [*J. Am. Chem. Soc.*, **70,** 1506–1510 (1948)] using a specific heat calorimeter found in a typical run that 1145.1 cal/mole of energy was required to raise the temperature from 132.242 to 136.095°K, the melting point being at 134.80°K. A correction of 2.7 cal/mole should be subtracted for a small quantity premelted at the starting temperature. The heat capacity of the solid being 20.22 cal/mole deg at 130°K, and 21.71 cal/mole deg just below its melting point, and the heat capacity of the liquid being 23.23 cal/mole deg just above the melting point, calculate the latent heat of fusion.

3-35. Using the table in Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement I, p. 706, 1927, find the molal internal energy $\bar{U} - \bar{U}^\circ_0$ of Ag(c) at 298.16°K relative to its value at 0°K, using for θ the value found in Prob. 3-21. What further information would be required in order to find the value of $\bar{H}^\circ - \bar{H}^\circ_0$ at 298.16°K and 1 atm? (Compare Prob. 3-1.)

CHAPTER 4

THERMOCHEMISTRY

In this chapter, we shall take up the applications of the first law of thermodynamics to processes in which changes take place in the composition of the thermodynamic system. The ultimate composition in terms of the chemical elements is of course assumed to remain fixed, in accordance with accepted chemical theory; but changes may take place in the forms in which the chemical elements are combined, each different combination entailing a characteristic quantity of energy. When such changes satisfy the law of definite proportions, they are regarded as true chemical changes; energy differences are associated also, however, with the process of forming a solution from its components, and from the purely thermodynamic viewpoint, no distinction can be made between the two cases. We shall discuss the treatment of both cases separately.

4-1. Heat of a Chemical Reaction. The heat of a chemical reaction is defined in general as the quantity of heat evolved when a given quantity of the reaction takes place, as represented by its chemical equation. For example, the combustion of methanol is represented by the thermochemical equation

$$CH_3OH(l) + \tfrac{3}{2}O_2(g) = 2H_2O(l) + CO_2(g); \qquad Q^\circ_{25^\circ C} = 173.64 \text{ kcal}$$

The heat of an endothermic reaction would be represented with a negative sign. One should note that this sign convention for Q in thermochemistry is opposite to that used in general chemical thermodynamics. In this chapter, therefore, following the general practice among thermochemists,[1] we shall be using the opposite sign convention for Q from that followed in other chapters. Since the heat of reaction may vary with the temperatures of the reacting substances, it is generally measured at or corrected to some particular constant temperature, *i.e.*, with each reactant originally at and each product finally at the same uniform temperature throughout. It varies also depending on whether one measures it at constant volume, as in a gas-combustion bomb, or at constant pressure, such as at the practically constant pressure of the atmosphere; it is generally convenient to correct all data, by methods that we shall pres-

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[1] See, for example, F. R. Bichowski and F. D. Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corporation, New York, 1936.

ently describe, to a uniform constant pressure of 1 atm throughout (except of course when one is deliberately concerned with heats of reactions taking place at controlled high pressures), and we shall use superscript zero, *e.g.*, as in the symbol Q°, to denote that this condition has been satisfied.[1]

The experimental method used to measure the heat of a chemical reaction depends on the nature of the reaction. The methods that have been directly applied may be divided into two general classes: isothermal and adiabatic. In isothermal or essentially constant-temperature calorimetry, the calorimeter has such a large heat capacity (*e.g.*, it may consist of a large water bath) that the measured temperature rise from which the heat of reaction is calculated is relatively small, of order several centigrade degrees; the surroundings are ordinarily at the approximately constant temperature of the room. Correction for thermal radiation is one of the most important sources of difficulty in isothermal calorimetry; such methods are therefore best adapted to reactions that go to completion rapidly, inasmuch as the radiation error tends to increase with time. For fast reactions taking place in liquid solution, such as the neutralization of a strong acid by a strong base in aqueous solution, the reaction may be set up conveniently in a Dewar flask, the solution itself then serving as the bulk of the calorimeter (the flask, stirring equipment, and thermometer also contribute to the total heat capacity, which can be determined from straightforward electrical heating by means of an immersion heater). Rapid mixing of the reactants and efficient stirring of the product mixture are essential in order that the temperature attained by the calorimeter may become uniform as soon as possible after mixing, before radiation effects have influenced seriously the total quantity of heat observed.

Combustions may be carried out in an isothermal calorimeter, consisting of a "bomb," or heavy-walled steel tube fitted with a hermetically tight cover, immersed in a body of water, whose temperature rise indicates the quantity of heat evolved by the reaction taking place within the bomb. The bomb, containing a weighed sample of the substance under investigation, is charged with oxygen gas at 20 to 30 atm pressure, and the reaction started by means of an electrically heated iron fuse wire dipping into the sample; the combustion reactions are practically instantaneous in oxygen under pressure, and the surrounding water is stirred mechanically in order to distribute the evolved heat rapidly throughout

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[1] For gaseous reactants and products, it is conventional to correct the heat of reaction at standard atmospheric pressure to what it would be if each gas satisfied the ideal-gas laws, Eqs. (3-60) and (3-62); however, the correction for deviation from ideal-gas behavior at 1 atm is practically negligible for most gases; it can be made from knowledge of $(d\bar{H}/dp)_T$ for each gaseous reactant and product, derived by the methods described in Chap. 3, and combined as shown in connection with Eq. (4-17).

its mass. The bomb calorimeter may be standardized fundamentally by means of electrical heating, the radiation correction being important, but more commonly it is standardized under actual working conditions by runs made on standard samples of high purity, whose heats of combustion have been established by fundamental electrical standardization; the National Bureau of Standards supplies standard samples of benzoic acid and of certain other combustion standards suitable for this purpose.

In adiabatic calorimetry, the calorimeter is surrounded by an insulated jacket heated independently at such a rate that its temperature is always maintained equal to that of the calorimeter. This type of calorimeter was first proposed by S. W. Holman in 1895, and was perfected largely through the work of T. W. Richards and his associates at Harvard University during the first quarter of the twentieth century. In the adiabatic bomb calorimeter, where the reaction is rapid, the temperature of the jacket may be controlled manually (e.g., by the admission of hot water as the temperature of the calorimeter proper rises; see, for example, the operating instructions furnished by the Parr Instrument Co., Moline, Ill., for its commercial adiabatic oxygen bomb calorimeters); but for slower reactions, the jacket temperature may be conveniently maintained by electrical heating, controlled automatically by means of a differential thermocouple having one junction set in the calorimeter and the other in the jacket; the deflection of a spotlight galvanometer, for example, connected to the thermocouple leads may be used in connection with a pair of photocell relays disposed on either side of the null point to activate or deactivate the jacket heater.

In the adiabatic calorimeter, thermal losses due to radiation are thus completely eliminated. Such a technique is essential to the precise measurement of the heats of comparatively slow reactions, and is well exemplified by the work of G. B. Kistiakowsky and his associates on the heats of hydrogenation of unsaturated hydrocarbons.[1] In this work, the calorimeter consisted of a tube containing the platinum catalyst on whose surface the reaction took place; the mixed reactant gases, *e.g.*, ethylene and hydrogen, preheated to about 82°C, were led into the calorimeter tube, which was surrounded by an automatically controlled insulated radiation shield maintained by independent electrical heating at the same temperature as the calorimeter tube within, and the rate at which heat was evolved by the reaction was measured by the rate at which the temperature of the tube containing the catalyst increased; the rate of reaction was simultaneously measured by gas analysis of the product gas issuing from the calorimeter. The calorimeter itself was equipped with its own

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[1] G. B. Kistiakowsky, H. Romeyn, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.*, **57**, 65–75 (1935).

heating coil, so that it could be standardized by means of electrical heating.

Gas-combustion reactions may be studied either in a constant-volume gas-combustion bomb, or by means of a constant-pressure flame calorimeter. An adiabatic flame calorimeter has been used by F. D. Rossini at the National Bureau of Standards to measure with high precision the heats of combustion of hydrogen with oxygen, hydrogen with chlorine, carbon monoxide with oxygen, and of many gaseous hydrocarbons with oxygen.[1] A substitution method is used, in which a measured quantity of electrical energy raises the temperature of the calorimeter (measured with a sensitive resistance thermometer) through the same interval as was observed for a measured quantity of the chemical reaction, the calorimeter itself thus serving merely as a comparator of the two kinds of energy.

The reader will find descriptions of other types of reaction calorimeters by A. Eucken[2] and also by W. P. White.[3]

One should note that an important indirect source of thermochemical data is based on measurement of the temperature variation of the equilibrium constant for the chemical reaction [van't Hoff's law, Eq. (8-2-2)]; the theory of this method, which depends on the second law of thermodynamics, is taken up in Chap. 8.

4-2. Hess's Law of Constant Heat Summation. In 1840, G. H. Hess proposed on the basis of available experimental evidence that the net heat of a chemical transformation was equal to the sum (with proper algebraic signs) of the heats of any intermediate reactions through which the transformation could be brought about. At the time of its discovery, Hess's so-called *law of constant heat summation* was supposed to provide excellent confirmation of the caloric fluid theory of heat still prevailing; apparently each reactant carried into and each product carried out of the reaction characteristic quantities of heat, the heat of reaction representing the excess of the heat "content" of the reactants over that of the products. In view of the first law of thermodynamics, we recognize now that Hess's law is true only under certain general restrictions. The heat of reaction is *not* independent of the path by which the reacting system passes from its initial to its final state. Thus, the quantity of heat evolved by the chemical reaction taking place in a galvanic cell from which energy in

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[1] F. D. Rossini, *J. Research Natl. Bur. Standards*, **6**, 1–35 (1931); **6**, 37–49 (1931); **6**, 791–806 (1931); **7**, 329–330 (1931); **9**, 679–702 (1932); etc. The calorimeter is described in detail in the first of these articles.

[2] A. Eucken, "Handbuch der experimental Physik," Vol. VIII, I.

[3] W. P. White, "The Modern Calorimeter," Reinhold Publishing Corporation, New York, 1928.

electrical form is being withdrawn is invariably smaller than the quantity of heat evolved when the same quantity of reaction is brought about directly, without the development of electrical energy.[1] Furthermore, the heat of a reaction carried out at constant pressure differs in general from the heat of the same reaction carried out at constant volume.

J. Thomsen suggested in 1853 that Hess's law is actually a special case of the general conservation law based on Joule's experiments. We have only to suppose that each reactant carries into and each product carries out of the reaction characteristic quantities of *internal energy* and of *enthalpy*, which depend solely on the states of the substances as they participate in the reaction. Thus, let

$$aA + bB + \cdots = lL + mM + \cdots \tag{4-1}$$

represent the equation of a chemical reaction involving the chemical substances A, B, . . . as reactants, and L, M, . . . as products, each being in some specified state. The corresponding net changes in internal energy and enthalpy for the amount of chemical reaction represented by Eq. (4-1) may be represented by

$$\Delta U = l\bar{U}_L + m\bar{U}_M + \cdots - a\bar{U}_A - b\bar{U}_B - \cdots \tag{4-2}$$
$$\Delta H = l\bar{H}_L + m\bar{H}_M + \cdots - a\bar{H}_A - b\bar{H}_B - \cdots \tag{4-3}$$

where $\bar{U}_A$, $\bar{U}_B$, . . . , $\bar{U}_L$, $\bar{U}_M$, . . . and $\bar{H}_A$, $\bar{H}_B$, . . . , $\bar{H}_L$, $\bar{H}_M$, . . . represent, respectively, the molal internal energies and the molal enthalpies of the chemical substances participating in the reaction, each in its specified state. The *internal energy of reaction*, ΔU, and the *enthalpy of reaction*, ΔH, thus clearly depend only on the initial states of the reactants and the final states of the products. The *heat of reaction*, on the other hand, is related to ΔU and ΔH through the general thermodynamic equations (3-18) and (3-37). Bearing in mind the sign convention for heats of reaction noted in Sec. 4-1, we find that the heat of reaction Q_v at *constant volume* is given by

$$Q_v = -\Delta U - W' \tag{4-4}$$

and the heat of reaction Q_p *at constant pressure* by

$$Q_p = -\Delta H - W' \tag{4-5}$$

When $W' = 0$, therefore, which is usually the case in straightforward thermochemical measurements by calorimetric means (except in such measurements as Jahn's, mentioned in the footnote below),

$$Q_v = -\Delta U \qquad (W' = 0) \tag{4-6}$$
$$Q_p = -\Delta H \qquad (W' = 0) \tag{4-7}$$

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[1] Such experiments, testing the first law of thermodynamics as applied to galvanic cells, were actually carried out by H. Jahn, *Z. physik. Chem.*, **18**, 399–425 (1895).

Thus, the conditions either of constant volume or of constant pressure, with no work possible except in the form of mechanical work of expansion, are sufficient to ensure that the heat of reaction shall be independent of the intermediate stages through which the system may pass on its way from the initial to the final state; under such conditions, therefore, Hess's law applies.

The relationship between Q_p and Q_v is readily inferred from the relationship between H and U,

$$\Delta H - \Delta U = \Delta(pV)$$
$$Q_p - Q_v = -\Delta(pV) \qquad (W' = 0) \qquad (4\text{-}8)$$

Thus, if ΔV represents the volume of the products less the volume of the reactants when the reaction takes place at the constant initial pressure p, then

$$Q_p - Q_v = -p(\Delta V) \qquad (W' = 0) \qquad (4\text{-}9)$$

The term on the right of Eq. (4-9) is equal to the work done on the system by the applied pressure p when the reaction takes place at constant pressure. For reactions involving only liquids and solids, the value of this term is usually so small that it may be neglected except in work of the highest precision. For reactions involving gases, each gas contributes to $p(\Delta V)$ a term pV which at sufficiently low pressures is equal to nRT, where n denotes the number of moles of that substance represented in Eq. (4-1) for the chemical reaction; thus, if $(\Delta n)_g$ denotes the total number of moles of *gaseous* products less the total number of moles of *gaseous* reactants, then Eq. (4-9) may be replaced by the approximation

$$Q_p - Q_v = -(\Delta n)_g RT \qquad (W' = 0) \qquad (4\text{-}10)$$

The corresponding approximate relation between the enthalpy and the internal energy of reaction at the constant temperature T is

$$\Delta H - \Delta U = (\Delta n)_g RT \qquad (4\text{-}11)$$

Thus, for the reaction,[1]

$$CH_3OH(l) + \tfrac{3}{2}O_2(g) = 2H_2O(l) + CO_2(g); \qquad Q^\circ_{25^\circ C} = 173.64 \text{ kcal};$$
$$(\Delta n)_g = -\tfrac{1}{2} \text{ mole}$$
$$\Delta H - \Delta U = -\tfrac{1}{2}RT = -0.30 \text{ kcal} \qquad (T = 298.16^\circ K)$$

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[1] The thermodynamic process actually taking place in a combustion bomb at constant volume, with oxygen under pressure, is by no means simple; corrections are necessary in order to reduce the observed heat evolved, $Q = -\Delta U_B$, representing the internal-energy change for the actual bomb process, corrected to a definite temperature, to what the heat would be if each reactant and product were in its standard state, at 1 atm. To the corrected ΔU, Eq. (4-11) may then be applied to find ΔH. These corrections, which are small but by no means negligible, have been analyzed in detail by E. W. Washburn, *J. Research Natl. Bur. Standards*, **10**, 525–558 (1933).

The heat of reaction at constant volume thus serves to measure directly the difference between the internal energies of the reactants and products, and the heat of reaction at constant pressure serves likewise to measure directly the difference between the enthalpies of the reactants and products. Because of the approximately constant pressure of the atmosphere, it is convenient for us to measure heats of reaction at or correct them to a constant standard pressure of 1 atm; they are furthermore always corrected to a constant uniform temperature for reactants and products. Thus, using the symbol Q_T° as introduced in Sec. 4-1 to denote the heat of reaction measured under such conditions, we have

$$\Delta H_T^\circ = l(\bar{H}_T^\circ)_L + m(\bar{H}_T^\circ)_M + \cdots - a(\bar{H}_T^\circ)_A - b(\bar{H}_T^\circ)_B - \cdots = -Q_T^\circ \qquad (W' = 0) \qquad (4\text{-}12)$$

for the general chemical reaction whose equation is represented by (4-1). Experimental measurement of Q_T° for a given reaction thus provides us with direct evidence concerning the relative values to be assigned to the standard molal enthalpies of the reactants and products in their respective standard states.

The law for the effect of temperature on the enthalpy of reaction (and by inference on the heat of reaction at constant pressure) is derived by the application of Eq. (3-39) to Eq. (4-12), after differentiation term by term,

$$\left(\frac{d\Delta H_T^\circ}{dT}\right)_P = \Delta C_p^\circ = l(\bar{C}_p^\circ)_L + m(\bar{C}_p^\circ)_M + \cdots - a(\bar{C}_p^\circ)_A - b(\bar{C}_p^\circ)_B - \cdots \qquad (4\text{-}13)$$

This relationship is known as *Kirchhoff's law.*[1] In integral form

$$\Delta H_T^\circ = \Delta H_{T_s}^\circ + \int_{T_s}^{T} \Delta C_p^\circ \, dT \qquad (4\text{-}14)$$

This integral may readily be evaluated if $\bar{C}_p^\circ$ for each reactant and product has been established as a function of temperature, as, for example, through empirical equations in the form (3-58) or (3-59) (see Appendix 3); one may thereby relate the enthalpy of reaction at any one fixed temperature T to the enthalpy of reaction at any other fixed temperature T_s. The equation may be used, for example, to deduce the enthalpy of reaction at some standard temperature T_s (such as 298.16°K) from the measured value of ΔH_T° determined at an arbitrary experimental temperature T found convenient for the study of the particular reaction.

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[1] After Gustav Kirchhoff, brilliant nineteenth-century German physicist, famous for his pioneer work in the field of thermal radiation, and in collaboration with Robert Bunsen, on chemical spectroscopy in general. He also made notable discoveries in the theory of electrical networks.

The effect of pressure on the enthalpy of reaction is likewise derived by the application of Eq. (3-44) to Eq. (4-3), after differentiation term by term,

$$\left(\frac{d\Delta H}{dp}\right)_T = \Delta L_p + \Delta V \tag{4-15}$$

In view of the relation (3-31) based on the second law of thermodynamics, Eq. (4-15) may be put in the equivalent form

$$\left(\frac{d\Delta H}{dp}\right)_T = \Delta[(1 - \alpha T)V] \tag{4-16}$$

from which we obtain the integral relationship

$$\Delta H_{T,p} = \Delta H_T^\circ + \int_{p_s}^{p} \Delta[(1 - \alpha T)V]dp \tag{4-17}$$

In this equation, according to our convention regarding the interpretation of ΔH_T°, $p_s = 1$ atm for liquid and solid chemical substances taking part in the reaction, but $p_s = 0$ for gases. The integral in Eq. (4-17) may be evaluated term by term from the appropriate equation-of-state data at the fixed temperature T for each reactant and product; its value is practically negligible unless p is of order several atmospheres or more. By combining Eq. (4-17) with Eq. (4-14), one sees how to calculate the value of $\Delta H_{T,p}$ at any arbitrary temperature and pressure from the value $\Delta H_{T_s}^\circ$ at some one standard temperature and pressure; it is necessary in principle for us to have thermochemical measurements for the reaction only at a single fixed temperature and pressure, for we can then "correct" the data to other temperatures and pressures from further knowledge solely of the thermodynamic properties of the reactant and product substances taken separately.

4-3. Standard Enthalpies of Formation. The heat of a chemical reaction at constant pressure represents the excess of the sum of the enthalpies of the reactants over the sum of the enthalpies of the products. Therefore direct calorimetric measurements of heats of reactions at constant pressure provide us with relative values of the molal enthalpies of the substances participating in the reaction. With the measurements carried out at or corrected to standard reference conditions p_s and T_s (*e.g.*, 1 atm and 298.16°K), we thus obtain values relative to one another of the hitherto arbitrary standard molal enthalpies $\bar{H}_{T_s}^\circ$, which were introduced originally in Eq. (3-47) merely as integration constants for particular chemical substances. For example, the heat of hydrogenation of ethylene, 32.824 kcal/mole as measured at 82°C and 1 atm by G. B.

Kistiakowsky and associates,[1]

$$C_2H_4(g) + H_2(g) = C_2H_6(g); \qquad \Delta H_{82^\circ C} = -32.824 \text{ kcal}$$

tells us that $\bar{H}_{C_2H_6}$ is algebraically smaller than the sum of $\bar{H}_{C_2H_4}$ and $\bar{H}_{H_2}$ at 82°C and 1 atm by 32.824 kcal; corrected to 25°C by means of Eq. (4-14), the difference becomes −32.575 kcal,

$$\Delta H^\circ_{298.16} = (\bar{H}^\circ_{298.16})_{C_2H_6} - (\bar{H}^\circ_{298.16})_{C_2H_4} - (\bar{H}^\circ_{298.16})_{H_2} = -32.575 \text{ kcal} .$$

Likewise, the heat of combustion of hydrogen with oxygen to form liquid water, 68.313 kcal/mole as measured at 25°C and 1 atm by F. D. Rossini,[2]

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(l); \qquad \Delta H_{25^\circ C} = -68.313 \text{ kcal}$$

measures directly the difference between the standard molal enthalpy of liquid water and the sum of the standard molal enthalpy of $H_2(g)$ and ½ the standard molal enthalpy of $O_2(g)$,

$$\begin{aligned}\Delta H^\circ_{298.16} &= (\bar{H}^\circ_{298.16})_{H_2O(l)} - (\bar{H}^\circ_{298.16})_{H_2(g)} - \tfrac{1}{2}(\bar{H}^\circ_{298.16})_{O_2(g)} \\ &= -68.313 \text{ kcal}\end{aligned}$$

For a chemical element, the value of the standard molal enthalpy in some one of its allotropic forms remains arbitrary, because transformations in the ordinary chemical sense of one element into another do not occur, and there is therefore no operational basis on which to intercompare their enthalpies.[3] The value of $\bar{H}^\circ_{T_s}$ for a chemical compound, however, relative to the standard molal enthalpies of its elements, whatever fixed values may be assigned to them, is a perfectly definite and reproducible quantity, which in some cases may be determined by direct calorimetric

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[1] G. B. Kistiakowsky, H. Romeyn, J. R. Ruhoff, H. R. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.*, **57**, 65–75 (1935); these results have not actually been adjusted for deviation from ideal-gas behavior, but the difference between $\Delta H_{25^\circ C, 1 \text{ atm}}$ and $\Delta H^\circ_{298.16}$ amounts only to about −0.004 kcal, whereas the experimental error in ΔH is ±0.050 kcal.

[2] F. D. Rossini, *J. Research Natl. Bur. Standards*, **6**, 1–35 (1931); **7**, 329–330 (1931). This result also has not actually been corrected for deviation of H_2 and O_2 from ideal-gas behavior, because the difference between $\Delta H_{25^\circ C, 1 \text{ atm}}$ and $\Delta H^\circ_{298.16}$ is only about +0.0008 kcal in this case.

[3] One could in principle accomplish such an intercomparison, of course, through measurements of the energies of nuclear transformation reactions. Thus, at some future time, it may become possible and convenient for us to assign to each nuclear species an enthalpy of formation with respect to its constituent neutrons and protons. Such a generalization would have no effect, however, on the relative values of the molal enthalpies of chemical compounds with respect to their constituent chemical elements, and, furthermore, in most cases the nuclear binding energies are not at present known with sufficient precision to make such a step feasible, even if it were advantageous for us to consider it.

measurements, as in the case of $H_2O(l)$, but in other cases may be inferred from calorimetric data for a series of intermediate reactions; the value of ΔH_T° for the hypothetical reaction $C(\text{graphite}) + 2H_2(g) = CH_4(g)$, for example, may be inferred from the heats or the enthalpies of combustion with $O_2(g)$ of graphite, hydrogen, and methane. Therefore it is convenient and customary in chemical thermodynamics for us to assign to each chemical element in its stable modification at standard-state conditions, 25°C and 1 atm, the arbitrary standard molal enthalpy $\bar{H}_{298.16}^\circ \equiv 0$. To each chemical compound (and to other metastable allotropic forms of the elements themselves) there is then assigned a value of $\bar{H}_{298.16}^\circ$ equal to its *molal enthalpy of formation*, or the negative of its *heat of formation from the elements* at the standard-state conditions: constant temperature of 25°C (298.16°K) and constant pressure of 1 atm [values for gases being corrected for deviation from the ideal-gas state at 25°C and 1 atm by means of Eq. (4-17) or equivalent thermodynamic relations, integrated between 0 and 1 atm with the aid of suitable equation-of-state data]. The standard enthalpy of reaction, $\Delta H_{298.16}^\circ$, for any chemical transformation for which the standard enthalpies of formation of all reactants and products have been established may then be represented as in Eq. (4-12) by the difference between the sum of the standard enthalpies of formation of the products and the sum of the standard enthalpies of formation of the reactants. Each independent direct calorimetric measurement of the heat of a reaction serves as a cross check on the self-consistency of the $\bar{H}_{298.16}^\circ$ values assigned to the participating compounds. Thus, the series of direct measurements by G. B. Kistiakowsky and his associates on the heats of hydrogenation of unsaturated hydrocarbons[1] contributed materially to the precision and self-consistency of the enthalpies of formation of the hydrocarbons, which had previously been established only from their heats of combustion.[2] Such data afford direct experimental verification of the first law of thermodynamics, in the sense that the energy absorbed or released during a chemical transformation comes within the scope of that law.

A table of standard molal enthalpies of formation is thus a compact means of summarizing the standard heats at 25°C and 1 atm of all actual and even hypothetical chemical transformations that may take place among the substances included in the table. The present objective of the thermochemist is to establish a best value of $\bar{H}_{298.16}^\circ$ for each chemical

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[1] G. B. Kistiakowsky, H. Romeyn, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.*, **57**, 65–75 (1935); G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *ibid.*, **57**, 876–882 (1935); **58**, 137–145, 146–153 (1936).

[2] See, for example, the review by F. D. Rossini and J. W. Knowlton, *J. Research Natl. Bur. Standards*, **19**, 249–262 (1937).

substance, consistent with all the experimental data available. Such a table hinges on the precise establishment of the $\bar{H}^\circ_{298.16}$ values for certain key compounds, such as CO_2, H_2O, HCl, SO_2, MgO, etc., whose heats of formation from the elements themselves can be directly measured; calorimetric measurements on reactions involving these key compounds and the chemical elements with a single additional compound can then be used to establish the $\bar{H}^\circ_{298.16}$ value of the new compound. Thus, the heat of combustion of CO(g) to form CO_2(g), taken in connection with the $\bar{H}^\circ_{298.16}$ value for CO_2(g) established from the heat of combustion of graphite with oxygen, serves to establish the $\bar{H}^\circ_{298.16}$ value of CO(g); likewise, the heat of combustion of CH_4(g) to form CO_2(g) and H_2O(l), taken in connection with the established $\bar{H}^\circ_{298.16}$ values of CO_2(g) and H_2O(l), serves to establish the $\bar{H}^\circ_{298.16}$ value of CH_4(g) relative to its elements. Reviews of the status of modern thermochemistry, particularly with reference to organic compounds, have been given by F. D. Rossini;[1] a group under his direction at the National Bureau of Standards has been at work on the compilation of such a table, which involves the revision of older tables, and the critical evaluation and incorporation of recent data; tables for the hydrocarbons have already been published in bound form. Appendix 2 consists of data taken from these sources.[2]

Standard enthalpies of formation for chemical substances in phases other than the stable allotrope at standard-state conditions may of course be inferred from knowledge of the enthalpy of formation of the stable allotrope, together with the appropriate latent heat of transition, as mentioned in connection with Eq. (3-48); thus, while $\bar{H}^\circ_{298.16}$ for H_2O(l) has been assigned the value −68.3174 kcal/mole, the value for H_2O(g) is −57.7979 kcal/mole, these two values differing by the latent heat of vaporization of water at 25°C; likewise, the value of $\bar{H}^\circ_{298.16}$ for diamond is 0.4532 kcal/mole, this representing the latent heat of transformation

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[1] F. D. Rossini, *Chem. Rev.*, **18**, 233–256 (1936); **27**, 1–16 (1940); *Ind. Eng. Chem.*, **29**, 1424–1430 (1937).

[2] "Selected Values of Chemical Thermodynamic Properties," issued quarterly in loose-leaf form since Dec. 31, 1947, by the National Bureau of Standards, Washington, D.C. See also Selected Values of Properties of Hydrocarbons, *Natl. Bur. Standards Circ.* C461 (1947). The most comprehensive previous publication is by F. R. Bichowsky and F. D. Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corporation, New York, 1936, in which the standard reference temperature was 18°C, and incidentally, all values for carbon compounds (of which only compounds containing 1 or 2 carbon atoms per molecule are listed) were taken with reference to diamond, instead of graphite, as the standard allotrope of carbon. The thermochemical data in the "International Critical Tables," Vol. V, McGraw-Hill Book Company, Inc., New York, 1929, are based on 20°C as the standard reference temperature, and the data are recorded in international joules.

from graphite, the stable allotrope of the element carbon at 25°C and 1 atm (its value has been established experimentally by the difference between the heats of combustion of diamond and graphite). It is convenient for us to include in the table $\bar{H}^\circ_{298.16}$ values even for substances that have only a hypothetical existence at the standard-state conditions; thus, for H(g), the value $\bar{H}^\circ_{298.16} = 52.089$ kcal has been assigned; this value has been established from spectroscopic determination of the dissociation energy of $H_2(g)$, and is in agreement with equilibrium data for the reaction $H_2(g) = 2H(g)$ obtained at high temperatures. Such hypothetical enthalpies of formation for substances in metastable states constitute a convenient way to include their thermochemical properties in the table under a uniform set of standard-state conditions; while such substances may have an actual stable existence only under conditions far removed from the conventional standard-state conditions, yet it is convenient for theoretical and practical purposes to have all the data reduced to a common standard temperature and pressure. In such cases, the correction usually calls for an assumed or a theoretical knowledge of the value of $\bar{C}^\circ_p$, so that Eq. (3-47) may be applied over the metastable range.

4-4. Bond Energies. It has long been recognized that many of the extensive physical properties of certain classes of chemical compounds can be represented approximately in terms of additive contributions characteristic of the particular elements present. The example of the homologous series encountered among the carbon compounds is a case in point, where one finds that between successive members of a given series the value of $\bar{C}^\circ_p$ for the gaseous state at given temperature and the value of $\bar{V}$ for the liquid at its normal boiling point increase by amounts that are approximately constant for the series, and therefore apparently represent the contributions per mole associated with the $—CH_2—$ group. Comparable additive relationships are found among the physical properties of the alkali halide group of compounds, where one can ascribe a certain set of properties to the Cl^- ion, for example, approximately independent of the particular alkali metal ion with which it may be associated. The additivity principle extends within certain limitations to the molal enthalpy of formation, provided that one takes into consideration the different types of bonds that may exist between atoms. The concept of bond energies is useful not only as a means of estimating enthalpies of formation where direct experimental data are not available but also as a means of measuring the relative strengths of interatomic valence forces. While this subject is not strictly within the scope of classical thermodynamics, yet it constitutes an interesting application of purely thermochemical data to a problem of considerable importance to theoretical chemistry.

Let us consider first compounds in which the atoms are bonded by covalent or shared-electron-pair bonds. In a review of heats of combustion of organic compounds prepared by M. S. Kharasch in 1929,[1] it was shown that the molal heat of combustion for the liquid state could generally be estimated with fair accuracy as a sum of empirical terms for each bond broken in the molecule, the term contributed by a particular bond, such as the C—H bond, or the C—C bond, being approximately independent of the size or shape of the molecule. Since during the combustion of an organic compound, the products are practically always the same, C atoms ending as CO_2 molecules, H atoms and O atoms as H_2O molecules, etc., the additivity rule for the heats of combustion implies more or less definite covalent bond energies, independent of the particular molecule in which the bond exists. This idea has been elaborated and extended to all kinds of covalent compounds by Linus Pauling.[2] In estimating bond energies from ordinary thermochemical data, Pauling first computed the enthalpy of formation of the appropriate compound in the gaseous state from its elements in the form of monatomic gases; in this way, he subtracted out, for example, the energy required to separate the atoms in gaseous H_2, and the energy required to separate the molecules of a crystalline compound, which are extraneous to the point under consideration. In principle, it would be desirable to work with thermochemical data extrapolated to 0°K, in order that the calculated bond energies should be free also of contributions from molecular thermal motion, but in practice the extrapolation is unwarranted in view of the approximate nature of the conclusions and of the fact that the data required for the extrapolation (low-temperature heat capacities) are in many cases not available. Table 4-1 presents some standard enthalpies of formation at 25°C of various elements in the hypothetical form of ideal monatomic gases at 1 atm; the data, taken from "Selected Values of Chemical Thermodynamic Properties," differ in some respects, particularly in the value assigned to C(g) about which there has been considerable controversy, from those used by Pauling in the reference cited. They have been derived in some cases from spectroscopic measures of dissociation energies and in others from high-temperature thermal equilibrium data, the results being corrected to 25°C by the assumption of the theoretical value of $\bar{C}_p^\circ = \frac{5}{2}R$ for each monatomic gas.

Thus, from the ordinary standard enthalpy of formation of methane,

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[1] M. S. Kharasch, *J. Research Natl. Bur. Standards*, **2**, 359–430 (1929); this review was prepared originally in connection with the "International Critical Tables" project.

[2] L. Pauling, "The Nature of the Chemical Bond," 2d ed., Cornell University Press, Ithaca, New York, 1940.

$$C(c, graphite) + 2H_2(g) = CH_4(g); \qquad \Delta H^\circ_{298.16} = -17.9 \text{ kcal}$$

combined with the data

$$C(c, graphite) = C(g); \qquad \Delta H^\circ_{298.16} = 171.7 \text{ kcal}$$
$$2H_2(g) = 4H(g); \qquad \Delta H^\circ_{298.16} = 208.4 \text{ kcal}$$

we derive for the enthalpy of formation of $CH_4(g)$ from gaseous atoms

$$C(g) + 4H(g) = CH_4(g); \qquad \Delta H^\circ_{298.16} = -398.0 \text{ kcal}$$

Thus, the average energy per C—H bond is 99.5 kcal; *i.e.*, this represents the average quantity of thermal energy required, per mole, to disrupt each C—H bond and separate the resulting gas atoms, under hypothetical conditions of constant pressure with each gas behaving as an ideal gas. Proceeding in a similar manner with ethane,

TABLE 4-1. STANDARD ENTHALPIES OF FORMATION FOR ELEMENTS AS MONATOMIC GASES*

($\bar{H}^\circ_{298.16}$, kcal/g-atom)

Li	37.07	Fe	96.68	Te	47.6
Na	25.98	Ni	101.61	N	85.566
K	21.51	Zn	31.19	P	75.18
Rb	20.51	Cd	26.97	As	60.64
Cs	18.83	Hg	14.54	Sb	60.8
Mg	35.9	H	52.089	Bi	49.7
Ca	46.04	F	32.25	C	171.698
Sr	39.2	Cl	29.012	Si	88.04
Ba	41.96	Br	26.71	Ge	78.44
Al	75.0	I	25.482	Sn	72
Cu	81.52	O	59.159	Pb	46.34
Ag	69.12	S	53.25		
Mn	68.34	Se	48.37		

* From "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D.C., as of March 31, 1950.

$$2C(c, graphite) + 3H_2(g) = C_2H_6(g); \qquad \Delta H^{\circ\prime}_{298.16} = -20.2 \text{ kcal}$$
$$2C(g) + 6H(g) = C_2H_6(g); \qquad \Delta H^\circ_{298.16} = -676.2 \text{ kcal}$$

Assuming the average value of 99.5 for each of the six C—H bonds, as derived from the data for methane, we are left with 79.2 kcal as the bond energy of the C—C covalent bond. From the data for the hydrocarbons in general, however, we find that the increment in $\bar{H}^\circ_{298.16}$ for the gaseous compounds per —CH_2— group has the average value −4.9 kcal,

$$C(c, graphite) + H_2(g) = \text{—}CH_2\text{—}(g); \qquad \Delta H^\circ_{298.16} = -4.9 \text{ kcal}$$
$$C(g) + 2H(g) = \text{—}CH_2\text{—}(g); \qquad \Delta H^\circ_{298.16} = -280.8 \text{ kcal}$$

Since introduction of an additional —CH_2— group into the molecule involves the net creation of one new C—C bond and two C—H bonds, we infer for the C—C bond the average bond energy: 81.8 kcal, slightly greater than the value deduced from the data for the single compound, ethane. This value, incidentally, is only 4 per cent less than the value inferred directly from the heat of sublimation of diamond:

$$\text{C(c, diamond)} = \text{C(g)}; \qquad \Delta H^\circ_{298.16} = 171.2 \text{ kcal}$$

where an average of *two* tetrahedral covalent bonds (four bonds per atom, shared by two atoms apiece) have to be broken per C atom liberated from the crystal lattice.

TABLE 4-2. COVALENT BOND ENERGIES* IN KILOCALORIES

H—H	104.2	C—H	99.5	C—Si	143.2
C—C	81.8	Si—H	77.8	C—N	60.3
Si—Si	44.0	N—H	84.3	C—O	82.3
Ge—Ge	39.2	P—H	76.4	C—S	60.1
N—N	20.2	As—H	58.6	C—F	115.8
P—P	47.9	O—H	110.6	C—Cl	78.3
As—As	34.5	S—H	81.1	C—Br	73.0
O—O	33.2	Se—H	66.0	C—I	50.1
S—S	50.2	Te—H	57.4	Si—O	104.0
F—F	64.4	H—F	148.5	Si—F	146.7
Cl—Cl	58.0	H—Cl	103.2	Si—Cl	87.4
Br—Br	46.1	H—Br	87.5	Ge—Cl	102.6
I—I	36.1	H—I	71.4		
Cl—F	86.9			C=C	146.6
Br—Cl	52.2			C≡C	201.9
I—Cl	50.3				
I—Br	42.4				

* Calculated essentially according to the methods outlined by L. Pauling, "The Nature of the Chemical Bond," 2d ed., pp. 52–58, Cornell University Press, Ithaca, New York, 1940; but the more recent thermochemical data given in "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D.C., 1950, have been used in the calculations.

From similar data for alkene hydrocarbons, we may infer an average bond energy of 146.6 kcal for the C=C bond, and from data for alkyne hydrocarbons, an average bond energy of 201.9 kcal for the C≡C bond. Table 4-2 presents other covalent bond energies derived in similar fashion, and Table 4-3 shows how well the experimental data are represented by the empirical bond energies for a number of aliphatic hydrocarbons.[1]

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[1] L. Gerö, *J. Chem. Phys.*, **16,** 1011–1013 (1948), has pointed out that the lower hydrocarbons, such as CH_4, C_2H_6, C_2H_4, etc., are "abnormal" with respect to the additivity of bond energies. By basing his calculations on the higher hydrocarbons, beginning with *n*-hexane, and 1-hexene, he has derived average bond-energy values (at 0°K) of [C—C] = 82.59 kcal/mole; [C—H] = 97.02 kcal/mole (in —CH_2— groups); [C=C] = 145.12 kcal/mole. He has estimated that the sum of the hydrogen bond energies in a methyl radical exceeds three times the $[\text{C—H}]_{CH_2}$ bond energy by 0.34 kcal/mole. See also J. G. Valatin, *ibid.*, 1018–1024.

TABLE 4-3. COMPARISON OF EXPERIMENTAL ENTHALPIES OF FORMATION OF ALIPHATIC HYDROCARBONS WITH VALUES DERIVED FROM BOND ENERGIES*

Formula	Compound (gas)	$\bar{H}^\circ_{298.16}$ from C(c, graphite) and H_2(g), kcal/mole	$-\Delta H^\circ_{298.16}$ from C(g) and H(g), kcal	Sum of bond-energy values, kcal
CH_4	Methane	−17.889	397.9	398.0
C_2H_6	Ethane	−20.236	676.2	678.8
C_3H_8	Propane	−24.820	956.6	959.6
C_4H_{10}	*n*-Butane	−29.812	1237.5	1240.4
C_4H_{10}	2-Methylpropane	−31.452	1239.1	1240.4
C_5H_{12}	*n*-Pentane	−35.00	1518.6	1521.2
C_5H_{12}	2-Methylbutane	−36.92	1520.5	1521.2
C_5H_{12}	2,2-Dimethylpropane	−39.67	1523.2	1521.2
C_6H_{14}	*n*-Hexane	−39.96	1799.4	1802.0
C_7H_{16}	*n*-Heptane	−44.89	2080.2	2082.8
C_8H_{18}	*n*-Octane	−49.82	2361.0	2363.6
C_2H_4	Ethylene	+12.496	539.3	544.6
C_3H_6	Propene	+ 4.879	822.7	825.4
C_4H_8	1-Butene	+ 0.280	1103.2	1106.2
C_4H_8	*cis*-2-Butene	− 1.362	1104.9	1106.2
C_4H_8	*trans*-2-Butene	− 2.405	1105.9	1106.2
C_4H_8	2-Methyl-propene	− 3.343	1106.8	1106.2
C_5H_{10}	1-Pentene	− 5.000	1384.4	1387.0
C_5H_{10}	*cis*-2-Pentene	− 6.710	1386.1	1387.0
C_5H_{10}	*trans*-2-Pentene	− 7.590	1387.0	1387.0
C_5H_{10}	2-Methyl-1-butene	− 8.680	1388.1	1387.0
C_5H_{10}	3-Methyl-1-butene	− 6.920	1386.3	1387.0
C_5H_{10}	2-Methyl-2-butene	−10.170	1389.6	1387.0
C_6H_{12}	1-Hexene	− 9.96	1665.2	1667.8
C_7H_{14}	1-Heptene	−14.89	1946.0	1948.6
C_8H_{16}	1-Octene	−19.82	2226.8	2229.4
C_2H_2	Acetylene	+54.194	393.4	400.9
C_3H_4	Propyne	+44.319	679.1	681.7
C_4H_6	1-Butyne	+39.70	959.6	962.5
C_4H_6	2-Butyne	+35.374	964.0	962.5
C_5H_8	1-Pentyne	+34.50	1240.7	1243.3
C_5H_8	2-Pentyne	+30.80	1244.4	1243.3
C_5H_8	3-Methyl-1-butyne	+32.60	1242.6	1243.3
C_6H_{10}	1-Hexyne	+29.55	1521.5	1524.1
C_7H_{12}	1-Heptyne	+24.62	1802.3	1804.9
C_8H_{14}	1-Octyne	+19.70	2083.1	2085.7

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* The $\bar{H}^\circ_{298.16}$ values for the hydrocarbons in the ideal-gas state are taken from Selected Values of Properties of Hydrocarbons, *Natl. Bur. Standards Circ.* C461 (1947). The $-\Delta H^\circ_{298.16}$ values are derived from them by using the $\bar{H}^\circ_{298.16}$ values for C(g) and H(g) given in Table 4-1. The C—H, C—C, C═C, and C≡C bond-energy values used in computing the sum of bond energies are those given in Table 4-2.

The observed standard enthalpies of formation of the hydrocarbons, given with high precision in the first numerical column of Table 4-3, show that bond energies can be only approximately additive, so long as no account is taken of detailed structure. These enthalpies of formation are derived mainly from highly precise measurements of the heats of combustion by F. D. Rossini and his associates. For the alkane hydrocarbons, there appears to be a real decrease (algebraic) in the value of $\bar{H}^\circ_{298.16}$ with increased degree of chain branching; this indicates in a general way that the more compact molecules tend to have greater stability than their straight-chain isomers.[1] For the unsaturated hydrocarbons, the position of the unsaturated bond, as well as the general configuration of the molecule, has a measurable effect on the apparent bond energies; this is clearly shown, for example, in the precise values obtained by G. B. Kistiakowsky and his associates for the heats of hydrogenation of the isomeric butenes:[2]

$$C_4H_8(g) + H_2(g) = C_4H_{10}(g)$$

Isomer, C_4H_8	$\Delta H^\circ_{82^\circ C}$, kcal/mole
1-Butene	−30.341
cis-2-Butene	−28.570
trans-2-Butene	−27.621
2-Methylpropene	−28.389

Here, the product is identical for the hydrogenation of the first three isomers (*i.e.*, *n*-butane), but nevertheless significant differences exist in the thermal energy released as the unsaturated bond becomes saturated by taking up a pair of hydrogen atoms. For this reason, bond energies cannot be construed as strictly additive; their average values are undoubtedly useful, however, as approximate relative measures of chemical affinity.

Pauling has also discussed in detail the quantum-mechanical concept of resonance energy and has shown how this quantity may be estimated from simple thermochemical data. The classic example is provided by the benzene nucleus; the existence of resonance energy is indicated by a straightforward examination of the heats of hydrogenation of benzene and of its intermediate products, 1,3-cyclohexadiene and cyclohexene, as

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[1] This statement could be put in more precise form in terms of the free energy of formation, as discussed in Chap. 8, rather than in terms of the enthalpy of formation; but for closely related members of a homologous series such as this, the enthalpy values are at any rate indicative, if not definitive measures of relative instability. One should note also that the relative stabilities of the isomers may vary with the temperature.

[2] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.*, **57**, 876–882 (1935).

measured at 82°C by Kistiakowsky and his associates:[1]

$$C_6H_6(g) + 3H_2(g) = C_6H_{12}(g); \qquad \Delta H^\circ_{82^\circ C} = -49.802 \text{ kcal}$$
$$C_6H_8(g) + 2H_2(g) = C_6H_{12}(g); \qquad \Delta H^\circ_{82^\circ C} = -55.367 \text{ kcal}$$
$$C_6H_{10}(g) + H_2(g) = C_6H_{12}(g); \qquad \Delta H^\circ_{82^\circ C} = -28.592 \text{ kcal}$$

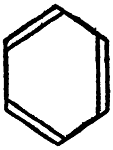
These data indicate that for the addition of the first pair of hydrogens to the cyclic benzene nucleus,

$$C_6H_6(g) + H_2(g) = C_6H_8(g); \qquad \Delta H^\circ_{82^\circ C} = +5.565 \text{ kcal}$$

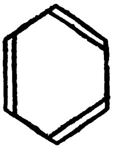
whereas for the addition of the second pair (*i.e.*, to 1,3-cyclohexadiene),

$$C_6H_8(g) + H_2(g) = C_6H_{10}(g); \qquad \Delta H^\circ_{82^\circ C} = -26.775 \text{ kcal}$$

Thus, the quantities of heat evolved when the second and the third pair of hydrogens are added have approximately the "normal" value for the addition of H_2 to the ordinary double bond, the heats of hydrogenation of the monoalkenes falling in the range 27 to 30 kcal/mole; but they differ radically, even to the extent of a reversal of sign, from the heat of hydrogenation for introduction of the first pair of hydrogens. Thus, as is well known, the conjugate bond system of the benzene ring, first postulated by A. Kekulé, is far more stable than one would expect from the consideration of ordinary alkene bonds, such as one finds in cyclohexene. In fact, if one compares the enthalpy of hydrogenation of benzene, −49.802 kcal (at 82°C), with three times the enthalpy of hydrogenation of cyclohexene, 3 × (−28.592) kcal, which is what one would expect for three independent alkene bonds, one obtains as a measure of the degree of stabilization in the benzene ring 35.97 kcal/mole. The exceptional stability of the benzene nucleus is attributed to resonance, involving mainly the two equivalent Kekulé structures:[2]



and



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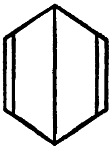
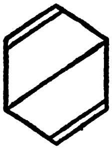
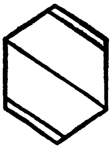
[1] *Ibid.*, **58**, 137–145, 146–153 (1936).

[2] The three equivalent Dewar structures







are supposed also to contribute to the normal state of the benzene molecule, but calculation shows that their energies are rather higher than those of the more stable Kekulé structures, and their contribution is therefore relatively slight.

These two structures differ from each other only in the distribution of certain electrons, but because of symmetry, their energies must be identical. In a situation like this, according to quantum mechanics, the actual normal state of the system consists of contributions from each such state of equal or nearly equal energy (there may in general be more than two such states), in the sense that if one makes repeated observations on the system, it will behave part of the times as though it were in one of the states and part of the times as though it were in the other, the probabilities being equal in a case such as this where there are two structures having exactly equal energies. The properties of the actual state, in other words, must be regarded as averages over such equivalent states contributing to the average state, but the actual state always possesses a lower energy than would be characteristic of the independent contributing states. This energy difference is called the *resonance energy* of the system; its existence permits the system to remain stable in a configuration which if it were not for resonance might have an appreciably higher energy. Thus, the resonance energy of benzene has the approximate empirical value 36 kcal/mole; Pauling has shown how a theoretical value in close agreement with this can be derived by a quantitative treatment of resonance from the point of view of the quantum theory of valence.[1]

The resonance energy associated with a given molecular structure may be determined empirically, of course, from bond-energy values. Thus, if one computes the enthalpy of formation of $C_6H_6(g)$ from C(g) and H(g) as in Table 4-3, starting with the experimental standard enthalpy of formation of $C_6H_6(g)$ from the elements in their ordinary standard states, $\bar{H}^\circ_{298.16} = 19.820$ kcal/mole, one obtains $-\Delta H^\circ_{298.16} = 1323.0$ kcal; whereas if one computes the sum of the bond energies according to either Kekulé structure, using the bond-energy values of Table 4-2, one obtains $6 \times 99.5 + 3 \times 81.8 + 3 \times 146.6 = 1282.2$ kcal, to which one must therefore add empirically 40.8 kcal/mole, representing resonance energy. The sum of the bond-energy values for the three equivalent Dewar structures, $6 \times 99.5 + 5 \times 81.8 + 2 \times 146.6 = 1299.2$ kcal, is slightly closer to the experimental result, and the fact that these structures contribute slightly to the normal state brings the empirical resonance-energy value down a little from what one would infer on the basis solely of the Kekulé structures. In applying covalent bond-energy values to estimate enthalpies of formation, one may therefore be quite in error if one overlooks the possibility of resonance stabilization; on the other hand, bond-energy data constitute in connection with empirical thermochemical data a simple and convenient means of testing proposed molecular structures and of detecting the existence of resonance energy.

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[1] Pauling, *op. cit.*, Chap. IV.

A different approach to the question of bonding energies is called for in the case of ionic compounds such as NaCl. Here, the electrostatic Coulomb forces of attraction and repulsion between the ions are of overwhelming importance. These forces, taken in connection with the spherical symmetry of the simpler types of ions and their established regular arrangement with respect to each other in the crystalline ionic compounds, are susceptible to exact theoretical treatment, leading to a reasonably satisfactory solution to the problem of the so-called *lattice energy,* the energy required to separate the ions from their normal distance in the crystal to an infinite distance apart [*e.g.*, the energy of the process, $NaCl(c) = Na^+(g) + Cl^-(g)$]. The theory has been developed through the work of many investigators, including in particular M. Born and his associates.[1] One assumes that the force holding the crystal together is the resultant of the Coulomb electrostatic forces, whose net effect is attractive, and a short-range interionic repulsive force, which is analogous to the van der Waals "b" effect, giving rise to finite ionic sizes or normal distance of closest approach between centers.[2] The potential energy of the entire crystal is then calculated by a summation over all ion pairs of the potential energy between a pair of ions. Now for diatomic crystals such as NaCl, MgO, CaF_2, Al_2O_3, etc., the total electrostatic potential energy per mole may always be expressed in the simple form

$$\bar{E}_e = -\frac{N_0 A e^2 z_+ z_-}{r_0} \tag{4-18}$$

where N_0 represents Avogadro's number, e the electron charge, z_+ and z_- the number of charge units on the cation and the anion (1 and 1 in the case of NaCl), r_0 the closest distance between centers of oppositely charged ions in the normal crystal lattice, and A a geometrical factor called the Madelung constant;[3] all interionic distances in a regular

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[1] M. Born and A. Landé, *Sitzber. preuss. Akad. Wiss., Physik.-Math. Klasse*, pp. 1048–1068 (1918); M. Born, *Ber. deut. physik. Ges.*, **20**, 224–229 (1918); M. Born and J. E. Mayer, *Z. Physik*, **75**, 1–18 (1932). The subject is reviewed by J. Sherman, *Chem. Rev.*, **11**, 93–170 (1932); excellent summaries are given by L. Pauling, "The Nature of the Chemical Bond," 2d ed., Chap. X, Cornell University Press, Ithaca, New York, 1940; R. C. Evans, "An Introduction to Crystal Chemistry," Chap. III, Cambridge University Press, New York, 1946; C. W. Stillwell, "Crystal Chemistry," Chap. VI, McGraw-Hill Book Company, Inc., New York, 1938; F. Seitz, "The Modern Theory of Solids," Chap. II, McGraw-Hill Book Company, Inc., New York, 1940.

[2] A more refined treatment by Born and Mayer, *loc. cit.*, takes account also of a van der Waals "a" effect of attraction between the ions; this, however, is much smaller than the Coulomb effect resulting directly from the ionic charges.

[3] E. Madelung, *Physik. Z.*, **19**, 524–532 (1918).

crystal lattice of a given type can be represented as more or less simple geometric functions of the single characteristic distance r_0, and the factor A arises when one sums the electrostatic potential energy between two ions over all possible interionic distances that may exist in the crystal. In the NaCl type of cubic lattice, for example, A has the value 1.7476; the value of this factor indicates that the average Coulomb electrostatic potential energy per ion pair in the NaCl type of lattice is about 75 per cent greater because of the influence of neighboring ions than the corresponding energy for an isolated pair of ions the same distance apart.[1] Values of A for other types of regular crystal structures are given in Table 4-4. The repulsive energy per mole, which prevents the crystal from collapsing altogether under the net attraction of the Coulomb forces, was originally assumed by Born and Landé to have the form

$$\bar{E}_r = \frac{B}{r_0^n} \tag{4-19}$$

where B and n are constants for the particular kind of crystal; if we assume that only nearest neighboring ions contribute significantly to $\bar{E}_r$, then Eq. (4-19) implies that individual ions repel each other with a force proportional to $1/r^{n+1}$. The value of n can be inferred from measurements of the coefficient of compressibility of the crystal; for most cubic ionic crystals, its value is about 9, but it varies with the size of the ions involved, being about 7 for ions of the Ne type and about 10 for ions of the Kr type,

TABLE 4-4. MADELUNG CONSTANTS*

Structure	A	N_0Ae^2, 10^2 kcal Å/mole
NaCl	1.747558	5.8019
CsCl	1.762670	5.8521
Wurtzite	1.641	5.448
Fluorite	2.51939	8.3644
Cuprite	2.05776	6.8318
Rutile	2.408	7.995
Corundum	4.17187	13.8506

* Values in the last column are computed with $N_0 = 6.0228 \times 10^{23}$/mole, $e = 4.8024 \times 10^{-10}$ esu, and with the conversion factor (1 kcal/4.1840×10^{10} erg) × 10^8Å/cm. The values of A given in Table 4-4 apply to Eq. (4-21) when r_0 represents the mean distance between closest ions of opposite sign; values may also be computed with r_0 standing for any other convenient geometrical function of this mean ionic "diameter," *e.g.*, the lattice constant itself, for cubic crystals.

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[1] The mathematical methods developed by E. Madelung, P. P. Ewald, M. Born, and others for the calculation of Madelung constants are briefly described by J. Sherman, *loc. cit.;* see also H. M. Evjen, *Phys. Rev.*, **39**, 675–687 (1932). See Prob. 2–17.

as seen in Table 4-5. The value of B can be found through the condition that the equilibrium distance r_0 must be such as to make the sum of $\bar{E}_e$ and $\bar{E}_r$ a minimum with respect to variations in r_0; thus

$$\frac{N_0Ae^2z_+z_-}{r_0^2} - \frac{nB}{r_0^{n+1}} = 0; \qquad B = N_0Ae^2z_+z_-\frac{r_0^{n-1}}{n}$$

Therefore the total potential energy per mole has the form

$$\bar{E}_e + \bar{E}_r = -\frac{N_0Ae^2z_+z_-}{r_0}\left(1 - \frac{1}{n}\right) \tag{4-20}$$

This represents the molal internal energy of the crystal relative to a state of complete separation of the independent ions ($r_0 \rightarrow \infty$); thus

$$\Delta U_0^\circ = \frac{N_0Ae^2z_+z_-}{r_0}\left(1 - \frac{1}{n}\right) \tag{4-21}$$

represents the energy required in order to separate the crystal into independent gas ions, *i.e.*, in the case of NaCl, the internal-energy change accompanying the reaction

$$\mathrm{NaCl(c)} = \mathrm{Na^+(g)} + \mathrm{Cl^-(g)} \tag{4-22}$$

TABLE 4-5. VALUES OF BORN EXPONENTS n*

Ion Type	n
He	5
Ne	7
A, Cu^+	9
Kr, Ag^+	10
Xe, Au^+	12

* From L. Pauling, "The Nature of the Chemical Bond," 2d ed., p. 339, Cornell University Press, Ithaca, New York, 1940. For two ions of different types, the average value of n is taken, *e.g.*, for KF, $n = 8.0$.

at 0°K. At ordinary temperatures, a correction should be introduced to take account of the thermal motion of the ions in the crystal as compared with the ideal-gas state, but up to 25°C, this correction amounts to but a few tenths of a kcal.[1] One sees that with n having a value of order 9, the Coulomb electrostatic energy accounts for approximately 90 per cent of the total, the balance being contributed by the interionic repulsive energy. In the case of NaCl, with $r_0 = 2.814$ Å and $n = 8$, the value of the lattice energy calculated according to Eq. (4-21) from the appropriate value of the Madelung constant is 180.4 kcal/mole; in the case of KI, with $r_0 = 3.526$ Å and $n = 10.5$, $\Delta U_0^\circ = 148.9$ kcal/mole. Lattice energies

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[1] The value of r_0 introduced in Eq. (4-21) should correspondingly be the equilibrium interionic distance between nearest ions of opposite charge at 0°K, but this too differs but slightly from the value at room temperature.

computed for a number of other ionic compounds are given in Tables 4-6 to 4-8; one will note that the only information about the crystal one needs in order to compute the value of ΔU_0° by the Born theory is its general structure and value of r_0, as given by X-ray analysis, together with the value of the Born-Landé repulsive force exponent n, which depends merely on the sizes of the ions concerned.

The value of ΔU_0° cannot be directly measured by thermochemical means, but it may be computed from thermochemical data available for a series of intermediate steps, as shown originally by M. Born and by F. Haber.[1] In order to work with the enthalpy function, in terms of which the thermochemical data are generally expressed, let us first write for a reaction such as (4-22)

$$\begin{aligned} \Delta H &= \Delta U + \Delta(pV) \\ &= \Delta U + \zeta RT \end{aligned}$$

where ζ represents the number of ions corresponding to the formula; thus, for NaCl, neglecting the correction of ΔU_0° itself to room temperature, but taking the 25°C value for the term $2RT$,

$$\Delta H_{298.16}^\circ = \Delta U_0^\circ + 1.2 \text{ kcal} \quad (\text{NaCl, etc.}; \zeta = 2)$$

Now, the reaction (4-22) to which the value of ΔU_0° applies may be brought about in principle through the following chain of independent steps:

$$\begin{array}{lrll} (1) & NaCl(c) = & Na(c) + \tfrac{1}{2}Cl_2(g); & \Delta H^\circ = -(\bar{H}_{298.16}^\circ)_{NaCl(c)} \\ (2) & Na(c) = & Na(g); & \Delta H^\circ = (\bar{L}_{cg})_{Na} = (\bar{H}_{298.16}^\circ)_{Na(g)} \\ (3) & \tfrac{1}{2}Cl_2(g) = & Cl(g); & \Delta H^\circ = (\bar{H}_{298.16}^\circ)_{Cl(g)} \\ (4) & Na(g) = & Na^+(g) + e; & \Delta H^\circ = I_{Na} \\ (5) & Cl(g) + e = & Cl^-(g); & \Delta H^\circ = -\epsilon_{Cl} \end{array}$$

The first of these steps represents simply the reverse of the formation of NaCl(c) from its elements in their ordinary standard states; its enthalpy is equal to the standard heat of formation of the compound, or the negative of its standard enthalpy of formation. The second step represents the sublimation of Na(c); its enthalpy at 298.16°K is derived essentially by means of the Clapeyron equation [Eq. (6-68)] and Eq. (3-48) from vapor-pressure measurements at higher temperatures. The third step represents the dissociation of $Cl_2(g)$ into atoms; its enthalpy at 298.16°K is derived both from spectroscopic indication of the dissociation energy of Cl_2 molecules, and from equilibrium data at high temperatures by extrapolation. The data needed for steps 2 and 3 are included in Table 4-1, which gives the standard enthalpies of formation of elements

[1] M. Born, *Ber. deut. physik. Ges.*, **21**, 13–24 (1919); F. Haber, *ibid.*, 750–768 (1919).

in the form of monatomic gases, as derived from the appropriate experimental evidence. If one adds steps 1, 2, and 3, one obtains, for the dissociation of the crystal into its gaseous *atoms*,

$$\mathrm{NaCl(c)} = \mathrm{Na(g)} + \mathrm{Cl(g)}; \qquad \Delta H^\circ = -(\bar{H}^\circ_{298.16})_{\mathrm{NaCl(c)}} + (\bar{H}^\circ_{298.16})_{\mathrm{Na(g)}} + (\bar{H}^\circ_{298.16})_{\mathrm{Cl(g)}} \quad (4\text{-}23)$$

This quantity has been tabulated in the ninth column of Tables 4-6 and 4-7, and in the eighth column of Table 4-8. Step 4 represents the ionization of Na(g), and I_{Na} the ionization potential of Na(g) (expressed in thermochemical units); the value of this quantity is known with high precision, both from analysis of the Na(g) spectrum and from direct resonance potential measurements on sodium vapor. The value of ϵ_{Cl} in step 5 is called the electron affinity of Cl; it represents the energy released per mole when gas ions are formed out of Cl(g) atoms, or what is equivalent, the ionization potential of $\mathrm{Cl^-(g)}$. For most anions, no way has been found to measure this quantity by direct independent means; in the case of $\mathrm{O^=}$, for example, its value is apparently negative and large in magnitude (Table 4-7), which means that $\mathrm{O^=(g)}$ could be produced from O(g) only with the absorption of a considerable quantity of energy. The theory has therefore generally been tested by the consistency with which the theoretical and the thermochemical data can be correlated upon the assignment of a suitable constant value to ϵ for a given anion throughout a series of its compounds. Thus, in the case of NaCl, we may compute the value of ϵ_{Cl} by difference from the equation

$$\Delta U^\circ_0 + 1.2\ \mathrm{kcal} = -(\bar{H}^\circ_{298.16})_{\mathrm{NaCl(c)}} + (\bar{H}^\circ_{298.16})_{\mathrm{Na(g)}} + (\bar{H}^\circ_{298.16})_{\mathrm{Cl(g)}} + I_{\mathrm{Na}} - \epsilon_{\mathrm{Cl}} \quad (4\text{-}24)$$

using the Born-Landé theoretical value of ΔU°_0; all the other terms in this equation are known from experiment. The values of I and ϵ refer to 0°K, but the correction to 298.16°K may be neglected. In Table 4-6, electron affinities for the halogen atoms and hydrogen have been so computed by difference from Born-Landé theoretical lattice energies and thermochemical data for the alkali halides and hydrides; one sees that in view of the extreme simplicity of the theoretical assumptions, the consistency of these data is excellent. In Table 4-7, similar data are presented for various oxides, sulfides, and selenides, leading to electron-affinity values for O, S, and Se; while there is evidence from other sources that capture of the first electron by these atoms is an exothermic process, capture of the second electron is evidently highly endothermic. In Table 4-8, values of ΔU°_0 (experimental) for certain other fluorides are computed from thermochemical data with $\epsilon_F = 96.3$ kcal/g-atom as derived from the data for the alkali fluorides, and these values are compared with ΔU_0° (theoretical) computed according to the Born-Landé theory; one sees that the agreement is in general quite good.

In the particular cases of Cl, Br, and I, the electron affinities have been directly measured by experiments ingeniously conceived by J. E. Mayer and his associates.[1] Equilibrium for the reaction

$$\mathrm{KI(g)} = \mathrm{K^+(g)} + \mathrm{I^-(g)} \tag{4-25}$$

was determined directly from measurements of the electrical conductivity of KI vapor at high temperatures (around 1000°K), and from the general thermodynamic relation between the variation of the equilibrium constant with temperature and the enthalpy of reaction (Chap. 8) the enthalpy of the gas reaction (4-25) was thus directly measured; by combining this information with the latent heat of sublimation of KI(c), and the thermochemical information corresponding to the reaction of the type (4-23), the value of $I_\mathrm{K} - \epsilon_\mathrm{I}$ was thereby experimentally established in terms of straightforward chemical thermodynamic data. The method was applied also to CsI, NaCl, and RbBr, and from the known ionization potentials of the metals, the values of ϵ for Cl, Br, and I were determined. The electron affinity of iodine was also determined independently from measurements of equilibrium (ratio of electron to negative ion emission from a W filament at 2000°K in I(g) at low pressure) for the process

$$\mathrm{I^-(g)} = \mathrm{I(g)} + e\mathrm{(g)}$$

The results of these experimental determinations are as follows:

$$\epsilon_{\mathrm{Cl}} = 88.3 \text{ kcal/g-atom}$$
$$\epsilon_{\mathrm{Br}} = 84.2 \text{ kcal/g-atom}$$
$$\epsilon_{\mathrm{I}} = 72.4 \text{ kcal/g-atom}$$

The value for I is rather lower than the value deduced from the Born-Landé theory in Table 4-6, but improvement in the theory by Born and Mayer, involving the use of an exponential instead of an inverse nth power repulsive-energy term and the introduction of a van de Waals term in addition to the Coulomb attractive energy, has resulted in closer agreement.[2]

We may conclude that the theory of ionic crystal lattice energies is in excellent shape. The theory accounts successfully for the relative stabil-

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[1] J. E. Mayer, *Z. Physik*, **61**, 798–804 (1930); L. Helmholtz and J. E. Mayer, *J. Chem. Phys.*, **2**, 245–251 (1934); P. P. Sutton and J. E. Mayer, *ibid.*, **3**, 20–28 (1935).

[2] M. Born and J. E. Mayer, *Z. Physik*, **75**, 1–18 (1932); see also J. E. Mayer and L. Helmholz, *ibid.*, 19–29; J. E. Mayer and M. M. Maltbie, *ibid.*, 748–752; J. E. Mayer, *J. Chem. Phys.*, **1**, 270–279 (1933).

TABLE 4-6. LATTICE ENERGIES OF THE ALKALI HALIDES AND HYDRIDES, AND ELECTRON AFFINITIES OF THE HALOGEN ATOMS AND OF HYDROGEN

Compound	Type of crystal structure	$AN_0e^2z_+z_-$, 10^2 kcal Å/mole	r_0, Å	n	ΔU_0° (theo.), kcal/mole	ΔH°_{298} (theo.), crystal to gas ions, kcal/mole	$-\bar{H}^\circ_{298}$, (thermochem.), kcal/mole	ΔH°_{298}, crystal to gas atoms, kcal/mole	I, metal gas atoms to gas ions, kcal	ϵ (calc.), kcal/g-atom
LiF	NaCl	5.8019	2.01	6.0	241.1	242.3	146.3	215.6	124.3	97.6
NaF	NaCl	5.8019	2.31	7.0	215.3	216.5	136.0	194.2	118.5	96.2
KF	NaCl	5.8019	2.67	8.0	190.5	191.7	134.5	188.3	100.1	96.7
RbF	NaCl	5.8019	2.82	8.5	181.9	183.1	131.3	184.1	96.4	97.4
CsF	NaCl	5.8019	3.00	9.5	172.8	174.0	126.9	178.0	89.9	93.9
LiCl	NaCl	5.8019	2.565	7.0	193.9	195.1	97.7	163.8	124.3	93.0
NaCl	NaCl	5.8019	2.814	8.0	180.4	181.6	98.2	153.2	118.5	90.1
KCl	NaCl	5.8019	3.14	9.0	164.2	165.4	104.2	154.7	100.1	89.8
RbCl	NaCl	5.8019	3.286	9.5	158.0	159.2	102.9	152.4	96.4	89.6
CsCl	CsCl	5.8521	3.559	10.5	148.8	150.0	103.5	151.3	89.9	91.2
LiBr	NaCl	5.8019	2.75	7.5	183.2	184.4	83.7	147.5	124.3	87.4
NaBr	NaCl	5.8019	2.98	8.5	171.8	173.0	86.0	138.7	118.5	85.4
KBr	NaCl	5.8019	3.29	9.5	157.8	159.0	93.7	141.9	100.1	83.0
RbBr	NaCl	5.8019	3.43	10.0	152.1	153.3	93.0	140.2	96.4	83.3
CsBr	CsCl	5.8521	3.71	11.0	143.3	144.5	94.3	139.8	89.9	85.2
LiI	NaCl	5.8019	3.00	8.5	170.6	171.8	64.8	127.4	124.3	79.9
NaI	NaCl	5.8019	3.23	9.5	160.7	161.9	68.8	120.3	118.5	76.9
KI	NaCl	5.8019	3.53	10.5	148.9	150.1	78.3	125.3	100.1	75.3
RbI	NaCl	5.8019	3.66	11.0	144.0	145.2	78.5	124.5	96.4	75.7
CsI	CsCl	5.8521	3.95	12.0	135.8	137.0	80.5	124.8	89.9	77.7
LiH	NaCl	5.8019	2.04	5.0	227.2	228.4	21.6	110.8	124.3	17.2
NaH	NaCl	5.8019	2.44	6.0	198.1	199.3	13.7	91.8	118.5	11.0
KH	NaCl	5.8019	2.85	7.0	174.5	175.7	13.6	87.2	100.1	11.6
RbH	NaCl	5.8019	3.02	7.5	166.6	167.8	12	85	96.4	14
CsH	NaCl	5.8019	3.19	8.5	160.6	161.8	12	83	89.9	12

TABLE 4-7. LATTICE ENERGIES OF OXIDES, SULFIDES, AND SELENIDES

Compound	Type of crystal structure	$An_0e^2z_+z_-$, 10^2 kcal Å/mole	r_0, Å	n	ΔU_0° (theo.), kcal/mole	ΔH_{298}° (theo.), crystal to gas ions, kcal/mole	$-\bar{H}_{298}^\circ$ (thermochem.), kcal/mole	ΔH_{298}°, crystal to gas atoms, kcal/mole	I, metal gas atoms to gas ions, kcal	ϵ (calc.), kcal/g-atom
Li_2O	Fluorite	16.729	2.00	6.0	697.0	698.8	142.4	275.2	248.6	−175.0
Na_2O	Fluorite	16.729	2.78	7.0	515.8	517.6	99.4	210.0	237.0	− 70.6
Cu_2O	Cuprite	13.663	1.84	8.0	649.7	651.5	39.8	261.4	356.8	− 33.0
Ag_2O	Cuprite	13.663	2.05	8.5	588.1	589.9	7.3	204.1	349.3	− 36.5
MgO	NaCl	23.208	2.10	7.0	946.3	947.5	143.8	238.3	522.8	−186.4
CaO	NaCl	23.208	2.40	8.0	846.8	848.0	151.9	256.5	414.6	−176.9
SrO	NaCl	23.208	2.55	8.5	803.0	804.2	141.1	238.9	385.6	−179.7
BaO	NaCl	23.208	2.75	9.5	755.1	756.3	133.4	234.0	350.8	−171.5
MnO	NaCl	23.208	2.22	8.0	914.7	915.9	92.0	218.9	531.9	−165.1
FeO	NaCl	23.208	2.14	8.0	948.1	949.3	63.7	219.0	551.0	−179.3
NiO	NaCl	23.208	2.09	8.0	973.5	974.7	58.4	218.6	596.3	−159.8
ZnO	Wurtzite	21.79	1.94	8.0	982.9	984.1	83.2	173.0	630.7	−180.4
CdO	NaCl	23.208	2.35	8.5	871.4	872.6	60.9	146.5	597.2	−128.9
PbO_2	Rutile	63.956	2.16	9.5	2649.2	2650.0	66.1	229.6	2231.7	− 94.4
Al_2O_3	Corundum	83.103	1.99	7.0	3654.0	3657.0	399.1	724.9	2456.0	−158.7
Na_2S	Fluorite	16.729	2.83	8.0	517.6	519.4	89.2	194.5	237.0	− 87.9
MgS	NaCl	23.208	2.60	8.0	781.0	782.2	83.0	172.2	522.8	− 87.2
CaS	NaCl	23.208	2.84	9.0	726.4	727.6	115.3	214.6	414.6	− 98.4
SrS	NaCl	23.208	3.00	9.5	692.2	693.4	108.1	200.6	385.6	−107.2
BaS	NaCl	23.208	3.18	10.5	660.3	661.5	106.0	201.3	350.8	−109.4
CaSe	NaCl	23.208	2.96	9.5	701.5	702.7	74.7	169.1	414.6	−119.0
SrSe	NaCl	23.208	3.11	10.0	671.6	672.8	78.7	166.3	385.6	−120.9
BaSe	NaCl	23.208	3.29	11.0	641.3	642.5	74.2	164.6	350.8	−127.1

ity of existing crystal structures and for the instability of hypothetical alternative structures.[1] It has been applied also in certain cases to demonstrate that the chemical binding may be partially covalent in character, rather than typically ionic; this appears to be true, for example, of AgI and CuI.[2] We shall return to the lattice energy theory in Chap. 9 (Sec. 9-4) in order to discuss its bearing on the relative magnitudes of standard electrode potentials in theoretical electrochemistry.

4-5. Heat and Enthalpy of Solution. The formation of a solution from its pure components, like a chemical transformation in the ordinary sense, is generally accompanied by exchange of energy with the surroundings. Since however, the proportions of the components can be varied, the quantity of energy released or absorbed is in general a function of the composition, whose form cannot be deduced from purely thermodynamic reasoning but must be established in particular cases by empirical observation or per-

TABLE 4-8. THEORETICAL AND EXPERIMENTAL LATTICE ENERGIES OF FLUORIDES

Compound	Type of crystal structure	$AN_0e^2z_+z_-$, 10^2 kcal Å/mole	r_0, Å	n	ΔU_0° (theo.), kcal/mole	$-\bar{H}_{298}$ (thermochem.), kcal/mole	ΔH_{298}°, crystal to gas atoms, kcal/mole	I, metal gas atoms to gas ions, kcal/g-atom	ϵ, $F(g) + e \rightarrow F^-(g)$, kcal	ΔH_{298}°, crystal to gas ions, kcal/mole	ΔU_0° (exp), kcal/mole
AgF	NaCl	5.8019	2.46	8.5	208.1	48.5	149.9	174.7	96.3	228.3	227.1
MgF_2	Rutile	15.989	1.96	7.0	699.2	263.5	363.9	522.8	192.6	694.1	692.3
CaF_2	Fluorite	16.729	2.36	8.0	620.2	290.3	400.8	414.6	192.6	622.8	621.0
SrF_2	Fluorite	16.729	2.54	8.5	581.8	290.3	394.0	385.6	192.6	587.0	585.2
BaF_2	Fluorite	16.729	2.68	9.5	558.9	286.9	393.4	350.8	192.6	551.6	549.8
NiF_2	Rutile	15.989	2.00	8.0	699.5	159.5	325.6	596.3	192.6	729.3	727.5
PbF_2	Fluorite	16.729	2.57	9.5	589.4	158.5	269.3	517.6	192.6	594.3	592.5

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[1] H. G. Grimm and K. F. Herzfeld, *Z. Physik*, **19**, 141–166 (1923), have accounted for the nonexistence of such hypothetical compounds as NeCl, $NaCl_2$, $MgCl_3$, etc., by showing that they would have large positive standard enthalpies of formation, based on reasonably assumed crystal structures; it turns out that $MgCl_2(c)$ is considerably more stable, by similar reasoning, than the hypothetical compound MgCl(c) would be; see also H. G. Grimm, *Z. Elektrochem.*, **34**, 430–437 (1928).

[2] J. E. Mayer, *J. Chem. Phys.*, **1**, 327–334 (1933); J. E. Mayer and R. B. Levy, *ibid.*, 647–648.

haps by theory based on extrathermodynamic evidence. In the case of binary solutions, particularly where water is one of the components, it has become the custom to represent the heat of solution, or quantity of heat evolved when the solution is prepared from its pure components, with reference to *one mole* of the one component, A, taken as solute; the so-called *integral molal heat of solution*, $\bar{Q}_s$, is then regarded as a function of n_1, the number of moles of the other component, S (*e.g.*, H_2O), taken as *solvent*. In other words, one divides the observed quantity of heat, as obtained by straightforward calorimetry for the mixing of arbitrary quantities of the two components, by the number of moles of the component regarded as the solute, and repeats the observations, varying the proportion of solvent to solute, so as to obtain a series of $\bar{Q}_s$ values corresponding to various values of n_1, the number of moles of solvent per mole of solute. Since one customarily measures heats of solution at or corrects them to conditions of uniform temperature and pressure throughout, the value of $-\bar{Q}_s$ represents in accordance with the general thermodynamic relation, Eq. (3-36), an enthalpy change corresponding to the process

$$A + n_1S = A(n_1S); \qquad \Delta H = H - n_1\bar{H}_1^\circ - \bar{H}_2^\circ = -\bar{Q}_s \qquad (4\text{-}26)$$

where H represents the enthalpy of the solution, per mole of A present, and $\bar{H}_1^\circ$ and $\bar{H}_2^\circ$ denote, respectively, the molal enthalpies of the pure solvent and pure solute at the given temperature and pressure. There is no distinction on purely thermodynamic grounds between solvent and solute; the choice affects the form in which one represents the experimental data, but is quite arbitrary, depending merely on one's point of view. Essentially, H is an extensive property of the solution, which for fixed temperature, pressure, and composition can vary only in direct proportion to the total mass.

In Table 4-9, data are presented for solutions of $H_2SO_4(l)$ in $H_2O(l)$ at 25°C and 1 atm, while in Table 4-10, similar data are presented for solutions of $HCl(g)$ in $H_2O(l)$.[1] With increasing n_1, the value of $\bar{Q}_s$ generally approaches asymptotically a terminal limit, $\bar{Q}_s^\circ$, called the *total molal heat of solution* or *heat of solution at infinite dilution* of the substance A in the solvent S. This quantity is of course a property of the particular solute and solvent, at given temperature and pressure; its value for $H_2SO_4(l)$ in water, derived by extrapolation of the experimental data obtained at finite solute concentrations, is given in parentheses at the bottom of the second column in Table 4-9. The range of dilute compositions over which $\bar{Q}_s$ differs insensibly from $\bar{Q}_s^\circ$ depends on the particular pair of

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[1] From "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D.C., 1947.

TABLE 4-9. HEAT OF SOLUTION, $H_2SO_4(l)$ IN $H_2O(l)$, AT 25°C AND 1 ATMOSPHERE*

$$H_2SO_4(l) + n_1H_2O(l) = H_2SO_4(n_1H_2O)$$

n_1, mole H_2O/ mole H_2SO_4	$\bar{Q}_s$, kcal/ mole H_2SO_4	Φ_h, kcal/ mole H_2SO_4	$\Phi_h - \overset{\circ}{\Phi}_h$, kcal/ mole H_2SO_4
0.0	......	−193.91	22.99
0.5	3.76	−197.67	19.23
1.0	6.71	−200.62	16.28
1.5	8.82	−202.73	14.17
2	10.02	−203.93	12.97
3	11.71	−205.62	11.28
4	12.92	−206.83	10.07
5	13.87	−207.78	9.12
6	14.52	−208.43	8.47
7	15.04	−208.95	7.95
8	15.44	−209.35	7.55
10	16.02	−209.93	6.97
12	16.41	−210.32	6.58
15	16.77	−210.68	6.22
20	17.09	−211.00	5.90
25	17.28	−211.19	5.71
30	17.37	−211.28	5.62
40	17.47	−211.38	5.52
50	17.53	−211.44	5.46
75	17.61	−211.52	5.38
100	17.68	−211.59	5.31
200	17.91	−211.82	5.08
300	18.09	−212.00	4.90
400	18.22	−212.13	4.77
500	18.34	−212.25	4.65
600	18.44	−212.35	4.55
700	18.54	−212.45	4.45
800	18.63	−212.54	4.36
900	18.71	−212.62	4.28
1,000	18.78	−212.69	4.21
2,000	19.33	−213.24	3.66
3,000	19.72	−213.63	3.27
4,000	19.99	−213.90	3.00
5,000	20.18	−214.09	2.81
6,000	20.34	−214.25	2.65
7,000	20.47	−214.38	2.52
8,000	20.60	−214.51	2.39
9,000	20.71	−214.62	2.28
10,000	20.81	−214.72	2.18
15,000	21.18	−215.09	1.81
20,000	21.42	−215.33	1.57
30,000	21.73	−215.64	1.26
40,000	21.93	−215.84	1.06
50,000	22.07	−215.98	0.92
70,000	22.24	−216.15	0.75
100,000	22.38	−216.29	0.61
200,000	22.59	−216.50	0.40
500,000	22.78	−216.69	0.21
∞	(22.99)	−216.90	0.00

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* SOURCE: "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D.C., Sept. 30, 1947.

TABLE 4-10. HEAT OF SOLUTION, HCl(g) IN $H_2O(l)$, AT 25°C AND 1 ATMOSPHERE*

$$HCl(g) + n_1H_2O(l) = HCl(n_1H_2O)$$

n_1, mole H_2O/ mole HCl	$\bar{Q}_s$, kcal/ mole HCl	Φ_h, kcal/ mole HCl	$\Phi_h - \Phi_h^\circ$, kcal/ mole HCl
0	....	−22.063	17.960
1	6.268	−28.331	11.692
2	11.668	−33.731	6.292
3	13.588	−35.651	4.372
4	14.628	−36.691	3.332
5	15.308	−37.371	2.652
6	15.748	−37.811	2.212
8	16.308	−38.371	1.652
10	16.608	−38.671	1.352
12	16.784	−38.847	1.176
15	16.967	−39.030	0.993
20	17.155	−39.218	0.805
25	17.272	−39.335	0.688
30	17.350	−39.413	0.610
40	17.453	−39.516	0.507
50	17.514	−39.577	0.446
75	17.602	−39.665	0.358
100	17.650	−39.713	0.310
200	17.735	−39.798	0.225
300	17.774	−39.837	0.186
400	17.796	−39.859	0.164
500	17.811	−39.874	0.149
700	17.832	−39.895	0.128
1,000	17.850	−39.913	0.110
2,000	17.883	−39.946	0.077
3,000	17.897	−39.960	0.063
4,000	17.905	−39.968	0.055
5,000	17.909	−39.972	0.051
7,000	17.919	−39.982	0.041
10,000	17.924	−39.987	0.036
20,000	17.935	−39.998	0.025
50,000	17.944	−40.007	0.016
100,000	17.949	−40.012	0.011
∞	(17.960)	−40.023	0.000

* SOURCE: "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D.C., Mar. 31, 1947.

components involved. Thus for H_2SO_4 in H_2O, a significant difference persists even at dilutions beyond $n_1 = 20{,}000$ moles H_2O/mole H_2SO_4, whereas for HCl in H_2O, the difference is less than 0.2 kcal/mole at dilutions beyond $n_1 = 400$ moles H_2O/mole HCl; the difference in the case of H_2SO_4 is no doubt associated with the progress of secondary ionization in the dilute range. We shall see in Sec. 7-3 that $\bar{Q}_s = \bar{Q}_s^\circ$ so long as the solvent satisfies Raoult's law, in the so-called ideal dilute solution; in fact, if both components satisfy Raoult's law and form solutions ideal over the entire composition range, then $\bar{Q}_s = 0$ for all compositions.

Now, aside from being interested in the heat of solution itself, because of its bearing on problems of heat transfer that may arise in chemical technology (*e.g.*, the removal of the heat released when sulfuric acid is diluted with water on a large scale), we are interested also in heats of chemical reactions involving one or more components present in solution, *e.g.*, reactions involving H_2SO_4 in aqueous solution. Two special situations call for our attention. We shall discuss them separately in the paragraphs immediately following.

In one situation commonly encountered, a substance A in solution, present originally at concentration $1:n_1$, is practically completely removed as a result of the reaction. If, for example, excess Zn(c) is added to $H_2SO_4(100\ H_2O)$, then the H_2SO_4 disappears practically completely from the solution, and is replaced by an equivalent quantity of $ZnSO_4$. In this case, it is evident according to the first law of thermodynamics that the substance A will contribute to the enthalpy of reaction a term equal to its standard molal enthalpy of formation in the pure state, less its integral molal heat of solution corresponding to the given initial concentration. Let us denote this term by the symbol Φ_h,

$$\Phi_h \equiv \bar{H}_2^\circ - \bar{Q}_s \qquad (T,\ p\ \text{const}) \qquad (4\text{-}27)$$

Then it follows from Eq. (4-26) that

$$\Phi_h = H - n_1\bar{H}_1^\circ \qquad (4\text{-}28)$$

that is, Φ_h represents the difference between the enthalpy of the solution, per mole of solute present, and the enthalpy of the pure solvent; it is called the *apparent molal enthalpy* of the solute. In the situation under consideration, to treat the solvent in solution as though it had the same enthalpy as in the pure state is an entirely consistent procedure, inasmuch as the reaction effects a complete separation between the solute (which is consumed by the reaction) and the solvent. Similar reasoning shows that Φ_h likewise represents the contribution per mole of A to the enthalpy of a reaction in which A appears as a product in solution at the ultimate concentration $1:n_1$, no A being originally present. Thus, we may write for the reaction between excess Zn(c) and $H_2SO_4(100\ H_2O)$, bearing in mind that the standard enthalpies of the elements in their normal allotropic forms are taken by convention to be zero,

$$\mathrm{Zn(c)} + \mathrm{H_2SO_4(100\ H_2O)} = \mathrm{ZnSO_4(100\ H_2O)} + \mathrm{H_2(g)};$$
$$\Delta H = (\Phi_h)_{\mathrm{ZnSO_4}} - (\Phi_h)_{\mathrm{H_2SO_4}} \qquad (4\text{-}29)$$

where in this case, both Φ_h values refer to the same stoichiometric concentration, $1:100\ H_2O$. Values of the quantity Φ_h are commonly tabulated directly in thermochemical tables, for various values of n_1, as the *enthalpy of formation in solution* of the substance A in the given solvent S. Such values are given in the third columns of Tables 4-9 and 4-10.[1] It is obvious that in order to construct a table of Φ_h values, one must have in addition to the heats of solution, the heat of some chemical transformation involving the compound, either in the pure state or in solution at a given concentration, with other substances whose standard enthalpies of formation have been established. In fact, the direct measurement of the heat of the reaction (4-29), combined with measurement of the heat of solution of $ZnSO_4(c)$, serves as one experimental method of establishing the value of $\bar{H}^\circ_{\mathrm{ZnSO_4(c)}}$, in relation to the independently established value of $(\Phi_h)_{\mathrm{H_2SO_4}}$.

The terminal value of Φ_h for a given solute at sufficiently dilute concentration in a given solvent is obtained from the total molal heat of solution, $\bar{Q}^\circ_s$, in accordance with the definition (4-27),

$$\Phi^\circ_h = \lim_{n_1 \to \infty} \Phi_h = \bar{H}^\circ_2 - \bar{Q}^\circ_s \qquad (4\text{-}30)$$

This is a characteristic property of the solute in the particular solvent at given temperature and pressure, independent of concentration, and is known as the *standard enthalpy of formation in solution* of the solute in the given solvent. For reasons that we shall discuss at length in Chap. 7, it is convenient for us to adopt as the standard reference state of a substance A in solution in a given solvent S, a hypothetical ideal dilute solu-

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[1] It is actually in such form, Φ_h values for selected values of n_1, that the thermochemical data for solutions, such as are represented in Tables 4-9 and 4-10, appear in the definitive compilation by the National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties." We have calculated the $\bar{Q}_s$ values given in Tables 4-9 and 4-10 by difference according to Eq. (4-27), for our purpose, though of course the original experimental data from which the tables in "Selected Values" were compiled consist essentially of $\bar{Q}_s$ measurements. In the older compilation by F. R. Bichowski and F. D. Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corporation, New York, 1936, the thermochemical data for substances in solution are tabulated in terms of $-\Phi_h$, the molal *heat* of formation in solution, for selected values of n_1.

tion at some specified finite concentration (generally 1 mole per kg of solvent, when the solvent happens to be water), in which the substance would have the same Φ_h value as at infinite dilution, namely, Φ_h°; the solvent is then supposed to have the same enthalpy as in the pure state, namely, $\bar{H}_1^\circ$. The reason for specifying a finite concentration for the hypothetical reference state, instead of merely the infinitely dilute solution itself, is that certain other important thermodynamic properties of the solute based on the second law of thermodynamics, while satisfying well-established empirical laws in the ideal dilute range, fail to remain finite as the solute concentration approaches zero. A similar situation is encountered in the behavior of pure gases; the values of $\bar{H}_T$ and $\bar{U}_T$, as well as of $\bar{C}_p$ and $\bar{C}_v$, approach finite limits as $p \rightarrow 0$, but the important entropy and free-energy functions introduced in Chap. 5 increase and decrease, respectively, without limit as $p \rightarrow 0$; therefore it is convenient to refer the thermodynamic properties to a hypothetical ideal-gas state at $p = 1$ atm, as shown in Sec. 6-1. The standard state of a solute in aqueous solution is generally indicated by the symbol (aq), *e.g.*, as in $H_2SO_4(aq)$.

It is convenient also for us to compute the *relative apparent molal enthalpy* with respect to the state of the solute in infinitely dilute solution,

$$\Phi_h - \Phi_h^\circ = -(\bar{Q}_s - \bar{Q}_s^\circ) \tag{4-31}$$

This quantity, tabulated in the fourth columns of Tables 4-9 and 4-10, clearly represents the negative of the quantity of heat that would be evolved per mole of solute if the solution of given composition, $1:n_1$, to which the value of $(\Phi_h - \Phi_h^\circ)$ refers were to be diluted with sufficient solvent until no thermal effect on further dilution would be observed. In view of the first law of thermodynamics, it is evident that the *heat of dilution* per mole of solute corresponding to a change from one concentration $1:n_1'$ to another $1:n_1''$ by the addition of pure solvent, is given by the difference between the $\bar{Q}_s$ values for the two concentrations, or what amounts to the same thing, by the negative of the difference between the corresponding $(\Phi_h - \Phi_h^\circ)$ values

$$\bar{Q}_d = \bar{Q}_s'' - \bar{Q}_s' = (\Phi_h' - \Phi_h^\circ) - (\Phi_h'' - \Phi_h^\circ) \tag{4-32}$$

Thus, from the data in Table 4-9, if sulfuric acid at $1H_2SO_4:2H_2O$ concentration is diluted with pure water to $1H_2SO_4:10H_2O$ concentration, then the quantity of heat liberated per mole of H_2SO_4 at 25°C and 1 atm is $16.02 - 10.02 = 6.00$ kcal. On the other hand, if sulfuric acid at original concentration of $1H_2SO_4:10H_2O$ were to be concentrated to $1H_2SO_4:2H_2O$ by the removal of water through evaporation, then 6.00

kcal of thermal energy per mole of H_2SO_4 present would be required, in addition to the latent heat of vaporization of the corresponding quantity of pure water removed at the given temperature. Practical methods for deriving the value of Φ_h° (or of $\bar{Q}_s^\circ$) precisely from heat-of-dilution data, combined with an accurate heat-of-solution measurement at some one low solute concentration, are described in an important paper by F. D. Rossini, in which results are given for aqueous solutions of a number of electrolytes.[1] The interionic attraction theory of P. Debye and E. Hückel discussed in Sec. 7-4 provides a theoretical basis for the precise extrapolation of thermal data for electrolytes to zero solute concentration.

The other situation arising in connection with the thermochemistry of solutions concerns virtual or infinitesimal transformations that leave the composition of the solution practically unchanged. Such transformations are of particular interest in the study of systems in equilibrium states, *e.g.*, as in the study of the vaporization of H_2O from a sulfuric acid solution at its own instantaneous partial vapor pressure. The theory is applicable also to the "differential" reaction

$$\mathrm{Zn(c)} + \mathrm{H_2SO_4}(n_1'\mathrm{H_2O}) = \mathrm{ZnSO_4}(n_1''\mathrm{H_2O}) + \mathrm{H_2(g)}$$

taking place in the galvanic cell

$$\mathrm{Zn(c)}|\mathrm{ZnSO_4}(n_1''\mathrm{H_2O})||\mathrm{H_2SO_4}(n_1'\mathrm{H_2O})|\mathrm{H_2(g)},\mathrm{(Pt)}$$

as a small quantity of electricity is discharged; this reaction differs from the "integral" reaction represented by Eq. (4-29) in that H_2SO_4 disappears from the right-hand compartment and $ZnSO_4$ appears in the left-hand compartment at the essentially constant concentrations, $1:n_1'$ and $1:n_1''$, respectively, so long as the quantity of electricity discharged remains small in comparison with the capacity of the cell; a situation similar with respect to the H_2SO_4, though not with respect to $ZnSO_4$, would arise if one were to add directly a small quantity of Zn(c) to a relatively large quantity of H_2SO_4 in solution. A knowledge of the differential enthalpies of the components of a solution may be of direct practical importance also in the control of continuous flow processes, in which one of the components is being consumed or produced through some chemical or physical transformation, but its concentration in the reaction mixture is maintained constant through continuous addition or removal (*e.g.*, by extraction or distillation) as the transformation proceeds.[2] Let us therefore define *differential* or so-called *partial molal enthalpies* of the com-

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[1] F. D. Rossini, *J. Research Natl. Bur. Standards*, **6**, 791–806 (1931).

[2] See, for example, T. S. Mertes and A. P. Colburn, *Ind. Eng. Chem.*, **39**, 787–796 (1947).

ponents by means of the symbolic operations

$$\eta_1 \equiv \left(\frac{dH}{dn_1}\right)_{T,p,c}; \qquad \eta_2 \equiv \left(\frac{dH}{dn_2}\right)_{T,p,c} \tag{4-33}$$

While we shall confine the discussion to binary solutions, the treatment may be generalized to include polycomponent systems, if the necessary thermochemical data are available. The subscript c following the differential coefficients in Eqs. (4-33) denotes that the composition is regarded as essentially constant during the operation by which the increase of H per mole of either component added is measured; this operation consists in principle of measuring the heat absorbed in the limit as Δn_1 or Δn_2, respectively, approaches zero (with T and p constant and $W' = 0$). We assume in other words that the quantities η_1 and η_2 themselves vary with the composition of the solution by infinitesimals of order higher than that of dn_1 and dn_2, an assumption borne out by the nature of the experimental data concerned. The values of η_1 and η_2 thus represent the terms properly contributed per mole of solvent S (designated as component 1) or per mole of solute A (designated as component 2), respectively, to the instantaneous enthalpy change of any process involving either substance, if it is carried out in such a way that the composition of the solution changes only infinitesimally. Thus, for the chemical reaction (4-29) as carried out in a galvanic cell, with discharge of a relatively small quantity of electricity, $\Delta H = \eta_{\mathrm{ZnSO}} - \eta_{\mathrm{H\,SO_4}}$; the two quantities $\eta_{\mathrm{ZnSO_4}}$ and $\eta_{\mathrm{H_2SO_4}}$ depend on the particular electrolyte concentrations, as well as on temperature and pressure.

Let us develop some of the mathematical properties of the quantities η_1 and η_2 and, in particular, devise methods for computing their values from experimental data in such forms as have been presented in Tables 4-9 and 4-10. To a first order of approximation, we may represent the change in the total enthalpy of the solution corresponding to changes in the quantities of the components present, at constant temperature and pressure, by means of the formal expression

$$\begin{aligned} dH &= \left(\frac{dH}{dn_1}\right)_{T,p,c} dn_1 + \left(\frac{dH}{dn_2}\right)_{T,p,c} dn_2 \\ &= \eta_1\,dn_1 + \eta_2\,dn_2 \qquad (T,\ p \text{ const}) \end{aligned} \tag{4-34}$$

This general functional relationship, which includes possible changes in the total mass of the solution, has, however, a special character resulting from the fact that H is necessarily an *extensive property* of the solution. No enthalpy change takes place when several portions of the *same solution*, all at the same temperature, pressure, and composition, are combined; therefore H must equal the sum of the enthalpy values of any portions of the solution, all having the same temperature, pressure, and composition, from which the solution may be regarded as made up, *i.e.*, it must increase in direct proportion to the total mass. The quantities η_1 and η_2 are equally clearly *intensive properties* of the solution, which may vary with temperature, pressure, and composition, but from the nature of their definition are independent of the total mass. If, then, n_1 and n_2 are increased in the *same proportion*, $dn_1 = \lambda n_1$, $dn_2 = \lambda n_2$, leaving the composition unchanged, η_1 and η_2 undergo no change, but H must likewise increase in the same proportion, $dH = \lambda H$, since the change under consideration is equivalent merely to an increase in the total quantity of the solution. Substituting these conditions in Equation (4-34), we infer that

$$H = n_1\eta_1 + n_2\eta_2 \qquad (4\text{-}35)$$

The partial molal enthalpies η_1 and η_2 represent in other words the properly additive contributions made by the components to the total enthalpy of the solution. If $\bar{Q}_s$ were zero for all compositions (as is actually the case for certain ideal mixtures, including in particular most gas mixtures at sufficiently low pressures), so that

$$H = n_1\bar{H}_1^\circ + n_2\bar{H}_2^\circ \qquad (\bar{Q}_s = 0)$$

then we should have $\eta_1 = \bar{H}_1^\circ$ and $\eta_2 = \bar{H}_2^\circ$ at all compositions, but in general, the values of η_1 and η_2 differ from the standard molal enthalpies of the pure components.

If we differentiate Eq. (4-35) in the most general manner with respect to changes in the variables n_1 and n_2,

$$dH = \eta_1\,dn_1 + n_1\,d\eta_1 + \eta_2\,dn_2 + n_2\,d\eta_2 \quad (T,\ p \text{ const})$$

and then compare the result with Eq. (4-34), we draw the inference that

$$n_1\,d\eta_1 + n_2\,d\eta_2 = 0 \qquad (T,\ p \text{ const}) \qquad (4\text{-}36)$$

Thus, the two partial molal enthalpies of a binary solution do not vary independently with composition, but are interrelated in such a way that if we have determined the value of either as a function of the composition, then we may calculate the value of the other by graphical or numerical integration of Eq. (4-36). The integration introduces an additive integration constant, whose value may be determined from knowledge of the terminal value of the partial molal enthalpy in question at either end of the composition scale; for in terms of the concepts embodied in Eqs. (4-27), (4-28), and (4-30), it is clear that

$$\lim_{(n_2/n_1)\to 0} \eta_1 = \bar{H}_1^\circ; \qquad \lim_{(n_2/n_1)\to 0} \eta_2 \equiv \eta_2^\circ = \Phi_h^\circ; \qquad \lim_{(n_2/n_1)\to \infty} \eta_2 = \bar{H}_2^\circ \quad (4\text{-}37)$$

Equation (4-36) is a special case of the general Gibbs-Duhem equation (3-16), introduced in Sec. 3-1.

We may proceed to evaluate η_1 and η_2 from empirical heat-of-solution data such as are presented in Tables 4-9 and 4-10 according to several mathematically equivalent forms, to suit our convenience. Thus, from Eqs. (4-28) and (4-35), if we bear in mind that the quantity Φ_h has been set up with $n_2 = 1$ mole by convention,

$$H = \Phi_h + n_1\bar{H}_1^\circ = n_1\eta_1 + \eta_2 \qquad (n_2 = 1 \text{ mole}) \qquad (4\text{-}38)$$

Applying the definition (4-33) of η_1 to the first equality in Eq. (4-38),

$$\eta_1 = \frac{d\Phi_h}{dn_1} + \bar{H}_1^\circ$$

whereupon, on substitution back in the second equality of Eq. (4-38),

$$\eta_2 = \Phi_h - n_1\frac{d\Phi_h}{dn_1}$$

These two equations express η_1 and η_2 in terms of Φ_h and its rate of change with n_1; it is of course impossible to derive the values of η_1 and η_2 at a given composition from heat-of-solution data obtained only at the one composition, since by their very nature, they imply a knowledge of how the enthalpy of solution varies with change in the composition. It is more convenient for us to work with $(\Phi_h - \Phi_h^\circ)$ rather than with Φ_h itself, since the values of $(\Phi_h - \Phi_h^\circ)$ may be derived directly from heat-of-solution data [by means of Eq. (4-31)] without explicit knowledge of the values of $\bar{H}_1^\circ$ and $\bar{H}_2^\circ$; thus

$$\eta_1 - \bar{H}_1^\circ = \frac{d(\Phi_h - \Phi_h^\circ)}{dn_1} \qquad (4\text{-}39)$$

$$\eta_2 - \Phi_h^\circ = (\Phi_h - \Phi_h^\circ) - n_1\frac{d(\Phi_h - \Phi_h^\circ)}{dn_1} \qquad (4\text{-}40)$$

Equations (4-39) and (4-40) express the values of η_1 and η_2, relative to their terminal values at infinite dilution in the component regarded as the solvent (component 1), in terms of $(\Phi_h - \Phi_h^\circ)$ and its rate of change with n_1 at the particular composition in question. The value of $d(\Phi_h - \Phi_h^\circ)/dn_1$ for any given value of n_1 may be read graphically from a plot of $(\Phi_h - \Phi_h^\circ)$ vs. n_1. Thus, from the lower curve in Fig. 4-1, where such a plot has been constructed for H_2SO_4-H_2O solutions from the data in Table 4-9, one finds that at $n_1 = 2000$ moles H_2O/mole H_2SO_4, the slope is -0.00047 kcal/mole H_2O; therefore

$$\begin{aligned}\eta_1 - \bar{H}^\circ_{H_2O(l)} &= -0.00047 \text{ kcal/mole}\\ \eta_2 - (\Phi_h^\circ)_{H_2SO_4(aq)} &= 3.66 - 2000(-0.00047)\\ &= 4.60 \text{ kcal/mole}\end{aligned}$$

The difference is almost insignificant for the solvent H_2O; but since for H_2SO_4, $\Phi_h^\circ - \bar{H}^\circ_{H_2SO_4(l)} = -22.99$ kcal/mole, one may infer that $\eta_2 - \bar{H}^\circ_{H_2SO_4(l)} = -18.39$ kcal/mole; thus, η_2 differs significantly at the given concentration both from its value at infinitely dilute solution and from the value of $\bar{H}^\circ_{H_2SO_4(l)}$ for the pure solute. Likewise, from the upper curve in Fig. 4-1, one reads at $n_1 = 400$ moles H_2O/mole H_2SO_4 the slope, -0.00128 kcal/mole H_2O; thus

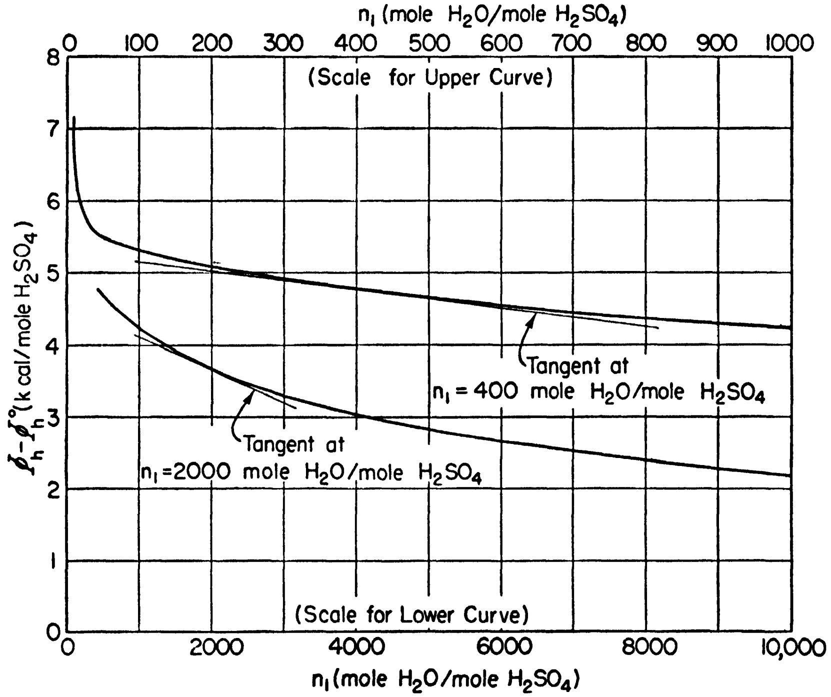

FIG. 4-1. $(\Phi_h - \Phi_h^\circ)$ vs. n_1 for solutions of $H_2SO_4(l)$ in $H_2O(l)$ at 25°C (data given in Table 4-9).

$$\begin{aligned} \eta_1 - \bar{H}^\circ_{H_2O(l)} &= -0.0013 \text{ kcal/mole} \\ \eta_2 - (\Phi_h^\circ)_{H_2SO_4(aq)} &= 4.77 - 400(-0.00128) \\ &= 5.28 \text{ kcal/mole} \end{aligned}$$

Where $(\Phi_h - \Phi_h^\circ)$ shows significant variation over as wide a range of n_1 values as in the case of H_2SO_4-H_2O solutions, it may be more convenient for us to plot $(\Phi_h - \Phi_h^\circ)$ vs. $\log n_1$, as in Fig. 4-2; Eqs. (4-39) and (4-40) may be put in the equivalent forms

$$\eta_1 - \bar{H}_1^\circ = \frac{1}{n_1} \frac{d(\Phi_h - \Phi_h^\circ)}{d \ln n_1} \tag{4-41}$$

$$\eta_2 - \Phi_h^\circ = (\Phi_h - \Phi_h^\circ) - \frac{d(\Phi_h - \Phi_h^\circ)}{d \ln n_1} \tag{4-42}$$

The differential coefficient appearing in this pair of equations may be read as 0.4343 times the slope of the $(\Phi_h - \Phi_h^\circ)$ vs. log n_1 graph. Thus,

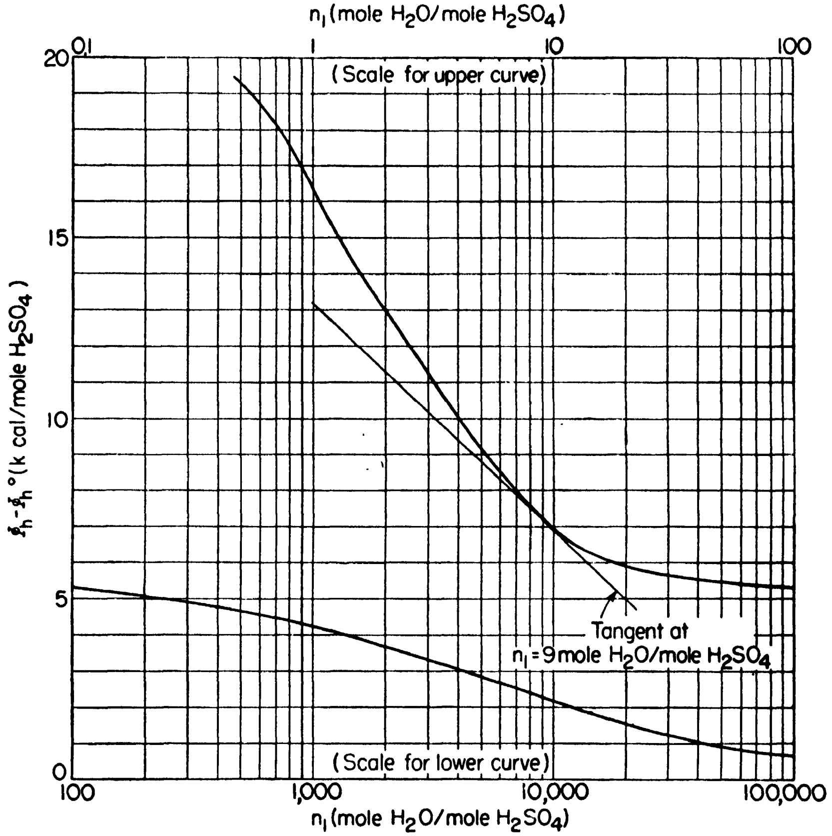

FIG. 4-2. $(\Phi_h - \Phi_h^\circ)$ vs. log n_1 for H_2SO_4-H_2O solutions at 25°C (same data as in Fig. 4-1).

from Fig. 4-2, one finds that at $n_1 = 9$ moles H_2O/mole H_2SO_4,

$$d(\Phi_h - \Phi_h^\circ)/d(\log n_1) = -6.29 \text{ kcal/mole } H_2SO_4;$$

therefore $d(\Phi_h - \Phi_h^\circ)/d(\ln n_1) = -2.73$ kcal/mole H_2SO_4, and thus

$$\eta_1 - \bar{H}^\circ_{H_2O(l)} = \tfrac{1}{9}(-2.73) = -0.303 \text{ kcal/mole } H_2O$$
$$\eta_2 - (\Phi_h^\circ)_{H_2SO_4(aq)} = 7.20 + 2.73 = 9.93 \text{ kcal/mole } H_2SO_4$$

The latter result is equivalent to $\eta_2 - \bar{H}^\circ_{H_2SO_4(l)} = -13.06$ kcal/mole H_2SO_4, since $\Phi_h^\circ - \bar{H}^\circ_{H_2SO_4(l)} = -\bar{Q}_s^\circ = -22.99$ kcal/mole H_2SO_4.[1]

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[1] Other functions of the composition may be used as independent variable, or plotting function. Thus, F. D. Rossini, *J. Research Natl. Bur. Standards*, **6**, 791–806 (1931), has used $\sqrt{m_2}$ when dealing with 1:1 electrolytes such as HCl and NaCl in aqueous solution. The *molality* m_2 represents the number of moles of solute per

An alternative graphical method for determining the relative partial molal enthalpies, $(\eta_1 - \bar{H}_1^\circ)$ and $(\eta_2 - \bar{H}_2^\circ)$, is based on a plot of the enthalpy of solution *per mole of solution formed* vs. the *mole fraction* of either component; this graph has certain practical advantages for the more concentrated solutions. Thus, from Eqs. (4-35) and (4-26), if we bear in mind that the heat-of-solution data corresponding to Eq. (4-26) have been expressed with $n_2 = 1$ mole throughout,

$$-\bar{Q}_s = (\eta_2 - \bar{H}_2^\circ) + n_1(\eta_1 - \bar{H}_1^\circ)$$

If we now divide by $(1 + n_1)$, the total number of moles of solution corresponding to $\bar{Q}_s$,

$$\begin{aligned} \frac{-Q_s}{1 + n_1} &= \frac{1}{1 + n_1}(\eta_2 - \bar{H}_2^\circ) + \frac{n_1}{1 + n_1}(\eta_1 - \bar{H}_1^\circ) \\ &= x_2(\eta_2 - \bar{H}_2^\circ) + x_1(\eta_1 - \bar{H}_1^\circ) \end{aligned}$$

where x_1 and x_2 denote, respectively, the mole fractions of the solvent (component 1) and the solute (component 2). Since in a binary solution $x_2 = 1 - x_1$, therefore

$$\frac{-\bar{Q}_s}{1 + n_1} = \Delta\bar{H} = (\eta_2 - \bar{H}_2^\circ) + x_1[(\eta_1 - \bar{H}_1^\circ) - (\eta_2 - \bar{H}_2^\circ)] \quad (4\text{-}43)$$

Thus, if one plots $-\bar{Q}_s/(1 + n_1)$ vs. x_1, as in Fig. 4-3, then the slope of the tangent to the curve at any value of x_1 is equal to $[(\eta_1 - \bar{H}_1^\circ) - (\eta_2 - \bar{H}_2^\circ)]$.

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kilogram of solvent, so that by definition,

$$n_1 = \frac{1}{m_2}\frac{1000\ g/kg}{\bar{M}_1}$$

where $\bar{M}_1$ represents the solvent's molecular weight (18.016 g/mole in the case of H_2O). One may thus readily prove that

$$\frac{d}{dn_1}(\ \ ) = -\frac{m_2^{3/2}}{2}\frac{\bar{M}_1}{1000\text{ g/kg}}\frac{d}{dm_2^{1/2}}(\ \ )$$

whence Eqs. (4-39) and (4-40) assume the forms

$$\eta_1 - \bar{H}_1^\circ = -\frac{m_2^{3/2}}{2}\frac{\bar{M}_1}{1000\text{ g/kg}}\frac{d(\Phi_h - \Phi_h^\circ)}{dm_2^{1/2}} \quad (4\text{-}41a)$$

$$\eta_2 - \Phi_h^\circ = (\Phi_h - \Phi_h^\circ) + \frac{1}{2}m_2^{1/2}\frac{d(\Phi_h - \Phi_h^\circ)}{dm_2^{1/2}} \quad (4\text{-}42a)$$

The differential coefficient appearing in Eqs. (4-41*a*) and (4-42*a*) may be read as the slope of the graphic plot of $(\Phi_h - \Phi_h^\circ)$ vs. $m_2^{1/2}$. The relationship between $(\Phi_h - \Phi_h^\circ)$ or Φ_h itself and $m_2^{1/2}$ for strong electrolytes tends to become linear as $m_2 \rightarrow 0$ [see Eq. (7-4-43*c*) and the accompanying discussion in Sec. 7-4], in the absence of hydrolysis or other complications (such as partial secondary ionization in the case of H_2SO_4 in dilute aqueous solution); this fact permits one to evaluate Φ_h° precisely by graphical extrapolation of the Φ_h vs. $m_2^{1/2}$ plot.

It follows that the intercept of the tangent to the curve on the $x_1 = 0$ axis is equal to $(\eta_2 - \bar{H}_2^\circ)$, while its intercept on the $x_1 = 1$ axis is equal to $(\eta_1 - \bar{H}_1^\circ)$. Applying this method at

$$x_1 = 0.75 (n_1 = 3 \text{ moles } H_2O/\text{mole } H_2SO_4),$$

we obtain $(\eta_1 - \bar{H}^\circ_{H_2O(l)}) = -1.46$ kcal/mole and

$$(\eta_2 - \bar{H}^\circ_{H_2SO_4(l)}) = -7.34 \text{ kcal/mole}$$

(the intercept on the $x_1 = 0$ axis is off the diagram, but may easily be computed from the slope and location of the tangent line).

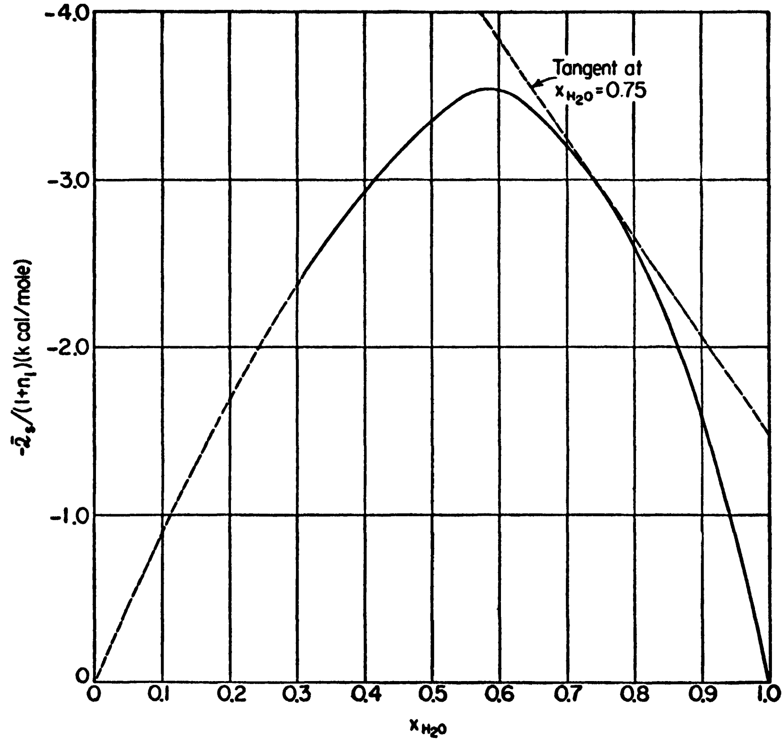

FIG. 4-3. Enthalpy of solution per mole of solution formed, plotted against x_1, for H_2SO_4-H_2O solutions at 25°C.

In Table 4-11, partial molal enthalpies relative to the pure liquid components are summarized for H_2SO_4-H_2O solutions at 25°C and 1 atm; they have been derived from the data in Table 4-9 by means of a combination of these graphic methods. Thus, if one wishes to represent precisely the differential enthalpy change of the chemical reaction taking place in the lead storage cell as a relatively small quantity of electricity is discharged, one will use the expression

$$\mathrm{Pb(c)} + \mathrm{PbO_2(c)} + 2\mathrm{H_2SO_4}(1\mathrm{H_2SO_4}{:}n_1\mathrm{H_2O}) = 2\mathrm{PbSO_4(c)} + 2\mathrm{H_2O}(1\mathrm{H_2SO_4}{:}n_1\mathrm{H_2O})$$

$$\Delta H = 2\bar{H}^\circ_{\mathrm{PbSO_4(c)}} + 2\eta_{\mathrm{H_2O}} - \bar{H}^\circ_{\mathrm{PbO_2(c)}} - 2\eta_{\mathrm{H_2SO_4}}$$

where $\eta_{\mathrm{H_2O}}$ and $\eta_{\mathrm{H_2SO_4}}$ differ from the standard molal enthalpies of formation of the pure liquid components by the amounts given in Table 4-11.[1]

TABLE 4-11. PARTIAL MOLAL ENTHALPIES IN H_2SO_4-H_2O SOLUTIONS AT 25°C AND 1 ATMOSPHERE

$x_{\mathrm{H_2SO_4}}$	$\frac{n_1}{n_2}$	Wt % H_2SO_4	$\eta_{\mathrm{H_2O}} - \bar{H}^\circ_{\mathrm{H_2O(l)}}$, kcal/mole	$\eta_{\mathrm{H_2SO_4}} - \bar{H}^\circ_{\mathrm{H_2SO_4(l)}}$, kcal/mole
0.00	∞	0.00	0	−22.99
0.01	99.0	5.19	−0.002	−17.48
0.05	19.0	22.27	−0.044	−16.24
0.10	9.0	37.70	−0.27	−13.06
0.15	5.67	49.00	−0.71	−10.36
0.20	4.0	57.63	−1.09	− 8.54
0.25	3.0	64.48	−1.46	− 7.34
0.30	2.33	70.00	−1.86	− 6.31
0.35	1.86	74.57	−2.16	− 5.69
0.40	1.50	78.40	−3.17	− 4.06
0.45	1.22	81.67	−4.43	− 2.34
0.50	1.00	84.48	−5.20	− 1.50
0.55	0.82	86.93	−5.55	− 1.19
0.60	0.67	89.09	−5.78	− 1.00
0.65	0.54	90.99	−6.29	− 0.71
0.70	0.43	92.71	−6.69	− 0.51
0.75	0.33	94.24	−7.12	− 0.32
0.80	0.25	95.61	−7.92	− 0.12
1.00	0	100.00	−10.65	0

The partial molal enthalpies are directly useful in straightforward thermal calculations involving the mixing or dilution of solutions of the two components. The basis of such computations is Eq. (4-35), which represents the total enthalpy of the solution in terms of its composition and the partial molal enthalpies of the components. If one combines this equation with the stoichiometric equation for the process under consideration, one has all the information necessary in order to compute the thermal effect from a table of partial molal enthalpies. Let us compute

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[1] The thermochemical properties of H_2SO_4-H_2O solutions have been treated comprehensively by D. N. Craig and G. W. Vinal, *J. Research Natl. Bur. Standards*, **24**, 475–490 (1940), with particular reference to the lead storage cell reaction.

from Table 4-11, for example, the enthalpy change (the negative of the quantity of heat evolved at constant temperature and pressure) when a sufficient quantity of 84.48 per cent H_2SO_4 is added to 100 g of 49.00 per cent H_2SO_4 so that the final concentration is 70.00 per cent. One readily calculates that the quantity of the more concentrated acid required is 145 g; thus, the change under consideration may be represented by the stoichiometric equation

$$\begin{aligned}0.50H_2SO_4(x_2 = 0.15) &+ 2.83H_2O(x_2 = 0.15)\\ &+ 1.25H_2SO_4(x_2 = 0.50) + 1.25H_2O(x_2 = 0.50)\\ &= 1.75H_2SO_4(x_2 = 0.30) + 4.08H_2O(x_2 = 0.30)\end{aligned}$$

where x_2 represents the mole fraction of H_2SO_4 in the sulfuric acid solutions. The corresponding enthalpy change, according to Eq. (4-35), has the form

$$\begin{aligned}\Delta H = 1.75\eta_2(x_2 = 0.30) &+ 4.08\eta_1(x_2 = 0.30)\\ &-0.50\eta_2(x_2 = 0.15) - 2.83\eta_1(x_2 = 0.15)\\ &-1.25\eta_2(x_2 = 0.50) - 1.25\eta_1(x_2 = 0.50)\end{aligned}$$

We may evidently substitute relative partial molal enthalpies, $(\eta_1 - \bar{H}_1^\circ)$ and $(\eta_2 - \bar{H}_2^\circ)$, in place of "absolute" values, η_1 and η_2, since the terms contributed by introducing $\bar{H}_1^\circ$ and $\bar{H}_2^\circ$ cancel out; thus, substituting from Table 4-11,

$$\begin{aligned}\Delta H = 1.75(-6.31) &+ 4.08(-1.86)\\ &-0.50(-10.36) - 2.83(-0.71)\\ &-1.25(-1.50) - 1.25(-5.20) = -3.07 \text{ kcal}\end{aligned}$$

The data for H_2SO_4-H_2O solutions have been extended by R. A. Morgen to include oleums containing up to 100 per cent free SO_3(l).[1] For this purpose, it is convenient to regard SO_3(l) and H_2O(l) as the components. Solutions containing less than $x_{SO_3} = 0.50$ are of course identical with H_2SO_4-H_2O solutions of equivalent concentrations; *i.e.*, a solution containing $x_{SO_3} = 0.100$ is identical with a solution containing $x_{H_2SO_4} = 0.111$. The value of η_{H_2O} for a particular composition is evidently the same, whether we express the composition in terms of SO_3 or of H_2SO_4 as the other component; this follows from the nature of the definition (4-33), which contains no reference to the manner in which the composition is defined. The value of η_{SO_3} is, however, equal to the value of $\eta_{H_2SO_4} - \eta_{H_2O}$ in a solution of the same actual composition, inasmuch as the addition of 1 mole of H_2SO_4(l) to a relatively large quantity of the solution, the process whose enthalpy change defines $\eta_{H_2SO_4}$, is identical in net effect with

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[1] R. A. Morgen, *Ind. Eng. Chem.*, **34**, 571–574 (1942).

the separate additions of 1 mole of $H_2O(l)$ plus 1 mole of $SO_3(l)$ to a relatively large quantity of the same solution. The partial molal enthalpies relative to the standard molal enthalpies of the pure compounds are therefore related through the equation

$$\begin{aligned}[\eta_{SO_3} - \bar{H}^\circ_{SO_3(l)}] = [\eta_{H_2SO_4} - \bar{H}^\circ_{H_2SO_4(l)}] - [\eta_{H_2O} - \bar{H}^\circ_{H_2O(l)}] \\ + [\bar{H}^\circ_{H_2SO_4(l)} - \bar{H}^\circ_{SO_3(l)} - \bar{H}^\circ_{H_2O(l)}]\end{aligned}$$

The last term on the right represents the enthalpy of the reaction

$$SO_3(l) + H_2O(l) = H_2SO_4(l)$$

which Morgen has shown to have the value $\Delta H = -21.18$ kcal (at 18°C and 1 atm). For solutions containing more than $x_{SO_3} = 0.50$ (*i.e.*, containing free SO_3, in excess of that theoretically required in order to form the compound H_2SO_4 with all the water present), one of course requires further experimental data beyond that contained in Table 4-9, *viz.*, heats of dilution with water for oleums of various free SO_3 concentrations. From a review of the existing data, Morgen computed the results summarized in Table 4-12. These data refer to 18°C and 1 atm; heat-capacity data are not known with sufficient accuracy for oleum mixtures to warrant correction of the data to 25°C. Examples illustrating the use of these data are given by Morgen in the reference cited (see also Prob. 4-29).

The mathematical treatment just described for the resolution of the enthalpy of a binary solution into partial molal enthalpy terms contributed by the components is quite general, and it may be applied to other extensive properties of the solution, such as its volume, its heat capacity, etc. The experimental data called for consist of measurements of the property in question for various compositions of the solution, in relation to the values of the property for the pure components. If B represents the extensive property, then the basic relationship involved may be expressed in the form

$$B = n_1\beta_1 + n_2\beta_2 = n_1\bar{B}^\circ_1 + n_2\bar{B}^\circ_2 + \Delta B \quad (T, p \text{ const}) \qquad (4\text{-}44)$$

where β_1 and β_2 represent the values of the two partial molal quantities corresponding to the composition $n_1:n_2$, $\bar{B}^\circ_1$ and $\bar{B}^\circ_2$ represent the values of the property for the two pure components in specified states, and ΔB represents the net change in the value of the property when the solution is formed from n_1 moles of the one component and n_2 moles of the other.

One may easily prove as a generalization of Eq. (3-39) that

$$\left(\frac{d\eta_i}{dT}\right)_{p,c} = \left(\frac{dC_p}{dn_i}\right)_{T,p,c} \equiv (\gamma_p)_i \qquad (4\text{-}45)$$

where $(\gamma_p)_i$ represents the *partial molal heat capacity at constant pressure* of component i in the solution. The partial molal heat capacities may be derived from measurements of C_p for solutions of various compositions and for the pure components by methods similar to those used for deriving

TABLE 4-12. PARTIAL MOLAL ENTHALPIES IN SO_3-H_2O SOLUTIONS* AT 18°C AND 1 ATMOSPHERE

x_{SO_3}	Per cent by weight			ΔH per mole of soln, kcal/mole	$\eta_{H_2O} - \bar{H}^\circ_{H_2O(l)}$, kcal/mole	$\eta_{SO_3} - \bar{H}^\circ_{SO_3(l)}$, kcal/mole
	SO_3	H_2SO_4	Free SO_3, based on H_2SO_4			
0.00	0.0	0.0	.....	....	0.00	(−43.25)
0.02	8.3	10.2	.....	−0.78	−0.01	−38.5
0.04	15.6	19.1	.....	−1.51	−0.02	−37.5
0.05	19.0	23.2	.....	−1.89	−0.08	−37.3
0.07	25.1	30.8	.....	−2.62	−0.21	−36.8
0.10	33.6	40.5	.....	−3.65	−0.50	−32.11
0.15	44.0	53.8	.....	−5.15	−0.85	−30.09
0.20	52.6	64.4	.....	−6.63	−1.21	−28.11
0.25	59.7	73.1	.....	−7.80	−2.59	−23.57
0.30	65.6	80.6	.....	−8.79	−3.98	−19.90
0.35	70.5	86.4	.....	−9.47	−5.16	−17.50
0.40	74.8	91.6	.....	−10.00	−6.33	−15.48
0.45	78.4	96.1	.....	−10.41	−7.80	−13.60
0.50	81.6	100.0	.....	−10.59	−10.59	−10.59
0.52	82.5	.....	6.4	−10.45	−15.92	−5.40
0.55	84.5	.....	15.4	−10.10	−17.17	−4.35
0.60	87.0	.....	29.0	− 9.37	−19.50	−2.60
0.65	89.2	.....	41.2	− 8.52	−19.50	−2.60
0.70	91.2	.....	52.1	− 7.68	−20.28	−2.22
0.75	93.0	.....	62.0	− 6.61	−23.35	−1.01
0.80	94.7	.....	71.0	− 5.48	−23.56	−0.95
0.85	96.2	.....	79.2	− 4.25	−23.95	−0.80
0.90	97.6	.....	86.7	− 3.03	−27.21	−0.39
0.95	98.8	.....	93.6	− 1.60	−31.0	−0.10
1.00	100.0	.....	100.0	....	(−37.0)	0.00

* R. A. Morgen, *Ind. Eng. Chem.*, **34**, 571–574 (1942), with permission.

η_i values from enthalpy data. F. D. Rossini has shown that for many 1 : 1 electrolytes in aqueous solution, the value of $(\Phi_c - \Phi_c^\circ)$ is empirically a linear function of $m_2^{1/2}$, of the form

$$\Phi_c - \Phi_c^\circ = A m_2^{1/2} \tag{4-46}$$

where A is a constant, at given temperature and pressure, characteristic of the particular electrolyte, and Φ_c represents the apparent molal heat capacity of the solute, defined analogously to Φ_h in Eq. (4-28); that is, Φ_c is computed from the specific heat c_p of the solution and the specific heat $(c_p^\circ)_1$ of the pure solvent (*e.g.*, 0.9989 cal/g deg for $H_2O(l)$ at 25°C and 1 atm) by means of the equation

$$\Phi_c = \left(\frac{1000\ \text{g/kg}}{m_2} + \bar{M}_2\right)c_p - \frac{1000\ \text{g/kg}}{m_2}(c_p^\circ)_1 \tag{4-47}$$

The first term on the right of Eq. (4-47) represents the total heat capacity of the solution per mole of solute, at molality m_2, and the second term represents the heat capacity of the corresponding quantity of pure solvent.[1] If the empirical finding, Eq. (4-46), is substituted in the equations analogous to (4-41*a*) and (4-42*a*), one obtains the semiempirical equations for the two partial molal heat capacities

$$(\gamma_p)_1 - (\bar{C}_p^\circ)_1 = -\frac{A}{2}\,\frac{\bar{M}_1}{1000\ \text{g/kg}}\,(m_2)^{3/2} \tag{4-48}$$

$$(\gamma_p)_2 - \Phi_c^\circ = \tfrac{3}{2}A(m_2)^{1/2} \tag{4-49}$$

where Φ_c° represents the terminal value of Φ_c and of $(\gamma_p)_2$ in infinitely dilute solution, another empirical property of the particular electrolyte in the given solvent. These simple equations apply over an astonishingly wide range of solute concentrations for many electrolytes in aqueous solution; thus, for HCl solutions at 25°C, Rossini has shown that with $\Phi_c^\circ = -32.5$ and $A = 7.2$ (in cal/mole deg), they are reasonably accurate over the range 0 to 16m. If Eq. (4-46) is valid over the composition range in which one is interested, then it is necessary to have experimental c_p values at but two different solute concentrations in order to establish the values of Φ_c° and A for the given electrolyte. Table 4-13 contains best values of these constants selected by Rossini for a number of 1:1 electrolytes at 25°C; the values of A are practically independent of temperature over the range 18 to 25°C, whereas $d\Phi_c^\circ/dT = d(\gamma_p)_2/dT$ has the approximate value 0.29 cal/mole (deg)^2.

The standard enthalpy of formation of a strong electrolyte in aqueous solution, $\Phi_h^\circ = \eta_2^\circ$, may be represented according to Arrhenius's ionization theory as a sum of independent terms contributed by the ions. In general, we cannot so represent Φ_h or η_2 at finite solute concentrations, because of interionic attraction and other more specific interactions between the ions and with the solvent. The Φ_h° or η_2° limit, however, refers to infinitely dilute solution in the given solvent, where general

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[1] F. D. Rossini, *J. Research Natl. Bur. Standards*, **4**, 313–327 (1930); **7**, 47–55 (1931); **9**, 679–702 (1932).

TABLE 4-13. PARTIAL MOLAL HEAT CAPACITIES OF 1:1 ELECTROLYTES IN AQUEOUS SOLUTION AT 25°C*

The constants A and Φ_c° in the semiempirical equations

$$(\gamma_p)_1 = (\bar{C}_p^\circ)_{H_2O(l)} - \frac{A(m_2)^{3/2}}{2(55.508 \text{ mole/kg})}$$

$$(\gamma_p)_2 = (\Phi_c^\circ) + \tfrac{3}{2}A(m_2)^{1/2}$$

[Equations (4-48) and (4-49)]; over the range 18 to 25°C, A may be taken as constant, whereas $d\Phi_c^\circ/dT = 0.29$ cal/mole deg².

Electrolyte	Φ_c°	A
HCl	−32.5	7.2
HBr	−33.0	12.4
HI	−33.7	15.9
HNO_3	−21.3	11.5
LiCl	−16.2	6.1
LiBr	−16.7	9.2
LiI	−17.4	11.8
$LiNO_3$	− 5.0	9.3
LiOH	−21.6	17.9
NaCl	−23.8	14.4
NaBr	−24.3	13.6
NaI	−25.0	16.6
$NaNO_3$	−12.6	20.0
NaOH	−29.2	19.0
KCl	−29.0	11.2
KBr	−29.5	10.8
KI	−30.2	13.6
KNO_3	−17.8	19.1
KOH	−34.4	16.1

* F. D. Rossini, *J. Research Natl. Bur. Standards*, **7**, 47–55 (1931).

electrostatic and specific interionic effects have presumably vanished. Thus, we may regard $\eta^\circ_{KCl(aq)}$ as made up of a sum of independent terms: $\eta^\circ_{K^+(aq)} + \eta^\circ_{Cl^-(aq)}$, where $\eta^\circ_{K^+(aq)}$ represents the value of the term contributed by K^+ ion to Φ_h° or η_2° of *any* strong electrolyte containing that ion, and $\eta^\circ_{Cl^-(aq)}$ represents similarly the value of the term contributed by Cl^- for *any* strong electrolyte containing that ion. The experimental fact that the Φ_h° values of strong electrolytes in aqueous solution (in particular) may be so represented in terms of additive contributions of the ions, constituted one of the most impressive pieces of evidence for Arrhenius's original theory.

Now, it is at present impossible for us to establish by any known technique the η° or Φ_h° value of any single ion independently in a particular solvent such as water. To be able to do so would imply that we had some means of preparing an aqueous solution containing only the single species of ion, or at any rate, an excess of one kind of ionic charge over the other. So far, no reliable experimental method has been discovered for preparing electrolytic solutions that are not electrically neutral. Therefore in order to construct a table of ionic η° values in the given solvent (water), we may begin by assigning an arbitrary η° value to any one standard ion; we may then construct a self-consistent table of values for the other ions by difference, relatively to this conventional base. The conventional standard is the H^+ ion, to which has been assigned the standard enthalpy of formation in solution (in any particular solvent, though most of the thermochemical data for solutions of electrolytes have been obtained in water as solvent): $\eta^\circ_{H^+} \equiv 0$. Thus, the observed Φ_h° value for any strong acid in aqueous solution is taken to define the η° value of the corresponding anion, in aqueous solution. For example, from the standard enthalpy of formation of HCl(g): $\bar{H}^\circ_{HCl(g)} = -22.063$ kcal/mole (as measured directly by F. D. Rossini, using the flame calorimeter), combined with the total molal enthalpy of solution of HCl(g) in $H_2O(l)$, $\Delta H_s^\circ = -17.960$ kcal/mole (Table 4-10), the value of

$$\Phi^\circ_{HCl(aq)} = -40.023 \text{ kcal/mole}$$

has been established at 25°C and 1 atm. Therefore, by convention, $\eta^\circ_{Cl^-(aq)} = -40.023$ kcal/mole, *i.e.*,

$$\tfrac{1}{2}Cl_2(g) + e = Cl^-(aq); \qquad \Delta H^\circ_{298} = \eta^\circ_{Cl^-(aq)} - \tfrac{1}{2}\bar{H}^\circ_{Cl_2(g)} = -40.023 \text{ kcal}$$

The electron appearing in this thermochemical equation has only formal significance, because the η° values for individual ions in solution have physical significance only when recombined with corresponding η° values for appropriate ions of opposite charge, whereupon any presumed thermochemical properties of the electron cancel out of the calculations.[1]

Likewise, from the limiting value at infinite dilution of the heats of neutralization of strong acids with strong bases,[2]

$$H^+(aq) + OH^-(aq) = H_2O(l); \qquad \Delta H^\circ_{298} = -13.360 \text{ kcal}$$

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[1] The situation is quite different for such real physical processes as

$$K(g) = K^+(g) + e,$$

whose energy is directly measured by the ionization potential, corresponding to escape of the electron with zero kinetic energy.

[2] See R. H. Lambert and L. J. Gillespie, J. *Am. Chem. Soc.*, **53**, 2632–2639 (1931).

combined with the standard molal enthalpy of formation of $H_2O(l)$, $\bar{H}^\circ_{H_2O(l)} = -68.317$ kcal/mole, we may infer for $OH^-(aq)$ the standard molal enthalpy of formation: $\eta^\circ_{OH^-(aq)} = -54.957$ kcal/mole; *i.e.*,

$$\tfrac{1}{2}O_2(g) + \tfrac{1}{2}H_2(g) + e = OH^-(aq); \qquad \Delta H^\circ_{298} = -54.957 \text{ kcal}$$

Proceeding stepwise, we may now infer from the additional thermochemical evidence afforded by the Φ°_h values for NaCl(aq), NaOH(aq), etc. (the enthalpies of formation of the pure compounds, combined with their total enthalpies of solution), a value of $\eta^\circ_{Na^+(aq)} = -57.476$ kcal/mole, *i.e.*,

$$Na(c) = Na^+(aq) + e; \qquad \Delta H^\circ_{298} = -57.476 \text{ kcal}$$

The agreement among the η° values for a particular cation obtained from independent thermochemical data for its various salts constitutes a check on the self-consistency of the data and the general validity of the scheme. Thus, Φ°_h values for strong electrolytes in solution in a given solvent are interrelated, in the sense that they may be resolved into additive contributions of the ions concerned. The Debye-Hückel interionic attraction theory, discussed in Sec. 7-4, shows how we may take first-order account of the deviation of Φ_h from Φ°_h in dilute solution from general principles; the thermochemical behavior of concentrated solutions of electrolytes remains more or less on an empirical basis at the present time.

We may in a similar manner resolve the limiting partial molal heat capacity of an electrolytic solute in infinitely dilute solution, Φ°_c or $(\gamma^\circ_p)_2$, into independent additive contributions of the ions, by first assigning to H^+ the conventional value: $(\gamma^\circ_p)_{H^+} \equiv 0$. Thus, from Rossini's value of $(\Phi^\circ_c)_{HCl(aq)}$ given in Table 4-13, we may assign to $(\gamma^\circ_p)_{Cl^-(aq)}$ the value -32.5 cal/mole deg at 25°C and 1 atm. We may then proceed in stepwise fashion to calculate (γ°_p) values for other ions. Such information is useful in the correction of η° values for individual ions in solution to other temperatures; *e.g.*, for the process

$$\tfrac{1}{2}Cl_2(g) + e = Cl^-(aq); \qquad \Delta H^\circ_{298} = -40.023 \text{ kcal}$$

we may write formally

$$\begin{aligned}\left(\frac{d\Delta H^\circ_T}{dT}\right)_p &= \Delta C^\circ_p = (\gamma^\circ_p)_{Cl^-(aq)} - \frac{1}{2}(\bar{C}^\circ_p)_{Cl_2(g)} \\ &= -32.5 - \frac{1}{2}(8.11) = -36.6 \text{ cal/deg}\end{aligned}$$

Thus, neglecting the relatively slight variation of ΔC°_p itself with temperature, we may conclude that at 18°C, $\eta^\circ_{Cl^-(aq)} = -39.767$ kcal/mole.

General References for Chapter 4

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Problems

4-1. The heat of formation of HCl(g) has been measured by F. D. Rossini [*J. Research Natl. Bur. Standards*, **9**, 679–702 (1932)] by direct union of H_2(g) and Cl_2(g) in the flame calorimeter, the calorimeter being immersed in water at a mean temperature of 30°C, and the heat being measured by substitution of an electric heating current to effect the same temperature rise in the system. In a typical run, the temperature of the calorimeter system rose by 0.95034 deg (as measured by means of a platinum resistance thermometer) as 0.159049 mole of HCl was being produced by the combustion, the electrical equivalent of the calorimeter system being 15,415.3 int joules/deg. To the total energy released during the run, 38.5 int joules representing net kinetic energy carried by the product gas must be added, and 10.3 int joules representing energy introduced by the ignition spark must be subtracted, as determined by blank runs. Calculate from these data the enthalpy of formation of HCl(g) at 30°C and 1 atm. From the heat-capacity data in Table 3-1, estimate the correction to 25°C. (The correction to the ideal-gas state is negligible in this case.)

4-2. The heat of the addition reaction between C_2F_4(g) and Cl_2(g) has been measured by J. R. Lacher and his associates [*J. Am. Chem. Soc.*, **71**, 1330–1334 (1949)], using an isothermal constant-flow calorimeter. In a typical run, in which the olefin flowing at a rate of 6.93×10^{-4} mole/min and chlorine flowing at a rate of 6.109×10^{-4} mole/min were mixed and passed over a catalyst at 1 atm and at a mean temperature of 90°C, energy was released at a rate equivalent to 35.02 cal/min, determined by electrical standardization of the calorimeter. Calculate ΔH at 90°C and 1 atm for the reaction $C_2F_4(g) + Cl_2(g) = C_2F_4Cl_2(g)$.

4-3. In measuring the heat of combustion of WC(c) in the oxygen bomb calorimeter, standardized by the combustion of standard benzoic acid, L. D. McGraw, H. Seltz, and P. E. Snyder [*J. Am. Chem. Soc.*, **69**, 329–331 (1947)] found for the process:

$$WC(c) + \tfrac{5}{2}O_2(g, 300.45°K, 35\ atm) = WO_3(c) + CO_2(g, 300.45°K, 2.15\ atm)$$
$$\Delta U = -284.76\ kcal$$

For $O_2(g)$, $(dU/dp)_T = -1.56$ cal/atm mole, from direct measurements by F. D. Rossini and M. Frandsen (see footnote 1, page 105), while for $CO_2(g)$

$$(dU/dp)_T = -6.79 \text{ cal/atm mole}$$

estimated from the Beattie-Bridgeman equation of state. Calculate ΔU for the reaction with each gas in the hypothetical ideal-gas state at 1 atm, and calculate $\Delta H^\circ_{300.45}$. Calculate $\Delta H^\circ_{298.16}$, using the $\bar{C}^\circ_p$ values: $O_2(g)$, 6.95 cal/mole deg; $WO_3(c)$, 19.55 cal/mole deg; WC(c), 8.63 cal/mole deg; $CO_2(g)$, 9.21 cal/mole deg.

From the enthalpies of combustion, C(c, graphite), $\Delta H^\circ_c = -94{,}051.8 \pm 10.8$ cal/g-atom, and W(c), $\Delta H^\circ_c = -195{,}700 \pm 900$ cal/g-atom, calculate the standard enthalpy of formation of WC(c) at 298.16°K.

4-4. Thermochemical data for $NaBH_4(c)$ of 99.61 per cent purity have been obtained by W. D. Davis, L. S. Mason, and G. Stegeman [*J. Am. Chem. Soc.*, **71,** 2775–2781 (1949)]. The heat of the reaction

$$NaBH_4(c) + 1.25HCl(200H_2O) = (NaCl + H_3BO_3 + 0.25HCl)(247H_2O) + 4H_2(g)$$

was measured in a constant-volume bomb calorimeter, the mean value of ΔU at 25°C being -66.25 ± 0.07 kcal. Calculate ΔH for this reaction.

The heat of mixing

$$\begin{aligned} &NaCl(60H_2O) + H_3BO_3(60H_2O) + 0.25HCl(508H_2O) \\ &\qquad = (NaCl + H_3BO_3 + 0.25HCl)(247H_2O); \qquad \Delta H_{298} = 0.057 \text{ kcal} \end{aligned}$$

and the heat of dilution of boric acid

$$H_3BO_3(60H_2O) + \infty H_2O(l) = H_3BO_3(aq); \qquad \Delta H_{298} = 0.068 \text{ kcal}$$

were then also measured. Calculate now the enthalpy of the reaction

$$\begin{aligned} &NaBH_4(c) + 1.25HCl(200\ H_2O) + 3H_2O(l) + \infty H_2O(l) \\ &\qquad = NaCl(60H_2O) + H_3BO_3(aq) + 0.25HCl(508H_2O) + 4H_2(g). \end{aligned}$$

Calculate the standard enthalpy of formation of $NaBH_4(c)$:

$$Na(c) + B(\text{solid, amorphous}) + 2H_2(g) = NaBH_4(c)$$

using the enthalpies of formation: $HCl(200H_2O)$, -39.798; $HCl(508H_2O)$, -39.875; $NaCl(60H_2O)$, -97.428; $H_3BO_3(aq)$, -255.2; $H_2O(l)$, -68.317 kcal. (Note that the enthalpy of formation of boric acid is the most uncertain piece of information entering these calculations.)

4-5. F. D. Rossini and J. W. Knowlton [*J. Research Natl. Bur. Standards*, **19,** 249–262 (1937)] have measured the heat of combustion of $C_2H_4(g)$, using the flame calorimeter. At 25°C and 1 atm, corrected to $H_2O(l)$ as product, they obtained $\Delta H = -337{,}280 \pm 70$ cal/mole. Using Rossini's values of $-68{,}313 \pm 10$ cal/mole for the enthalpy of combustion of $H_2(g)$, and $-372{,}810 \pm 110$ cal/mole for the enthalpy of combustion of $C_2H_6(g)$, calculate a value of ΔH at 25°C and 1 atm for the reaction $C_2H_4(g) + H_2(g) = C_2H_6(g)$; estimate its precision, and compare with the directly observed value of $-32{,}580 \pm 60$ obtained by G. B. Kistiakowsky and coworkers (corrected from 82°C to 25°C), on a sample that probably contained 0.25 mole per cent C_2H_6 originally.

Using also the "best" value of $\Delta H^\circ_{298.16} = -94{,}051.8 \pm 10.8$ cal/mole for the combustion of C(c, graphite), selected by E. J. Prosen, R. S. Jessup and F. D. Rossini

[*J. Research Natl. Bur. Standards*, **33**, 447–449 (1944)], calculate the standard enthalpy of formation of $C_2H_4(g)$ at 25°C.

4-6. The heat of combustion of cyanamide has recently been measured by D. J. Salley and J. B. Gray [*J. Am. Chem. Soc.*, **70**, 2650–2653 (1948)]. From the result

$$CH_2N_2(c) + \tfrac{3}{2}O_2(g) = CO_2(g) + H_2O(l) + N_2(g); \qquad \Delta H^\circ_{298.16} = -177.20 \text{ kcal}$$

calculate the standard enthalpy of formation, and also the standard enthalpy at 25°C of the reaction

$$CH_2N_2(c) + 2H_2O(l) = CO_2(g) + 2NH_3(g)$$

using additional data given in Appendix 2.

4-7. The heat of combustion of $D_2(g)$, and the heat of vaporization of $D_2O(l)$ have been measured by F. D. Rossini, J. W. Knowlton, and H. L. Johnston [*J. Research Natl. Bur. Standards*, **24**, 369–388 (1940)], with the following results:

$$D_2(g) + \tfrac{1}{2}O_2(g) = D_2O(l); \qquad \Delta H^\circ_{298.16} = -70{,}414 \text{ cal}$$
$$D_2O(l) = D_2O(g); \qquad \Delta H^\circ_{298.16} = 10{,}850 \text{ cal}$$

Using data for H_2O given in Appendix 2, calculate $\Delta H^\circ_{298.16}$ for the isotope exchange reaction

$$D_2(g) + H^1_2O(g) = D_2O(g) + H^1_2(g)$$

4-8. Calculate the heating value at 25°C in Btu per cubic foot saturated with water vapor at 15°C and 1 atm, of a natural gas consisting of 31.8 per cent ethane, 67.7 per cent propane, and 0.5 per cent nitrogen by volume. Use the standard heats of combustion at 25°C [to $CO_2(g)$ and $H_2O(l)$]: $C_2H_6(g)$, 372.82 kcal/mole; $C_3H_8(g)$, 530.60 kcal/mole [E. J. Prosen and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 263–269 (1945)].

Calculate also the heating value under similar conditions of a water gas consisting of 43.4 per cent CO, 3.5 per cent CO_2, 51.8 per cent H_2, and 1.3 per cent N_2 by volume, using thermochemical data contained in Appendix 2.

4-9. The heats of formation of the four known borates of calcium have been determined by D. R. Torgeson and C. H. Shomate [*J. Am. Chem. Soc.*, **69**, 2103–2105 (1947)] by dissolving them in 1*M* HCl, the amounts in each case being adjusted to be equivalent to 1 g CaO per 1845.5 g of 1*M* HCl. Separate experiments were made on the heat of solution of boric oxide in the same quantity of HCl containing 1 g of CaO. The mean results follow:

Compound	Enthalpy of Solution, cal/mole, in 1.000*M* HCl at 298.16°K
$3CaO{\cdot}B_2O_3$	$-82{,}423 \pm 12$
$2CaO{\cdot}B_2O_3$	$-50{,}287 \pm 20$
$CaO{\cdot}B_2O_3$	$-20{,}259 \pm 8$
$CaO{\cdot}2B_2O_3$	$-10{,}080 \pm 10$
CaO	$-46{,}380 \pm 11$
B_2O_3(0.4139 g in 1845.5 g 1.000*M* HCl)	-3286 ± 7
B_2O_3(0.6209 g in 1845.5 g 1.000*M* HCl)	-3289 ± 7
B_2O_3(1.2418 g in 1845.5 g 1.000*M* HCl)	-3298 ± 7
B_2O_3(2.4836 g in 1845.5 g 1.000*M* HCl)	-3316 ± 7

Calculate the enthalpies of the borates relative to the oxides. Using −151,900 cal/mole as the enthalpy of formation of CaO(c) and −302,000 cal/mole as the enthalpy of formation of B_2O_3(c), calculate the enthalpies of formation of the four calcium borates from the elements.

4-10. The heats of solution of $CaSO_4$(c) and its hydrates in 2.09*m* HCl at 25°C have been measured by E. S. Newman and L. S. Wells [*J. Research Natl. Bur. Standards*, **20**, 825–836 (1938)], the samples taken being all equivalent to 2.000 g of $CaSO_4 \cdot 2H_2O$, dissolved in 640.0 g of the acid. The mean results were as follows:

	Q_s
$CaSO_4 \cdot 2H_2O$(c)	−33.01 cal/g
$CaSO_4 \cdot \frac{1}{2}H_2O$(c)	−11.05 cal/g
$CaSO_4$(c)	−12.67 cal/g

Furthermore, for the reaction,

$$H_2O(l) = H_2O(2.09m\ HCl); \qquad \Delta H_{298.16} = -17 \text{ cal/mole}$$

Calculate the enthalpies of hydration of $CaSO_4$(c) and $CaSO_4 \cdot \frac{1}{2}H_2O$(c) to $CaSO_4 \cdot 2H_2O$(c).

4-11. Given the heat of solution of Na(c) in H_2O(l) at 25°C and 1 atm, devise a system of thermochemical measurements by which the standard enthalpy of formation of NaCl(c) may be determined, using this information.

4-12. Suppose you wished to undertake a thermochemical investigation of the standard enthalpy of formation of Na_2CO_3(c). How would you set up the investigation? What calorimetric measurements would you undertake to determine, and upon what established heats of reaction would your final result depend?

4-13. From the standard enthalpies of combustion given by F. D. Rossini [*J. Research Natl. Bur. Standards*, **22**, 407–414 (1939)]:

$$\begin{aligned} H_2(g) + \tfrac{1}{2}O_2(g) &= H_2O(g); & \Delta H^\circ_{298.16} &= -57{,}798.4 \pm 10.0 \text{ cal} \\ CO(g) + \tfrac{1}{2}O_2(g) &= CO_2(g); & \Delta H^\circ_{298.16} &= -67{,}636.1 \pm 28.7 \text{ cal} \\ C(c, \text{graphite}) + O_2(g) &= CO_2(g); & \Delta H^\circ_{298.16} &= -94{,}051.8 \pm 10.8 \text{ cal} \end{aligned}$$

calculate the standard enthalpy of formation of CO(g) at 25°C, and also the standard enthalpies at 25°C of the water gas reaction

$$H_2(g) + CO_2(g) = H_2O(g) + CO(g)$$

and the producer gas reaction

$$C(c, \text{graphite}) + CO_2(g) = 2CO(g)$$

4-14. Using the data in the preceding problem, and the empirical heat-capacity equations given in Appendix 3, calculate the standard enthalpy of the water gas reaction

$$C(c, \text{graphite}) + H_2O(g) = H_2(g) + CO(g)$$

at 1000°C.

If the heat of this reaction is supplied by the combustion of C(c, graphite) to CO_2(g) at 1000°C, what proportion of C must be burned to the quantity converted to water gas in order to obtain a heat balance?

4-15. The heat of combustion of CH_3OH(g) has been measured at 25°C and 1 atm in the flame calorimeter by F. D. Rossini [*J. Research Natl. Bur. Standards*, **13**, 189–202 (1934)], the result corrected to H_2O(l) as product being 182.58 ± 0.05 kcal/

mole. Calculate $\Delta H_{298.16}$ for the methanol synthesis

$$2H_2(g) + CO(g) = CH_3OH(g)$$

using other data from Appendix 2.

Using for $CH_3OH(g)$ the approximate empirical heat-capacity equation,

$$\bar{C}_p = 2.0 + 0.03T,$$

given by G. S. Parks and H. M. Huffman ("Free Energies of Some Organic Compounds," p. 114, Reinhold Publishing Corporation, New York, 1932) and for $H_2(g)$ and $CO(g)$ the empirical heat-capacity equations given in Appendix 3, calculate ΔH for the reaction at 400°C.

Using Berthelot's equation of state for the three gases, estimate the effect on ΔH of increasing the pressure to 50 atm at 400°C (recall Prob. 3-13).

4-16. The internal energy of combustion of isoprene, $C_5H_8(l)$, was measured by R. S. Jessup [*J. Research Natl. Bur. Standards*, **20**, 589–597 (1938)] in an oxygen combustion bomb standardized by the combustion of standard benzoic acid. The mean result, corrected to 30°C and 1 atm, was

$$C_5H_8(l) + 7O_2(g) = 5CO_2(g) + 4H_2O(l); \qquad \Delta U = -753.28 \pm 0.38 \text{ kcal}$$

(*a*) Calculate ΔH at 30°C and 1 atm.

(*b*) Using for $C_5H_8(l)$ the heat-capacity value, $\bar{C}_p^\circ = 36.7$ cal/mole deg, and for the other substances the values given in Appendix 2, calculate ΔH at 25°C.

(*c*) The heat of combustion of rubber hydrocarbon $(C_5H_8)_x$ was measured by R. S. Jessup and A. D. Cummings [*J. Research Natl. Bur. Standards*, **13**, 357–369 (1934)], who obtained at 25°C and 1 atm, $\Delta H = -(736.76 \pm 1.44)x$ kcal/mole. Calculate the quantity of heat evolved in the reaction

$$x\, C_5H_8(l) = (C_5H_8)_x \qquad \text{(rubber hydrocarbon)}$$

4-17. Calculate the theoretical maximum flame temperature when methane originally at 25°C is burned with the stoichiometric proportion of air containing 21 per cent O_2 and 79 per cent N_2 by volume. [Express $H_T - H_{298}$ for the product of combustion of 1 mole of $CH_4(g)$ as a function of T, using the heat-capacity equations for $CO_2(g)$, $H_2O(g)$, and $N_2(g)$ given in Appendix 3, and equate to the heat of combustion at 25°C corrected to $H_2O(g)$ as product; solve for T by trial. The dissociation of CO_2 and of H_2O at the flame temperature is neglected in this calculation.]

4-18. G. B. Kistiakowsky and his associates [*J. Am. Chem. Soc.*, **57**, 65–75 (1935); **57**, 876–882 (1935); **58**, 146–153 (1936)] have measured the heats of hydrogenation of a number of unsaturated hydrocarbons in the gaseous state, including the following (at 82°C and 1 atm):

Compound	$-\Delta H_{355°K}$
1-Butene	30,341 cal
2-Butene (*trans*)	27,621
2-Butene (*cis*)	28,570
1,3-Butadiene	57,067

Show that the reaction $C_4H_6(g) + H_2(g) = C_4H_8(g)$ is more exothermic when Thiele addition of 1 H atom to each end of the resonant system of unsaturated bonds in 1,3-butadiene takes place than when 1 H atom adds to each member of the pair of adjoining carbons at either end of the chain.

4-19. The standard enthalpies of formation of $CH_3Cl(g)$, $CH_2Cl_2(g)$, and $CHCl_3(g)$ at 25°C are, respectively, −19.58, −21, and −24 kcal/mole. Test these data for consistency of the bond-energy values given in Table 4-2.

4-20. The heat of vaporization of isoprene, corrected to 25°C, is 6200 cal/mole [from vapor-pressure data by N. Bekkedahl, L. A. Wood, and M. Wojciechowski, *J. Research Natl. Bur. Standards*, **17**, 883–894 (1936)]. (*a*) Using the results of Prob. 4-16, calculate the heat of combustion of $C_5H_8(g)$ at 25°C and 1 atm, and the standard enthalpy of formation. (*b*) Calculate the heat of the reaction

$$5C(g) + 8H(g) = C_5H_8(g)$$

and by comparison with hydrocarbon bond-energy data, estimate the resonance energy of the isoprene molecule.

4-21. $SrCl_2(c)$ has the fluorite structure, and $r_0 = 3.02$ Å. Calculate the lattice energy, and using data given in the text, calculate a value for the standard heat of formation. The observed heat [from Sr(c) and $Cl_2(g)$] is 198.0 kcal/mole.

4-22. KCN(c) has the same structure as KCl(c) and the CN^- ion, because of rotation, probably is spherically symmetrical, like the Cl^- ion. Using 3.275 Å as the distance of closest approach between K^+ and CN^-, from X-ray crystallography, and $n = 8$ in Eq. (4-21), calculate the lattice energy of the KCN crystal and $\Delta H^\circ_{298.16}$ for the reaction

$$KCN(c) = K^+(g) + CN^-(g)$$

The standard enthalpy of formation of KCN(c)

$$K(c) + C(c, \text{graphite}) + \tfrac{1}{2}N_2(g) = KCN(c)$$

is −26.9 kcal/mole, from measurements of the heat of combustion, solution, and neutralization of HCN, combined with the heat of solution of KCN(c) itself, while the enthalpy of combustion of $C_2N_2(g)$ is −260 kcal/mole [F. R. Bichowski and F. D. Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corporation, New York, 1936]. Calculate the enthalpy of the process

$$\tfrac{1}{2}C_2N_2(g) + e = CN^-(g)$$

(using data given in the text). Assuming an electron affinity of 84.3 kcal/mole for the CN(g) molecule, estimate the dissociation energy of the $C_2N_2(g)$ molecule into 2CN(g) [compare G. Glockler, *J. Chem. Phys.*, **16**, 600–601 (1948)].

4-23. $NH_4Br(c)$ has the CsCl(c) structure, and $NH_4I(c)$ the NaCl(c) structure, at 25°C, the lattice constants being, respectively, 4.047 and 7.244 Å. Calculate the lattice energies, according to Eq. (4-21), selecting n from Table 4-5 on the basis that NH_4^+ is a Ne-type ion (note that for the CsCl structure, $r_0 = (\sqrt{3}/2)a$, and for the NaCl structure, $r_0 = (\tfrac{1}{2})a$, where a is the lattice constant, or edge of the unit cell).

Using the standard enthalpies of formation, −64.61 kcal/mole for $NH_4Br(c)$, −48.30 kcal/mole for $NH_4I(c)$, −11.04 kcal/mole for $NH_3(g)$, 367.08 kcal/mole for $H^+(g)$, and other data given in the text, calculate the energy of the reaction

$$NH_3(g) + H^+(g) = NH_4^+(g)$$

from the data for each salt [compare J. Sherman, *Chem. Revs.*, **11**, 150–152 (1932)].

4-24. Calculate the lattice energy of the hypothetical compound MgCl(c), assuming that it would crystallize in the NaCl lattice, and assuming for Mg^+ the same ionic radius, 0.65 Å, as for Mg^{++} (the Cl^- radius has the value 1.81 Å). The first ionization potential for $Mg(g) = Mg^+(g) + e$ is 7.61 volts; calculate the standard enthalpy of formation of the hypothetical compound, and compare with that of the actual compound, $MgCl_2(c)$, which is -153.40 kcal/mole.

4-25. (a) Using the data in Table 4-10, plot $\bar{Q}_s$ vs. $m_2^{1/2}$ for HCl concentrations below 1:500 H_2O and confirm by extrapolation the $\bar{Q}_s^\circ$ value given in the table.

(b) From your graph, using Eqs. (4-41a) and (4-42a), calculate $\eta_{H_2O} - \bar{H}^\circ_{H_2O(l)}$ and $\eta_{HCl} - \bar{H}^\circ_{HCl(g)}$ at $m_2 = 0.001, 0.01$, and 0.1 mole HCl/kg H_2O. [Note that the slope of your graph is simply the negative of the differential coefficient appearing in Eqs. (4-41a) and (4-42a).]

(c) From a plot of $\Phi_h - \Phi_h^\circ$ between $n_1 = 2$ and $n_1 = 10$ moles H_2O/mole HCl, calculate the values of $\eta_{H_2O} - \bar{H}^\circ_{H_2O(l)}$ and $\eta_{HCl} - \bar{H}^\circ_{HCl(g)}$ in HCl-H_2O solutions containing 35 per cent and 20 per cent by weight of HCl. What are the differential molal heats of vaporization of the two components from these solutions? [Compare, F. D. Rossini, *J. Research Natl. Bur. Standards*, **9**, 679–702 (1932).]

4-26. Letting $\Delta\bar{H} = -\bar{Q}_s/(1 + n_1)$ in Eq. (4-43) denote the enthalpy of solution per mole of solution formed, prove with the aid of Eq. (4-36) that for a binary solution

$$\frac{d\Delta\bar{H}}{dx_1} = (\eta_1 - \bar{H}_1^\circ) - (\eta_2 - \bar{H}_2^\circ)$$

and show that

$$\eta_1 - \bar{H}_1^\circ = \Delta\bar{H} + (1 - x_1)\frac{d\Delta\bar{H}}{dx_1}$$

$$\eta_2 - \bar{H}_2^\circ = \Delta\bar{H} - x_1\frac{d\Delta\bar{H}}{dx_1}$$

4-27. The enthalpy of formation of solid solutions of NaCl and NaBr

$$x_{NaCl}NaCl(c) + x_{NaBr}NaBr(c) = x_{NaCl}NaCl, x_{NaBr}NaBr(c)$$

was measured at 25°C by M. A. Fineman and W. E. Wallace [*J. Am. Chem. Soc.*, **70**, 4165–4169 (1948)] from the difference between the heats of solution in water of the solid solutions and of physical mixtures of the two salts having corresponding compositions. The following results were obtained:

x_{NaBr}	$\Delta\bar{H}_{298.16}$, cal/mole of Solid Solution
0.1018	136.7
0.2019	220.5
0.2982	291.9
0.4029	323.5
0.4927	335.5
0.5977	319.9
0.7007	271.0
0.7922	213.7
0.8947	122.6

The authors showed that the results could be represented by the empirical equation

$$\Delta\bar{H} = 1433x_{NaBr} - 1616x_{NaBr}^2 + 182.8x_{NaBr}^3$$

(Test this equation at several of the given experimental compositions.) Calculate $(\eta_1 - \bar{H}_1^\circ)$ for NaBr and $(\eta_2 - \bar{H}_2^\circ)$ for NaCl at 0.1 mole-fraction intervals, using the equations derived in Prob. 4-26.

4-28. From the data in Table 4-9 and the standard enthalpies of formation

	$\bar{H}^\circ_{298.16}$
$PbO_2(c)$	−66.12 kcal/mole
$PbSO_4(c)$	−219.50 kcal/mole
$H_2O(l)$	−68.317 kcal/mole

(from "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D.C., 1947), calculate the enthalpy of the reaction

$$Pb(c) + PbO_2(c) + 2H_2SO_4(10H_2O) = 2PbSO_4(c) + 2H_2O(l)$$

Using the data in Table 4-11, calculate the enthalpy of the actual lead storage-cell reaction

$$Pb(c) + PbO_2(c) + 2H_2SO_4(1H_2SO_4{:}10H_2O) = 2PbSO_4(c) + 2H_2O(1H_2SO_4{:}10H_2O)$$

as an infinitesimal quantity of electricity is discharged.

4-29. Using the data in Table 4-12, calculate the quantity of heat evolved when 96.1 per cent H_2SO_4 is mixed with sufficient oleum containing 29.0 per cent free SO_3 to form 1000 g of 100 per cent H_2SO_4 at 18°C.

Taking the specific heat of $H_2SO_4(l)$ as given approximately by the formula

$$c_p = 0.32 + 0.0005t \text{ cal/g deg},$$

between 20 and 80°C (Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIIc, p. 2277, 1936) estimate the maximum temperature rise, in the absence of heat losses.

4-30. K. S. Pitzer [*J. Am. Chem. Soc.*, **59**, 2365–2371 (1937)] measured the heat of neutralization at 25°C of $NaOH{\cdot}1065.5H_2O$ with $HCl{\cdot}46.5H_2O$ to form $NaCl{\cdot}1113H_2O$, the quantity of heat evolved being 13,828 ± 12 cal per mole of acid and base reacting. In a separate experiment, he measured the heat of dilution of $HCl{\cdot}46.5H_2O$ to $HCl{\cdot}1112H_2O$, the quantity of heat evolved being 352 ± 8 cal per mole of HCl (compare Table 4-10). Calculate the standard enthalpy of ionization of H_2O to form $H^+(aq) + OH^-(aq)$ at infinite dilution, using the heats of dilution extrapolated to zero concentration: for $HCl{\cdot}1112H_2O$, +100 cal; for $NaOH{\cdot}1065.5H_2O$, +86 cal; and for $NaCl{\cdot}1113H_2O$, +73 cal. Using the standard enthalpy of formation of $H_2O(l)$ at 25°C, −68,313 ± 10 cal, as determined by F. D. Rossini from direct combustion of $H_2(g)$ with $O_2(g)$ in the flame calorimeter, calculate $\eta^\circ_{OH^-(aq)}$.

4-31. K. S. Pitzer [*J. Am. Chem. Soc.*, **59**, 2365–2371 (1937)] has measured the heats of ionization of a number of weak acids and bases by straightforward calorimetry. Thus, upon mixing exactly 10 ml of 1.162*M* HCl with 875 ml of 0.015*M* $NaHCO_3$, he observed that 26.6 ± 0.6 cal of heat was evolved (measured by substitution of an equivalent quantity of electrical energy to heat the calorimeter and contents through the same temperature rise). Assuming 452 cal/mole as the heat of dilution of the HCl to infinite dilution, and neglecting the heats of dilution of the other solutes, calculate the enthalpy of ionization of $H_2CO_3(aq)$ to $H^+(aq)$ and $HCO_3^-(aq)$.

In another series of experiments, he found that upon mixing exactly 10 ml of 1.162*M* HCl with 875 ml of a solution containing 0.015*M* Na_2CO_3 and 0.015*M* $NaHCO_3$ (added to repress hydrolysis of $CO_3^=$), the quantity of heat evolved was 46.7 ± 0.5 cal. In this case, part of the HCl reacted with the OH^- present in the buffer mixture; using 4.70×10^{-11} as the secondary ionization constant of H_2CO_3, correct for the quantity of HCl consumed and the energy liberated by the reaction with the free OH^- present, as well as for the heat of dilution of HCl, and calculate finally the standard enthalpy of ionization in infinitely dilute solution of $HCO_3^-(aq)$ to $H^+(aq) + CO_3^=(aq)$.

4-32. The enthalpy of solution of $CO_2(g)$ at infinite dilution in water is −4,640 cal/mole at 25°C. Combining this information with the standard enthalpy of formation of $CO_2(g)$, −94,051.8 ± 10.8 cal/mole, and the results of the preceding problem, calculate $\eta°$ of $HCO_3^-(aq)$ and of $CO_3^=(aq)$.

Using Pitzer's value of 865 ± 30 cal/mole as the enthalpy of ionization of $NH_4OH(aq)$ and 13,358 cal/mole as the enthalpy of ionization of $H_2O(l)$, calculate the standard enthalpy of the reaction

$$CO_2(g) + NH_4OH(aq) = NH_4^+(aq) + HCO_3^-(aq)$$

4-33. B. J. Fontana and W. M. Latimer [*J. Am. Chem. Soc.*, **69**, 2598–2599 (1947)] found that when $NaClO_2(c)$ was dissolved in a solution containing $HClO_4$ and KI, the heat of the reaction between $ClO_2^-(aq)$, $I^-(aq)$ and $H^+(aq)$ was 105.76 ± 0.06 kcal per mole of $ClO_2^-(aq)$, corrected for the heat of solution of $NaClO_2(c)$ in water (−0.10 ± 0.01 kcal/mole). Under the conditions of the calorimetric runs, the equilibrium between $I_2(aq)$ and $I_3^-(aq)$ was estimated to be such that 98.6 per cent of the total iodine produced was in the form of $I_3^-(aq)$. Using the data,

$$\begin{aligned} \tfrac{1}{2}H_2(g) + \tfrac{1}{2}I_2(c) &= HI(aq); & \Delta H_{298} &= -13.37\ \text{kcal} \\ I_2(c) &= I_2(aq); & \Delta H_{298} &= 5.0\ \text{kcal} \\ I^-(aq) + I_2(aq) &= I_3^-(aq); & \Delta H_{298} &= -\ 4.22\ \text{kcal} \end{aligned}$$

and also the standard enthalpies of formation of $Cl^-(aq)$ and $H_2O(l)$ given in Appendix 2, calculate the enthalpy of formation of $ClO_2^-(aq)$.

4-34. From the data in Table 4-13, calculate the specific heat of 20 per cent HCl at 25°C. Using the results of Prob. 4-25*c*, estimate also the values of $\eta_{H_2O} - \bar{H}^\circ_{H_2O(l)}$ and $\eta_{HCl} - \bar{H}^\circ_{HCl(g)}$ at 20°C.

4-35. The specific heat of NaOH solution relative to that of pure water at 25°C is 0.9526 cal_{25}/g deg at m_2 = 1.00 mole/kg, and 0.9105 cal_{25}/g deg at m_2 = 2.55 mole/kg [selected from measurements by F. T. Gucker and K. H. Schminke, *J. Am. Chem. Soc.*, **55**, 1013–1019 (1933)]. Calculate the values of Φ_c° and A according to Eq. (4-46), and compare with those given in Table 4-13. Calculate therefrom the values of $(\gamma_p)_{H_2O}$ and $(\gamma_p)_{NaOH}$ in 1.00*m* solution at 25°C.

4-36. The heat of solution of Na(c) in $H_2O(l)$ to form $NaOH(100\ H_2O)$ is given by F. R. Bichowski and F. D. Rossini ("Thermochemistry of Chemical Substances," Reinhold Publishing Corporation, New York, 1936) as 43.7 kcal/mole at 18°C, and the heat of dilution to infinitely dilute solution as 0.039 kcal. Using the established heat of formation of $H_2O(l)$ at 18°C, 68.372 kcal/mole, calculate Φ_h° of NaOH(aq) at 18°C. Using the data in Table 4-13, correct Φ_h° to 25°C, and using the value of $\eta^\circ_{OH^-(aq)}$ given in the text (from heat-of-neutralization data), calculate $\eta^\circ_{Na^+(aq)}$ at 25°C.

4-37. Calculate from the data in Table 4-13 the value of $(\gamma_p^\circ)_{K^+(aq)}$, and using the value of $\eta^\circ_{K^+(aq)} = -60.270$ kcal/mole at 18°C and 1 atm given by F. R. Bichowski and F. D. Rossini ("Thermochemistry of Chemical Substances," Reinhold Publishing Corporation, New York, 1936), calculate $\eta^\circ_{K^+(aq)}$ at 25°C and 1 atm. [The heat capacity of K(c) is given in Appendix 2.]

Combining this result with $\eta^\circ_{OH^-(aq)}$ given in the text, and with the total enthalpy of solution of KOH(c), $\Delta H_s^\circ = -13.20$ kcal, calculate the standard enthalpy of formation of KOH(c) at 25°C.

4-38. The partial *specific* volumes of the components of a binary solution are the intercepts on the 0 and 100 per cent axes of the tangent to the specific volume (reciprocal of the density) vs. weight per cent curve. The partial *molal* volumes may then be obtained by multiplying the partial specific volumes by the molecular weights of the respective components. From the density data for H_2SO_4-H_2O solutions at 25°C given in the "International Critical Tables," Vol. III, pp. 56–57, 1928, plot the specific volume vs. weight per cent, and determine the partial molal volumes of H_2SO_4 and H_2O at 10 weight per cent intervals by application of this graphic method.

CHAPTER 5

THE SECOND LAW OF THERMODYNAMICS

The experiments of Rumford, and particularly the quantitative experiments of Joule proved beyond any doubt that energy in mechanical or electrical form can be converted *without limit* into thermal form, *e.g.*, into raising the temperature of a material body, or into effecting some phase transition that ordinarily requires the absorption of heat, etc. In this chapter, we shall examine the conditions attending the reverse transformation, that of energy from a thermal source into energy in nonthermal forms, such as is accomplished by a heat engine. To such transformations, Joule's law of course applies; there is a quantitative relation between the net quantity of thermal energy consumed and the quantity of energy appearing in nonthermal forms, 1 cal_{15} being equivalent according to the best modern measurements to 4.1855 ± 0.0004 joules of energy in mechanical or electrical form.[1] It is well known, however, that the availability of energy in thermal form is limited; thus, no heat engine will operate continuously unless the source of thermal energy is at a higher temperature than that of the surroundings. This simple general observation contains as we shall presently see the germ of the principle known as the second law of thermodynamics. The subject was first explored by the young French engineer Nicolas Léonard Sadi Carnot in some notes, "Reflexions sur la puissance motrice du feu," written in 1824. Carnot was particularly concerned with how heat was utilized in the steam engine, which had recently been developed as a practical machine, but whose principles were but vaguely understood. He perceived, however, that his treatment of the problem was quite general, within the scope of the caloric fluid theory of heat then prevailing. The significance of Carnot's ideas was not fully comprehended until they were recalled by William Thomson (Lord Kelvin) in 1848, many years after Carnot's death. Kelvin and R. J. E. Clausius generalized Carnot's treatment to bring it into accord with the principle of conservation of energy based on Joule's work, and thus established the foundations of modern thermodynamics.

5-1. Maximum Work and Thermodynamic Reversibility. Let us consider some devices for transforming thermal energy into energy in nonthermal forms. A real heat engine always consists of some material sys-

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[1] R. T. Birge, *Rev. Modern Phys.*, **13**, 233–239 (1941).

tem (steam in the steam engine; air mixed with combustion-product gases in the internal-combustion engine) that undergoes certain changes of state, during which it absorbs net thermal energy Q (derived from the combustion of coal or fuel oil under the boiler of the steam engine, or from the combustion of gasoline or light fuel oil within the cylinder itself of the internal-combustion engine), and does work W. The net heat absorbed and the net work done during any sequence of changes always satisfy the first law of thermodynamics,

$$\Delta U = Q - W \tag{5-1}$$

where ΔU represents the net change in internal energy of the system undergoing the changes.[1] Now, in a practical engine, the working substance is generally put through a cyclic process that in principle restores it periodically to the same state; otherwise the engine would run down before the thermal source had been depleted of its energy. Because water and air are cheap and so readily available, the particular sample of water put through the steam-engine cycle and the particular sample of air put through the internal-combustion engine cycle are generally not recycled, but are continually being replaced by fresh samples; this practical consideration does not, however, affect the general principle that the water and the air are ultimately resorted to the respective bodies from which they were originally withdrawn, without having undergone permanent changes of state, except possibly for a gradual thermal change of a general nature in the state of the entire world, which as we shall presently see, constitutes the subject proper of the second law of thermodynamics.

A heat engine that is to operate continuously, then, withdrawing energy from a thermal source and doing work without permanently changing the state of the working substance, must be designed on a cyclic principle, such that each complete cycle leaves the working substance in the same state, ready for the next cycle. Therefore, during each complete cycle (starting at any particular phase), $\Delta U = 0$ [compare Eq. (2-23)], and

$$Q = W \qquad (\Delta U = 0) \tag{5-2}$$

It might appear at first sight that an indefinitely large quantity of work might be done by the heat engine, simply through some arrangement whereby the net heat Q absorbed during each cycle is made indefinitely large. Certainly, energy originally in nonthermal form expended *on* the material system and passing to the surroundings in the form of heat (such

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[1] In a steam turbine or in a jet-propulsion engine, work is done mainly at the expense of kinetic energy of the gas, whose change must be included with ΔU on the left of Eq. (5-1). In the ordinary gas-expansion engine, however, the kinetic energy of the working substance is inappreciable.

as through friction, mechanical stirring, effect of an electric-resistance coil, etc.) can be made indefinitely large in amount [Q and W having negative values in Eq. (5-2)], as shown by Rumford's and Joule's experiments. There is nothing inherent in the first law of thermodynamics that would imply any restriction on the reverse transformation, that of thermal into mechanical or electrical energy, beyond equivalence between the net quantity of heat absorbed and the net quantity of work done, as embodied in Eqs. (5-1) and (5-2). Yet, experience shows that every actual process has natural limitations to its capacity for absorbing thermal energy and releasing an equivalent amount of energy in nonthermal form.

One general type of limitation arises from our inability to free the process completely from dissipative losses. Our process for the generation of mechanical or electrical energy cannot be utilized with perfect efficiency, because some of the nonthermal energy developed by the heat engine is consumed (*i.e.*, restored to thermal form) in overcoming friction, electric resistance of the dynamo and leads, etc.; when, for example, steam expands in the cylinder of a steam engine, some of the energy potentially available in mechanical form is expended as heat in overcoming friction between the piston and the cylinder. This type of limitation raises no new theoretical questions; it is perfectly comprehended within the scope of the first law of thermodynamics. There is an ideal upper limit to the quantity of work that can be produced by a given change of state taking place in a real system, which is approached as we reduce the effects of dissipative influences. Let us discuss this situation further in terms of specific examples; in Sec. 5-2, we shall then proceed to consider a different type of limitation, imposed by the relation of the temperature of our source of thermal energy to the temperature of the surroundings.

Consider a gas confined in a cylinder by means of a movable piston, to which an external pressure is applied whose instantaneous value is represented by the symbol P; then as the gas expands from volume V_1 to volume V_2, the work done by the gas against the external pressure P is $\int_{V_1}^{V_2} P\,dV$. Suppose that the expansion is carried out at constant temperature; then since we know that to a first approximation in the low-pressure range, $(\Delta U)_T = 0$ (the Joule experiment), therefore $Q = W$; in other words, the isothermal expansion of an ideal gas constitutes a simple method of drawing thermal energy from the surroundings (which serve to maintain the temperature of the gas constant) and doing an equivalent amount of work. For a real gas at finite pressures, $(\Delta U)_T$ would differ somewhat from zero, and W would then be related to Q by means of the general relationship, Eq. (5-1); but as we shall see presently, there is no loss of generality for our present purpose in considering the gas to be ideal. Now, the external pressure P applied to the piston confining the gas may be given any value from 0 up, the quantity of work done for the given volume change increasing in proportion. If for example $P = 0$, as when the gas expands freely into a vacuum (the Joule experiment), then no work at all is done, and no heat is absorbed from the surroundings (to a first approximation, at least, for real gases). If the gas is to do work, then P must be given a finite value, but it cannot be as large as the static equilibrium pressure p of the gas consistent with its instantaneous volume V at any stage of the expansion, because a value of P somewhat smaller than p would be sufficient in view of friction to prevent the piston from moving at all. In the ideal limiting case of a frictionless piston, however, there is then clearly an upper limit to the work that can be done by the expanding gas, given by the value of $\int_{V_1}^{V_2} p\, dV$; for if one attempted to increase the value of the work done by the gas by making P any larger than p, the process would actually be reversed, and the gas instead of expanding would be compressed at the expense of work done on it by the external applied pressure. In other words, the *maximum work* that can theoretically be obtained from the expansion of the gas is obtained when the gas is permitted to expand with frictional losses reduced to zero against an external pressure maintained at a value never more than infinitesimally below the value of its instantaneous static equilibrium pressure. Now, in compressing the gas from volume V_2 back to volume V_1, one will observe that the work of compression (the negative of the work $\int_{V_2}^{V_1} P\, dV$ done *by* the gas) may be made to assume a numerical value as large as one pleases, by the application of a sufficiently high pressure P; if the temperature is maintained constant, a quantity of heat equal within a first approximation to the quantity of work done on the gas then passes on to the surroundings. The high pressure P might be maintained, for example, if there were considerable friction to overcome between the piston and the cylinder, or if the gas were compressed rapidly; in any event, the presence of some degree of friction would make it necessary that P exceed p, the instantaneous static pressure of the gas, in order that the piston move at all. In the ideal limiting case of a frictionless piston, there is thus a lower limit to the work that must be done in order to compress the gas (*upper* limit in the algebraic sense to the work done *by* the gas), given by the value of $\int_{V_2}^{V_1} p\, dV$. This quantity is equal in magnitude but opposite in sign to the maximum work that can be done by the gas during the reverse process of expansion along the same path connecting the same pair of end states. Thus, we may write in general

$$W \leqq \int_{V_1}^{V_2} p\,dV \qquad (5\text{-}3)$$

where V_1 denotes the initial and V_2 the final volume of the gas and p denotes its equilibrium or static pressure corresponding to the instantaneous volume V; Eq. (5-3) applies in the algebraic sense along a given path (assumed relation between p and V during the change of state), regardless of direction, *i.e.*, whether V_2 is greater than V_1, or V_1 is greater than V_2. The specification of constant temperature fixes exactly in the case of an ideal gas the form of the relationship between p and V during a change of state, and Eq. (5-3) then reduces to

$$W \leqq nRT \ln \frac{V_2}{V_1} \quad (T \text{ const; ideal gas}) \qquad (5\text{-}4)$$

A thermodynamic process carried out under conditions differing insensibly from those of equilibrium throughout is said to be *thermodynamically reversible.* This expression implies that infinitesimal changes in appropriate directions of the variables determining the state at any stage of the process would be sufficient to send the system in exactly the opposite direction along the same path. In particular, the work done by the system during a thermodynamically reversible change is the same in magnitude but exactly opposite in sign for the two opposing directions, and sets an algebraic upper limit to the work that can actually be done by the system during a corresponding real change of state. Real changes, of course, are never reversible in the thermodynamic sense. One cannot in practice, for example, take full advantage of the energy of a compressed gas, because if one were to attempt to derive the maximum work by continually adjusting the external pressure on the confining piston to a value but infinitesimally lower than the instantaneous value of the equilibrium pressure as the gas expanded, the process would require an infinitely long time to be completed. However, the reversible process conceived as the *ideal limit* of some real process, whose work may be calculated in operational terms as precisely as one pleases from a series of data taken under static or equilibrium conditions (*e.g.*, measurement of p as a function of V for a gas at given constant temperature), is an idea of the utmost theoretical importance, as perceived by Carnot.

To take another illustration of the same basic idea, let us consider a different device for obtaining work at the expense of energy that would ordinarily appear in thermal form, the galvanic cell. In the Daniell cell, for example, the chemical reaction taking place during discharge is essentially

$$\mathrm{Zn(c)} + \mathrm{CuSO_4}(C_1 \text{ in } \mathrm{H_2O}) = \mathrm{ZnSO_4}(C_2 \text{ in } \mathrm{H_2O}) + \mathrm{Cu(c)} \qquad (5\text{-}5)$$

If the concentrations of the two electrolytes are both approximately 0.1 mole/liter, then from straightforward thermochemical measurements, $\Delta H_{298} = -51.8$ kcal; when the reactants are directly mixed, all this energy is released in thermal form. In the Daniell cell, however, the zinc does not come into direct physical contact with the $CuSO_4$ solution, and part of the energy released by the cell reaction can then be made available in electrical form. Let E' denote the instantaneous value of the potential difference across the electrodes as the cell is discharged; then the work done by the cell on the external circuit as j g-eq of Zn(c) and $Cu^{++}(C_1 \text{ in } H_2O)$ are consumed is equal to $\int_0^j E'\,dj$, the direction of spontaneous flow of negative electricity (electrons) in the external circuit being from the zinc to the copper electrode. If E' is measured in volts and j in coulombs through Faraday's law, 1 g-eq = 96,485 ± 10 coulombs, then the quantity of electrical energy sent into the external circuit, given by the value of this integral, is measured in joules; we may also replace dj by $I\,d\tau$, where I represents the instantaneous value of the current (in amperes) and τ represents time (in seconds). Now, E' may be made to assume any value, from 0 up, the quantity of energy sent in electrical form into the external circuit increasing in proportion. Thus, one may short-circuit the cell by means of a heavy copper bar, whose electric resistance is negligible compared with the internal electric resistance of the cell itself; the value of E' is then zero, and no work at all is done by the cell; a quantity of heat equal to $-\Delta H$ for the cell reaction is released within the cell, just as though the reactants had been brought into direct contact with each other. If the external circuit consists simply of a metallic conductor of resistance R_e, while the internal resistance is R_i, then, in general, $E' = ER_e/(R_e + R_i)$, where E is a property of the cell, its so-called emf, or potential difference on open circuit [Eq. (2-11)]. The value of E is determined by the cell reaction, and it varies with the states of the reactants and products, as determined by temperature, pressure, and the concentrations of the electrolytes; its value for the Daniell cell at room temperature and pressure, when the Zn^{++} and the Cu^{++} concentrations are equal, is about 1.08 volts. The maximum quantity of energy in electrical form is sent into the external circuit, therefore, when R_e is very large in comparison with R_i, so that E' approaches in value its uppermost limit, E; thus

$$W' = \int_0^j E'\,dj \leqq \int_0^j E\,dj \tag{5-6}$$

When the external circuit consists simply of a metallic conductor, all this energy is dissipated as heat in the external circuit; discharge of the cell in such circumstances, even when R_e is extremely large, cannot be regarded as thermodynamically reversible. We may, however, connect the cell to an external circuit that includes another source of electrical energy, *e.g.*, a different cell set up in a potentiometer circuit, by which means a potential difference E' either smaller or larger than E may be impressed on the electrodes. Then it becomes clear that Eq. (5-6) is valid in general; for if we increase E' beyond E, we find that the direction of the current is reversed, so that instead of withdrawing a greater quantity of electrical energy from our cell, we are putting energy into it, charging it at the expense of electrical energy withdrawn from the external circuit (*i.e.*, from the battery of the potentiometer). The upper limit to the quantity of work in electrical form that can be done by our cell is therefore $\int_0^j E\,dj$; this maximum work would be attained if the cell were allowed to discharge against a potential difference maintained not more than infinitesimally below the potential difference on open circuit. Now, Eq. (5-6) continues to apply in the algebraic sense when E' exceeds E, the signs of dj and W' then being reversed; in other words, the value of $-\int_0^j E\,dj$ (with dj negative) represents the *lower* limit to the work in electrical form $-W'$ that must be done *on* the cell in order to charge it, the cell reaction being driven backward. If E' exceeds E, then the energy difference between $-W'$ and $-\int_0^j E\,dj$ (both of these quantities having positive values, in accordance with our sign conventions) appears in the form of Joule heat generated in overcoming the electric resistance of the cell.

Thus, when the galvanic cell is coupled to a potentiometer, adjusted close to the potential difference of the cell on open circuit, so that current practically ceases to flow through the cell (precisely the condition sought when one uses the potentiometer in the ordinary way to measure the emf of the cell), one is then in effect setting up the chemical reaction from which the cell derives its energy under conditions closely approaching thermodynamic reversibility. A slight displacement of the applied potential difference up or down from the equilibrium potential difference E is sufficient to drive the chemical reaction in either of the two opposite directions, in circumstances such that the work done by the cell for either direction is practically the same in magnitude, but exactly opposite in sign; a larger displacement from E would of course destroy the condition of thermodynamic reversibility, in accordance with the general relation (5-6). Not every galvanic cell can be set up to operate in a strictly reversible manner; in fact, the types available are severely limited, as we shall see in Chap. 9. One must be sure that the chemical change taking place as the cell is charged by the application of a higher potential difference is the exact reverse in every detail of the spontaneous reaction taking place as the cell is discharged. This is not quite true of the ordinary Daniell cell, because of irreversible migration of ions across the liquid junction between the two electrolytes; thus, during discharge, Zn^{++} ions migrate into the $CuSO_4$ electrolyte, while when the direction of the current is reversed, Cu^{++} ions migrate instead into the $ZnSO_4$ electrolyte; these processes, which tend to take place slowly even in the absence of an electric current, through ordinary thermal diffusion, are not included in the simple chemical equation (5-5), which therefore does not quite accurately represent the true change taking place in the cell. It is sufficient for our present purpose, however, to note that of the 51.8 kcal decrease in enthalpy that accompanies the chemical reaction (5-5), a maximum of but 49.8 kcal [= (1.08 volts) (2 g-eq)(96,485 coulombs/g-eq)(1 kcal/4184 volt-coulombs)] is available in electrical form; at least 2.0 kcal must still be released directly in thermal form. Conversely, at the same temperature, pressure, and electrolyte concentrations, one must expend a minimum of 49.8 kcal of energy in electrical form in order to drive the chemical reaction (5-5) in the reverse direction (to cause Cu to displace Zn from a solution of its sulfate), and only the balance, 2.0 kcal, required by the conservation principle can at most be taken in from the surroundings in thermal form.

5-2. The Second Law of Thermodynamics. Equations (5-4) and (5-6) express limitations imposed by nature on the quantities of energy in nonthermal form that can be derived from two particular kinds of processes, one involving changes in the state of an ideal gas, and the other involving a chemical oxidation-reduction reaction. In either case, we have seen that the maximum work is derived when the system is maintained throughout in a state differing but infinitesimally from the equilibrium state characteristic of the external conditions instantaneously prevailing. A slight shift in the appropriate direction of these conditions is then sufficient to reverse exactly the direction in which the system's state tends to change, changing the sign of W_r; a change of state executed hypothetically under such conditions is said to be executed reversibly.

These equations suggest, however, a far more general limitation on the utilization of thermal energy, first perceived by Carnot; for so long as the temperature is fixed, they imply that at least as much energy in nonthermal form must be expended on the respective systems in order to restore them to their original states as they are capable of producing. Suppose, for example, we attempt to base a heat engine on the cyclic expansion and compression of a gas, as in the ordinary steam engine or the internal-combustion engine; for simplicity, we shall treat the gas as ideal, but this involves no real loss of generality, as we shall presently see.

So long as the temperature of the gas remains constant (*e.g.*, at the temperature of the potential source of thermal energy), Eq. (5-4) implies that the net work W done by the gas during a complete cycle that restores it to its original state must necessarily satisfy the condition

$$W \leqq 0 \qquad (T \text{ const}) \tag{5-7}$$

For Eq. (5-4) applies in the algebraic sense both as the gas expands (the expression on the right then having a positive value) and as it is compressed (the expression on the left then being negative). The equality sign in Eq. (5-7) applies in fact only if both the expansion and the restoring compression are executed under thermodynamically reversible conditions. Otherwise, an irreversible or permanent transfer of energy from mechanical to thermal form takes place during each cycle. The transfer may be effected in the present instance through mechanical friction, temporary eddy currents set up in the gas, etc., but whatever the mechanism, it tends to make W algebraically smaller (more negative) than the ideal value for reversible change, whether during expansion or compression.

If, however, the gas can be compressed at some lower temperature than the temperature at which it is permitted to expand, then within the limitation represented by Eq. (5-4), it is possible for the gas to do a positive quantity of net work during each cycle. To be explicit, let W' denote the quantity of work done by n moles of an ideal gas as it expands from volume V_1 to volume V_2 at the constant (higher) temperature T'; then

$$W' \leqq nRT' \ln \frac{V_2}{V_1}$$

Likewise, let W'' denote the quantity of work done by the same quantity of gas as it is compressed from volume V_2 back to volume V_1 at the constant (lower) temperature T'' (its value will of course be negative); then

$$W'' \leqq nRT'' \ln \frac{V_1}{V_2}$$

The cycle may be completed by means of intermediate steps in which the gas at constant volume V_2 is cooled from T' to T'', and at constant volume V_1 is heated from T'' back to T'; neither of these steps involves work, and for an ideal gas, the heat given up during the one exactly counterbalances the heat absorbed during the other, since $\bar{C}_v$ is independent of the pressure, as shown by the application of the general thermodynamic relations, (3-49) and (3-41), to a gas satisfying the ideal-gas equation of state, Eq. (3-60).[1] Thus, for the net work done by the gas during one complete

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[1] In the cycle we have just described, if the gas is cooled at the constant volume V_2 from T' to T'' by direct contact with the lower temperature medium and later is

cycle,

$$W = W' + W'' \leqq nR(T' - T'') \ln \frac{V_2}{V_1} \tag{5-8}$$

which may have a positive value, so long as $T' > T''$ (on the assumption by hypothesis that $V_2 > V_1$). Now, the quantity of heat Q' absorbed from the source of thermal energy at the constant temperature T' is equal to W', inasmuch as for an ideal gas, $(\Delta U)_{T'} = Q' - W' = 0$ [see Eq. (3-62)]; therefore only the fraction

$$\frac{W}{Q'} \leqq \frac{T' - T''}{T'} \tag{5-9}$$

is converted into mechanical form, the balance $[1 - (W/Q')]$ representing the fraction passed on to the surroundings at the temperature T'' still in thermal form. Since $W = Q' + Q''$, where $-Q''$ represents the quantity of thermal energy transferred to the lower temperature part of the surroundings, at the constant temperature T'', Eq. (5-9) may be put in the equivalent form

$$\frac{-Q''}{Q'} \geqq \frac{T''}{T'} \tag{5-10}$$

Thus, the utilization of the thermal energy absorbed by the gas at the higher temperature is necessarily incomplete, even when the gas is put through a cycle of reversible changes of state. Equation (5-9) represents the efficiency with which the cyclic heat engine transforms thermal into mechanical energy, without itself undergoing permanent change. The efficiency of such an engine, operating between two fixed temperatures, thus has as an upper limit the function of the two temperatures given by the right-hand member of Eq. (5-9). Unless provision is made for com-

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warmed at the constant volume V_1 from T'' back to T' by direct contact with the higher temperature thermal source, then at least the quantity of thermal energy, $n \int_{T''}^{T'} \bar{C}_v^\circ \, dT$, would be irreversibly transferred from T' to T'' during each cycle. This irreversibility could be eliminated, in principle, if a series of intermediate bodies were available, at temperatures differing by infinitesimal degrees between T' and T''; the thermal energy released by the gas as it cooled from T' to T'', by successive contacts with the intermediate bodies, could then be stored reversibly, available for restoring the gas back through the reverse sequence of stages to the initial temperature T'. In Carnot's original treatment, he conceived the idea of cooling the gas from T' to T'' by means of a further expansion under adiabatic conditions and likewise of restoring the gas to its original temperature by an adiabatic compression. No heat leaves or enters the system during these adiabatic stages; one may prove through Eqs. (3-83) and (3-84) that if the entire cycle is carried out reversibly, the work of the two adiabatic steps cancels (since $\bar{C}_v^\circ$ is a function only of temperature for an ideal gas), and the net work satisfies the equalities represented in Eqs. (5-8) and (5-9).

pressing the gas at a lower temperature than the temperature at which it was allowed to expand, there is no way to restore it to its original state without the expenditure of at least as much energy from the surroundings in nonthermal form as was yielded by the gas in expanding.

Carnot perceived that what is true of the expansion and compression of an ideal gas[1] is but a special case of a far-reaching principle, which has come to be known as the *second law of thermodynamics*. Every real thermodynamic process leaves a permanent change in the world, either immediate or deferred in character, the deferred change (which may be used to counteract the immediate change that has taken place in the system itself) being equivalent ultimately either to the transformation of energy from nonthermal to thermal form or to the transfer of thermal energy from a higher temperature to a lower temperature level. *No process has ever been discovered whose sole result is the transfer of energy from thermal to nonthermal forms.* In the cyclic heat engine, which transforms thermal energy to nonthermal energy without itself undergoing permanent change, the permanent change in the world at large consists invariably of the transfer during each cycle of a certain quantity of unutilized thermal energy from the source to surroundings at a lower temperature than the source; this is fundamentally an irreversible or one-directional change, which would tend to take place of its own accord if the thermal source and the lower temperature surroundings were to be exposed to each other's influence directly (compare Sec. 1-1) instead of through the intermediate agency of the heat engine. In the absence of lower temperature surroundings, however, the energy of the thermal source is completely unavailable for the continued production of work, even if the heat engine is supposed to operate reversibly [compare Eq. (5-9)]. To be sure, one may transfer thermal energy back from the lower temperature to the higher temperature level by means of a cyclic refrigerating engine, or heat engine driven in reverse, but this can be accomplished only through the expenditure of additional energy in nonthermal form, passed on ultimately to the surroundings in the form of heat. As we shall note in the following section, the second law of thermodynamics implies that we cannot so counteract the "permanent" change effected by the operation of the heat engine without expending at least as much work on the refrigerating engine as the output of the heat engine; thus, in attempting to do so, we should merely be substituting a different and even more permanent

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[1] The behavior of steam in an actual steam engine is only slightly more complex, involving the phase transition between liquid water and steam, as well as changes in state of the real gas, steam; in the internal-combustion engine, there is the added complexity of a chemical reaction taking place within the cylinder, whereby thermal energy is made available during each cycle.

irreversible change (one requiring the expenditure of a still greater quantity of nonthermal energy for its compensation) in place of the change we had succeeded in counteracting.

The second law of thermodynamics is expressed in the form of a negative statement, or denial. We obviously cannot produce for such a statement direct experimental proof, such as corresponds to Joule's law in relation to the first law of thermodynamics. Its generality rests rather on the failure of all attempts to disprove it. Such attempts are always equivalent to the construction of a so-called "perpetual motion" machine of the second class (a perpetual motion machine of the first class being one that would violate the principle of conservation of energy), which might operate for example by drawing upon thermal energy from a source originally at the same temperature as its surroundings (such as a portion of the ocean, or the atmosphere), doing work without itself undergoing permanent change (*i.e.*, by means of a cyclic process), and ultimately lowering thereby the temperature of the source in relation to the surroundings; ordinary thermal interchange between the source and surroundings could then be relied on to restore thermal energy to the depleted source, and thereby keep the machine in operation indefinitely, transforming thermal energy drawn ultimately from the surroundings into mechanical form without the need of an elevated temperature. Experience teaches us that every device considered potentially suitable for this purpose has failed. Upon the hypothesis that *all* such devices are necessarily doomed to failure, we may of course construct a set of logical implications, applying in particular to relationships among the states of a thermodynamic system; for any thermodynamic system is potentially a device for transforming thermal into nonthermal energy. Such thermodynamic relationships are subject to direct experimental verification; the truth of such relationships then constitutes indirect proof of the second law of thermodynamics as the coordinating principle. The importance of the second law of thermodynamics to chemistry rests in the fact that every chemical transformation is potentially a means for transforming thermal energy into mechanical or electrical energy, and the general limitation imposed by the second law constitutes, as we shall presently see, the foundation for the entire theory of chemical equilibrium. Our faith in the second law is based in part on the precision and logical consistency of the results that have been accomplished in this field.

5-3. Carnot's Principle. An immediate inference from the second law of thermodynamics is that *any reversible* cyclic process operating between two given fixed temperatures must yield the same net quantity of work W_r from a given quantity of heat Q' drawn from the higher temperature source. For let us first compare the behavior of a reversible cyclic heat engine with that of any nonreversible one, doing net work W from heat Q' drawn from the higher temperature source. If W were greater than W_r, we could then use the nonreversible engine to drive the reversible one backward so that it would function as a refrigerating engine, transmitting the quantity of heat $-Q'$ to the higher temperature source as the quantity of work $-W_r$ is expended in running it; by hypothesis, the reversible engine would require exactly the same quantity of work to drive it backward, for a given quantity of heat then delivered to the higher temperature source, as it would do in running normally as a heat engine upon absorbing that same quantity of heat; on the other hand, the nonreversible engine, as we have already noted in Sec. 5-1, in general would require a greater expenditure of nonthermal energy to drive it in reverse than it delivers when running in the forward direction. Now, the net result would be that for each complete compound cycle of both engines, the net quantity of work $W - W_r$ would be done, at the expense of thermal energy (the difference between $Q' - W_r$ taken up from the lower temperature body by the reversible engine running in reverse, and $Q' - W$ delivered to that body by the nonreversible engine) drawn from the lower temperature surroundings; this would be the sole result, since the reversible engine would have restored to the higher temperature body all the thermal energy withdrawn from it by the nonreversible engine. Such a possibility is denied by the second law of thermodynamics; it follows therefore that

$$W - W_r \leqq 0$$

$$W \leqq W_r \tag{5-11}$$

No heat engine operating between two given fixed temperatures can be more efficient than one operating reversibly. If, however, we compare any two *reversible* cyclic processes operating between the same two temperatures, one doing net work W_r^1 and the other W_r^2 upon drawing the same quantity of heat Q' from the higher temperature source, then by similar reasoning we can show that

$$W_r^1 \leqq W_r^2 \qquad \text{and} \qquad W_r^2 \leqq W_r^1$$

Both of these conditions can be satisfied only if

$$W_r^1 = W_r^2 \tag{5-12}$$

In other words, *any* reversible cyclic process operating between two given fixed temperatures is equally efficient in transforming thermal energy drawn from the higher temperature source into work.

The value of W_r/Q' is therefore a universal function of the two fixed temperatures concerned, entirely independent of the particular material system undergoing the cyclic change. This important generalization is known as *Carnot's principle.* It follows that we can establish the form of this universal function by studying empirically the limiting behavior as one approaches thermodynamically reversible conditions of any particular system. We have already found in Eq. (5-9) that for a system consisting of an ideal gas (whose behavior has been inferred from the behavior of real gases in the limit as $p \rightarrow 0$, as shown in Sec. 1-2), the upper limit to the efficiency of the cyclic process, attained by thermodynamically reversible changes of state, is given by

$$\frac{W_r}{Q'} = \frac{T' - T''}{T'} \tag{5-13}$$

where T represents the temperature measured on the absolute ideal-gas temperature scale, as defined by Eq. (1-3). Equation (5-13) therefore applies to any material system whatever, undergoing in principle a cycle of reversible changes of state between the two fixed temperatures T' and T''.

5-4. The Thermodynamic Temperature and the Entropy. We may treat Carnot's principle in a more elegant way, first conceived by William Thomson, Lord Kelvin, in 1852. Kelvin noted that Carnot's principle in effect defines a universal temperature scale independent of the particular material system used as the thermometer. For let us consider two different bodies, each momentarily at some fixed temperature (such as might be maintained by ice melting at normal atmospheric pressure, or by liquid oxygen boiling at normal atmospheric pressure), and let θ' and θ'' be their temperature measures derived naïvely as by means of Eq. (1-1) from any appropriate thermometric property, such as the length of a copper bar or the resistance of a platinum coil. Now, up to this point, at which we introduce the second law of thermodynamics, the temperature scale has had no numerical significance beyond that of ordering different systems in relation to each other. A scale sufficient for coping with all problems arising in relation purely to the first law of thermodynamics could have been derived in terms of any measure θ, single-valued, continuously defined, and increasing in regular sequence as the body whose temperature is being measured is made hotter,[1] without the need for attaching any meaning to the quantitative relationships among the temperature measures of different systems; thus, the numbers 0, 100, and 444.6°C assigned, respectively, to the ice point, the steam point, and the

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[1] The direction of increase here is purely conventional; an equally practical scale would be obtained if the value of θ decreased steadily as the body became qualitatively hotter; one would then discover by experience that the senses of the inequalities between the θ values in expression (5-14) would have to be reversed.

sulfur point order these systems in relation to each other, and in relation to other bodies whose temperature measures may be similarly assigned, but we have had no occasion to attach physical significance to the concept of precisely how much hotter a substance at the boiling point of sulfur is than a substance at the boiling point of water. The absolute ideal-gas temperature scale has had such special significance in relation to certain physical properties of gases, but this has been a rather narrow field of application. We are now prepared to assign a temperature scale on which the numerical values have quantitative significance in general, in relation to the second law of thermodynamics. For let us use as the thermometer, in principle, any material system that could be put through a reversible cycle, during which it absorbs thermal energy Q'_r from the one body, Q''_r from the other body (under the sign convention that when heat is actually given up by the system, Q_r will be assigned a negative value), and does net work: $W_r = Q'_r + Q''_r$. Then the general content of Carnot's principle is summarized qualitatively in the form of the following statements:

$$\left.\begin{array}{ll}\text{If } \theta' > \theta'', \text{ then } W_r \text{ is positive}, & \text{that is, } Q'_r > -Q''_r \\ \text{If } \theta' = \theta'', \text{ then } W_r = 0, & \text{that is, } Q'_r = -Q''_r \\ \text{If } \theta' < \theta'', \text{ then } W_r \text{ is negative}, & \text{that is, } Q'_r < -Q''_r \end{array}\right\} \quad (5\text{-}14)$$

Thus, we see that the absolute value of Q_r has the same qualitative numerical properties as the temperature measure θ itself; the relative magnitudes of the quantities of heat exchanged by the system with the two bodies, as the system goes through one complete reversible cycle, could be used to place the two bodies, and any others by extension of the scheme of measurement, in qualitative temperature order. But according to Carnot's principle, the value of the ratio $W_r/Q'_r = 1 + (Q''_r/Q'_r)$ is determined solely by the temperatures of the two bodies, however they may be measured, and independently of the particular material system undergoing the reversible cycle of changes between them. Therefore we may use the ratio $-Q''_r/Q'_r$, as measured empirically using *any* material system whatsoever, to *define* the relative temperature measures of the two bodies, according to the quantitative law,

$$\frac{\Theta''}{\Theta'} \equiv -\frac{Q''_r}{Q'_r} \qquad (5\text{-}15)$$

(the negative sign in this equation merely ensures a positive value of the ratio Θ''/Θ', since Q''_r and Q'_r will themselves have opposite signs). The temperature scale Θ so defined is known as the *absolute thermodynamic temperature scale.* Such a scale has all the essential qualitative features of ordinary temperature scales, but has in addition the universal property that *any* system used to measure the values of Q_r'' and Q_r', and thereby serving as an empirical thermometer through Eq. (5-15), will yield the same value of Θ''/Θ'. We have already seen in Eq. (5-10) that if we choose as our thermodynamic thermometer an ideal gas (whose behavior has been inferred from empirical observation of the limiting behavior of actual gases as $p \rightarrow 0$), then

$$-\frac{Q_r''}{Q_r'} = \frac{T''}{T'} \tag{5-16}$$

where T' and T'' represent the absolute ideal-gas temperatures, as measured independently of thermodynamics by means of an ordinary gas thermometer corrected for deviation from Boyle's law at finite pressures [compare Eq. (1-3)]; therefore we conclude in general that

$$\Theta = CT \tag{5-17}$$

where the proportionality factor C may be set equal to 1 merely through assignment of the same numerical scale to Θ as has already been assigned to T. Equations (5-9) and (5-10), to which we were led by empirical observations based on the properties of gases at sufficiently low pressures, therefore apply generally to any thermodynamic system whatever, where T stands for the absolute ideal-gas temperature.

Equation (5-15) is evidently not the only way in which one might proceed to define a universal temperature scale based on the second law of thermodynamics. Kelvin in fact first proposed a scale essentially defined by the relation

$$\Xi'' - \Xi' \equiv \ln\left(-\frac{Q_r''}{Q_r'}\right) \tag{5-18}$$

This so-called "first" scale of Kelvin evidently satisfies the qualitative requirements of ordinary scales, as embodied in relations (5-14), and, like any other function of $-Q_r''/Q_r'$, must be universal in view of Carnot's principle. If we apply the definition (5-18) to some particular material system, such as an ideal gas, we evidently obtain

$$\Xi = \Xi_0 + \ln T \tag{5-19}$$

where T represents the absolute ideal-gas temperature, and Ξ_0 is a constant merely locating the zero point on the Ξ scale in relation to the zero point on the T scale. The Θ scale defined by Eq. (5-15), however, to which T is proportional, has one important property not possessed by other "thermodynamic" scales. If we transpose terms in Eq. (5-15), then

$$\frac{Q'_r}{\Theta'} + \frac{Q''_r}{\Theta''} = 0 \tag{5-20}$$

In other words, the quantity Q_r/Θ, where Q_r denotes in the algebraic sense the quantity of heat absorbed by the system during a reversible change of state at the constant thermodynamic temperature Θ, when summed over a complete cycle of changes that restores the system ultimately to its original state, vanishes. Equation (5-20) applies to a system absorbing heat reversibly only at the two fixed temperatures Θ' and Θ''; we may generalize to take account of reversible changes of state during which the temperature of the system undergoes change by invoking the methods of the calculus. Thus, let us define a function S by means of the equation

$$dS \equiv \frac{d'Q_r}{\Theta} \tag{5-21}$$

Then we may infer from the second law of thermodynamics that the integral of dS around any closed reversible path that ultimately restores the system to its original state vanishes; this statement is merely a generalization of Eq. (5-20). In other words, the value of S itself, except possibly for a constant of integration for the particular system, must be determined completely by the state, and is therefore an extensive property of the system (extensive because the value of Q_r for a given kind of material substance will evidently be proportional to the total mass of it under consideration).

We may in fact set up the temperature scale Θ originally in such a way as to ensure that dS defined by Eq. (5-21) is determined completely by the changes taking place in the variables fixing the state, independently of the particular path along which they vary. Let us forget for the moment our previous definition of Θ [Eq. (5-15)], and concentrate on this new aspect, since the creation of a physical property of the system in terms of which the second law of thermodynamics can be expressed in mathematical form would be an achievement equivalent in value to the creation of U and H in relation to the first law. The value of Q_r is clearly *not* determined solely by the initial and final states of the system, as we have indicated by using the notation $d'Q_r$ for its differential. Equation (5-21) suggests, however, that by dividing the value of $d'Q_r$ by some particular temperature measure Θ, whose relation to any ordinary (*i.e.*, nonthermodynamic) method of measuring the temperature, such as by means of a platinum resistance thermometer, or a constant-volume nitrogen thermometer, is to be determined by empirical observation. The quantity $1/\Theta$ is thus to serve in the capacity of an *integrating factor* (to use the language of differential equations) of the differential expression represented by $d'Q_r$. Now, according to Carnot's principle, the relationship between Θ and any particular ordinary temperature scale, based on some thermometric property of a particular type of thermometric system, must be a universal one; in other words, the temperature scale Θ which transforms $d'Q_r/\Theta$ into a perfect differential in terms of the variables determining the state for any one system will serve in the same capacity for any other system. We can therefore discover the form of the general relationship between Θ and any ordinary temperature measure by studying empirically the behavior of any particular material system. We can express in detail, for example, the behavior of an ideal gas by means of the empirical equations

$$p = \frac{nRT}{V} \qquad \text{(from equation-of-state data for real gases at low pressures)} \qquad (5\text{-}22a)$$

$$dU = n\bar{C}_v\,dT \qquad \text{(from Joule-Thomson experiments on real gases at low pressures)} \qquad (5\text{-}22b)$$

where T represents the absolute ideal-gas temperature defined by Eq. (1-3) independently of thermodynamic considerations. Now, in general, for any system,

$$d'Q = dU + p\,dV \qquad (W' = 0;\ \text{first law})$$

Let us divide by Θ, a function as yet unspecified of the ordinary temperature as represented, for example, by the absolute ideal-gas temperature T,

$$dS \equiv \frac{d'Q_r}{\Theta} = \frac{dU + (p\,dV)_r}{\Theta} \qquad (W' = 0) \qquad (5\text{-}23)$$

and introduce the ideal-gas data, noting that for reversible changes of state, the gas is maintained throughout at a pressure equal to its equilibrium static pressure, as represented by Eq. (5-22a). Thus

$$dS = \frac{n\bar{C}_v}{\Theta}\,dT + \frac{nRT}{\Theta}\frac{dV}{V} \qquad \text{(ideal gas)} \qquad (5\text{-}24)$$

One sees at a glance that in order for dS to be a perfect differential in terms of the variables T and V, it is necessary and sufficient that

$$\Theta = CT \qquad (5\text{-}25)$$

where C is a universal constant, which merely fixes the size of the degree on the Θ scale in terms of the arbitrary degree fixed by convention on the T scale. Equation (5-25) follows rigorously from Eq. (5-24) if one applies Euler's criterion

$$\frac{d}{dT}\left(\frac{nRT}{\Theta V}\right)_V = \frac{d}{dV}\left(\frac{n\bar{C}_v}{\Theta}\right)_T$$

$$\frac{R}{\Theta V} - \frac{RT}{\Theta^2 V}\frac{d\Theta}{dT} = 0$$

$$\frac{d \ln \Theta}{dT} = \frac{1}{T}$$

$$\Theta = CT$$

[Eqs. (5-22*a*) and (5-22*b*) are sufficient, taken in connection with the first law of thermodynamics, to ensure that $\bar{C}_v$ is independent of V and of p.] Equation (5-25) represents of course the same conclusion we previously reached by a different approach in Eq. (5-17). In other words, $1/T$, where T represents the absolute ideal-gas temperature, is itself an integrating factor for $d'Q_r$, and the function S, hereafter defined by

$$dS \equiv \frac{d'Q_r}{T} \tag{5-26}$$

is for a particular thermodynamic system an extensive property determined entirely by its state

$$\Delta S = S_2 - S_1 = \int_{\text{state 1}}^{\text{state 2}} \frac{d'Q_r}{T} \tag{5-27}$$

This completes the identification of the absolute thermodynamic temperature scale with the absolute ideal-gas temperature scale, to which we referred in Sec. 1-2; the gas thermometer, corrected for deviation of the particular gas from Boyle's law, thus constitutes an experimental method of realizing temperature measures on the thermodynamic scale, which has the properties implied by Eq. (5-27).

The function S defined by Eq. (5-26) or Eq. (5-27) is known as the *entropy* function, and was first introduced by R. J. E. Clausius in 1865. It is important for one to realize that while the defining equations, (5-26) and (5-27), apply only to thermodynamically reversible changes of state, the value of ΔS is a property solely of the initial and final states of the system. Therefore if the value of ΔS between two given states can be established, for example by applying Eq. (5-27) to any reversible path connecting the states, then the entropy *of the system* undergoes that same change whenever the same change of state is brought about, by whatever process, reversible or nonreversible. The accompanying entropy change taking place in the surroundings is another matter, which we shall discuss at further length in the following section. For changes of state taking place in an ideal gas, from Eq. (5-24), neglecting change of $\bar{C}_v^\circ$ with temperature,

$$\bar{S}_2 - \bar{S}_1 = \bar{C}_v^\circ \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \quad \text{(ideal gas)} \quad (5\text{-}28a)$$

or, in terms of T and p as state variables,

$$\bar{S}_2 - \bar{S}_1 = \bar{C}_p^\circ \ln \frac{T_2}{T_1} - R \ln \frac{p_2}{p_1} \quad \text{(ideal gas)} \quad (5\text{-}28b)$$

While the ratio of the absolute thermodynamic temperatures of two bodies, T''/T', is thus given general quantitative significance in the light of the second law of thermodynamics, represented, for example, by Eq. (5-16), the number assigned to any one fixed temperature point remains arbitrary, as seen in Eq. (5-25); the absolute thermodynamic temperature measures could be multiplied throughout by a constant scale factor, without effect of any kind on the thermodynamic relations involved, although of course the choice of scale would affect the numerical values assigned to S. As explained in Sec. 1-2, the *Kelvin* or absolute thermodynamic centigrade scale has been defined since Kelvin's time by the arbitrary assignment of 100°K to the difference between the steam-point and the ice-point temperatures; the *Rankine* or absolute thermodynamic Fahrenheit scale in use by chemical and mechanical engineers has been defined similarly by the arbitrary assignment of 180°R to the difference between the steam-point and the ice-point temperatures. It then follows from experiment that T_0, the absolute thermodynamic ice-point temperature, has the value 273.16 ± 0.01°K on the Kelvin scale and 491.69 ± 0.02°R on the Rankine scale. A movement is under way to redefine the Kelvin scale by the arbitrary assignment of the number 273.16°K (or whatever number may be agreed upon by convention) to the ice point, or possibly by the assignment of a suitable conventional number to the triple point of water, which is perhaps more reproducible than the ordinary ice point. This change would of course have no immediate practical effect on absolute temperature measures now in use.

If in Eqs. (5-26) and (5-27) defining dS and ΔS, $d'Q_r$ is represented in calories and T in degrees Kelvin, then dS and ΔS are measured in calories per degree, or so-called *entropy units* (eu). The second law of thermodynamics defines only changes in the value of S; the entropy of a given thermodynamic system, like the internal energy and the enthalpy, is therefore indeterminate to the extent of an arbitrary additive constant of integration, concerning which, however, we shall have more to say in Sec. 8-3.

5-5. Thermodynamic Measures of Irreversibility and Criteria of Equilibrium. We have discussed the entropy function so far only in relation to reversible changes of state, by means of which changes in its value can be directly established experimentally according to Eq. (5-26), or its integral form, Eq. (5-27). The second law of thermodynamics implies, however, that its difference, ΔS, between two given states does not depend on how the change of state is brought about, although Eq. (5-27) itself is valid only along a reversible path. Let us now see what kind of information we can derive from the entropy function concerning real changes of state, which in general are not thermodynamically reversible.

From the general discussion given in Secs. 5-2 and 5-3, it is clear that for any real change taking place in the state of the system *at constant temperature*, the following condition is always satisfied:

$$Q \leqq T\,\Delta S \qquad (T \text{ const}) \tag{5-29}$$

For if Q represents the quantity of heat absorbed and W the quantity of work done by the system during the actual change of state, and if Q_r and W_r represent the quantity of heat absorbed and the quantity of work done if the same net change of state were brought about by means of any thermodynamically reversible process, then in principle one could always restore the system to its original state by putting it through the reversible process in the reverse direction; the net work $W - W_r$ done by the system during the complete cycle must then satisfy the general second-law condition

$$W - W_r \leqq 0 \qquad (T \text{ const}) \tag{5-30}$$

Since, however, in view of the first law of thermodynamics,

$$Q - W = \Delta U = Q_r - W_r$$

it follows therefore from Eq. (5-30) that

$$Q - Q_r \leqq 0 \qquad (T \text{ const}) \tag{5-31}$$

But at constant temperature T, according to Eq. (5-27) defining ΔS in general,

$$Q_r = T\,\Delta S \qquad (T \text{ const}) \tag{5-32}$$

Therefore condition (5-29), which is actually a generalization of Eq. (5-32), follows; the equality sign in (5-29) applies to the special case in which the change of state under consideration happens to be carried out reversibly.

The generalization of condition (5-29) for real changes of state during which the temperature of the system changes is

$$d'Q \leqq T\,dS \tag{5-33}$$

or

$$Q \leqq \int_{\text{state 1}}^{\text{state 2}} T\,dS \tag{5-34}$$

where the integral is evaluated along the actual path followed by the system. For we may conceive the actual path to be approximately equivalent to a path made up of a sequence of changes at successive constant temperatures, connected by intermediate steps during which the temperature is changed to the next value under adiabatic conditions; during the adiabatic connecting steps, $d'Q = d'Q_r = T\,dS = 0$, while during the isothermal steps, condition (5-29) or its limiting form (5-33) for infinitesimal changes applies. In the limit as the steps are shortened and their number correspondingly increased, the approximation to the actual path can be made as close as one pleases, always under the assumption that below the limit of experimental error in the measurement of quantities such as T and Q there is still some distance to go before the discrete ultimate structure of the material system causes these quantities to lose the precision with which they may ordinarily be defined (we shall presently see that when one takes into account the molecular constitution of material substances, one must assume that the second law of thermodynamics has a statistical foundation, as have such concepts as temperature itself and the distinction between thermal and mechanical energy).

In general, both terms involved in Eq. (5-34) depend on the path actually followed by the system during the change of state under consideration. We may, however, rearrange Eq. (5-33) before integrating, so that the condition it imposes on real changes of state may be expressed in terms of the quantity ΔS, whose value depends only on the initial and final states,

$$\int_{\text{state 1}}^{\text{state 2}} \frac{d'Q}{T} \leqq \Delta S = S_2 - S_1 \tag{5-35}$$

This relation is the generalization of Eq. (5-27), which defines ΔS; the equality sign in condition (5-35) applies to the special case of a thermodynamically reversible process.

Condition (5-35) is a concise statement in elegant mathematical form of the second law of thermodynamics. It expresses the general limitation on the utilization of thermal energy embodied in that law by setting an upper limit to the quantity of heat any given material system may take in during a change of state (by means of which some or all of the thermal energy might conceivably be converted to mechanical or other nonthermal form); this limit is set through the abstract relation (5-35) in terms of a function of the state of the system, whose change, ΔS, depends only on the initial and final states of the system for the change of state under contemplation. In particular, if the system goes through a cycle of changes, which restores it ultimately to its original state, so that

$$\Delta S = \Delta U = 0,$$

then

$$W = \oint d'Q \qquad \text{(first law)} \qquad (5\text{-}36a)$$

where

$$\oint \frac{d'Q}{T} \leqq 0 \qquad \text{(second law)} \qquad (5\text{-}36b)$$

Carnot's equation, (5-13), and the various relations for cyclic heat engines developed in Sec. 5-2, are merely special cases of the general relation represented by Eqs. (5-36). More generally, condition (5-35) sets bounds to the thermodynamic feasibility of conceivable changes of state; only such changes as satisfy (5-35) are consistent with the second law of thermodynamics. If, for example, one has established the value of ΔS between two given states, then the system can get from one state to the other only along such paths as satisfy (5-35), *i.e.*, paths over which $\int d'Q/T$ does not exceed the value of ΔS. This condition evidently determines the direction in which the system will tend to move, or can move, under a given set of constraints imposed on it. This powerful criterion may be applied in particular to determine the direction in which a chemical reaction tends to take place under a given set of constraints, as we shall see later; it is evident, for example, that an endothermic reaction at constant temperature demands a positive entropy of reaction, but this condition is evidently not sufficient to ensure that the reaction tends to take place in the endothermic direction.

The case of the thermally insulated system is particularly significant. If the system is constrained to changes of state such that $d'Q = 0$, then the general condition (5-35) reduces to

$$\Delta S \geqq 0 \qquad (Q = 0) \qquad (5\text{-}37)$$

Therefore during real adiabatic changes of state, the entropy of the system cannot decrease; it must increase, or for hypothetical reversible changes of state, remain stationary. Condition (5-37) applies a fortiori to changes taking place in an isolated system, which exchanges no energy in any form with the outside world; in this case, since, in general,

$$d'Q = dU + p\,dV + d'W'$$

we may write explicitly

$$(\Delta S)_{U,V} \geqq 0 \qquad (W' = 0) \qquad (5\text{-}38)$$

Since according to Eq. (5-38), the entropy of an isolated system cannot decrease, the ultimate state of such a system must tend to be the one of maximum entropy consistent with its fixed total energy and volume. When the system has reached such a state, no further changes can take place consistently with the second law of thermodynamics; the system will be in a state of stable equilibrium, with all its energy completely unavailable for effecting further change.

Consider, for example, the simple case of a heated piece of iron that has just been dropped into a Dewar flask containing water originally at room temperature. The iron cools down and the water warms up until ultimately both have reached a common temperature (compare Secs. 1-1 and 2-2), from which no further change takes place except for gradual loss of heat from the Dewar flask to the surroundings. Now, all the energy, both thermal and mechanical, introduced with the iron is still present in the flask, and there would be no contradiction of the conservation principle if the iron and the water were to return of their own accord to their respective original temperatures, or for that matter, if the iron were to gather together energy in mechanical form and jump back out of the flask. Experience tells us, however, that such changes never take place. Condition (5-38) is an abstract means of putting such experience in the form of a mathematical statement; once the iron has entered the flask, the entropy of the resulting "isolated" system can only increase or remain stationary, and as it increases, the energy of the system becomes increasingly unavailable for effecting further changes.

The entropy change as the iron cools and the water warms may be analyzed in detail as follows: let the total heat capacity of the iron body be represented by C_1 and its instantaneous temperature by T_1, and let the total heat capacity of the water (neglecting that of the container itself) be represented by C_2 and its instantaneous temperature by T_2. Then if the temperature of the iron were to change by dT_1 and the temperature of the water correspondingly by dT_2, subject to the conservation condition

$$C_1\,dT_1 + C_2\,dT_2 = 0$$

the total entropy change would be given by

$$\begin{aligned} dS &= \frac{C_1}{T_1}\,dT_1 + \frac{C_2}{T_2}\,dT_2 \\ &= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) C_1\,dT_1 \end{aligned}$$

Thus, so long as $T_1 > T_2$, dS can be positive only if dT_1 is negative, *i.e.*, if the iron cools, which is of course what actually happens. Had T_1 been smaller than T_2, that is, the iron body initially colder than the water, then dS would be positive only for a change such that dT_1 would be positive. Now when ultimately $T_1 = T_2$, then for further small change of state represented by dT_1, the value of dS would be zero, but the second-order effect if T_1 were to be increased sufficiently (and T_2 correspondingly decreased) would be to make the coefficient of $C_1\,dT_1$ in the above expression for dS become negative; *i.e.*, a small but finite increase in T_1 would be accompanied by negative ΔS. A precisely similar argument shows that a small but finite increase in T_2, starting with the condition $T_1 = T_2$, would likewise be accompanied by negative ΔS. Neither change can actually take place so long as the system remains isolated. Thus, the statement that the entropy of an isolated system cannot decrease symbolizes in general what experience teaches us in detail about this particular situation: that the temperatures of the two bodies tend to become equal and to remain equal thereafter. This idea is implicit, of course, in the use of a thermometer to measure the temperature of a body with which it has come to thermal equilibrium, free from the influence of other external bodies.

The "dissipation" of mechanical energy associated with the motion of the iron body as it drops into the insulated flask also corresponds to an entropy increase. In order to consider this question, let us suppose for simplicity that the iron body and the water are initially at the same temperature T_0, and let E then represent the kinetic energy with which the iron drops into the water. This energy is transformed into internal energy of the combined system, and neglecting the small volume change associated with the rise in temperature,

$$\Delta U = E = (C_1 + C_2)\Delta T$$

Now, since the entropy change of the system depends only on the initial and final thermodynamic states, we can compute its value from the moment the kinetic energy of the iron body vanishes until the combined system has come to thermal equilibrium by calculating what the value of $\int d'Q_r/T$ would be if the same change of state were brought about through any reversible process, such as by reversible heating (*i.e.*, by means of heat supplied by an external body whose instantaneous temperature is maintained only infinitesimally higher than the instantaneous internal equilibrium temperature of the system itself); thus

$$\Delta S = \int_{T_0}^{T_0+\Delta T} \frac{d'Q_r}{T} = \int_{T_0}^{T_0+\Delta T} \frac{dU}{T} \sim (C_1 + C_2)\frac{\Delta T}{T_0}$$

to a first approximation, under the assumption that ΔT is small compared with T_0. In other words

$$\Delta S \sim \frac{E}{T_0}$$

So long as the content of the flask remains isolated, all the energy E becomes unavailable through temperature equalization, just as in the case of energy introduced directly in thermal form (as when the iron body was introduced at an original temperature higher than that of the water). What physical significance may we attach to the value of ΔS itself in the present instance? Suppose that lower temperature external surroundings exist, at some temperature T^*. Then through a Carnot process, the fraction $(T_0 - T^*)/T_0$ of the assimilated energy E (and of any other thermal energy withdrawn from the combined iron-water system, so long as it remains essentially at the temperature T_0) might be converted back to mechanical form; but the balance $E(T^*/T_0)$ would remain unavailable, and even under the most efficient conditions consistent with the second law of thermodynamics would be passed on to the low-temperature surroundings still in thermal form. Thus, the quantity

$$T^* \Delta S = E \frac{T^*}{T_0}$$

represents energy rendered "permanently" unavailable when the mechanical energy of the falling body is "dissipated" within the flask in thermal form. This interpretation of ΔS as a measure of the extent to which energy, thermal or mechanical, has been made unavailable is quite general. The unavailability depends on the lowest available temperature to which one can divert the unutilized thermal energy; in a closed system, such that all parts are ultimately at the same temperature, *all* the thermal energy is unavailable. We have supposed in the example under consideration that ΔT was sufficiently small to leave T_0 sensibly unchanged; if the temperature within the flask is increased significantly through accretion of the energy introduced by the iron body, then the value of ΔS is correspondingly smaller, indicating that the extent to which this energy has been made unavailable (which depends on the ratio of the lowest available external temperature to the temperature finally prevailing within the system that has acquired the energy) is likewise smaller.

Now, thermodynamic changes taking place in the world at large may be regarded ultimately as changes taking place within an isolated or self-contained system; for any change occurring in a system that is not itself isolated consists of an interaction between the system and its environment, during which energy may be exchanged (in thermal and nonthermal forms) but according to the first law of thermodynamics is never created or destroyed. Therefore by the inclusion of enough of the environment to encompass all parts influenced by the energy transfer, the system plus environment constitutes a supersystem that is in effect isolated; its total energy and its total volume are both constant. The classic expression of this viewpoint was given by R. J. E. Clausius in 1865 and was quoted by J. Willard Gibbs at the outset of his monumental treatise, "On the Equilibrium of Heterogeneous Substances," published 10 years later:

> "Die Energie der Welt ist constant.
> Die Entropie der Welt strebt einem Maximum zu."

In Sec. 5-2, we introduced the second law of thermodynamics in the form of a statement expressed in terms of ordinary experience: *no process* *has ever been discovered whose sole result is the transformation of energy from thermal to nonthermal form.* We may now replace that statement by the mathematically equivalent abstract but more powerful generalization: *the entropy of a closed thermodynamic system never decreases.* The entropy of any nonisolated portion of the system may decrease (just as thermal energy may be transformed into nonthermal energy by means of a heat engine, which itself undergoes no permanent change as a result of the operation), but only when the decrease is compensated by an at least equal increase in the entropy of the surroundings. So far as we know, this law applies universally to all physical and chemical transformations involving matter in bulk.

When the entropy of a closed thermodynamic system has reached a maximum value consistent with its fixed total energy and volume, then no further changes in it can take place, without violating the second law of thermodynamics; the system will have attained a state of equilibrium. All thermodynamic changes may thus be regarded as steps on the way toward ultimate equilibrium of the world in general. This aspect of the second law has of course influenced cosmology, and man's outlook on his place in the universe. We are concerned here, however, only with the modest aim of studying its implications with respect to equilibrium in chemical systems. The main lesson we learn is how to take advantage of nature so as to benefit by changes that tend to take place of their own accord, and to assess the cost, in terms of an immediate or a deferred change of a permanent nature in the environment, of effecting a desired transformation that ordinarily does not take place of its own accord. But one is always faced with the necessity of working within the limitations imposed by the second law. Thus, the criterion for stable equilibrium in an isolated system is that for all conceivable changes the system may undergo, consistent with general chemical and physical principles (conservation of mass, conservation of the chemical elements, general stoichiometry, mechanical principles governing motion, etc.),

$$(\Delta S)_{U,V} \leqq 0 \qquad (W' = 0) \qquad (5\text{-}39)$$

When in particular we are dealing with a system in dynamic equilibrium, such that the same equilibrium state may be approached from either of two opposite directions (as in the equilibrium between liquid water and steam, or in the gas-phase equilibrium for the reaction $N_2 + 3H_2 = 2NH_3$ at sufficiently high temperatures), then since the entropy change that would be associated with a virtual displacement of the system in the one direction from the equilibrium state is in general equal in magnitude but exactly opposite in sign to the entropy change for a virtual displacement in the opposite direction, the general equilibrium condition (5-39) reduces to

$$(\Delta S)_{U,V} = 0 \qquad (W' = 0) \qquad (5\text{-}40)$$

The inequality sign in (5-39) merely implies that there may be other conceivable changes of state, denied by the second law of thermodynamics, other than the particular reversible change in which we are interested to which the equality (5-40) applies. Thus, if we can establish conditions under which for a given thermodynamic system Eq. (5-40) applies, then we shall have established ultimate equilibrium conditions in that system, consistent with given values of U and V.[1]

Before discussing Eq. (5-40) and its implications in detail, it is important for us to note two serious limitations on its usefulness. In the first place, while the general condition (5-35) [of which (5-38) is a special case] is a necessary condition satisfied by every real change of state, it is not a sufficient condition; the second law denies the existence of changes contradicting (5-35), but it does not ensure that a thermodynamically feasible change will in fact take place under a given set of conditions or under any set of conditions. We are familiar with many examples of metastable states in which the system may remain indefinitely, even though more stable states are known to exist to which the system could conceivably pass by means of a change of state satisfying (5-35). Thus, we may show that (5-35) is satisfied by the transformation of water into ice at atmospheric pressure and all temperatures below 0°C; nevertheless, it is entirely possible for one to supercool liquid water below 0°C and to maintain it in that metastable state for an indefinitely long period of time. However, the change at atmospheric pressure and temperatures below 0°C will go only in the one direction, from water into ice; no one has ever succeeded in transforming ice into water under such conditions. In the same sense, diamond at room temperature and pressure is metastable toward transformation into graphite, although here the evidence is more indirect, since we cannot actually induce the transformation to take place in either direction at ordinary temperatures and pressures. TNT and many other explosives are metastable with respect to their decomposition products; the decomposition can be initiated by an effect small out of all proportion to the over-all result. Likewise, a mixture of CO and H_2 at atmospheric pressure and room temperature is in a metastable state with respect to

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[1] A steady state differing in important aspects from the stable equilibrium states discussed in this book may be maintained through a balance between incoming and outgoing energy and material substances. The thermodynamics of such open systems, which may have significant biological applications, has been explored by I. Prigogine, "Étude thermodynamique des phénomènes irréversibles," Éditions Desoer, Liége, 1947.

chemical combination to form methanol, although no reaction takes place in the absence of a suitable catalyst. In some of these cases, there may be an energy barrier to be overcome as a preliminary to the over-all change of state satisfying condition (5-35); for example, in the methanol synthesis, H_2 molecules may have to be disassociated, partially or completely, in order for reaction to take place; in the freezing of supercooled water, crystal nuclei below a certain critical submicroscopic size may have higher energy than larger crystals, because of the relatively larger proportion of surface molecules. In other cases, one might regard the transformation to the more stable state as under way, but proceeding with extreme slowness. Certain explosives, such as PETN (pentaerythritol tetranitrate), might be put in this class, for here the decomposition takes place at a measurable rate, at a slightly elevated temperature such as 120°C; the rate increases rapidly with increasing temperature until one reaches a point at which it becomes self-accelerating because heat cannot be conducted away as fast as it is being released by the decomposition. The distinction between an extremely slow rate of change and a change hindered by an energy barrier is perhaps artificial, but in any event the information given by the second law of thermodynamics is essentially negative in character.

The other limitation on (5-35) and its various special forms such as (5-38) is that even when the system is known to be actually moving toward a stable equilibrium state and is not resting in a metastable or suspended state the magnitude of the inequality represented by (5-35) for the change actually occurring gives no clue to the speed with which equilibrium will be attained. Certain spontaneous changes take place with explosive speed under suitable conditions, such as the reaction between H_2 and O_2 to form H_2O, while others, such as the polymerization of styrene, may take days. Many chemical reactions are speeded up, or even initiated altogether, by specific catalytic agents, which have no effect on the ultimate equilibrium state. Within these limitations, however, the information to be derived from thermodynamic criteria of equilibrium, such as Eq. (5-40) and other related equations, is of the utmost theoretical and practical value. Entire chemical industries, such as the Haber process for synthetic ammonia and the synthetic methanol process, have been founded on such information.

Now, if we introduce the general second-law condition (5-33) for real changes of state into Eq. (2-20) representing the first law, we may derive the conditions for thermodynamic change in terms of the internal-energy function

$$dU \leqq T\,dS - p\,dV - d'W' \tag{5-41}$$

Thus

$$(\Delta U)_{S,V} \leqq -W' \qquad (5\text{-}42)$$

$$\leqq 0 \qquad (W' = 0) \qquad (5\text{-}43)$$

The internal energy of a thermodynamic system thus tends to be a minimum consistent with its total entropy and volume. The condition for stable thermodynamic equilibrium at fixed entropy and volume is therefore that for all conceivable changes

$$(\Delta U)_{S,V} \geqq 0 \qquad (W' = 0) \qquad (5\text{-}44)$$

This criterion for stable equilibrium is entirely equivalent to (5-39). For a reversible process in a state of equilibrium, we may apply (5-44) to either direction, and therefore the equilibrium criterion reduces to

$$(\Delta U)_{S,V} = 0 \qquad (W' = 0) \qquad (5\text{-}45)$$

The general condition (5-41) for thermodynamic change provides further insight into the significance of the entropy function. Let us rearrange that equation in the form

$$d'W \leqq T\,dS - dU \qquad (5\text{-}46)$$

where $d'W$ includes both work of expansion and any other work done by the system. The value of $(T\,dS - dU)$ therefore sets an upper limit to the work that can be done by the system during a given infinitesimal change of state. Consider a process for which $dS = 0$; then $d'W \leqq -dU$, or $W \leqq -\Delta U$. Any work done by the system under this condition can at most equal the decrease in the system's own internal energy, *i.e.*, it cannot be at the expense of energy drawn from the surroundings in thermal form. Therefore whenever the system receives net energy from a thermal source, its entropy necessarily increases [this is not necessarily true when it receives energy from a nonthermal source; for example, if one compresses a gas by doing work on it mechanically through a piston, say at constant temperature, then its entropy actually decreases, as shown by Eq. (5-28); but if one increases its pressure by heating it, say at constant volume, then its entropy increases]. Now, the value of $T\,dS$, according to (5-33), sets algebraically an upper limit to the quantity of heat that the system may take in during the change of state under consideration. Therefore if the system undergoes the change in such a manner that the actual quantity of heat it absorbs, $d'Q$, is algebraically smaller than the value of $T\,dS$, then an opportunity for the potential utilization of thermal energy in the amount $(T\,dS - d'Q)$ has been lost. In this sense, the change has been *irreversible*, and the essentially positive quantity

$$T\,dS - d'Q = T\,dS - dU - d'W \geqq 0 \qquad (5\text{-}47)$$

therefore serves as a measure, in energy units, of the degree of irreversibility with which the particular change of state has been brought about. In general, the integral of $T\,dS$ for a finite change of state depends on the particular path followed by the system; for a change of state taking place at constant temperature, however, its value depends only on the initial and final states; this condition greatly increases the usefulness of (5-47), as we shall see in the following section.

5-6. The Free-energy Functions. In practical thermodynamic investigation, we are more often concerned with systems maintained at constant temperature than with isolated systems. It is generally easier for us to let the system interact with surroundings at a controlled temperature (*e.g.*, a thermostatic air bath, or liquid bath) than to free it completely, even for a short time, from interaction with its surroundings. At constant temperature, the general condition (5-46) satisfied by real thermodynamic changes assumes the form

$$W \leqq T\,\Delta S - \Delta U \qquad (T \text{ const}) \qquad (5\text{-}48)$$

Let

$$A \equiv U - TS \qquad (5\text{-}49)$$

Then condition (5-48) may be put in the form

$$W \leqq -\Delta A \qquad (T \text{ const}) \qquad (5\text{-}50)$$

The quantity A so defined is evidently like U and S an extensive property of the system, whose value for given total mass is determined completely by the state; it is known as the *Helmholtz free-energy* function, or as the *maximum-work* function.[1] At constant temperature, only those changes of state can take place for which any work done by the system does not exceed in the algebraic sense the decrease in its Helmholtz free energy. The decrease in the value of A between two states at the same temperature thus sets an upper limit to the quantity of work that may be done by the system in passing from the one state to the other; the limit, represented by the equality sign in (5-50), is attained when the system passes from one state to the other by means of a thermodynamically reversible process. One will note that the reversible work W_r thus becomes a function only of the initial and final states under the restriction of constant temperature, although this is not true in general when the temperature is

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[1] G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York, 1923; the letter A is based on the German word *Arbeit.* Some authors have used the letter F for this function, but this practice should not be encouraged, because of possible confusion with the Gibbs free-energy function, defined by Eq. (5-59).

permitted to change. This fact, of course, we recognized in Sec. 5-2; it now appears as a special case of the second law of thermodynamics.

It is convenient for us to separate W into mechanical work of expansion, and W' representing all work done in a form other than mechanical work of expansion [Eq. (3-17)]; then (5-50) assumes the form

$$W' \leqq -\Delta A - \int_{V_1}^{V_2} p\,dV \qquad (T \text{ const}) \tag{5-51}$$

Therefore for changes of state taking place *at constant temperature and constant volume,*

$$(\Delta A)_{T,V} \leqq -W' \tag{5-52}$$
$$\leqq 0 \qquad (W' = 0) \tag{5-53}$$

Condition (5-53) is entirely equivalent to condition (5-38), or to condition (5-43). For a system maintained at constant temperature and volume, and so constituted that no energy enters or leaves the system in nonthermal form, A can only decrease, or ultimately, when equilibrium has been attained, remain stationary. For stable equilibrium in a process at constant temperature and volume that may go in either of two opposite directions,

$$(\Delta A)_{T,V} = 0 \qquad (W' = 0) \tag{5-54}$$

or, more generally,

$$(\Delta A)_{T,V} = -W' \tag{5-55}$$

These criteria of equilibrium are the equivalent of (5-40) and of (5-45).

If instead of constant temperature and constant volume, we have the generally more convenient conditions of constant temperature and constant pressure, then Eq. (5-51) assumes the form

$$W' \leqq -\Delta A - p\,\Delta V \qquad (T, p \text{ const}) \tag{5-56}$$

Let

$$F \equiv A + pV \tag{5-57}$$

We may then write the condition (5-56) for thermodynamic change in the simple form

$$W' \leqq -\Delta F \qquad (T, p \text{ const}) \tag{5-58}$$

The quantity F, like A, is another extensive property of the system, whose value is determined completely by the thermodynamic state; it is known as the *Gibbs free-energy* function, or simply as the *free energy.* It bears to A the same relation that H bears to U; in fact, Eq. (5-57) defining F could have been put in the form

$$F \equiv U - TS + pV \equiv H - TS \tag{5-59}$$

One sees that F bears to H the same relation that A bears to U. Thus, at constant temperature and pressure, only those changes of state can take place for which any work done by the system in forms other than mechanical work of expansion does not exceed algebraically the decrease in its Gibbs free energy. The decrease in the value of F between two states at the same temperature and pressure thus sets an upper limit to the quantity of energy theoretically available, consistently with the second law of thermodynamics, in nonthermal forms other than mechanical work of expansion. Chemical reactions, however, excluding electrochemical processes, are generally carried out under such conditions that no such energy is actually expended, either by the system or on it. Therefore the condition for thermodynamic change *at constant temperature and pressure* has the form

$$(\Delta F)_{T,p} \leqq 0 \qquad (W' = 0) \qquad (5\text{-}60)$$

This condition is entirely equivalent to (5-38) or to (5-43) or to (5-53). Thus, for a system maintained at constant temperature and pressure, and so constituted that no energy enters or leaves the system in nonthermal form excepting as work of expansion associated with change in its volume, the value of F can only decrease, or ultimately, when equilibrium has been attained, remain thereafter stationary. The condition for stable equilibrium in a reversible process at constant temperature and pressure is therefore

$$(\Delta F)_{T,p} = 0 \qquad (W' = 0) \qquad (5\text{-}61)$$

or, more generally,

$$(\Delta F)_{T,p} = -W' \qquad (5\text{-}62)$$

The latter condition finds special application in the equilibrium theory of galvanic cells, as we shall see in Chap. 9. The fact that constant temperature and constant pressure are such convenient working conditions to set up in the chemical laboratory and in the chemical plant endows F with particular usefulness in the theory of chemical equilibrium; we encountered a similar situation in thermochemical theory, where for practical experimental reasons H proved to be more useful in many situations than U, which is perhaps the more fundamental quantity from the purely theoretical point of view.

Further insight into the significance of ΔF and ΔS for changes of state taking place at constant temperature and pressure may be obtained from the application of the general definition (5-59) to such a change

$$\begin{aligned} \Delta F &= \Delta H - T\,\Delta S \qquad && (T,\ p \text{ const}) \\ &= Q - W' - T\,\Delta S && (T,\ p \text{ const}) \end{aligned}$$

Thus

$$Q - W' = T\,\Delta S + \Delta F \qquad (T,\ p \text{ const}) \qquad (5\text{-}63)$$

Now, the terms on the left of Eq. (5-63) depend on how the change of state is brought about, but, according to Eq. (5-58), the maximum value

W' may assume is equal to $-\Delta F$, while at the same time the maximum value assumed by Q is equal to $T\,\Delta S$. These limits represent the case of a reversible change of state; for real changes, W' may be as much smaller algebraically than $-\Delta F$ as one pleases, Q being correspondingly smaller algebraically than $T\,\Delta S$. The difference, $Q - W'$, is of course determined solely by the initial and final states; in fact

$$Q - W' = T\,\Delta S + \Delta F = \Delta H \quad (T, p \text{ const}) \qquad (5\text{-}64)$$

The Daniell cell reaction (5-5) already discussed in Sec. 5-1 is a case in point. The value of ΔH for that reaction has been found to be -51.8 kcal at 25°C and 1 atm, from straightforward calorimetry (with $W' = 0$). Of this net quantity of energy released (which excludes energy expended or absorbed in the form of work of expansion, negligible anyhow in the present instance), we found that a maximum of $W'_r = 49.8$ kcal was available in electrical form, this being the amount hypothetically derived when the cell is discharged under reversible conditions (*i.e.*, at a potential difference equal to that of the cell's on open circuit); this quantity therefore represents the value of $-\Delta F$ for the cell reaction. At least the balance, 2.0 kcal, is necessarily released in thermal form (although it is possible for as much as the entire magnitude of $-\Delta H$ to be so released, if the reaction is permitted to take place with $W' = 0$); this quantity represents the value of $-T\,\Delta S$ for the cell reaction, and with $T = 298$°K, $\Delta S = -6.7$ eu.

According to Eq. (5-64), we may regard $-\Delta H$, the net energy released during a change of state at constant temperature and pressure, excluding work of expansion, as made up of two terms: $-\Delta F$, representing *available energy*, and $-T\,\Delta S$, *unavailable energy*. By available energy, we mean energy potentially available in nonthermal form (excluding mechanical work of expansion associated merely with the volume change taking place in the system), even though in a particular application, it may not so appear; by unavailable energy, we mean energy that even under ideal conditions can appear only in thermal form. Now, the equality sign in condition (5-58) applies only to thermodynamically reversible processes; we may therefore regard the essentially positive quantity

$$-\Delta F - W' \geqq 0 \qquad (T, p \text{ const}) \qquad (5\text{-}65)$$

as a numerical measure of the degree of thermodynamic irreversibility with which a given change of state at constant temperature and pressure has been carried out; this replaces the more general measure, (5-47). For a change in which the value of ΔF is negative, the expression on the left of (5-65) measures the quantity of available energy that was not actually utilized in nonthermal form as the change was carried out; for a change in which the value of ΔF is positive, (5-65) measures the excess energy in nonthermal form (available energy drawn from some other system in the surroundings) expended on the system over the least quantity theoretically needed to effect the change. In either case, the total available energy in the world has gone down (*i.e.*, has been converted to thermal energy released to the surroundings at the constant temperature T) by the amount represented by (5-65), and this represents the irreversible effect of the change as carried out. If for example one discharges a Daniell cell by short-circuiting the electrodes by means of a heavy copper bar, or if one merely dips the zinc electrode directly into the $CuSO_4$ electrolyte, then $-\Delta F = 49.8$ kcal, just as in reversible discharge of the cell, but all this energy is now "dissipated" as heat, along with $-T\,\Delta S = 2.0$ kcal. The chemical reaction has then been carried out irreversibly, to the extent of 49.8 kcal. This much energy (per mole of Zn and Cu^{++} reacting) previously available has passed on to the surroundings in thermal form, where it is no longer available unless one can produce a heat engine and a lower temperature body to serve as condenser. If one wishes to restore the resulting chemical system, $Cu + Zn^{++}$, to its original state without changing the temperature and pressure, one can do this only by the expenditure of "available" energy to the extent of at least 49.8 kcal in electrical form from some other source; the balance, 2.0 kcal, can then be taken in from the surroundings in thermal form, but this represents the upper limit to the quantity of thermal energy that can be taken back in this form.

For a reaction taking place in a chemical system so constituted that $W' = 0$, the sign of ΔF, and not the sign of ΔH or of ΔU, evidently determines the direction of change at constant temperature and pressure; only those reactions for which ΔF is negative can take place. The value of ΔF depends of course on the states of the reactants and products. Since ΔF differs from ΔH by the value of $T\,\Delta S$ [Eq. (5-64)], endothermic reactions may occur, provided that they have sufficiently large entropies of reaction. On the other hand, a reaction such as the decomposition of $H_2O(l)$ into $H_2(g)$ and $O_2(g)$, for which at room temperature and all finite pressures the value of ΔF is positive and large in magnitude, can be made to take place only through the application of nonthermal energy in forms other than work of compression, in accordance with (5-65) (with W' negative); thus, one may decompose water by the expenditure of electrical energy. Now, electrical energy, in particular, is measured by the product of the potential difference across the electrodes by the quantity of electricity passing through the system; the quantity of electricity for electrochemical processes in general, including the action of galvanic cells, is measured by the quantity of chemical reaction according to Faraday's law, and has a fixed value for the quantity of reaction represented, for example, by the conventional chemical equation for the reaction. There is therefore a general connection between the value of ΔF and the smallest applied potential difference theoretically sufficient to make the reaction (such as the electrolysis of water) take place; or, in the case of a galvanic cell, between the value of $-\Delta F$ and the cell emf. This connection will be developed at length in Chap. 9.

In the two chapters immediately following, we shall develop some of the properties of the free-energy function for simple chemical substances and for mixtures. In Chap. 8, we shall then apply the results to the general theory of chemical equilibrium.

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Problems

5-1. The enthalpy of the lead storage cell reaction at 25°C and 1 atm for $1H_2SO_4$:$10H_2O$ electrolyte concentration was calculated in Prob. 4-28. The emf of the cell is 2.11 volts under the same conditions [D. N. Craig and G. W. Vinal, *J. Research Natl. Bur. Standards*, **24**, 475–490 (1940)]. If the cell is discharged through a resistance relatively high compared with its own internal resistance, at such a rate that a current of 1 amp is flowing, what is the rate at which heat is evolved within the cell in calories per second?

5-2. Compare the ideal thermodynamic efficiencies with which the combustion energy of fuel oil may be utilized for the production of work: (*a*) by using it to drive a steam engine operating at boiler pressure of 39.18 psi (130°C) and condenser temperature of 25°C, and (*b*) by burning it in a diesel engine, the temperature of the combustion products reaching 1800°C and the cylinder block being cooled to 80°C.

5-3. Compare the ideal thermodynamic efficiencies of a cyclic mercury-vapor engine operating at boiler pressure of 1 atm and condenser temperature of 25°C and of a steam engine operating under the same conditions.

5-4. Calculate the net work done on 1 kg of ammonia in the following ideal refrigeration cycle: the ammonia at 10°C under 1 atm is compressed isothermally and reversibly to its vapor pressure, 6.06 atm, the equation of state for the gas at 10°C being

$pV = (1364 - 20p)$ ml atm/g, and condensed to the liquid state, whose specific volume is 1.61 ml/g; within the refrigerating unit, the liquid is reduced to 1 atm by passing through a throttle valve, whereupon its temperature drops to the normal boiling point, $-33.35°C$, and the liquid evaporates; the specific volume of the liquid under this condition is 1.46 ml/g, and that of the gas is 1124 ml/g; the cold gas is now led out of the refrigerating unit, where it picks up thermal energy from the room at 10°C, and returns to its original state, at constant pressure of 1 atm. Which of the steps in this cycle are not carried out under thermodynamically reversible conditions? Calculate the net quantity of heat Q'' removed from the refrigerator during each cycle, using the following information: the latent heat of vaporization at the normal boiling point is 327.5 cal/g, and the mean specific heat of the equilibrium liquid phase between 10°C and $-33.35°C$ is 1.09 cal/g deg. Compare the coefficient of performance, $-Q''/W$ (W being negative), with that of a reversible Carnot engine operating between the same two temperatures.

5-5. If a self-contained household electric refrigerator were left running with the door open, what would happen to the temperature of the room?

5-6. Calculate the theoretical least quantity of nonthermal energy that must be expended in order to quick-freeze 10 kg of green peas. Assume that the peas contain 25 per cent of solids, having a mean specific heat of 0.35 cal/g deg, and 75 per cent water; the heat given up by the freezing peas, originally at 25°C, is removed from the freezer at the constant temperature of $-25°C$ and transferred by the refrigerator to the room at 20°C. Neglect thermal leakage through the refrigerator.

5-7. Describe a series of reversible steps by which supercooled water at $-5°C$ could be transformed into ice at $-5°C$, and looking up the necessary experimental information, calculate the entropy change for the process. Compare with the value of Q/T for the actual transformation at $-5°C$.

5-8. Construct to scale a temperature vs. entropy diagram for an ideal reversible heat engine based on the cyclic process described in Sec. 5-2, using 1 mole of air ($\bar{C}_v^\circ = 5.0$ cal/mole deg) as the working substance, operating between temperatures of 0 and 100°C, and at a maximum pressure of 10 atm (the air may be regarded as an ideal gas). Note that the area enclosed by the curve traced by the gas during one complete cycle represents the *net* reversible heat absorbed, *i.e.*, the maximum work done per cycle. What graphical feature represents the quantity of heat absorbed from the high-temperature source?

5-9. Plants are able to synthesize carbohydrates and starches from $CO_2(g)$ and $H_2O(l)$, the by-product being $O_2(g)$. The reaction clearly tends to go ordinarily in the opposite direction, as shown by the combustion of these materials. Do these facts constitute a violation of the second law of thermodynamics? Explain.

5-10. The rusting of iron is evidently a thermodynamically irreversible process. What irreversible changes ordinarily accompany the manufacture of iron from iron oxide?

5-11. Do U^{235} fission and plutonium manufacture constitute violations of the second law of thermodynamics? Explain.

5-12. What is the change in free energy of the lead storage cell reaction under the conditions given in Prob. 5-1? If 1 mole of $PbO_2(c)$ is consumed, while the electrical energy at 2.11 volts is used to heat 10 kg of water originally at 25°C in a thermally insulated flask, what is the change of entropy within the cell (neglecting change of emf with the electrolyte concentration), and what is the change of entropy of the water within the flask? What fraction of the total energy received by the water in the flask could be recovered in nonthermal form by means of a cyclic heat engine operating between its temperature and that of the room, 25°C?

CHAPTER 6

THERMODYNAMIC BEHAVIOR OF SIMPLE SYSTEMS

In this chapter, we consider the thermodynamic properties of a simple system consisting of a pure chemical substance of fixed composition. We shall discuss in particular how its free energy depends on its state, and shall derive the special conditions for equilibrium during phase transitions and for the equilibrium of the interface between the phases.

6-1. Free Energy of a Chemical Substance. The *molal free energy* of a homogeneous chemical substance of fixed composition, defined in accordance with Eq. (5-59) by

$$\bar{F} = \bar{H} - T\bar{S} \tag{6-1}$$

is evidently one of its intensive properties, and therefore in the absence of special influence of gravity, electric fields, magnetic fields, etc., on the state of the substance it may be represented formally as a function of temperature and pressure by

$$\bar{F} = \bar{F}(T, p) \tag{6-2}$$

$$d\bar{F} = \left(\frac{d\bar{F}}{dT}\right)_p dT + \left(\frac{d\bar{F}}{dp}\right)_T dp \tag{6-3}$$

We may proceed to develop this form as follows; from (6-1),

$$\begin{aligned} d\bar{F} &= d\bar{H} - T\,d\bar{S} - \bar{S}\,dT \\ &= d'Q + \bar{V}\,dp - d'W' - T\,d\bar{S} - \bar{S}\,dT \end{aligned}$$

Now, if the system is supposed to follow a *reversible* path, for which by definition,

$$d'Q_r = T\,d\bar{S}$$

then

$$d\bar{F} = -\bar{S}\,dT + \bar{V}\,dp - d'W' \tag{6-4}$$

If furthermore the path is of such a nature that $W' = 0$, then

$$d\bar{F} = -\bar{S}\,dT + \bar{V}\,dp \qquad (W' = 0) \tag{6-5}$$

The reversibility of the path will be ensured if we substitute in Eq. (6-5) for $\bar{S}$ and $\bar{V}$ their equilibrium values, established in principle from a series of data obtained under static equilibrium conditions, represented as functions of T and p. The value of $\Delta\bar{F}$ for a given change of state may then be calculated by the integration of Eq. (6-5) between the initial and final state along such a path, as will be shown presently; but its value, thereby established, will of course be a function only of the end states, and will be the same for any path by which the change is brought about, though Eq. (6-5) itself would not be valid for the irreversible path.

Taking advantage of the fact that $\bar{F}$ is determined solely by the state (*i.e.*, by T and p, except for a disposable additive constant of integration for the particular system), we may derive an important thermodynamic relationship from Eq. (6-5) by applying Euler's criterion for $d\bar{F}$ to be a perfect differential in terms of the independent variables T and p [compare Eq. (3-7)]:

$$-\left(\frac{d\bar{S}}{dp}\right)_T = \left(\frac{d\bar{V}}{dT}\right)_p \tag{6-6}$$

This is known as one of J. C. Maxwell's relations, the other three analogous relations being given in Sec. 6-3. Since we may write

$$\left(\frac{d\bar{S}}{dp}\right)_T = \frac{1}{T}\left(\frac{d'Q_r}{dp}\right)_T = \frac{1}{T}\bar{L}_p \tag{6-7}$$

where $\bar{L}_p$ represents the molal latent heat of pressure variation, introduced in Eq. (3-28), therefore Eq. (6-6) leads to

$$\bar{L}_p = -T\left(\frac{d\bar{V}}{dT}\right)_p = -T\bar{V}\alpha \tag{6-8}$$

where α represents the coefficient of cubical expansion, introduced in Eq. (3-4). This establishes the proof of Eq. (3-31), which we used throughout Chap. 3.

Two other important relationships follow from a comparison of Eq. (6-5) with Eq. (6-3):

$$\left(\frac{d\bar{F}}{dT}\right)_p = -\bar{S} \tag{6-9}$$

$$\left(\frac{d\bar{F}}{dp}\right)_T = \bar{V} \tag{6-10}$$

We may use Eq. (6-9) to eliminate $\bar{S}$ from Eq. (6-1), and thus obtain the temperature coefficient of $\bar{F}$ expressed in a different form

$$\bar{F} = \bar{H} + T\left(\frac{d\bar{F}}{dT}\right)_p \tag{6-11}$$

This equation may be reduced to either of the equivalent forms

$$\left[\frac{d(\bar{F}/T)}{dT}\right]_p = -\frac{\bar{H}}{T^2} \tag{6-12}$$

$$\left[\frac{d(\bar{F}/T)}{d(1/T)}\right]_p = \bar{H} \tag{6-13}$$

Thus, whether Eq. (6-9), or one of the equations (6-12) or (6-13) is the more suitable for integration to find the value of $\bar{F}$ at one temperature relative to its value at another temperature, both at the same constant pressure, depends on whether one has experimental data for the entropy $\bar{S}$ or for the enthalpy $\bar{H}$. On the other hand, the experimental measurement of $(d\bar{F}/dT)_p$ serves as one means of establishing directly the value of $\bar{S}$, according to Eq. (6-9); and one may combine such information with experimental measurement of $\bar{F}$ itself in one of the forms (6-11), (6-12), or (6-13) to establish indirectly the value of $\bar{H}$. The value of $\bar{F}$ for a homogeneous chemical substance of fixed composition has no particular significance in itself, since the principal use of the free-energy function is in connection with the equilibrium criteria represented by Eqs. (5-61) and (5-62). We shall therefore find that Eqs. (6-9) to (6-13) are primarily useful when applied to two or more different substances (including different phases of the same chemical substance) in equilibrium with each other. We can then use these general thermodynamic equations, applied term by term to the expression for ΔF of the chemical or physical process under consideration, to derive the effects of temperature and pressure on the equilibrium conditions. For the moment, however, let us continue to develop their integral forms for individual homogeneous chemical substances.

Since the second law of thermodynamics, like the first law, contains information applicable only to *changes* of state [each law sets up in mathematical form a difference equation, or first-order differential equation, (2-22) and (2-23) for the first law and (5-33) and (5-36*b*) for the second law], the value of F for a particular material system, like the value of H, is indeterminate to the extent of an arbitrary additive constant independent of the state (an integration constant). Extending the notation introduced in Chap. 3, let $\bar{F}^\circ_{T_s}$ denote the *standard molal free energy* of a given homogeneous chemical substance of fixed composition *at standard temperature* T_s (by convention, taken to be 25°C or 298.16°K) and *standard pressure* p_0 (by convention, 1 atm for liquids and solids; for gases, however, we adopt a hypothetical ideal-gas standard state at 1 atm, in which the free energy has been corrected for deviation from Boyle's law at that pressure, as will be shown presently). In Chap. 8, we shall identify this standard molal free-energy constant with the standard molal free energy of formation from the chemical elements, just as we identified $\bar{H}^\circ_{T_s}$ with the standard molal enthalpy of formation from the chemical elements in Chap. 4. Then, according to Eq. (6-12), the molal free energy $\bar{F}^\circ_T$ at standard pressure and temperature T is given by the equation

$$\frac{\bar{F}^\circ_T}{T} = \frac{\bar{F}^\circ_{T_s}}{T_s} - \int_{T_s}^{T} \frac{\bar{H}^\circ_T}{T^2}\, dT \qquad (p = p_0) \qquad (6\text{-}14)$$

The integral in Eq. (6-14) may be evaluated from purely thermal data at standard pressure, in the form of $\bar{H}^\circ_T$ expressed as a function of T [Eq. (3-47)]:

$$\bar{H}^\circ_T = \bar{H}^\circ_{T_s} + \int_{T_s}^{T} \bar{C}^\circ_p\, dT \qquad (p = p_0) \quad (6\text{-}15)$$

where $\bar{H}^\circ_{T_s}$ represents the standard molal enthalpy constant (the standard molal enthalpy of formation) of the chemical substance at T_s and p_0, derived from thermochemical data by the means discussed in Chap. 4. As has already been indicated, Eq. (6-14) is seldom applied directly to an individual pure substance, but if, for example, $\bar{F}^\circ_{T_s}$ stands for the standard free energy of the chemical reaction of forming the substance from its elements, then Eq. (6-14) describes in terms of the enthalpy of formation how the free energy of formation varies with temperature.

Equation (6-10) describes how the molal free energy of a homogeneous chemical substance varies with pressure at given constant temperature. Therefore if $\bar{F}_{T,p}$ denotes the molal free energy in general at T and p, then

$$\bar{F}_{T,p} = \bar{F}^\circ_T + \int_{p_0}^{p} \bar{V}\, dp \qquad (T \text{ const}) \qquad (6\text{-}16)$$

The integral in this equation may be evaluated from equation-of-state data for the substance at the fixed temperature T. If we combine Eqs. (6-14) and (6-16), we may then calculate the value of $\bar{F}_{T,p}$ relative to that of $\bar{F}^\circ_{T_s}$ from purely thermal data obtained at the constant pressure p_s (*i.e.*, 1 atm), and equation-of-state data at the temperature T.

In the case of a pure liquid or solid phase, the value of the pressure integral in Eq. (6-16) is insignificant for ordinary variations in the barometric pressure, and is quite small up to pressures even of several hundred atmospheres; thus, for $H_2O(l)$ at 25°C, with $\bar{V} = 0.018$ liter/mole, its value between 1 and 100 atm is only 0.043 kcal/mole. Therefore at moderate pressures, we may take $\bar{F}_{T,p} = \bar{F}^\circ_T$ as a satisfactory approximation for such substances, regardless of the exact value of p. For gases, however, the effect of pressure on the value of $\bar{F}_{T,p}$ is significant, even for rather small changes. In the low-pressure range, we may assume as a first approximation the ideal-gas law

$$\bar{V} = \frac{RT}{p}$$

Thus

$$\bar{F}_{T,p} = \bar{F}^\circ_T + RT \ln p \quad (p \text{ in atm; ideal gas}) \qquad (6\text{-}17)$$

This equation is generally satisfactory for gases up to several atmospheres pressure, except for the most precise purposes, where it becomes necessary to introduce actual equation-of-state data. At higher pressures, of course, it is always necessary to introduce actual equation-of-state data, or a more accurate equation of state for the gas in Eq. (6-16).

Actual equation-of-state data for gases are conveniently represented by means of a power series in p with empirical coefficients, of the form

$$pV = c_1 + c_2p + c_3p^2 + c_4p^3 + \cdots \quad (T \text{ const}) \qquad (6\text{-}18)$$

This form of equation is known as the *virial equation of state,* and was first introduced by H. K. Onnes in 1901; the numbers c_1, c_2, c_3, . . . , which vary with temperature, are known as first, second, third, . . . virial coefficients. If they were represented for 1 mole of gas, then the value of c_1 would be simply equal to RT. More commonly, however, the data are expressed relatively to an arbitrary quantity of the particular gas, usually such that $pV = 1.0000$ at 0°C and 1 atm; if the data happen to be so represented, then

$$p\bar{V} = \bar{V}_0(c_1 + c_2p + c_3p^2 + c_4p^3 + \cdots) \quad (T \text{ const}) \qquad (6\text{-}19)$$

where $\bar{V}_0$ represents the standard molal volume of the gas, at 0°C and 1 atm, and $c_1\bar{V}_0 = RT$. Special interest attaches to the second virial coefficient, which determines the course of $p\bar{V}$ over the low-pressure range; it changes sign at the Boyle point for the particular gas, being negative below and positive above. By the use of four or five terms in the series, (6-18) or (6-19), the behaviors of many gases can be represented with high accuracy over a range of several hundred atmospheres, at temperatures and pressures not too close to the region of liquefaction. Table 6-1 gives, for example, virial coefficients for $N_2(g)$ at temperatures between 0 and 150°C. If the experimental equation-of-state data have been summarized in such a form, then the integral in Eq. (6-16) is readily evaluated analytically by the substitution for $\bar{V}$ of the appropriate function in terms of p, given by (6-18) or (6-19). Even when virial coefficients have not been explicitly worked out, however, p-V-T data for gases are commonly given in the form of the pressure-volume product, pV, measured at various pressures for given temperatures; a particularly convenient form consists of the experimentally determined *compressibility* *factor*

$$z \equiv \frac{p\bar{V}}{RT} \qquad (6\text{-}20)$$

whose value approaches 1 in the low-pressure range as $p \rightarrow 0$. If z has been determined at various pressures for a given uniform temperature, then the integral in Eq. (6-16) is conveniently evaluated graphically from a plot of z vs. $\log p$:

$$\bar{F}_{T,p} = \bar{F}^\circ_T + 2.3026\,RT \int_{p_0}^{p} z\, d\log p \qquad (6\text{-}21)$$

The area under the curve between the abscissas p_0 and p represents the value of the integral in Eq. (6-21).[1] Now, where direct experimental data are lacking for a particular gas, an excellent approximation may be obtained in many cases through application of the theory of corresponding states. B. F. Dodge has shown that if one plots the value of z against the *reduced pressure* of the gas, p/p_c, for various values of the *reduced temperature*, T/T_c, then the resulting curves are nearly identical for many gases over a wide range of pressures.[2] Figures 6-1*a* and *b* show a master plot, based on the average behavior of several gases. This generalized graphical form of the real-gas equation of state is very useful where exact data for the particular gas are not available; one must of course know the values of the critical temperature and the critical pressure.

TABLE 6-1. COMPRESSIBILITY DATA FOR NITROGEN*

$$pV = c_1 + c_2 p + c_3 p^2 + c_4 p^3 + c_5 p^4 + c_6 p^5 \qquad (p \text{ in atm})$$

$$(pV = 1.00000 \text{ at } 0°\text{C and 1 atm}; \ \bar{V}_0 = 22.4040 \text{ liter/mole})$$

t, °C	c_1	$c_2 \times 10^3$	$c_3 \times 10^6$	$c_4 \times 10^{12}$	$c_5 \times 10^{18}$	$c_6 \times 10^{24}$
0	1.00045	−0.45890	2.90964	23.1895	−587.22	4503.8
25	1.09201	−0.22110	2.65436	5.06187	−159.266	1008.8
50	1.18358	−0.01616	2.23372	2.64600	−95.758	535.08
75	1.27515	+0.15299	1.92483	−0.46531	−31.6196	163.97
100	1.36671	+0.28848	1.69106	−1.68806	−8.2022	47.065
125	1.45828	+0.41812	1.37824	−0.56983	−11.4400	43.566
150	1.54985	+0.52421	1.19192	−0.91694	−4.5638	18.788

* From measurements up to 400 atm by J. Otto, A. Michels, and H. Wouters, *Physik. Z.*, **35**, 97–100 (1934).

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[1] When the experimental data happen to be given in the form of pV relative to $pV = 1.0000$ at standard conditions, such as 0°C and 1 atm, one can see that $z = (pV)/\lim_{p \rightarrow 0} (pV)$, where both numerator and denominator refer to the same temperature.

[2] B. F. Dodge, *Ind. Eng. Chem.*, **24**, 1353–1363 (1932).

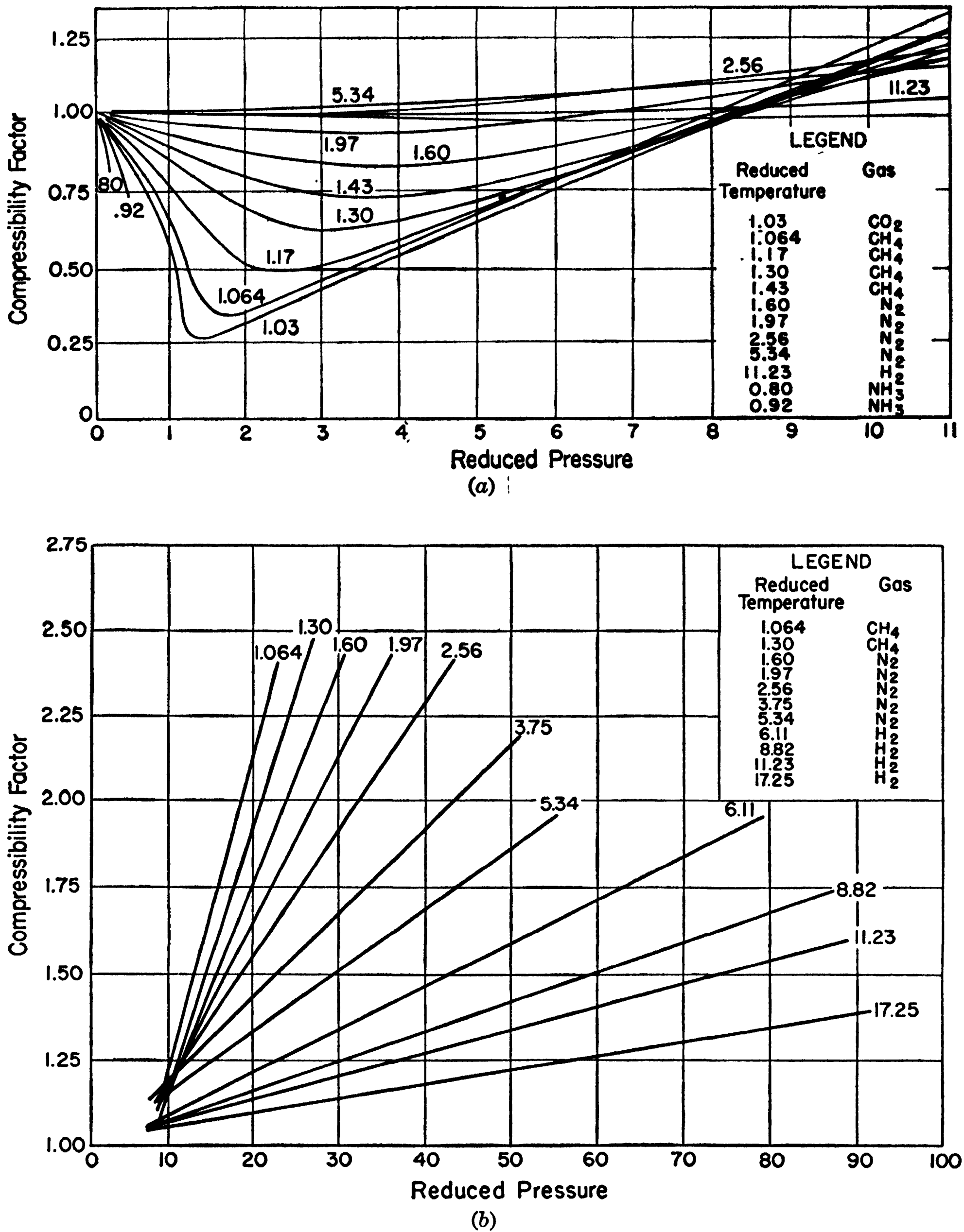

FIG. 6-1. Compressibility factor for gases as a function of reduced temperature and pressure: (*a*) intermediate-pressure region; (*b*) high-pressure region. [*B. F. Dodge, Ind. Eng. Chem.*, **24**, 1355 (1932), *with permission.*]

Now, the value of $\bar{F}_{T,p}$ for a gas approaches $-\infty$ as $p \rightarrow 0$, which is unfortunate, since we know most about the general behavior of gases in this range. Because of the universal form of the relationship between $\bar{F}_{T,p}$ and p in this range, Eq. (6-17), it is convenient for us to represent the thermodynamic properties of real gases in terms of the so-called *fugacity* function, f, introduced originally by G. N. Lewis;[1] this function is defined by the equation

$$\bar{F}_{T,p} \equiv \bar{F}_T^\circ + RT \ln f \qquad (6\text{-}22)$$

Thus, f is by definition related to $\bar{F}_{T,p}$ at all pressures in the same way that p itself is related in the ideal-gas limit. In other words, the experimental value of f is equal to the value of p at which an ideal gas would have the same relative molal free energy as the actual gas. The ratio

$$\nu \equiv \frac{f}{p} \qquad (6\text{-}23)$$

is called the *fugacity coefficient* of the gas.[2] It is convenient for us to set the numerical scale of f values in accordance with the convention

$$\lim_{p\rightarrow 0} \frac{f}{p} = 1 \qquad (T \text{ const}) \qquad (6\text{-}24)$$

Then f is measured in the same unit as p (*e.g.*, atm), and ν is a dimensionless number, whose deviation from 1 thus measures the effect of the deviation of the gas from ideal-gas behavior on its thermodynamic properties [the deviation of the compressibility factor z from 1 measures directly its deviation from Boyle's law, but this only indirectly influences its thermodynamic behavior, as we shall see presently, in Eq. (6-29)].

We may calculate the value of ν directly from equation-of-state data by introducing the definitions (6-22) and (6-23) in the general thermodynamic relation (6-16)

$$\begin{aligned} RT \ln \frac{f}{f_0} &= \int_{p_0}^{p} \bar{V}\, dp && (T \text{ const}) \\ RT \ln \frac{\nu}{\nu_0} &= \int_{p_0}^{p} \bar{V}\, dp - RT \ln \frac{p}{p_0} \\ &= \int_{p_0}^{p} \left(\bar{V} - \frac{RT}{p}\right) dp && (T \text{ const}) \qquad (6\text{-}25) \end{aligned}$$

---

[1] G. N. Lewis, *Proc. Am. Acad. Arts Sci.*, **37**, 49–69 (1901); *Z. physik. Chem.*, **38**, 205–226 (1901).

[2] R. H. Newton, *Ind. Eng. Chem.*, **27**, 302–306 (1935), has proposed to call this quantity the activity coefficient of the gas, but this term is perhaps better reserved for its original purpose, in connection with the thermodynamic properties of solutions, as described in Chap. 7.

where f_0 and ν_0 denote the values of the fugacity and fugacity coefficient at the pressure p_0. In accordance with the convention (6-24), we let $\nu_0 \rightarrow 1$ as $p_0 \rightarrow 0$; thus

$$RT \ln \nu = \int_0^p \left(\bar{V} - \frac{RT}{p} \right) dp \qquad (T \text{ const}) \qquad (6\text{-}26)$$

$$= \int_0^p (p\bar{V} - RT) d \ln p \qquad (T \text{ const}) \qquad (6\text{-}27)$$

The value of the integral in Eq. (6-27), which always converges if the gas does not undergo dissociation or other chemical change with changing pressure (it would vanish altogether for an ideal gas), may be evaluated from equation-of-state data for the gas at the given temperature T. The evaluation is particularly convenient if the experimental data have been expressed in terms of virial coefficients, as in Eq. (6-19),

$$RT \ln \nu = \bar{V}_0 \int_0^p (c_2 p + c_3 p^2 + c_4 p^3 + \cdots) \frac{dp}{p}$$

$$= \bar{V}_0 \left(c_2 p + \frac{c_3}{2} p^2 + \frac{c_4}{3} p^3 + \cdots \right) \qquad (6\text{-}28)$$

Or, if the experimental data have been given in the form of z, defined by Eq. (6-20), at various values of p, then we may write

$$\log \nu = \int_0^p (z - 1) d \log p \qquad (6\text{-}29)$$

and thus evaluate the integral by taking the area under the graphical plot of $z - 1$ vs. $\log p$ between the abscissas 0 and p, for the given value of T. The exact relationship between $\bar{F}_{T,p}$ and p may then be put in the form

$$\bar{F}_{T,p} = \bar{F}_T^\circ + RT \ln p\nu \qquad (6\text{-}30)$$

No new thermodynamic information has been introduced by the use of ν; ν is merely a mathematically convenient alternative means of representing free-energy data for gases, in place of $\bar{F}_{T,p}$ itself. It has three advantages over $\bar{F}_{T,p}$ as a means of recording experimental free-energy data, such as are implied by Eq. (6-16): (1) while the value of $\bar{F}_{T,p}$ at each temperature approaches $-\infty$ as $p \rightarrow 0$, the value of ν remains finite, and approaches in fact the value 1; (2) while $\bar{F}_{T,p}$ varies to a first order as a logarithmic function of p, the value of ν varies much less rapidly with p, and is therefore a sensitive means, particularly convenient for graphical representation, of describing accurately the actual thermodynamic properties of the gas; and (3) we shall discover in Chap. 8 that f, or its equivalent, $p\nu$, is the exact term appearing for each mole of gaseous reactant or product in the familiar law-of-mass-action expression for the equilibrium state of a chemical reaction.

In view of our convention (6-24), the value of the molal free-energy constant $\bar{F}_T^\circ$ for a pure gas in Eq. (6-30) has a slightly different significance, depending on the extent to which the gas deviates from ideality, from the value for a pure liquid or solid, where by convention it represents the value of $\bar{F}$ at T and 1 atm, and is in fact but slightly dependent on the particular standard pressure chosen. According to Eq. (6-30), $\bar{F}_T^\circ$ represents the value of $\bar{F}$ for a state of the gas at temperature T in which f, rather than p, equals 1 atm, or what amounts to the same thing, a hypothetical ideal-gas state (that is, $\nu = 1$) at $p = 1$ atm. With this understanding, $\bar{F}_T^\circ$ then varies with temperature according to Eq. (6-14), with $\bar{H}_T^\circ$ representing the limiting value of the molal enthalpy as $p \to 0$; the value of $\bar{H}_{T,p}$, of course, remains finite as $p \to 0$, being independent of p for an ideal gas, as we have noted in Chap. 3. From precise equation-of-state data for the gas, it is quite simple for us to relate the value of $\bar{F}_T^\circ$ to the actual value of $\bar{F}_{T,p}$ at $p = 1$ atm; for example, if the virial coefficients in Eq. (6-28) have been represented with p in atmospheres (based on an arbitrary quantity of the gas such that $pV = 1.0000$ at 0°C and 1 atm), then the value of ν at 1 atm is given by

$$RT \ln \nu_{1\,\text{atm}} = \bar{V}_0 \left(c_2 + \frac{c_3}{2} + \frac{c_4}{3} + \cdots \right)$$

Since the values of the higher virial coefficients are generally much smaller than the value of the second virial coefficient (their contributions becoming important only at the higher pressures), this formula reduces to

$$RT \ln \nu_{1\,\text{atm}} \sim \bar{V}_0 c_2 \sim RT(z_{1\,\text{atm}} - 1) \tag{6-31}$$

and $\bar{F}_{T,1\,\text{atm}}$ may be related to $\bar{F}_T^\circ$ by the substitution of the value of $\nu_{1\,\text{atm}}$ so derived in Eq. (6-30)

$$\bar{F}_{T,1\,\text{atm}} = \bar{F}_T^\circ + \bar{V}_0 c_2 \tag{6-32}$$

The correction is generally quite small, as one can perceive from the values of c_2 in the case of nitrogen, given in Table 6-1; thus, at 25°C, the difference between $\bar{F}_{1\,\text{atm}}$ and $\bar{F}^\circ$ is only

$$(-0.221 \times 10^{-3}) \times (22.4) \text{ liter atm/mole} = -0.00012 \text{ kcal/mole}$$

It would be rather larger in magnitude for a gas well below its critical point.

Just as the value of z may be estimated from the theory of corresponding states (Fig. 6-1), so in view of Eq. (6-29) must a similar situation exist

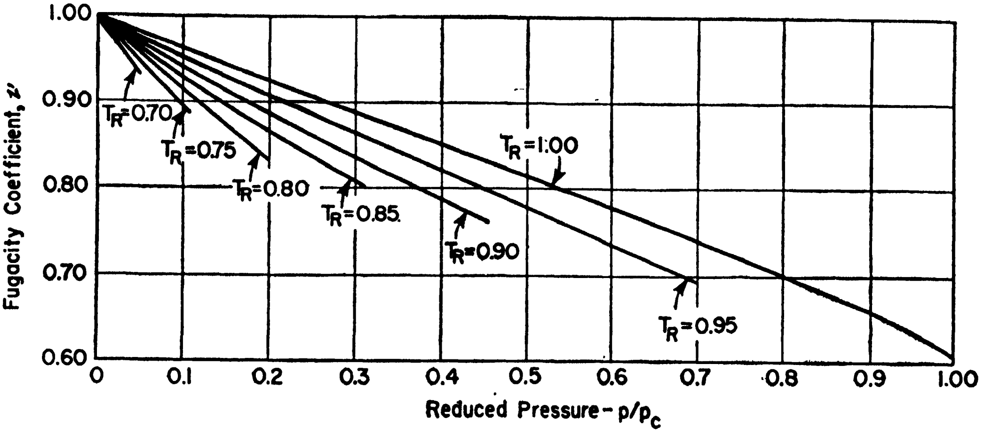

FIG. 6-2. Fugacity coefficient for gases below the critical temperature. [*R. H. Newton, Ind. Eng. Chem.*, **27**, 302–306 (1935), *with permission.*]

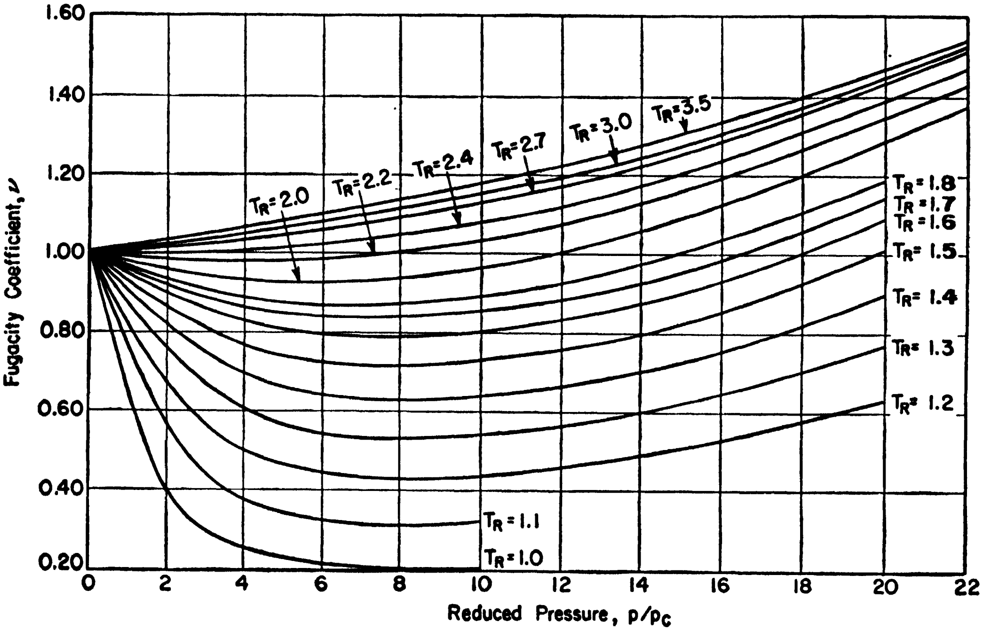

FIG. 6-3. Fugacity coefficient for gases at intermediate temperatures. [*R. H. Newton, Ind. Eng. Chem.*, **27**, 302–306 (1935), *with permission.*]

with regard to ν. By applying Eq. (6-29) to the generalized equation-of-state data represented by Fig. 6-1, one may construct generalized values of ν as a function of p/p_c for various values of T/T_c. This work has been done by R. H. Newton, and Figs. 6-2 to 6-4 represent his results.[1] These curves fit the experimental data for many gases with astonishing accuracy, and may be used to estimate fugacity coefficients of gases for which pre-

[1] *Ibid.*

cise equation-of-state data are not available. Their application to gas mixtures will be discussed in Sec. 7-2.

6-2. Entropy of a Chemical Substance. The entropy of a chemical substance of fixed composition may always be calculated except for an arbitrary additive constant from its free energy and enthalpy by means of Eq. (6-1) defining $\bar{F}$,

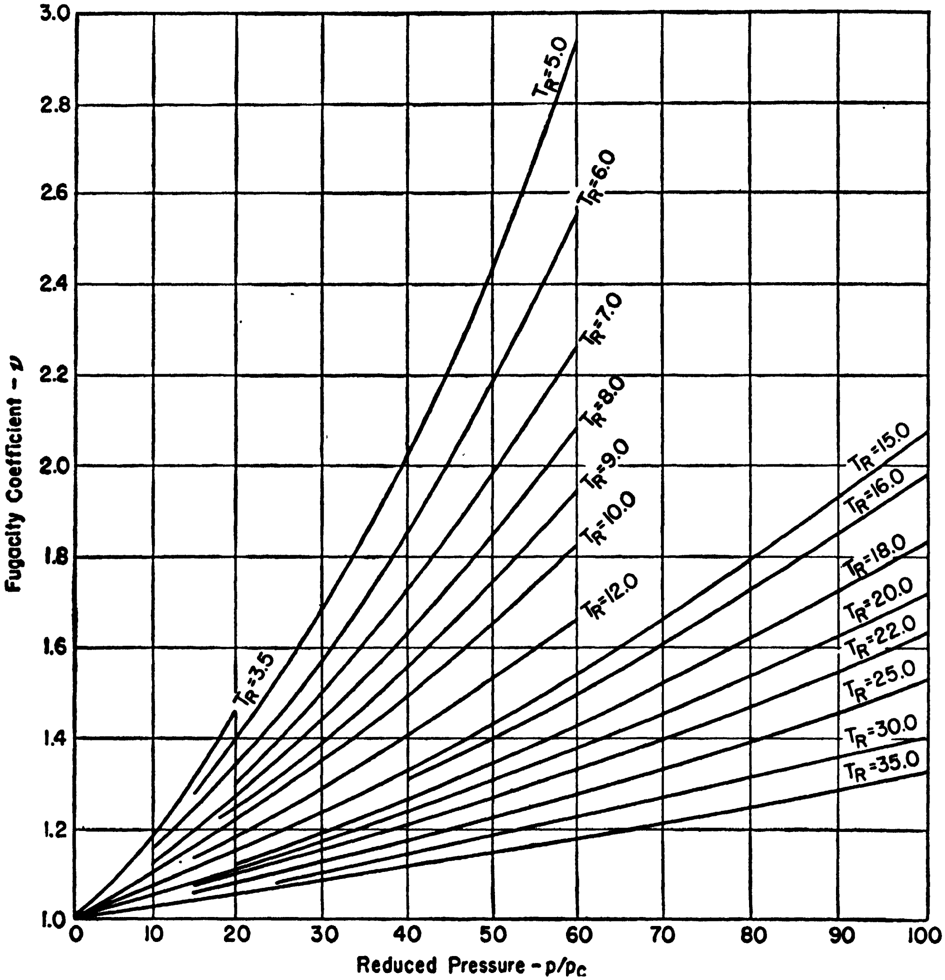

Fig. 6-4. Fugacity coefficient for gases at high temperatures. [*R. H. Newton, Ind. Eng. Chem.*, **27**, 302–306 (1935), *with permission.*]

$$\bar{S} = \frac{\bar{H} - \bar{F}}{T} \tag{6-33}$$

If in this equation $\bar{H}$ and $\bar{F}$ represent the molal enthalpy of formation and the molal free energy of formation with respect to the chemical elements, then $\bar{S}$ will likewise represent the molal entropy of formation with respect to the chemical elements, as we shall see in Chap. 8. In Sec. 8-3, however, we shall examine a method based on the so-called third law of thermodynamics whereby the value of $\bar{S}$ may be determined independently from purely thermal data. For this and other reasons to be discussed presently, the entropy function has a primary physical significance in its own right, and we wish now to express its dependence on the state in terms of familiar properties of the substance. Formally, we may write

$$\bar{S} = \bar{S}(T, p) \tag{6-34}$$

$$d\bar{S} = \left(\frac{d\bar{S}}{dT}\right)_p dT + \left(\frac{d\bar{S}}{dp}\right)_T dp \tag{6-35}$$

If the state depends on other independent variables, such as height above the earth's surface, magnetic field strength, etc., then corresponding additional terms would have to appear in Eq. (6-35), but we shall assume that such effects are not present.

Now, for changes of state carried out reversibly,

$$d\bar{S} = \frac{d'Q_r}{T} \tag{6-36}$$

We may therefore write

$$\left(\frac{d\bar{S}}{dT}\right)_p = \frac{1}{T}\left(\frac{d'Q_r}{dT}\right)_p = \frac{\bar{C}_p}{T} \tag{6-37}$$

$$\left(\frac{d\bar{S}}{dp}\right)_T = \frac{1}{T}\left(\frac{d'Q_r}{dp}\right)_T = \frac{\bar{L}_p}{T} \tag{6-38}$$

where $\bar{C}_p$ and $\bar{L}_p$ represent, respectively, the instantaneous values of the molal heat capacity at constant pressure and the molal latent heat of pressure variation, as introduced originally in Chap. 3. Therefore, introducing our conventional notation and taking into account the value of $\bar{L}_p$ given by the general thermodynamic relationship (6-8) [or introducing Eq. (6-6) directly in place of (6-38)],

$$\bar{S}^\circ_T = \bar{S}^\circ_{T_s} + \int_{T_s}^{T} \frac{\bar{C}^\circ_p}{T}\, dT \qquad (p = p_0) \tag{6-39}$$

$$\bar{S}_{T,p} = \bar{S}^\circ_T - \int_{p_0}^{p} \alpha\bar{V}\, dp \qquad (T \text{ const}) \tag{6-40}$$

These equations permit us to calculate the molal entropy $\bar{S}_{T,p}$ at any temperature and pressure relative to the standard-state value $\bar{S}^\circ_{T_s}$ at T_s and p_0, from heat-capacity data at the constant pressure p_s and equation-of-state data at the constant temperature T.

If the homogeneous chemical substance with which we are dealing happens to be a liquid or a solid, then the values of α and $\bar{V}$ in Eq. (6-40) are relatively small, and the effect of pressure on the value of $\bar{S}$ is comparatively slight. Therefore at ordinary pressures, we may take $\bar{S}_{T,p}$ as equal to $\bar{S}_T^\circ$, its value at $p = 1$ atm. For gases at moderate pressures, satisfying approximately the ideal-gas equation of state, Eq. (6-40) reduces to

$$\bar{S}_{T,p} = \bar{S}_T^\circ - R \ln \frac{p}{p_0} \qquad \text{(ideal gas)} \qquad (6\text{-}41)$$

Thus, $\bar{S}$ for a gas is quite sensitive to the pressure, and it increases without limit as $p \to 0$. If in Eq. (6-41) we took $p_0 = 1$ atm as our standard pressure, then the value of $\bar{S}_T^\circ$ would refer likewise to the state (T, 1 atm). It is convenient, however, for us to use the same hypothetical reference state to which the value of $\bar{F}_T^\circ$ refers, *viz.*, a state in which the gas at a hypothetical pressure of 1 atm would still conform precisely to the thermodynamic laws that it satisfies in the limit as $p \to 0$, as represented by the ideal-gas equation of state. Now according to Eqs. (6-9) and (6-30), we may express $\bar{S}_{T,p}$ for a real gas in terms of the fugacity coefficient by means of the general equation

$$\bar{S}_{T,p} = -\frac{d\bar{F}_T^\circ}{dT} - R \ln p\nu - RT\left(\frac{d \ln \nu}{dT}\right)_p \qquad (6\text{-}42)$$

If the gas continued to satisfy the ideal-gas equation of state exactly from 0 to 1 atm at all temperatures, then the value of ν in Eq. (6-42), which is an exact thermodynamic relation, would equal 1, and therefore the value of $\bar{S}$ in the hypothetical ideal-gas state at 1 atm satisfies the relationship

$$\bar{S}_T^\circ = -\frac{d\bar{F}_T^\circ}{dT} \qquad (6\text{-}43)$$

The precise relationship between $\bar{S}_{T,p}$ and $\bar{S}_T^\circ$ at $p = 1$ atm, or any other pressure, is then given by

$$\bar{S}_{T,p} = \bar{S}_T^\circ - R \ln p\nu - RT\left(\frac{d \ln \nu}{dT}\right)_p \qquad (6\text{-}44)$$

where the derivative in the last term on the right is taken at the particular constant pressure p to which the value of $\bar{S}_{T,p}$ refers. By comparing with Eq. (6-31), one may easily convince oneself that

$$\bar{S}_{T,1\,\text{atm}} = \bar{S}_T^\circ - \bar{V}_0\left(\frac{dc_2}{dT}\right) \qquad (6\text{-}45)$$

where c_2 represents the second virial coefficient in the empirical equation of state having the form (6-19) [assuming as in Eq. (6-31) itself that the higher virial coefficients may be neglected for this purpose in comparison with c_2]; thus, for $N_2(g)$ at 25°C, from the data in Table 6-1,

$$\bar{S}_{1\,\mathrm{atm}} - \bar{S}^\circ = -(22.4) \times (0.009 \times 10^{-3}) \text{ liter atm/mole deg}$$
$$= -0.0048 \text{ eu/mole}$$

This correction is always small, the more so the closer the gas approximates ideal-gas behavior at $p = 1$ atm; and one may estimate the value of c_2 with sufficient accuracy for the purpose, when its value is not explicitly given, by means of the approximation $c_2 \sim (pV)_{1\,\mathrm{atm}} - \lim\limits_{p \to 0} (pV)$. With this understanding concerning the physical significance of $\bar{S}_T^\circ$, we may then use in Eq. (6-39) for gases the ideal-gas value of $\bar{C}_p^\circ$, which represents $\lim\limits_{p \to 0} \bar{C}_p$, as described in Chap. 3. One may of course apply Eq. (6-37) directly to data for a gas at the actual constant pressure of 1 atm, or for that matter at any other constant pressure.

The ideal-gas result, Eq. (6-41), which we may put in the equivalent form

$$S_2 - S_1 = nR \ln \frac{V_2}{V_1} \quad (T \text{ const; ideal gas}) \quad (6\text{-}46)$$

provides us with further valuable insight into the physical significance of the entropy function, particularly in relation to the kinetic molecular theory. Let us reexamine the Joule experiment, in which a gas, confined originally in a flask joined by means of a stopcock to another previously evacuated flask, is permitted to expand freely, without doing work, as the stopcock is opened. To a first approximation, one finds that practically no net change in temperature tends to occur in this experiment, or, if one ensures that the temperature remains essentially constant by immersing the flasks in a body of water, then it turns out that practically no heat is actually exchanged with the surrounding medium. From this fact, we have already concluded empirically that for an ideal gas (which merely represents any actual gas at sufficiently low pressures), the internal energy is determined solely by the temperature, independently of pressure or volume [compare Eq. (3-62)]. Thus, so far as the surroundings are concerned, no immediate effect of any kind is perceived by which one could infer without actually opening the system (*e.g.*, by introducing a manometer) that a change has taken place upon the opening of the connecting stopcock. The first law of thermodynamics is powerless in this case to define precisely in what respect the system differs in its relationship to the external world, before and after the stopcock has been opened.

Now, the entropy function affords a quantitative measure of the difference that we intuitively know must exist between the states of the system before and after the change, even though this difference is reflected in no way by the energy. For according to Eq. (6-46), if the gas is allowed to expand at constant temperature into a total volume twice as large as the original volume, then its entropy increases by the amount $R \ln 2$ per mole. If it should be allowed to expand into a total volume four times as large as the original, then the entropy increase would be $R \ln 4$ per mole, the larger value reflecting the fact that if the gas is first expanded to twice its original volume, it will expand irreversibly still further if the doubled container is then connected to another evacuated receiver. The entropy in fact increases without limit as the gas becomes more and more attenuated at the given temperature.

The irreversible nature of the change taking place in the Joule experiment, and its deferred effect upon the surroundings, is appreciated when one begins to consider how the gas may be restored to its original state. It is not sufficient merely to leave the stopcock open and wait for the gas to accumulate again on the original side; one must, for example, introduce a piston into the second flask, and force the gas back through the stopcock against its own pressure, doing work on it at the expense of some nonthermal source of energy outside the system (*e.g.*, a falling weight, which some external agency had previously lifted into position, etc.). One could effect a partial restoration alternatively by cooling the first flask well below the temperature of the second; reflection shows, however, that such an operation would not obviate but would only defer the ultimate consumption of "available" energy (either nonthermal energy, or thermal energy drawn from a higher temperature level, as by means of a heat engine), *e.g.*, to run the refrigerating engine providing the lower temperature. Now, the quantity of nonthermal energy one must so expend is at least equal to $T^* \Delta S$, where T^* represents the temperature (assumed constant for simplicity) at which one compresses the gas [Eqs. (6-46) and (5-4); compare also the discussion of the entropy increase accompanying simple thermal exchange, on page 215]. In this sense, the entropy increase taking place in the temporarily effectively isolated system consisting of the two flasks and the gas contained within, during the free expansion, constitutes a deferred charge against the available energy of the outside world, the system's own available energy having decreased by the amount $-\Delta F = nRT \ln (V_2/V_1)$ without having been utilized.

Now, according to the kinetic theory of gases, the mean translational kinetic energy of the molecules does not change when the gas expands at constant temperature. When the stopcock is first opened, however, there is an overwhelming probability on the basis of pure chance that gas molecules will move into the evacuated flask, against an overwhelming improbability of their returning. Only when the concentrations on either side have become almost equal will the probability of an individual molecule's returning to the original flask become almost equal to its probability of leaving that flask. The opening of the stopcock opens the way to a greater randomness in the molecular distribution, and renders the original distribution highly improbable in comparison. In fact, if one assumes that with the stopcock open, and with both flasks having equal capacities, the chance of an individual molecule's being in the original flask becomes ultimately $\frac{1}{2}$ (after sufficient time has elapsed so that the random molecular motion will have given all the molecules the opportunity of access to either half of the joined containers), then the probability that all the molecules will simultaneously be back in the original half of the container will be $(\frac{1}{2})^N$, on the basis of the probability 1 (the certainty) that they will be somewhere within both halves of the container. With N of order 10^{23}, this relative probability of the system's being in its original state, out of all the states made available to it by the opening of the stopcock, becomes a fantastically small number, though it is not quite zero.

For the point of view of molecular theory, the second law of thermodynamics is thus a statistical law, resulting from the randomness of ordinary molecular motion, combined with the relative coarseness of our perceptions and instruments. We cannot harness the energy of random molecular motion (heat) in the same way that we can harness the energy of a massive moving body (mechanical or nonthermal energy), in which presumably all the molecules have superimposed on their random thermal motion a drift motion in a common direction. Irreversible changes consist of changes from states of relatively ordered molecular motion to states of greater randomness. Such changes are irreversible in the sense that an enormously improbable coincidence would be required in order that on the basis of pure chance, unaided by energy directed from an outside agency, the enormous numbers of molecules present in the thermodynamic system should recapture the relatively greater degree of order characteristic of the original state once they have been permitted to spread.

The fact that the entropy change for an ideal gas at constant temperature depends for a given quantity of the gas only on the ratio of the final to the initial volume is highly suggestive. Generalizing the preceding argument, we may say that V_2/V_1 represents the relative probability of an individual molecule's being anywhere throughout the volume V_2 to its probability of being confined within a particular region of volume V_1, representing the volume in which all the molecules were confined before the expansion. Therefore if the molecules behave completely independently of each other (ideal-gas hypothesis), $(V_2/V_1)^N$ represents the relative probability of a state in which the N molecules are distributed at random throughout the volume V_2 compared with a state in which all N are confined within the volume V_1 (this argument assumes that volume elements of equal size are equally probable to individual molecules). Let P_2/P_1 represent the probability ratio for the two states of the gas in this particular type of problem

$$\frac{P_2}{P_1} = \left(\frac{V_2}{V_1}\right)^N \tag{6-47}$$

Comparing with the thermodynamic equation (6-46), we may infer the relationship

$$S_2 - S_1 = k \ln \frac{P_2}{P_1} \tag{6-48}$$

where $k = R/N_0$. We thus perceive the entropy as a measure of the probability of the state in question, when the state is viewed from the standpoint of the variety of changing molecular configurations that constitute it. This concept was first developed by the genius of Ludwig Boltzmann in 1877, and k is known as Boltzmann's constant. The meaning of the probability of a thermodynamic state, in general, with regard to changes more complex than the one considered here, raises several subtle questions, which we shall explore at length in Chap. 10. Meanwhile, let us note that the tendency for the entropy of an isolated system to increase, which we found in Sec. 5-5 to contain the essence of the second law of thermodynamics, turns out to be purely a statistical effect, resulting from the completely random nature of molecular motion and the enormous numbers of molecules present in ordinary material systems; the enormous numbers of individuals give the statistical laws for the assembly overwhelming reliability—hence the great generality of the second law. Needless to say, the second law rests on a firm experimental basis, quite independent of its statistical molecular interpretation; nevertheless, this interpretation has been of immense value in supplementing formal thermodynamics with data derived from molecular structure, as we shall see in Chap. 10.

Before passing on to the next section, let us note two useful relationships that may be derived from the general equations (6-35), (6-37), and (6-38) for reversible *adiabatic* changes of state ($d\bar{S} = 0$). Thus

$$\left(\frac{dT}{dp}\right)_{\bar{S}} = -\frac{\bar{L}_p}{\bar{C}_p} = \frac{\alpha\bar{V}T}{\bar{C}_p} \tag{6-49}$$

$$\left(\frac{d\bar{V}}{dp}\right)_{\bar{S}} = \left(\frac{d\bar{V}}{dT}\right)_p \left(\frac{dT}{dp}\right)_{\bar{S}} + \left(\frac{d\bar{V}}{dp}\right)_T \qquad \text{[Eq. (3-3)]}$$

$$= \frac{\alpha^2\bar{V}^2T}{\bar{C}} - \beta\bar{V} \tag{6-50}$$

Equations (6-49) and (6-50) find particular application to the theory of sound, which consists of compression waves propagated under essentially adiabatic conditions through a material medium.

6-3. General Thermodynamic Relationships for a Homogeneous Chemical Substance. Let us now reexamine the forms of the internal energy and the enthalpy functions for fixed mass (*e.g.*, 1 mole) of a homogeneous chemical substance of fixed composition, in view of the further information furnished by the second law of thermodynamics. The first law resulted in the equation

$$\begin{aligned} dU &= d'Q - d'W \\ &= d'Q - p\,dV - d'W' \end{aligned}$$

where certain general restrictions were imposed on the kinds of energy changes taken into consideration (for example, changes in the kinetic and potential mechanical energy of the system as a whole were not included). The second law results in the equation

$$dS = \frac{d'Q_r}{T}$$

Therefore for thermodynamically reversible changes of state

$$dU = T\,dS - p\,dV - d'W' \qquad (6\text{-}51)$$

If we confine our attention to changes of state for which $W' = 0$, so that the only nonthermal energy exchanged with the surroundings is in the form of mechanical work of expansion, then Eq. (6-51) sets up for us the differential equation for U as a function of S and V as state-determining independent variables. We may recall from the discussion in Sec. 3-1 that for a homogeneous substance of fixed composition, the values of *any two* independently variable properties serve to determine the state (in the absence of special influences, such as that of a magnetic field, etc.). Thus, for 1 mole of the substance,

$$d\bar{U} = T\,d\bar{S} - p\,d\bar{V} \qquad (W' = 0) \qquad (6\text{-}52)$$

The companion equation for $d\bar{H}$, from Eq. (3-57), is easily shown to have the form

$$d\bar{H} = T\,d\bar{S} + \bar{V}\,dp \qquad (W' = 0) \qquad (6\text{-}53)$$

From these general thermodynamic relationships, we draw the conclusions

$$\left(\frac{d\bar{U}}{d\bar{S}}\right)_V = T = \left(\frac{d\bar{H}}{d\bar{S}}\right)_p \qquad (W' = 0) \qquad (6\text{-}54)$$

$$\left(\frac{d\bar{U}}{d\bar{V}}\right)_S = -p; \qquad \left(\frac{d\bar{H}}{dp}\right)_S = \bar{V} \qquad (W' = 0) \qquad (6\text{-}55)$$

By the application of Eqs. (6-52) and (6-53) to Eqs. (5-49) and (5-59) defining the functions $\bar{A}$ and $\bar{F}$, complementary equations follow for $d\bar{A}$ and $d\bar{F}$:

$$d\bar{A} = -\bar{S}\,dT - p\,d\bar{V} \qquad (W' = 0) \tag{6-56}$$

$$d\bar{F} = -\bar{S}\,dT + \bar{V}\,dp \qquad (W' = 0) \tag{6-57}$$

The second of these equations has already been introduced in Sec. 6-1 as Eq. (6-5).

We may apply Euler's criterion to Eqs. (6-52), (6-53), (6-56), and (6-57), for $d\bar{U}$, $d\bar{H}$, $d\bar{A}$, and $d\bar{F}$ to be perfect differentials in terms of the respective pairs of independent variables, any of which serves to determine the state; in this way we obtain a set of four useful thermodynamic relationships known as *Maxwell's equations:*[1]

$$\left(\frac{dp}{d\bar{S}}\right)_V = -\left(\frac{dT}{d\bar{V}}\right)_S \tag{6-58}$$

$$\left(\frac{d\bar{V}}{d\bar{S}}\right)_p = \left(\frac{dT}{dp}\right)_S \tag{6-59}$$

$$\left(\frac{d\bar{S}}{d\bar{V}}\right)_T = \left(\frac{dp}{dT}\right)_V \tag{6-60}$$

$$\left(\frac{d\bar{S}}{dp}\right)_T = -\left(\frac{d\bar{V}}{dT}\right)_p \tag{6-61}$$

Maxwell's equations provide a compact and flexible scheme for transposing from one pair of independent variables to another. As an illustration, let us transpose Eq. (6-53) from $\bar{S}$ and p to T and $\bar{V}$ as independent variables defining the state; thus

$$\left(\frac{d\bar{H}}{dT}\right)_V = \left[\frac{d}{dT}(\bar{U} + p\bar{V})\right]_V = \left(\frac{d\bar{U}}{dT}\right)_V + \bar{V}\left(\frac{dp}{dT}\right)_V = \bar{C}_v + \frac{\alpha\bar{V}}{\beta} \tag{6-62}$$

[according to (3-23) and (3-6)]. At the same time, from (6-53) and (6-60),

$$\begin{aligned}\left(\frac{d\bar{H}}{d\bar{V}}\right)_T &= T\left(\frac{d\bar{S}}{d\bar{V}}\right)_T + V\left(\frac{dp}{d\bar{V}}\right)_T \\ &= T\left(\frac{dp}{dT}\right)_V - \frac{1}{\beta} = T\frac{\alpha}{\beta} - \frac{1}{\beta}\end{aligned} \tag{6-63}$$

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[1] Named after the brilliant nineteenth-century physicist James Clerk Maxwell, who among many great achievements contributed with Ludwig Boltzmann to the creation of the statistical molecular theory of thermodynamics.

Therefore, for $\bar{H}$ in the form

$$
\begin{aligned}
\bar{H} &= \bar{H}(T, \bar{V}) \\
d\bar{H} &= \left(\frac{d\bar{H}}{dT}\right)_V dT + \left(\frac{d\bar{H}}{d\bar{V}}\right)_T d\bar{V} \\
&= \left(\bar{C}_v + \frac{\alpha\bar{V}}{\beta}\right) dT + \left(\frac{\alpha T - 1}{\beta}\right) d\bar{V} \qquad (6\text{-}64)
\end{aligned}
$$

Equation (6-64) thus provides the differential equation satisfied by $\bar{H} = \bar{H}(T, \bar{V})$, in terms of familiar thermal and equation-of-state data for the substance.

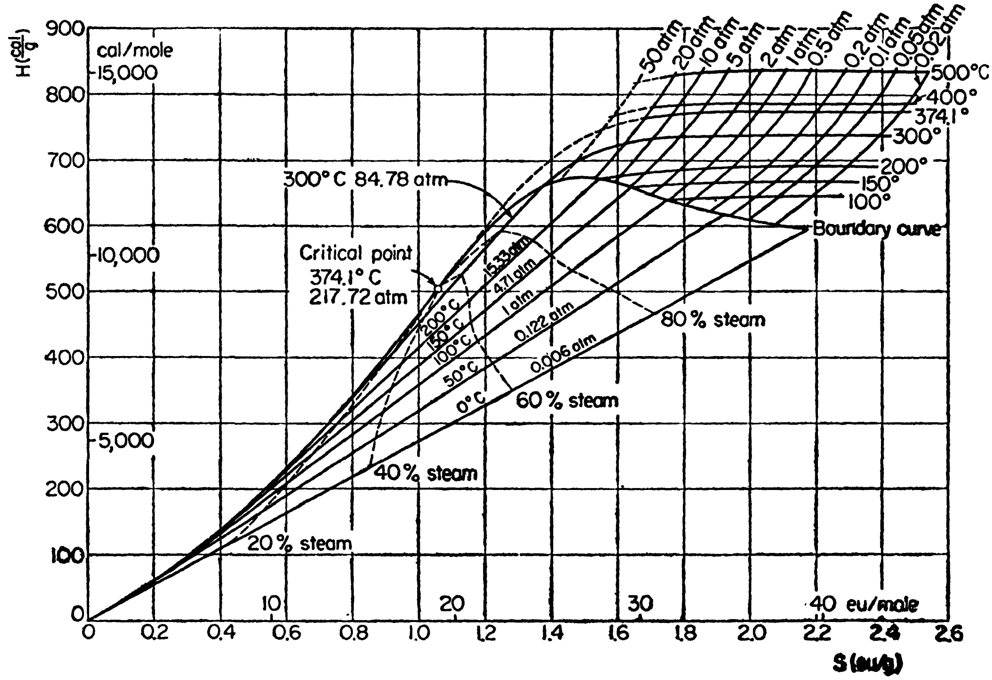

FIG. 6-5. Mollier diagram for steam.

A convenient form of graphical representation of the thermodynamic properties of a fluid substance, whether gas, or liquid, or equilibrium mixture of both phases, is the Mollier diagram, introduced by R. Mollier in 1904, and widely used in engineering practice. In this diagram, $\bar{H}$ is plotted against $\bar{S}$. Figure 6-5 shows on a small scale the Mollier diagram for steam; larger charts showing much greater detail are available, from which the thermodynamic properties may be read with high precision. The boundary curve shown in the diagram separates the region of dry steam from the region of heterogeneous mixtures of steam with liquid water (whose equilibrium we shall discuss in the following section). According to Eq. (6-53), the slopes of the isopiestics (lines of constant pressure) in the Mollier diagram, $(d\bar{H}/d\bar{S})_p$, are everywhere equal to T; in the "wet" region, therefore, below the boundary curve, the isopiestics are straight lines, inasmuch as in this region, a unique temperature corresponds to each value of the pressure (the vapor pressure at the given temperature). Furthermore, the slopes of isothermals (lines of constant temperature), $(d\bar{H}/d\bar{S})_T$, according to (6-53) and (6-61), are everywhere equal to $T - 1/\alpha$; at the lower pressures and higher temperatures, where steam behaves approximately as an ideal gas, these isothermals become straight lines parallel to the $\bar{S}$ axis. Since the diagram is drawn for a fixed mass of the substance under consideration, each point within the "wet" or two-phase region corresponds to some particular ratio of vapor to liquid; it is customary in this region to connect up points of equal "dryness" (expressed as a percentage of the total mass in the vapor state), as shown in Fig. 6-5. As one follows an isopiestic down from the boundary curve in this region, the change in $\bar{H}$ represents the latent heat of vaporization for the particular quantity of vapor condensing to liquid between the corresponding pair of points on the curve; *e.g.*, between the lines corresponding to 90 per cent and 80 per cent dryness, the difference in $\bar{H}$ values along any isopiestic (isothermal, in this region) corresponds to the latent heat of vaporization for 0.1 mole at the given pressure and temperature; the change in $\bar{S}$ along an isopiestic in this region represents the proportional entropy of vaporization ($\Delta\bar{S} = \Delta\bar{H}/T$) for the particular quantity of vapor condensing to liquid between the corresponding pair of points on the curve. A reversible adiabatic change of state is represented on the diagram by a line parallel to the $\bar{H}$ axis ($\Delta\bar{S} = 0$), passing through the point representing the initial state (or any other state through which the system may pass during the change). Joule-Thomson expansion ($\Delta\bar{H} = 0$) is represented by a line parallel to the $\bar{S}$ axis, running to the right from the point representing the initial state of the fluid.

One may show that the decrease in $\bar{H}$ along an adiabatic (line of constant $\bar{S}$) between two states of the fluid represents the reversible work that may be done per mole of the substance when it enters the cylinder in the first state and leaves the cylinder in the second state during the so-called *Rankine cycle,* for the conversion of thermal into mechanical energy. The Carnot cycle described in Sec. 5-2, in which a gas is alternately expanded within a cylinder at a higher temperature and compressed again at a lower temperature, is not technically feasible for the design of an actual heat engine, because too much energy would be wasted in heating and cooling the cylinder.[1] In actual steam engines,

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[1] This problem is solved in the internal-combustion engine by the fact that combustion takes place extremely rapidly in relation to the thermal conductivity of the product gases; the expansion is therefore practically adiabatic, and the gas immediately

steam is generated from water heated in a separate boiler, and after it passes into the cylinder, where it works against the piston and cools, it is then expelled into a separate condenser, from which the water may be returned to the boiler. The Rankine cycle is an idealized cycle of this nature, conceived as follows. Let steam be generated in a boiler, and let it pass into the cylinder at the constant pressure p_1; this boiler pressure represents the vapor pressure of water at the boiler temperature, but the steam may be superheated to a higher temperature without change in the pressure by further heating of the pipes that convey it to the cylinder. The reversible work done by the steam in entering the cylinder and displacing the piston is $p_1\bar{V}_1$ per mole, where $\bar{V}_1$ is its molal volume in the state in which it enters the cylinder. At a certain stage of the piston's forward stroke, the steam entering the cylinder is cut off, but it continues to expand the rest of the way under practically adiabatic conditions, which reduce its temperature at the end of the stroke practically to that of the condenser. During the adiabatic expansion, the work done per mole is equal to $\bar{U}_1 - \bar{U}_2$ [Eq. (2-24)], where $\bar{U}_1$ represents the molal internal energy in the state in which the substance enters the cylinder, and $\bar{U}_2$ represents its molal internal energy in the state in which it leaves the cylinder; in the latter state, it may be partially condensed to the liquid form, but $\bar{U}_2$ is taken to represent its total molal internal energy, in whatever manner in which it may be distributed between the liquid and the gas phases. If $\bar{V}_2$ denotes the total molal volume in the condition in which the substance leaves the cylinder, and p_2 the pressure (generally speaking, the vapor pressure at the temperature of the condenser, into which the spent steam passes), then the work done by the piston *on* the spent steam in forcing it from the cylinder on the return stroke is $p_2\bar{V}_2$. A small additional term, $(p_1 - p_2)\bar{V}_1$, should be subtracted from the total work, representing the work that must be done by the feed pump in order to transfer the cold water, at molal volume $\bar{V}_1$, from the condenser into the boiler, thereby completing the cycle. Thus, the total work, per mole per cycle, is

$$W = p_1\bar{V}_1 + \bar{U}_1 - \bar{U}_2 - p_2\bar{V}_2 - (p_1 - p_2)\bar{V}_1$$

where $\bar{U}_1$, p_1, and $\bar{V}_1$ are connected with $\bar{U}_2$, p_2, and $\bar{V}_2$ through an adiabatic change. Therefore, neglecting the work done by the boiler feed pump,

$$W = \bar{H}_1 - \bar{H}_2 \qquad (\bar{S} \text{ const})$$

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after the combustion, before it begins to expand, may attain a temperature much higher (about 2000°C) than the temperature of the cylinder block, which is generally cooled by a current of water, oil, or air.

This applies, whether the steam is dry, saturated, or wet, where H_1 denotes the total molal enthalpy for the state in which it enters the cylinder and $\bar{H}_2$ the total molal enthalpy for the state in which it leaves the cylinder. For given operating conditions, the value of $\bar{H}_1 - \bar{H}_2$ at constant $\bar{S}$ is easily read from the Mollier diagram, which therefore serves as a particularly convenient form for analyzing the ideal behavior of a steam engine, or other heat or refrigerating engine operating on similar principles.

6-4. Equilibrium in Phase Transitions. When a chemical substance of fixed composition undergoes a phase transition, then in general, if both phases are at the same temperature and pressure, a change in free energy satisfying Eq. (5-60) takes place, as well as changes in the internal energy and the enthalpy. For example,

$$\text{S(I, monoclinic, 25°C, 1 atm)} = \text{S(II, rhombic, 25°C, 1 atm)}; \qquad \Delta F = -0.016 \text{ kcal}$$

(How ΔF for this transformation is measured will be explained presently.) Since the sign of ΔF is determined solely by the thermodynamic states of the two phases, therefore at an arbitrary temperature and pressure, in general, only one of the states is thermodynamically stable, though other phases may exist in metastable states. Now, for reversible equilibrium between the two phases (not metastatic equilibrium, such as exists between diamond and graphite at room temperature and pressure), the general equilibrium condition (5-61) must apply; for example,

$$\text{H}_2\text{O(l, 100°C, 1 atm)} = \text{H}_2\text{O(g, 100°C, 1 atm)}; \qquad \Delta F = 0$$

This condition sets up a restriction on the possible equilibrium states, because while the molal free energies, $\bar{F}_1$ and $\bar{F}_2$, of the substance in the two phases vary independently with temperature and pressure, yet the equilibrium condition

$$\bar{F}_1 = \bar{F}_2 \qquad (T_1 = T_2;\ p_1 = p_2) \qquad (6\text{-}65)$$

sets up a thermodynamic relation between the pair of variables T and p (which are by hypothesis respectively equal for the two phases). Thus, to each value of T, there corresponds a unique value of p at which the two phases may be in equilibrium, or what amounts to the same thing, to each value of p there corresponds a unique value of T at which the two phases may be in equilibrium. The variance of the two-phase equilibrium system is 1, instead of 2, such as would characterize the behavior of a single homogeneous phase of fixed composition (compare Sec. 3-1).

We may discover the relationship between T and p for reversible equilibrium between the two phases by equating the changes in $\bar{F}_1$ and $\bar{F}_2$

with T and p as we follow the system from one equilibrium state to another; thus, according to Eq. (6-5),

$$d\bar{F}_1 = d\bar{F}_2$$
$$-\bar{S}_1\,dT + \bar{V}_1\,dp = -\bar{S}_2\,dT + \bar{V}_2\,dp$$

So long as this condition is maintained, then if $\bar{F}_1 = \bar{F}_2$ at any one temperature and pressure, Eq. (6-65) will continue to be satisfied at other temperatures and pressures. The equilibrium temperature and pressure therefore satisfy the equation

$$\frac{dp}{dT} = \frac{\bar{S}_2 - \bar{S}_1}{\bar{V}_2 - \bar{V}_1} \tag{6-66}$$

Now, the transformation from one phase to the other at the equilibrium temperature and pressure is a thermodynamically reversible process, for which

$$\bar{S}_2 - \bar{S}_1 = \frac{\bar{L}_{12}}{T} \tag{6-67}$$

where $\bar{L}_{12}$ represents the molal latent heat of the transition from phase 1 to phase 2 ($= \bar{H}_2 - \bar{H}_1$; its value is taken to be positive in the sense that heat is absorbed by the substance in passing from phase 1 to phase 2). Therefore

$$\frac{dp}{dT} = \frac{\bar{L}_{12}}{T(\bar{V}_2 - \bar{V}_1)} \tag{6-68}$$

This is the well-known *Clapeyron-Clausius equation.*[1]

Equation (6-68) is entirely general, applying to equilibrium between any two phases of a chemical substance of fixed composition. Characteristically, it gives only the rate of change of the equilibrium pressure with temperature, but not the equilibrium pressure itself at any one temperature; this latter information has to be introduced empirically, as an integration constant to the integral form of Eq. (6-68). If, for example, we have determined the so-called "normal" transition temperature (at $p = 1$ atm, by convention), then Eq. (6-68) upon introduction of the necessary thermal and equation-of-state data may be used to deduce the transition temperature at other pressures, or the equilibrium pressure at other temperatures. Thus, for the transition between rhombic and monoclinic sulfur at the normal transition temperature, 95.5°C, the latent

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[1] It was first deduced by the French engineer B. P. E. Clapeyron in 1832 from Carnot's theory. A rigorous derivation was later given by the German physicist R. J. E. Clausius in the light of the first law of thermodynamics.

heat of transformation as determined by J. N. Brønsted is 0.095 kcal/g-atom;[1] *i.e.*,

$$\text{S(II, rhombic)} = \text{S(I, monoclinic)}; \qquad \Delta H^\circ_{368.7} = 0.095 \text{ kcal}$$

while $\Delta\bar{V} = 0.442$ cm³/g-atom; therefore at the normal transition temperature

$$\begin{aligned}\frac{dp}{dT} &= \frac{0.095 \text{ kcal/g-atom}}{368.7 \text{ deg} \times 0.442 \text{ cm}^3\text{/g-atom}} \times 41.3 \times 10^3 \text{ cm}^3 \text{ atm/kcal} \\ &= 24.1 \text{ atm/deg}\end{aligned}$$

This result agrees well with the experimental value of 26.4 atm/deg obtained by G. Tammann, who followed the transition equilibrium up to the rhombic-monoclinic-liquid triple point at 151°C and 1288 atm.[2] The value of dp/dT of course varies in general with the particular equilibrium temperature and pressure at which it is determined. Its sign is fixed by the sign of $\bar{V}_2 - \bar{V}_1$, in accordance with the sign convention for $\bar{L}_{12}$, being positive when $\bar{V}_2$ exceeds $\bar{V}_1$, as in the equilibrium between rhombic and monoclinic sulfur, and negative when $\bar{V}_2$ is smaller than $\bar{V}_1$, as in the ice-water equilibrium.

Equation (6-68) may be used conversely to determine the value of $\bar{L}_{12}$ from purely nonthermal data. For example, ordinary ice (ice I) at −30°C undergoes a transition at 2087 atm to a different allotropic form, ice III, the volume decreasing by 3.46 cm³/mole. The system has been studied by G. Tammann and by P. W. Bridgman[3] who found that at that temperature $dp/dT = -3.1$ atm/deg, this being the slope of the transition curve at the given point on the phase diagram. Thus, for the transformation, ice I = ice III, at −30°C and 2087 atm,

$$\begin{aligned}\bar{L}_{\text{I,III}} &= (-3.1 \text{ atm/deg}) \times (243 \text{ deg}) \times (-3.46 \text{ cm}^3\text{/mole}) \\ &\qquad \times \frac{1 \text{ kcal}}{41.3 \times 10^3 \text{ cm}^3 \text{ atm}} = 0.063 \text{ kcal/mole}\end{aligned}$$

When one of the phases is a gas, at equilibrium pressures not greater than several atmospheres, we may introduce certain approximations that improve the usefulness of Eq. (6-68). Thus, $\bar{V}_2 \sim RT/p \gg \bar{V}_1$; introducing these approximations in (6-68), we obtain

$$\frac{d \ln p}{dT} = \frac{\bar{L}_{1g}}{RT^2} \quad \text{(vapor-phase ideal gas)} \qquad (6\text{-}69)$$

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[1] J. N. Brønsted, *Z. physik. Chem.*, **55**, 371–382 (1906).

[2] G. Tammann, *Ann. Physik u. Chem.*, (3) **68**, 629–657 (1899).

[3] See "International Critical Tables," Vol. IV, pp. 11, 17, McGraw-Hill Book Company, Inc., New York, 1928.

In this equation, p stands for the vapor pressure, and $\bar{L}_{1g}$ for the molal latent heat of vaporization or sublimation, depending on whether the first phase is a liquid or a solid. Over a range of temperatures sufficiently narrow so that $\bar{L}_{1g}$ may be regarded as sensibly constant (the heat of vaporization of water, for example, decreases by about 0.1 per cent per degree Kelvin between its freezing point and its normal boiling point), we may integrate Eq. (6-69) immediately, to obtain a familiar vapor-pressure equation

$$\log p = -\frac{\bar{L}_{1g}}{2.303RT} + B \qquad (6\text{-}70)$$

whose empirical form

$$\log p = -\frac{A}{T} + B \qquad (6\text{-}70a)$$

is known as Young's equation; B is an integration constant, whose value can be determined only by extrathermodynamic means; its value for a liquid can be calculated, for example, from knowledge of its normal boiling point, *i.e.*, the value of T for which $p = 1$ atm. One may put Eq. (6-70) alternatively in the form

$$\log \frac{p}{p_0} = \frac{\bar{L}_{1g}}{2.303R}\left(\frac{1}{T_0} - \frac{1}{T}\right) \qquad (6\text{-}71)$$

where p_0 denotes the vapor pressure at the temperature T_0. These equations are extremely useful for the approximate correlation of vapor-pressure data; they suggest that if one plots $\log p$ vs. $1/T$, an approximately straight line will result (depending on how much $\bar{L}_{1g}$ varies with temperature over the range in question); its slope may be used to calculate the value of $\bar{L}_{1g}$. This constitutes in fact an important method of determining latent heats of vaporization and latent heats of sublimation, though higher precision in the integral form of the vapor pressure equation is obtained if one takes account of the change of $\bar{L}_{1g}$ with temperature.

Now, the general equation for the change of $\bar{L}_{1g}$ with the equilibrium temperature and pressure is Eq. (3-48). If we confine our attention to pressures not greater than several atmospheres, a necessary restriction if Eq. (6-69) itself is to be valid, then Eq. (3-48) reduces to

$$\bar{L}_{1g} = (\bar{L}_{1g})_0 + \int_{T_0}^{T} \Delta\bar{C}_p^\circ \, dT \qquad (\text{low } p) \qquad (6\text{-}72)$$

where $\Delta\bar{C}_p^\circ = (\bar{C}_p^\circ)_g - (\bar{C}_p^\circ)_1$ represents the difference between the molal heat capacity of the gas and that of the liquid or solid phase at constant pressure of 1 atm; the explicit effect of changing pressure on the value of $\bar{L}_{1g}$ may be neglected for all practical purposes at pressures of order 1 atm or lower, though this would not be true at high pressures. We may introduce empirical heat-capacity equations of the form (3-58) or (3-59) for the two phases, and thus express $\bar{L}_{lg}$ as an empirical function of T by means of Eq. (6-72), from a knowledge of its value $(\bar{L}_{lg})_0$ at any one temperature T_0 [obtained either by thermal measurement, or by the application of Eq. (6-69) itself to vapor-pressure measurements around the temperature T_0]. Since the heat capacities do not vary rapidly with temperature, however, a good approximation may be obtained by treating them as constant, and using their mean values over the temperature range for which one wishes to represent the vapor pressure. Thus, we may put Eq. (6-72) in the approximate form

$$\bar{L}_{lg} = (\bar{L}_{lg})_0 + \Delta\bar{C}_p^\circ\,(T - T_0) \tag{6-72a}$$

Introducing this form in Eq. (6-69) and integrating, we obtain

$$\log p = -\frac{(\bar{L}_{lg})_0 - (\Delta\bar{C}_p^\circ)T_0}{2.303RT} + \frac{(\Delta\bar{C}_p^\circ)}{R}\log T + C \tag{6-73}$$

This vapor-pressure equation, with C an integration constant, has the form of the empirical Kirchhoff-Rankine equation

$$\log p = -\frac{A'}{T} + B'\log T + C \tag{6-73a}$$

but it provides theoretical values for the constants A' and B'. Let us apply it to water, using the data $\bar{L}_{lg} = 9717$ cal/mole at $T_0 = 373.16$°K, $(\bar{C}_p^\circ)_l = 18.03$ cal/mole deg, $(\bar{C}_p^\circ)_g = 8.05$ cal/mole deg. Substituting in Eq. (6-73) and solving for C by making use of the information $p_0 = 1$ atm when $T_0 = 373.16$°K, we obtain

$$\log p = -\frac{2937.5}{T} - 5.022\log T + 20.788 \quad (p \text{ in atm})$$

Testing this equation at 25°C ($T = 298.16$°K), we obtain

$$\log p = -1.491$$
$$p = 0.0323 \text{ atm} = 24.5 \text{ mm Hg}$$

This result may be compared with the experimental value, $p = 23.8$ mm Hg; part of the small deviation is a consequence of the deviation of steam from ideal-gas behavior at 100°C and 1 atm; the rest follows from variation of the heat capacities with temperature.

We may treat vaporization equilibrium in a more rigorous manner that includes the effect of significant deviation of the gas phase from ideal-gas behavior. The free-energy change in general for the process

A(liquid) = A(gas), or for the comparable solid-gas transition, is given at a particular temperature T and pressure p by

$$\Delta F = (\bar{F}_{T,p})_g - (\bar{F}_{T,p})_1 \qquad (6\text{-}74)$$

where subscript 1 stands for either the liquid or the solid, as the case may be. Now, up to moderately high pressures, well beyond the ideal-gas range for the vapor phase, we may assume that pressure has comparatively little effect on the value of $(\bar{F}_{T,p})_1$ of the liquid or solid phase [compare Eq. (6-16)]; we may therefore assume that $(\bar{F}_{T,p})_1$ is practically equal to $(\bar{F}^\circ_T)_1$, the 1 atm value, regardless of the exact value of p. For the vapor phase, however, we may use Eq. (6-30), where ν represents the fugacity coefficient of the gas at temperature T and pressure p, measured by the methods described in Sec. 6-1. Thus

$$\Delta F = \Delta F^\circ_T + RT \ln p\nu \quad (p = \text{any pressure}) \qquad (6\text{-}75)$$

where the only assumption introduced has been the independence of $(\bar{F}_{T,p})_1$ for the liquid or solid phase of the value of p. Thus, for equilibrium,

$$\ln p\nu = -\frac{\Delta F^\circ_T}{RT} \quad (p = \text{vapor pressure}) \qquad (6\text{-}76)$$

Measurement of the vapor pressure at a given temperature thus serves essentially to determine the value of ΔF°_T, the standard free-energy change for the vaporization process (liquid or solid phase at 1 atm, and vapor phase in the hypothetical ideal-gas state at 1 atm, at the given temperature). At sufficiently low values of the vapor pressure, one may assume that $\nu = 1$ in Eq. (6-76), but in general, this assumption is not warranted. If we make use of Eq. (6-12), then

$$\frac{d \ln (p\nu)}{dT} = \frac{\Delta H^\circ}{RT^2} \qquad (6\text{-}77)$$

where ΔH° represents the standard enthalpy of vaporization at the given temperature; Eq. (6-77) constitutes a generalization of Eq. (6-69), but of course, it contains the empirically determined quantity ν, whose value cannot be deduced from theory. One may use this equation, however, to determine the value of ΔH° precisely from precise vapor-pressure measurements; for this purpose, one may write it in the equivalent form

$$\frac{d \ln (p\nu)}{d(1/T)} = -\frac{\Delta H^\circ}{R} \qquad (6\text{-}78)$$

from which one sees that by plotting log $p\nu$ instead of log p itself against $1/T$, the slope of the resulting curve gives the instantaneous value of

$-\Delta H_T^\circ/2.303R$, where ΔH_T° represents the molal heat absorbed in the transition from liquid or solid at 1 atm to ideal gas.

Many empirical rules have been developed for the estimation of the vapor-pressure curve of a liquid from scant data. One of the simplest of these rules is that of Ramsay and Young[1] who found that the ratio of the absolute temperatures at which two liquids have the same vapor pressures is approximately constant, the more so the closer the relationship between the two substances compared. Thus, letting T_1' and T_1'' denote the respective temperatures at which the two liquids have the common vapor pressure p_1, and T_2' and T_2'' the respective temperatures at which the same two liquids have the common vapor pressure p_2, then according to the empirical rule of Ramsay and Young

$$\frac{T_1'}{T_1''} = \frac{T_2'}{T_2''} \quad (p_1' = p_1'' = p_1;\, p_2' = p_2'' = p_2) \tag{6-79}$$

The following example serves to illustrate how the rule may be applied: the normal boiling points ($p_1 = 1$ atm) of benzene and bromobenzene are, respectively, 80.2°C and 156.2°C; let us estimate the vapor pressure of bromobenzene at 100°C, from complete empirical knowledge of the vapor-pressure curve for benzene. Now, $T_1'/T_1'' = 353°\text{K}/430°\text{K}$, from which one concludes according to Eq. (6-79) that if $T_2'' = 373°\text{K}$, then $T_2' = 306°\text{K}$; in other words, bromobenzene at 100°C should have the same vapor pressure as benzene at 33°C, *viz.*, 135 mm Hg. Its actual vapor pressure turns out to be 141 mm Hg.

If we compare Eq. (6-79) with the approximate vapor-pressure equation (6-71), which we may put in the form

$$\log\frac{p}{p_0} = \frac{(\bar{L}_{lg})'}{2.303RT_0'}\left(1 - \frac{T_0'}{T'}\right) = \frac{(\bar{L}_{lg})''}{2.303RT_0''}\left(1 - \frac{T_0''}{T''}\right)$$

we must draw the conclusion that for substances satisfying both the empirical rule of Ramsay and Young and the nonthermodynamic assumptions involved in the derivation of Equation (6-71),

$$\frac{(\bar{L}_{lg})'}{T_0'} = \frac{(\bar{L}_{lg})''}{T_0''} \tag{6-80}$$

In other words, the value of $\bar{L}_{lg}/T_0$ must be approximately the same for many substances, where T_0 represents a temperature at which the given substance has some particular vapor pressure, the same throughout. This vapor pressure may be selected as 1 atm, in which case T_0 represents the normal boiling point, and $\bar{L}_{lg}/T_0$ the molal entropy of vaporization

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[1] W. Ramsay and S. Young, *Phil. Mag.*, (5) **21,** 33–51 (1886).

at the normal boiling point. The rule represented by Eq. (6-80) turns out to be approximately satisfied by many liquids, and when the temperature is taken to be the normal boiling point ($p_0 = 1$ atm), it is known as Trouton's rule;[1] the value of the Trouton constant, $\bar{L}_{lg}/T_0$, is approximately 21 eu/mole. For liquids whose molecules are strongly polar and tend to associate, the value of the Trouton ratio tends to be larger; *e.g.*, for water, it is 26.0 eu/mole, and for ammonia, 23.2 eu/mole; such substances generally have exceptionally high molal heats of vaporization and boiling points in relation to their molecular weights.[2] On the other hand, those substances having the lowest boiling points and critical points show lower values of the Trouton ratio; *e.g.*, for He it is only 5.2 eu/mole; for H_2, 10.6 eu/mole; for N_2, 17.3 eu/mole; and for O_2, 18.1 eu/mole. Many attempts have been made to provide a theoretical foundation for the regularities implied by the rule of Ramsay and Young and the rule of Trouton. In particular, one can derive more consistent values for the Trouton ratio by means of a semiempirical adaptation of the theory of corresponding states. An empirical generalization proposed by H. von Wartenberg:

$$\frac{\bar{L}_{lg}}{T_0} = 7.4 \log T_0$$

gives good results for nonpolar liquids,[3] while an equation of similar form involving only the natural constant R has been derived on semiempirical grounds by V. A. Kistyakovskii:[4]

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[1] F. T. Trouton, *Phil. Mag.*, (5) **18,** 54–57 (1884).

[2] From the statistical molecular viewpoint developed in Chap. 10, the tendency of polar molecules to organize into polymolecular aggregates introduces relatively greater order in the liquid state as compared with the more completely random orientation of the molecules in a nonpolar liquid. Therefore, aside from other considerations such as entropy terms contributed by the molecular internal configuration, which is essentially the same for the liquid as for the equilibrium vapor state, the entropy of the polar liquid substance tends to be relatively lower than that of a nonpolar liquid substance in comparable circumstances, leading to a larger entropy change on vaporization when the corresponding vapor phases are in states of equivalent degrees of disorder.

[3] H. von Wartenberg, *Z. Elektrochem.*, **20,** 444 (1914).

[4] V. A. Kistyakovskii, *J. Russ. Phys. Chem. Soc.*, **53,** 256–264 (1921); *Z. physik. Chem.*, **107,** 65–73 (1923). In his argument, RT_0 stands for the molal volume of the equilibrium vapor phase at T_0 (the normal boiling point) and 1 atm; therefore the value of the R after the logarithm sign is expressed in ml atm/mole deg, whereas the R before the logarithm sign is expressed in cal/mole deg, if $\bar{L}_{lg}/T_0$ is to be so expressed. Kistyakovskii's equation is not as inconsistent with Wartenberg's as one might at first suppose; neither is particularly sensitive to the value of T_0 in the range of most general applicability, 300 to 2000°K, and over this range, the two equations give $\bar{L}_{lg}/T_0$ values differing by at most 9 per cent.

$$\frac{\bar{L}_{l0}}{T_0} = R \ln RT_0$$
$$= 8.76 + 4.576 \log T_0$$

J. H. Hildebrand has modified Trouton's rule by taking the entropy of vaporization not at the normal boiling point, where the various liquids have the same vapor pressure, but at corresponding temperatures at which the concentration of the equilibrium vapor phase is the same (*e.g.*, 0.005 mole/liter).[1] None of these rules, however, is much better for liquids consisting of polar molecules than Trouton's original rule, and while such attempts have had practical value, they have not been sufficiently general to have much theoretical significance. A similar interesting empirical rule, for which no theoretical explanation has been found to date, is that of C. M. Guldberg concerning the relationship between the normal boiling point and the critical point on the absolute thermodynamic scale: he pointed out that for many liquids, T_0 is approximately two-thirds of T_c.[2]

Actual vapor-pressure data for inorganic compounds have been reviewed critically by K. K. Kelley.[3] More recently, a comprehensive tabulation for more than 1500 organic and inorganic substances has been published by D. R. Stull.[4] These tables give the temperatures at which the various substances attain certain arbitrarily selected values of the vapor pressure, and they include all the references to the original literature consulted. They are of inestimable value in practical applications of liquid-vapor or solid-vapor equilibrium theory.

In considering equilibrium between two phases of a chemical substance, we have so far confined our attention to the ordinary situation in which both phases are in mechanical contact with each other, at the same pressure. It is possible, however, to establish equilibrium across a semipermeable barrier, which permits diffusion but does not transmit pressure. Under this condition, one phase may be subjected to a higher pressure than the other, and we seek then the condition for stable reversible thermodynamic equilibrium. Since at equilibrium, we may conceive the hypothetical transfer of the substance through the semipermeable barrier to take place with essentially no change in pressure on either side, we may apply the general equilibrium condition (5-61), in the form

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[1] J. H. Hildebrand, *J. Am. Chem. Soc.*, **37**, 970–978 (1915).

[2] C. M. Guldberg, *Z. physik. Chem.*, **5**, 374–382 (1890).

[3] K. K. Kelley, Contributions to the Data on Theoretical Metallurgy. III. The Free Energies of Vaporization and Vapor Pressures of Inorganic Substances, *U.S. Bur. Mines Bull.* 383 (1935).

[4] D. R. Stull, *Ind. Eng. Chem.*, **39**, 517–550 (1947).

$$\bar{F}_1(T_1, p_1) = \bar{F}_2(T_2, p_2) \qquad (T_1 = T_2)$$

As we follow the system from one equilibrium state to another with changing p_1 and p_2, both phases being maintained at the same constant temperature,

$$d\bar{F}_1 = d\bar{F}_2$$

whence according to Eq. (6-5), applied to each phase,

$$\bar{V}_1\, dp_1 = \bar{V}_2\, dp_2 \qquad (T_1 = T_2 = \text{const})$$

Thus

$$\left(\frac{dp_2}{dp_1}\right)_T = \frac{\bar{V}_1}{\bar{V}_2} \tag{6-81}$$

This general thermodynamic relationship is known as the *Gibbs-Poynting equation*;[1] it applies to equilibrium between any two phases of the substance, separated by a mechanism that prevents the transmission of pressure but does not interfere with the transfer of material from one region to the other. A case of special interest arises when one of the phases is the gas phase and the other is the liquid phase subjected to a pressure different from the equilibrium vapor pressure; let us assume that the gas phase, phase 2 in Eq. (6-81), is at a sufficiently low equilibrium pressure p so that it satisfies the ideal-gas law, $\bar{V}_2 = RT/p$; then

$$\frac{d \ln p}{dp_1} = \frac{\bar{V}_1}{RT} \tag{6-82}$$

This equation is the analogue of Eq. (6-69), which gave the effect of temperature of the liquid phase on the equilibrium vapor pressure (on the assumption, however, that both phases were at the *same* temperature). Since the compressibility of the liquid phase is generally quite small, we may treat the right-hand member of Eq. (6-82) as sensibly constant with p_1, up to rather high pressures, and so integrate, starting from the limit $p_1 = p = p°$, where $p°$ represents the ordinary vapor pressure, when the liquid is subjected directly to the pressure of its own equilibrium vapor,

$$\ln \frac{p}{p°} = \frac{\bar{V}_1}{RT}(p_1 - p°) \tag{6-83}$$

Thus, the equilibrium vapor pressure increases with the pressure applied to the liquid phase (a precisely similar equation applies of course to solid-

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[1] Named after J. Willard Gibbs, who first established the general conditions for equilibrium among several phases separated by semipermeable barriers in his classic work, "On the Equilibrium of Heterogeneous Substances," 1876–1878, and J. H. Poynting, who derived Eq. (6-81) for the special case of liquid-vapor equilibrium, *Phil. Mag.*, (5) **12**, 32–48 (1881).

vapor equilibrium under similar conditions), but since the value of $\bar{V}_1$ is comparatively small in relation to RT at ordinary temperatures, the effect is slight. For $H_2O(l)$ at 25°C, with $\bar{V}_1 = 18.069$ ml/mole,

$$\log \frac{p}{p^\circ} = \frac{18.069 \text{ ml/mole}}{(2.303)(82.05\text{ml atm/mole deg})(298.16 \text{ deg})} (p_1 - p^\circ)$$
$$= 0.0003208 \text{ atm}^{-1} (p_1 - p^\circ)$$

In order to effect an increase of 1 per cent in the vapor pressure, corresponding to $\log (p/p_0) = 0.00432$, it would be necessary for p_1 to equal 13.47 atm.

It would be extremely difficult to test Eq. (6-83) by direct experiment, in view of the slowness with which equilibrium would be attained through the materials available to serve as semipermeable barriers and the smallness of the effect. This equation finds a useful application, however, to the estimation of the vapor pressures of tiny droplets, where, as we shall see in Sec. 6-5, the curvature of the surface is correlated with higher pressure on the liquid within than the pressure under a plane surface, from which the vapor pressure is ordinarily measured. A modification of Eq. (6-81), applicable to equilibrium across a semipermeable membrane between a liquid solution and the pure liquid solvent, constitutes also the basis of the thermodynamic theory of osmotic pressure, as we shall see in Sec. 7-5.

We may compute the standard free-energy change for a phase transition taking place at conditions other than the equilibrium ones by applying Eq. (6-14) to each phase and taking the difference, making use of the fact that $\Delta F_T^\circ = 0$ at the normal transition temperature, or other equilibrium state. We may establish the value of ΔH_T° either by direct calorimetric means or indirectly by the application of Eq. (6-68) or Eq. (6-69) to equilibrium data obtained at temperatures and pressures beyond the normal (1 atm) values. Thus, for the transition,

$$\text{S(I, monoclinic)} = \text{S(II, rhombic)}$$

we have the equilibrium condition $\Delta F_{368.7}^\circ = 0$, together with Brønsted's value $\Delta H_{368.7}^\circ = -95$ cal for the latent heat of transformation. In addition, the following empirical equations represent the two heat capacities over the range 250 to 368.7°K, from experimental data of Eastman and McGavock,[1]

$$\bar{C}_p^\circ \text{ (rhombic)} = 3.493 + 0.00636T \text{ cal/mole deg}$$
$$\bar{C}_p^\circ \text{ (monoclinic)} = 3.556 + 0.00698T \text{ cal/mole deg}$$

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[1] E. D. Eastman and W. C. McGavock, *J. Am. Chem. Soc.*, **59**, 145–151 (1937).

Expressing ΔH_T° as a function of T by means of Eq. (6-15) applied to each phase,

$$\begin{aligned}\Delta H_T^\circ &= -95 \text{ cal} + \int_{368.7^\circ\text{K}}^{T} (-0.063 - 0.00062\text{T})dT \\ &= -30 - 0.063T - 0.00031T^2\end{aligned}$$

Substituting in Eq. (6-14), we may now calculate the value of ΔF_T°, at standard temperature of 298.16°K,

$$\begin{aligned}\frac{\Delta F_{298.16}^\circ}{298.16 \text{ deg}} &= 0 + \int_{298.16^\circ\text{K}}^{368.7^\circ\text{K}} (-30 - 0.063T - 0.00031T^2)\frac{dT}{T^2} \quad \cdot \\ &= \left[\frac{30}{T} - 0.063 \ln T - 0.00031T\right]_{298.16}^{368.7} \\ &= -0.0544 \text{ cal/deg} \\ \Delta F_{298.16}^\circ &= -16 \text{ cal/mole}\end{aligned}$$

Alternatively, we may compute the standard free-energy change at a given temperature by applying Eq. (6-16) to each phase, if we know the equilibrium pressure at that temperature; thus, for the transition,

$$H_2O(l) = H_2O(g)$$

we know from experiment that at 25°C, $\Delta F = 0$ if $p = 23.756$ mm Hg $= 0.031258$ atm. In this case, Eq. (6-16) reduces to (6-75), where at the low pressure involved, $\nu = 1$. Thus

$$\begin{aligned}\Delta F_{298.16}^\circ &= -RT \ln 0.031258 \\ &= (-1364.3 \text{ cal/mole})(\log 0.031258) \\ &= 2053.3 \text{ cal/mole}\end{aligned}$$

This represents the free-energy change for the hypothetical transition from H_2O(l, 25°C, 1 atm) to H_2O(g, 25°C, 1 atm), with H_2O(g) behaving as an ideal gas. We could equally well have derived the value of this constant by applying Eq. (6-14), integrating down from 100°C where ΔF at 1 atm is zero. In order to calculate $\Delta F_{373.16}^\circ$ precisely at that temperature, one would have to introduce the value of ν for steam at 100°C and 1 atm in Eq. (6-75); from the observed molal volume of steam at 100°C and 1 atm, $\bar{V} = 30.149$ liters/mole, one finds that $z = 0.9846$, whence according to the approximation (6-31), $\ln \nu_{373^\circ\text{K}, 1\,\text{atm}} = -0.0154$; therefore, according to Eq. (6-76), $\Delta F_{373.16}^\circ = -RT(-0.0154) = 11.4$ cal/mole, the difference from zero reflecting the effect of deviation of steam from ideal-gas behavior at 100°C and 1 atm.

By suitable modifications of these procedures, we may thus derive $\bar{F}_T^\circ$, values at standard-state conditions for the various phases of a chemical substance, relative to the value assigned to some one phase, the phase stable at T_s and 1 atm. When one is dealing with a phase whose range of existence is far removed from standard-state conditions, this may be impractical in view of the doubtful extrapolation one would have to make of the experimental data for the phase in question. We shall see in Chap. 10 that an independent method exists for the calculation of solid-vapor or liquid-vapor equilibrium, based on statistical molecular analysis of the spectrum for the gas phase, combined with third-law treatment of the condensed phase (Sec. 8-3).

6-5. Surface Tension Effects. When two different phases are in equilibrium, certain effects may be observed that are associated with the boundary region separating the phases. These effects are particularly noticeable when the two phases are fluid, so that their boundary is mobile, *i.e.*, when one phase is a liquid and the other a gas, or when both phases are liquids. The boundary in such cases (unless one is working close to the critical temperature and pressure, or the critical solution temperature, as the case may be) is extremely sharp. Optical methods based on the polarization of light reflected from the interface show that for a clean air-water interface the transition region is of order one molecule deep.[1] Therefore the region of heterogeneity over which the properties of the two phases differ significantly from those they show separately in bulk cannot extend over more than a few molecular diameters.

The most striking property of a mobile interface is its tendency to shrink to minimum area consistent with the mechanical constraints imposed on it (such as by gravity, adhesion to solid surfaces, incompressibility of liquid phases, etc.). This tendency was demonstrated in an elaborate investigation by J. A. F. Plateau in 1873; Plateau experimented with drops of olive oil suspended in alcohol-water solutions adjusted to the same density, so as to eliminate the effect of gravity; he used wire frames to establish contours of various shapes, and the surface of the oil drop was found invariably to assume minimum area consistent with its volume, as constrained by the frame.[2]

The spontaneous tendency for the interface between two fluid phases to contract may be represented mathematically by means of a surface-energy term increasing with the area σ of the interface. We may thus represent the internal energy of the system consisting of two fluid phases and their interface by means of the equation

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[1] N. K. Adam, "The Physics and Chemistry of Surfaces," 3d ed., p. 5, Oxford University Press, New York, 1941.

[2] For a brilliant exposition of this simple principle as applied to the shapes assumed by growing cells and cell aggregates, see D'Arcy Wentworth Thompson, "On Growth and Form," Chaps. V, VII, and VIII, The Macmillan Company, New York, 1942.

$$\begin{aligned} dU &= d'Q - d'W \\ &= T\,dS - p_1\,dV_1 - p_2\,dV_2 + \gamma\,d\sigma \end{aligned} \tag{6-84}$$

The presence of the interface between the phases apparently does not disturb the condition of thermal equilibrium, and we shall suppose therefore that both phases, including the boundary region, are at a common temperature; dS in Eq. (6-84) then represents the change in the total entropy of the system, which will in general include entropy associated with the presence of the interface over and above the sum of the entropies of the two separate phases. The pressures of the two phases, however, will not necessarily be equal, but may be influenced by the shape of the interface, as we shall presently discover. The quantity γ, defined in accordance with Eq. (6-84) by

$$\gamma = \left(\frac{dU}{d\sigma}\right)_{S,V_1,V_2} \tag{6-85}$$

is a property of the interface, and represents the energy required per unit increase in the interfacial area in order to increase the surface against its spontaneous tendency to contract. We may readily show that Eq. (6-84), with both phases and the boundary region all at the same temperature, is equivalent to

$$dF = -S\,dT + V_1\,dp_1 + V_2\,dp_2 + \gamma\,d\sigma \tag{6-86}$$

Hence a definition of γ equivalent to Eq. (6-85) is given by

$$\gamma = \left(\frac{dF}{d\sigma}\right)_{T,p_1,p_2} \tag{6-87}$$

In the case of a gas-liquid interface, γ is called the *surface tension;* the gas is generally air at atmospheric pressure, but for a few liquids, data have been obtained for the liquid against its own equilibrium vapor.[1] In the case of a liquid-liquid interface, γ is called the *interfacial tension.* The value of γ is generally expressed in ergs per square centimeter; thus, for the air-water interface at 20°C and 1 atm, $\gamma = 72.73$ erg/cm^2, as determined by the capillary height method whose theory we shall presently describe.[2]

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[1] The surface tension of a liquid against its own equilibrium vapor at pressures below atmospheric pressure is slightly, almost imperceptibly, higher than its surface tension against air; the difference is partly the result of the difference in pressure, but may also result from air solubility in the liquid. See T. W. Richards and E. K. Carver, *J. Am. Chem. Soc.*, **43**, 847 (1921).

[2] *Ibid.*, pp. 827–847.

The physical meaning of the term $\gamma\, d\sigma$ is brought out by a model suggested by P. Dupré in 1869 (Fig. 6-6). Imagine a thin liquid film occupying a rectangular frame consisting of three fixed sides, and a movable edge that can slide in a direction normal to its own length along the adjacent parallel fixed sides. The film may be surrounded by a gas, or if one wishes to study interfacial tension, by another liquid phase with which it is immiscible. Because of the spontaneous tendency for the interface between the liquid film and the surrounding medium to contract, work must be done on the system in order to enlarge the surface area. Thus, one could pull on the sliding wire edge by means of weights under the influence of gravity, and by measuring their descent determine directly the work required to increase the surface area by a given amount (since there is a surface on either side of the frame, the increase in the surface area would be twice the area generated by the moving edge of the frame). The ratio of the work thus done reversibly on the system to the increase in the surface area would measure the value of γ. While the Dupré balance serves most simply in principle to bring out the physical operations implied by the surface tension concept, it is not a practical device for the precise study of surface properties.

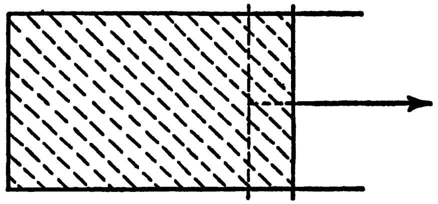

FIG. 6-6. Dupré balance illustrating the concept of surface energy.

Characteristically, the value of γ does not depend on the area of the surface.[1] In this respect, the surface between two fluids differs radically from a stretched membrane, to which it otherwise bears a formal resemblance. The tension in an elastic membrane, such as a rubber balloon, increases as the surface is stretched; there is no such effect when the surface area between two fluid phases is enlarged.[2] The reason for the difference is of course inherent in the molecular origin of the surface tension effect. We may picture a typical gas-liquid interface as in Fig. 6-7*a*, or a liquid-liquid interface as in Fig. 6-7*b*. In either case a molecule that happens to be in the surface layer will presumably be subject to a resultant van der Waals force tending to draw it into the body of the liquid. In the case of the gas-liquid interface, the comparatively large distances to

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[1] For a discussion, however, of the effect of droplet size on the surface tension of small droplets, see R. C. Tolman, *J. Chem. Phys.*, **17**, 333–337 (1949).

[2] One can easily demonstrate that the pressure within a large soap bubble is actually smaller than the pressure within a small one [in accordance with Eq. (6-88) following]. Thus, if one connects a larger to a smaller soap bubble blown at the ends of a T tube, having a central two-way stopcock to facilitate the operation, one will observe that the larger bubble expands at the expense of the smaller one.

the nearest neighbors on the gas side of the boundary will diminish the relative attraction of these molecules for the surface molecules. In the case of the liquid-liquid interface, we must suppose that van der Waals' attraction between the two different kinds of molecules is weaker than the attractions between like molecules; otherwise the two phases would mix with each other; therefore the molecules that happen to be in the surface layer on either side of the boundary will likewise be subject to a resultant attractive force tending to draw them back into the body of the liquid on their respective sides. The tendency for the interface to contract to minimum area consistent with the imposed constraints thus follows automatically from the tendency of molecules comprising the surface layer to retreat back into the body of the liquid; but the size of the surface area does not affect in any way the nature of the surface region, or the tendency for molecules to retreat out of it.

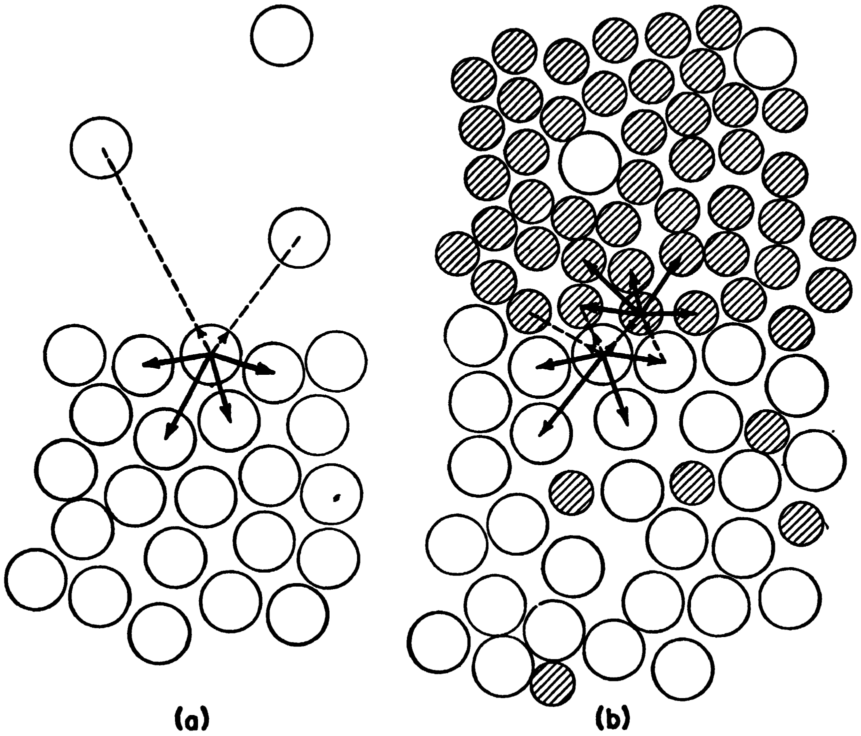

Fig. 6-7. Diagram showing the molecular origin of the tendency for the interface between two fluid phases to contract to minimum area consistent with the volumes of the phases and other constraints imposed. (a) Case of a liquid against a gas phase. (b) Case of two slightly miscible liquid phases.

In order for us to develop the thermodynamic theory of surface behavior, however, it is not necessary that we form a molecular picture of its origin. Equation (6-84), together with empirical knowledge that γ is an intensive property of the interface, independent of σ, is sufficient for our purpose. Let us apply to Eq. (6-84) the general thermodynamic criterion (5-45) for stable reversible equilibrium: U shall be a minimum consistent with given total entropy and volume. Since under these conditions $dV_1 = -dV_2$,

$$(p_1 - p_2)dV_1 = \gamma\, d\sigma \tag{6-88}$$

This equilibrium criterion applies to any virtual displacement of the interface, which might change its area but would at the same time alter the relative volumes of the two phases. In other words, the interface tends to assume such a shape and position that any work done by virtue of the pressure difference existing across it, if it were to be displaced in such a way as to generate the volume dV_1 on the one side at the expense of the other [left-hand member of Eq. (6-88)], would be exactly counterbalanced by the work required in order to increase the surface area correspondingly, against its spontaneous tendency to contract [right-hand member of Eq. (6-88)].

Let us apply Eq. (6-88) to the equilibrium of a spherical drop or bubble suspended in another fluid medium (ignoring for the moment the distorting effect of gravity, which would increase with the size of the drop and with the difference between its own density and that of the surrounding medium). Let the equilibrium radius be denoted by r; then for a virtual displacement of the surface normal to itself through the distance dr [any other kind of displacement changing the spherical shape would increase the ratio of surface area to volume, and hence could not satisfy Eq. (6-88) for given instantaneous values of $(p_1 - p_2)$ and γ]

$$\begin{aligned} dV_1 &= 4\pi r^2\, dr \\ d\sigma &= 8\pi r\, dr \end{aligned}$$

Substituting these relations in Eq. (6-88), we have as the equilibrium situation

$$p_1 - p_2 = \frac{2\gamma}{r} \tag{6-89}$$

The generalization of Eq. (6-89) for a surface of any shape is readily derived. Let r_1 and r_2 denote the two principal radii of curvature at a given point on the surface, and consider an element of area about the point, subtending the small angle ϵ at the two centers of curvature, so that its edges are to a first order of approximation arcs of length $r_1\epsilon$ and $r_2\epsilon$. Imagine the surface to be displaced parallel to itself through the distance dr (Fig. 6-8). Note that $d\sigma$ in Eq. (6-88) will have the same sign as dV_1, provided that p_1 and dV_1 refer to the phase on the more concave side of the surface; in other words, the pressure is necessarily greater on the more concave side of the interface. Neglecting infinitesimals of order higher than that of $\epsilon^2\,dr$,

$$\begin{aligned} dV_1 &= (r_1\epsilon)(r_2\epsilon)dr \\ d\sigma &= (r_1 + dr)(r_2 + dr)\epsilon^2 - r_1r_2\epsilon^2 \\ &= (r_1 + r_2)\epsilon^2\,dr \end{aligned}$$

Hence

$$p_1 - p_2 = \gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \tag{6-90}$$

Equation (6-90) is known as *Laplace's fundamental equation of capillarity.*[1] It reduces to Eq. (6-89) wherever the two principal radii of curvature are equal, as in the case of a spherical surface, or in general, at the center of any surface of revolution. For a plane mobile surface, one sees that the pressure difference across the interface vanishes.

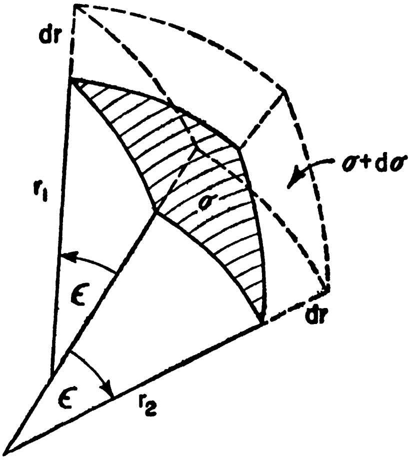

FIG. 6-8. Displacement of a surface element having two different principal radii of curvature.

From Eq. (6-90), we may derive ideal equations for all the static equilibrium methods of measuring surface or interfacial tension. One method, for example, consists of measuring the maximum bubble pressure that can just be maintained in a vertical tube of known radius dipping to a known depth below the surface of the liquid (the method could be adapted to the measurement of interfacial tension, but it is more feasible for air-liquid surface tensions). If the internal radius of the tube is sufficiently small, we may assume that the bubble surface at the end of the tube will tend to be spherical (Fig. 6-9), and we may apply Eq. (6-89). A more rigorous calculation would make use of Eq. (6-90), and would take into account the variation of the external hydrostatic pressure p_2 with increasing depth from the tip of the tube to the bottom of the bubble; the greater hydrostatic pressure at the bottom tends to flatten the bubble to an oblate hemispheroid shape. As one increases the pressure p_1 within the tube, the radius of curvature of the bubble decreases, according to Eq. (6-89), until ultimately it becomes no larger than that of the tube itself; the bubble is then hemispherical in shape, provided that the radius is sufficiently

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[1] It was given by Pierre Simon de Laplace in his celebrated "Mécanique céleste," published in 1806, but was also known in nonmathematical form by Thomas Young, *Trans. Roy. Soc.* (*London*), (A) **1**, 65 (1805).

small so that gravity distortion arising from the difference in hydrostatic pressure between the end of the tube and the bottom of the bubble is negligible. If one further decreases the radius of the bubble by increasing p_1, the bubble becomes unstable since it now tends to be slightly smaller than the tube, and it therefore detaches itself from the end of the tube.

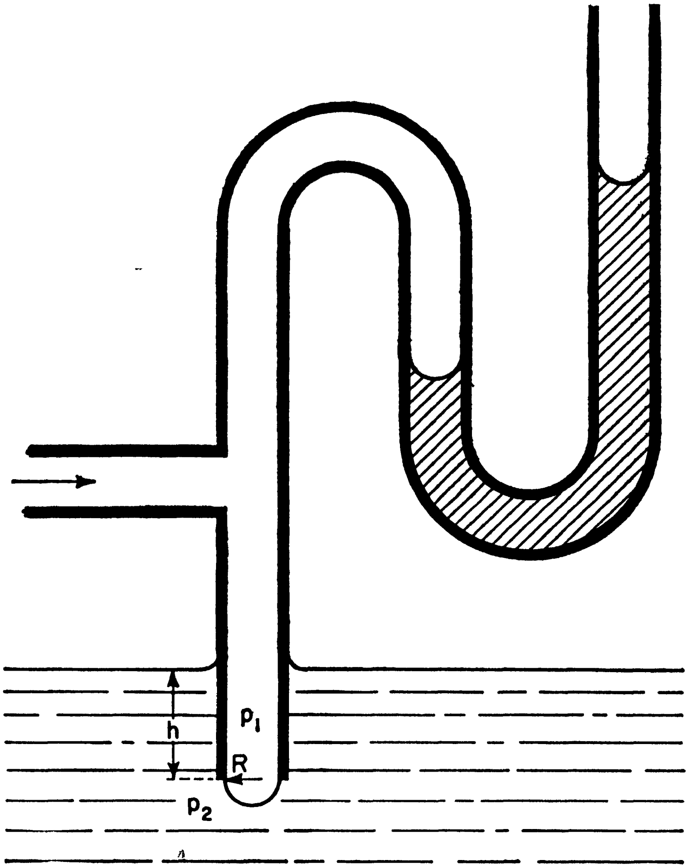

Fig. 6-9. Diagram illustrating the maximum-bubble-pressure method of measuring surface tension.

Thus, applying Eq. (6-89) to the situation just as the bubble is about to become unstable,

$$p_{\max} - h(d_2 - d_1)g = \frac{2\gamma}{R}$$

where R represents the internal radius of the tube, d_2 the density of the liquid, d_1 the density of the gas, and h the mean distance of the bubble below the plane surface of the liquid.

Another common method for measuring surface tension consists of measuring the capillary rise (Fig. 6-10). Here, the determining factor is the limiting angle at which the gas-liquid interface meets the surface of the capillary. For many liquids against glass in air, this contact angle has been shown to be 0 deg;[1] this condition is generally satisfied by those liquids that "wet" glass, *i.e.*, that tend to spread to an unlimited extent over a horizontal clean glass surface. For mercury against glass in air, however, the contact angle is about 130 deg. Let us denote the contact angle by θ; then if the internal radius of the tube is sufficiently small so that the hydrostatic pressure p_2 is necessarily practically uniform over the entire gas-liquid interface and if the tube is perfectly circular in cross section, the gas-liquid interface will assume a spherical shape with radius r determined by the tube radius R and the contact angle θ through the relation

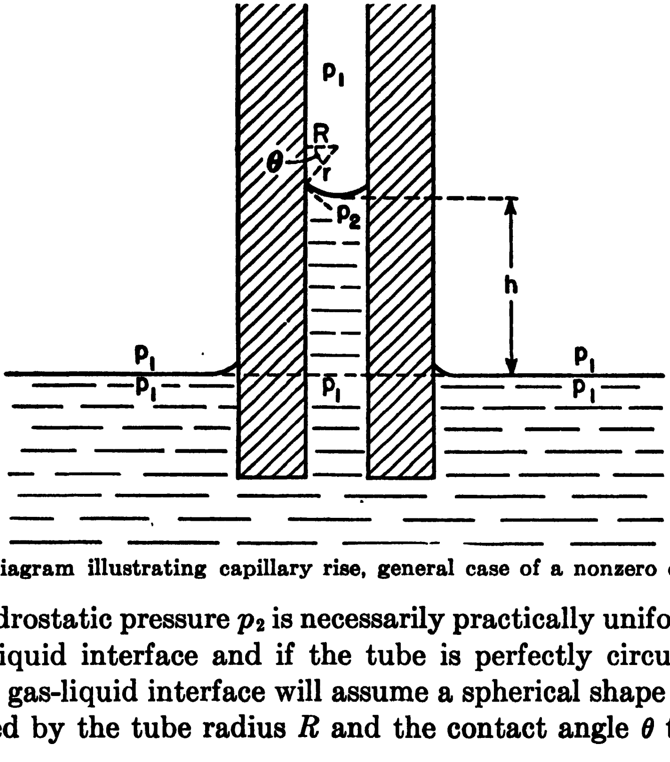

FIG. 6-10. Diagram illustrating capillary rise, general case of a nonzero contact angle.

$$r = \frac{R}{\cos\theta}$$

Otherwise, one must calculate the shape of the surface by means of Eq. (6-90), taking into account the variation of p_2 with height.[2] Substituting

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[1] Richards and Carver, *loc. cit.*

[2] The exact solution cannot be obtained in finite terms consisting of familiar functions. For $\theta = 0$ deg in a tube of circular cross section, Rayleigh gave as an approximation the solution

$$\frac{2\gamma}{R(d_2 - d_1)g} = h_0\left(1 + \frac{1}{3}\frac{R}{h_0} - 0.1288\frac{R^2}{h_0^2} + 0.1312\frac{R^3}{h_0^3}\right)$$

which reduces to the familiar form as $R/h_0 \to 0$, h_0 representing the height of the lowest point of the meniscus above the plane surface outside the tube. Numerical tables have been prepared by S. Sugden, *J. Chem. Soc.*, **119**, 1483–1492 (1921), by means in Eq. (6-89),

$$p_1 - p_2 = \frac{2\gamma \cos \theta}{R}$$

Now, the pressure p_1 of the gas phase is essentially the same as the pressure in the liquid just below the plane surface outside the tube; hence if θ is smaller than 90 deg, p_2 will necessarily be smaller than p_1, and the liquid will rise in the capillary until its hydrostatic pressure within the tube at the level of the plane surface outside counterbalances the difference $(p_1 - p_2)$ imposed by the curvature of the surface within the tube. Thus, for equilibrium of the column,

$$h(d_2 - d_1)g = \frac{2\gamma \cos \theta}{R}$$

where in this case, d_2 represents the density of the lower phase (the liquid), d_1 the density of the upper phase (the gas), and h the mean height of the meniscus above the plane surface outside; if one measures h_0 to the lowest point of the meniscus, then one may easily show that for $\theta = 0$ deg, $h = h_0 + \frac{1}{3}R$, the correction $\frac{1}{3}R$ representing the mean height of the liquid contained within the meniscus itself above the plane tangent to its lowest point. In the case of a liquid like mercury within a glass capillary, with θ greater than 90 deg, the surface becomes concave on the mercury side of the interface, and the mercury is accordingly depressed below the level of the plane surface outside.

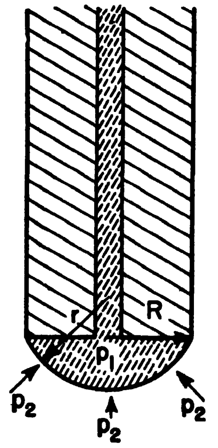

FIG. 6-11. Diagram showing the growth of a drop at the tip of a capillary tube.

The fundamental equation (6-90) may be used to calculate the shapes of sessile and pendant drops in terms of surface or interfacial tension and the influence of gravity. We may apply Eq. (6-89) naïvely to calculate also "ideal" formulas for falling drops, and for the ring-balance method of measuring surface tension. These equations are instructive in showing how surface tension influences the phenomena, but they cannot be taken seriously, because of complicating circumstances; the very derivations show, however, the respects in which the formulas fail to represent the facts. If a drop is permitted to grow slowly at the end of a vertical capillary tube (Fig. 6-11), then at any instant, equilibrium would be maintained between the weight of the pendant drop and the force it exerts

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of which one may calculate γ accurately from h in a tube of any radius, using successive approximations; the use of these tables is described completely by Adam, *op. cit.*, Chap. IX.

against the end of the tube as a result of the higher pressure p_1 within the drop over the pressure p_2 outside. If the instantaneous weight of the drop is Mg (corrected for the weight of air displaced) and if the *external* radius of the tube from which it is hanging is R, then the excess pressure within the drop is equivalent to a force, $(p_1 - p_2)\pi R^2$, which is exactly countered by the weight Mg. Now, as the drop increases in weight, its radius of curvature must decrease approximately according to Eq. (6-89) [a more rigorous treatment of the hanging drop would take into account the varying hydrostatic pressure over the depth of the drop itself, and would make use of Eq. (6-90) in determining the shape]. When the radius of curvature has become no larger than that of the tube from which it is suspended, then further growth in the weight can only result in destroying the stability of the drop, and thus the "ideal" weight M_0g of the falling drop should be given by the formula

$$M_0g = 2\gamma\pi R$$

This argument explains in a general way why the drop ultimately loses its stability and falls. The dynamic act of detachment is, however, far more complicated, as has been shown by high-speed photography;[1] the drop invariably "necks down" before falling off, and a secondary droplet, formed by the breaking up of the drawn-out neck, invariably follows the main drop after it has finally become detached. Therefore the "ideal" formula does not give correctly the true weight of the falling "drop." A most thorough experimental study has been made of the drop-weight method by W. D. Harkins and F. E. Brown; they established an empirical function relating the size of the actual drop delivered by a tube of given radius to the surface tension.[2] When their table is applied, the drop-weight method becomes a highly precise means of establishing surface tensions; it is not a fundamental method, however, inasmuch as Harkins and Brown had to determine their function empirically by the use of standard liquids whose surface tensions had been established by other methods (in particular, the capillary-rise method).

In the ring-balance method (Fig. 6-12), a circular platinum ring of 0.5 to 1 cm radius is pulled against the surface by means of a load that is gradually increased, and the weight that is just sufficient to pull the ring through the surface is measured. As one starts to pull on the ring, the

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[1] P. A. Guye and F. L. Perrot, *Arch. sci. phys. et nat.* (Geneva), **15**, 132–188 (1903); E. A. Hauser, H. E. Edgerton, B. M. Holt, and J. T. Cox, *J. Phys. Chem.*, **40**, 973–988 (1936).

[2] W. D. Harkins and F. E. Brown, *J. Am. Chem. Soc.*, **41**, 499–524 (1919); their table is reproduced in the "International Critical Tables," Vol. IV, p. 435, McGraw-Hill Book Company, Inc., New York, 1928.

surface within the ring tends to be constrained to an approximately spherical shape, to which we may apply Eq. (6-89); actually, however, one should apply Eq. (6-90), taking into account the variation of the hydrostatic pressure p_2 with depth, which tends to flatten the bottom of the meniscus.[1] One sees that the air pressure p_1 acts against the lowered pressure p_2 beneath the surface within the ring, the resultant force required to maintain equilibrium at any stage being equal to $(p_1 - p_2)$ multiplied by the area of the surface. As one increases the pull, the increased pressure difference $(p_1 - p_2)$ is accompanied by a reduction in the radius of curvature of the surface, until ultimately, if it were not for distortion resulting from the variation of p_2 with depth, the surface within the ring would become hemispherical in shape, with radius no larger than that of the ring itself. Further increase in the pull on the ring could then result only in decreasing the radius of curvature below that of the ring, with consequent instability and rupture of the surface. According to Eq. (6-89), therefore, the "ideal" maximum weight w_0 that can be applied before the ring breaks through the surface is given by

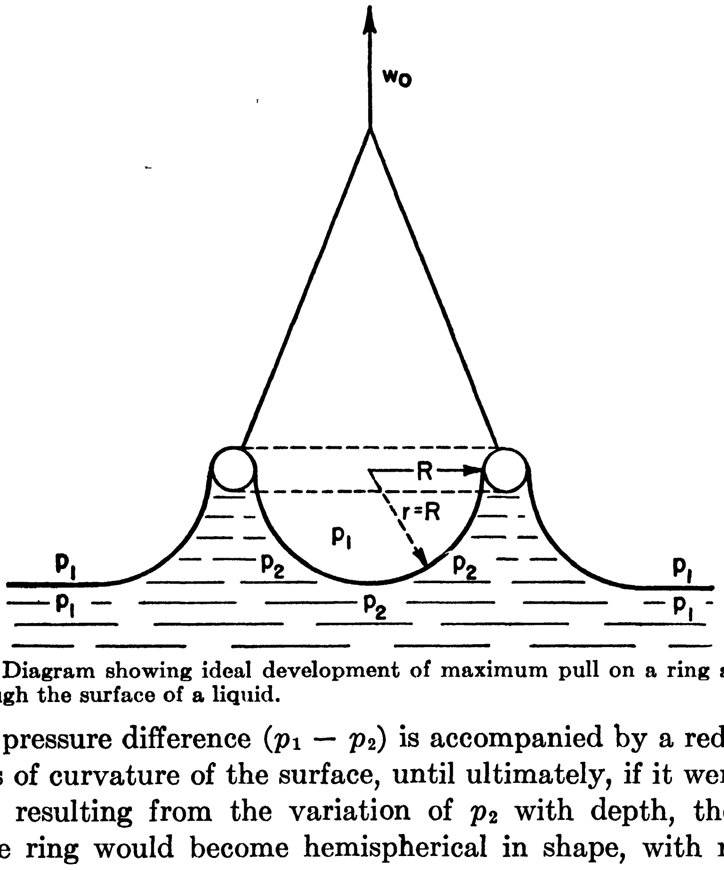

FIG. 6-12. Diagram showing ideal development of maximum pull on a ring about to be drawn through the surface of a liquid.

$$\begin{aligned} w_0 &= \frac{2\gamma}{R} 2\pi R^2 \\ &= 4\gamma\pi R \end{aligned}$$

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[1] See B. B. Freud and H. Z. Freud, *J. Am. Chem. Soc.*, **52**, 1772–1782 (1930).

where R represents the internal radius of the ring. Again, the actual dynamics of the process is more complicated than this simple picture would indicate;[1] furthermore, the shape of the surface just before rupture is modified not only by the variation in hydrostatic pressure of the liquid over the surface's depth but also by the finite thickness of the wire ring in comparison with the ring's radius. W. D. Harkins and H. F. Jordan have made an experimental study of this method, resulting in an empirical correction factor to the observed maximum pull, varying with the size and shape of the ring.[2] By the application of the proper value of the correction factor, the surface tension may then be computed with reasonable accuracy. It was necessary, of course, to use standard liquids whose surface tensions had been established by other methods, in order to establish the form of the correction factor.

We may combine Eq. (6-89) with Eq. (6-83) to derive a significant relationship between the vapor pressure and the radius of a small liquid droplet. The pressure within the small droplet is higher than the pressure outside, in accordance with Eq. (6-89), but according to Eq. (6-83), the effect of greater pressure on a liquid is to increase its equilibrium vapor pressure. Thus

$$\ln \frac{p}{p^\circ} = \frac{2\gamma}{r} \frac{\bar{V}_l}{RT} \tag{6-91}$$

where p represents the vapor pressure of the droplet, whose radius is r, and p° represents the ordinary vapor pressure, from a plane surface. Introducing data for water at 25°C, $2\gamma\bar{V}_l/RT = 1.05 \times 10^{-7}$ cm, we obtain from Eq. (6-91) the results shown in Table 6-2.

TABLE 6-2. CALCULATED VAPOR PRESSURES OF WATER DROPLETS

r, cm	p/p°, at 25°C
10^{-3}	1.0001
10^{-4}	1.001
10^{-5}	1.01
10^{-6}	1.11
10^{-7}	2.86

These results show why it is quite easy to produce supersaturation in dust-free water vapor. An aggregation of about 150,000 molecules is required to produce a droplet of water having a radius of only 10^{-6} cm, but even a submicroscopic droplet as large as this has a vapor pressure 11 per cent higher than the ordinary vapor pressure as measured with respect to a plane surface. The influence of dust particles as nuclei promoting condensation may well result from the irregular shapes of the

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[1] See Hauser, Edgerton, Holt, and Cox, *loc. cit.*

[2] W. D. Harkins and H. F. Jordan, *J. Am. Chem. Soc.*, **52**, 1751–1772 (1930).

surfaces they present, reducing the curvatures of the incipient droplets that chance to form on them. Soluble dust particles may of course function as nuclei also by lowering the vapor pressure sufficiently to make up for the surface tension effect. On the other hand, from a concave surface, as in a small bubble of vapor within the liquid, the vapor pressure is correspondingly lower than from a plane surface,

$$\ln \frac{p}{p^\circ} = -\frac{2\gamma}{r}\frac{\bar{V}_l}{RT} \tag{6-92}$$

This equation has been verified experimentally by M. Thomä,[1] who used a differential method to compare the vapor pressures of various liquids over plane surfaces and over curved surfaces in capillary tubes. The lowered vapor pressure from a concave surface accounts for the ease with which superheating may be induced in a liquid; one must raise the temperature above the ordinary boiling point in order to permit the first small bubbles to develop (in a deep column of the liquid, there will also be a greater hydrostatic pressure at the bottom as compared with the top). As the bubbles grow in size, of course, the vapor pressure of the liquid at their surfaces increases, approaching the ordinary value for a plane surface at the same temperature. The boiling liquid thus has a tendency to "bump" more or less violently, with corresponding fluctuations in its temperature. By introducing boiling stones having plane or irregular surfaces, or by drawing a stream of comparatively large air bubbles through the liquid, superheating with its attendant violent fluctuations during the boiling of the liquid may be greatly reduced. As an illustration, for water at 100°C, $\bar{V}_l = 18.8$ ml/mole and $\gamma = 58.9$ erg/cm^2; by applying Eq. (6-92), one finds that the equilibrium pressure within a vapor bubble of 10^{-6} cm radius is only 747.4 mm Hg, insufficient to maintain the bubble against normal atmospheric pressure acting on the liquid. Now, the vapor pressure of water around its normal boiling point increases by about 27 mm Hg/deg; therefore, a bubble of 10^{-6} cm radius would become stable if the liquid were superheated to 100.47°C at normal atmospheric pressure. But as such a bubble begins to grow in size, through evaporation into it from the liquid phase, its vapor pressure rapidly approaches the value characteristic of a plane surface, *e.g.*, 772.6 mm Hg at 100.47°C. Since the pressure within the enlarged bubble is thus appreciably greater than the pressure over the plane surface of the liquid, it is not surprising that the pure air-free liquid boils in violent spurts, the temperature fluctuating by as much as half a degree between spurts, when no provision is made to reduce superheating.

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[1] M. Thomä, *Z. Physik*, **64**, 224–236 (1930).

6-6. Magnetization Effects. When a homogeneous chemical substance of fixed composition is in the field of a magnet, then, in general, its properties depend on the magnetic field strength, $\mathcal{H}$, as well as on temperature and pressure. Let $\bar{J}$ represent its intensity of magnetization, as measured by the magnetic moment per mole; then by straightforward extension of the mechanical energy concept to magnetic behavior, the work $d'W'$ done on the substance by a magnetic field of instantaneous strength $\mathcal{H}$ in changing its intensity of magnetization by the amount $d\bar{J}$ is measured by $\mathcal{H}\,d\bar{J}$.[1] No special name has been given to the unit in which $\bar{J}$ is commonly represented, but it is so chosen that if $\mathcal{H}$ is in *gauss*, then the expression $\mathcal{H}\,d\bar{J}$ is given in ergs per mole. Thus, we may write as the general expression for the internal energy

$$\begin{aligned} d\bar{U} &= d'Q - d'W \\ &= T\,d\bar{S} - p\,d\bar{V} + \mathcal{H}\,d\bar{J} \qquad (6\text{-}93) \end{aligned}$$

for thermodynamically reversible changes of state. Now, in general, $\mathcal{H}$ and $\bar{J}$ are vectorial quantities whose relative directions depend on the orientation of the substance with respect to the magnetic field; for isotropic substances, however, whose properties are uniform in all directions, such as a gas, a liquid, or a cubic crystalline solid, $\bar{J}$ tends to assume either the same or exactly the opposite direction to that of $\mathcal{H}$. In the former case, the substance is said to be *paramagnetic*, and the term $\mathcal{H}\,d\bar{J}$ in Eq. (6-93) is positive in sign; a magnetic moment is induced in the substance in such a sense that it is attracted by the applied magnet, and tends to be drawn deeper into its field (measurement of the strength of this attraction by means of a balance constitutes one of the methods of measuring $\bar{J}$). In the latter case, the substance is said to be *diamagnetic*, and the term $\mathcal{H}\,d\bar{J}$ is negative in sign; the induced magnetic moment in this case is usually quite small, and has such a sense that the substance is repelled by the applied magnet, and tends to be ejected from its field. For anisotropic crystalline solids, the magnitude of $\bar{J}$ for given field

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[1] A uniformly magnetized body is formally equivalent to a magnet with poles of strength $+m$ and $-m$ separated by distance l, though only the magnetic moment ml (not the separate factors) has immediate physical significance; *i.e.*, the magnetic moment $\bar{J}$ per mole can be directly measured by observation of the substance's interaction with an applied magnetic field, but how one might choose to represent it as made up of separate factors m and l is quite arbitrary, if not meaningless. Now, if the intensity of magnetization is changed by the amount $d\bar{J}$, then formally the change is equivalent to a change dl in the displacement between poles; since the force acting on the one pole $(+m)$, the other being regarded as stationary, is $\mathcal{H}m$, therefore $\mathcal{H}m\,dl = \mathcal{H}\,d\bar{J}$ represents the work of magnetization, in accordance with the general definition (2-4), assuming that $\mathcal{H}$ and $d\bar{J}$ have the same direction.

strength is generally different for different directions through the crystal; the behavior of an aggregation of such crystals is accordingly complex. For ordinary diamagnetic or paramagnetic substances, the induced magnetic moment disappears as soon as the exciting magnetic field is removed, but *ferromagnetic* substances, such as iron itself, show not only extraordinarily strong paramagnetism but also saturation and hysteresis effects; thus, a comparatively weak magnetic field can induce in iron a high value of $\bar{J}$ practically independent of $\mathcal{H}$, which if the iron has been suitably prepared may persist after the external field has been removed. We shall not be concerned in this section with ferromagnetic materials, but one should note that if a "permanent" magnet is introduced into a magnetic field, then it may have ordinary mechanical potential energy depending on its orientation with respect to the field, as well as internal energy satisfying Eq. (6-93).

According to the atomic-molecular theory of magnetism, developed during the nineteenth century by the work of A. M. Ampère, W. Weber, M. Faraday, J. C. Maxwell, J. A. Ewing, P. Curie, and others, diamagnetic substances consist of atoms or molecules having no net magnetic moments in the undisturbed state; the diamagnetism results from the interaction of the applied magnetic field on the electronic "currents" within the atom or molecule, disturbing their normal state of symmetry (for example, as in the case of paired electrons constituting a covalent bond).[1] Paramagnetic substances, on the other hand, consist of atoms or molecules having permanent individual magnetic moments; superimposed on their diamagnetism, therefore, is a tendency for the individual atomic or molecular magnets to orient themselves with respect to the exciting field, against the tendency of their thermal motion to disorient them at random; in true paramagnetic substances, the paramagnetic effect prevails over the relatively weak diamagnetic effect, which is always present. In ferromagnetic substances, according to the domain theory first proposed by P. Weiss, the individual atomic magnets give rise to a magnetic field capable of orienting their neighbors in the same direction over a limited domain. Quantum mechanics has of course played an increasingly important role in the modern development of atomic-molecular magnetic theory, particularly in the quantitative calculation of magnetic

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[1] Many of the metals, notably bismuth, exhibit a structural diamagnetism associated with the collective susceptibility of the "free" electrons shared by the metal atoms and serving to bind them together in the crystalline state; this structural diamagnetism decreases with increasing temperature, and disappears if the metal is melted. Other metals show similarly a structural paramagnetism, independent of the atomic magnetic properties.

properties in terms of atomic structure, but we do not need such information for our immediate purpose.[1]

Now, for isotropic diamagnetic and paramagnetic substances at moderate field strengths (low intensities of magnetization), the value of $\bar{J}$ turns out empirically to be proportional to $\mathcal{H}$,

$$\bar{J} = \bar{X}\mathcal{H} \qquad (T, p \text{ const}) \qquad (6\text{-}94)$$

where $\bar{X}$ is a characteristic property of the substance known as its *molal magnetic susceptibility*;[2] its sign is generally written as positive for paramagnetic substances, and negative for diamagnetic substances. Thus, for chrome alum ($K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$) at 20°C and 1 atm,

$$\bar{X} = 12{,}500 \times 10^{-6} \text{ erg/mole gauss}^2$$

whereas for water at 20°C and 1 atm, $\bar{X} = -13.005 \times 10^{-6}$ erg/mole gauss^2. In order to take advantage of the empirical relationship (6-94), let us define a generalized Gibbs free-energy function

$$\bar{F} \equiv \bar{U} - T\bar{S} + p\bar{V} - \mathcal{H}\bar{J} \qquad (6\text{-}95)$$

where clearly $\bar{F}$, like $\bar{U}$, is a function of the state of the substance, whether determined by $\bar{S}$, $\bar{V}$, and $\bar{J}$ as independent variables, or by T, p, and $\mathcal{H}$. Differentiating (6-95) in the most general manner, and introducing Eq. (6-93),

$$d\bar{F} = -\bar{S}\,dT + \bar{V}\,dp - \bar{J}\,d\mathcal{H} \qquad (6\text{-}96)$$

Let us now introduce the empirical relationship (6-94), where $\bar{X}$ depends on T and p but not on $\mathcal{H}$,

$$d\bar{F} = -\bar{S}\,dT + \bar{V}\,dp - \bar{X}\,d\left(\frac{\mathcal{H}^2}{2}\right) \qquad (6\text{-}97)$$

This equation does *not* apply to ferromagnetic substances, nor does it apply to anisotropic crystalline solids without reservations; but it is extremely useful for isotropic diamagnetic or paramagnetic substances. Thus, let us apply to Eq. (6-97) Euler's criterion for $\bar{F}$ to be a function of

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[1] See, for example, J. H. VanVleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, New York, 1932; E. C. Stoner, "Magnetism and Matter," Methuen & Co., Ltd., London, 1934. For experimental methods of measuring magnetic properties, with particular application to chemistry, see P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, 1943.

[2] It is equal to the *specific susceptibility* (or magnetic susceptibility per unit volume divided by the density), as commonly reported in tables of magnetic properties, multiplied by the molecular weight.

the state, as defined by the values of T, p, and $\mathcal{H}$ as independent variables,

$$\left(\frac{d\bar{X}}{dT}\right)_p = \left[\frac{d\bar{S}}{d(\mathcal{H}^2/2)}\right]_{T,p} \qquad (6\text{-}98)$$

Since $\bar{X}$ is supposedly independent of $\mathcal{H}$ for the substances with which we are presently concerned, it is not necessary for us to indicate explicitly that $\mathcal{H}$ is constant in taking the left-hand derivative in Eq. (6-98); this equation thus gives us a thermodynamic equation for the temperature coefficient of $\bar{X}$, subject to the empirical condition (6-94) defining $\bar{X}$.

Now, the magnetic susceptibility of most diamagnetic substances is practically constant with temperature; there are reasons why this should be so from the atomic theory of magnetism, which we need not discuss.[1] It follows, according to Eq. (6-98), that for such substances no change in entropy takes place when the substance is magnetized at constant temperature and pressure. But for paramagnetic substances, $\bar{X}$ generally decreases with T in accordance with P. Curie's law,

$$\bar{X} = \frac{\bar{A}}{T} \qquad (p \text{ const}) \qquad (6\text{-}99)$$

where $\bar{A}$ is the molal Curie constant for the particular substance; this approximate empirical law, which also has a foundation in atomic-molecular theory, has been tested over a wide range of temperatures, and in particular cases, has been found valid down to 1°K; according to the atomic-molecular theory, its validity depends on the assumptions that the diamagnetic effect is comparatively negligible and that the individual atomic magnets have little interaction with each other. Both assumptions are apparently satisfied by the more strongly paramagnetic substances even in the crystalline state, down to extremely low temperatures. The fact that $\bar{X}$ for isotropic paramagnetic substances invariably decreases with rising temperature implies according to Eq. (6-98) that the entropy of such a substance decreases if one magnetizes it at constant temperature and pressure.[2] Suppose one has magnetized such a substance, allowing any energy put in over and above $\Delta U + p\,\Delta V$ to pass on to the constant-temperature surroundings in thermal form; if one now thermally insulates it and removes the exciting magnetic field, then its entropy cannot change during the ensuing adiabatic demagnetization. The substance will thereby end in a state at zero field strength characteristic of its lowered

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[1] See, however, the footnote on page 278.

[2] From the statistical molecular viewpoint, this entropy decrease corresponds to the degree of order introduced by the partial alignment of the atomic magnets induced by the application of the magnetic field, against the tendency for thermal motion to produce completely random orientations.

entropy value; in general, this state, at constant pressure throughout, will be one of lower temperature (barring a phase transition, or some other "latent" means by which the loss of energy associated with demagnetization might make itself manifest without a change in temperature). Specifically, if the substance satisfies Curie's law (6-99) at the original constant temperature T_0 at which it is magnetized, then, according to Eq. (6-98),

$$\Delta S = -\frac{\bar{A}}{T_0^2}\frac{\mathcal{H}^2}{2} \qquad (T_0,\ p \text{ const}) \qquad (6\text{-}100)$$

If the substance is now adiabatically demagnetized so that its entropy undergoes no further change, its final state at zero field strength will be the same as though it had undergone the same entropy change at zero field strength and constant pressure throughout. But the entropy change for a homogeneous substance of fixed composition at constant pressure in the absence of the magnetic field is given by

$$\Delta S = \int_{T_0}^{T} \frac{\bar{C}_p}{T}\,dT \qquad (p \text{ const};\ \mathcal{H} = 0) \qquad (6\text{-}101)$$

Therefore

$$\int_{T_0}^{T} \frac{\bar{C}_p}{T}\,dT = -\frac{\bar{A}}{T_0^2}\frac{\mathcal{H}^2}{2} \qquad (6\text{-}102)$$

where $\mathcal{H}$ represents the magnetic field strength applied at the constant initial temperature T_0 and T' represents the ultimate temperature ideally attained under thermodynamically reversible conditions after adiabatic demagnetization.

At ordinary initial temperatures, the degree of cooling that can be attained by adiabatic demagnetization is insignificant. Thus, for chrome alum, the Curie constant has the value 3.66 erg deg/mole gauss^2; therefore at 20°C, even if one had available a field strength as high as 50,000 gauss (which would call for an electromagnet of huge size), the value of $-\Delta S$ according to Eq. (6-100) would be only 53,300 ergs/mole deg, or 0.0013 eu/mole. Compared with a molal heat capacity of about 324 cal/mole deg, one sees that the degree of cooling according to Eq. (6-102) would be less than 0.0012°K. At extremely low temperatures, however, such as may be attained initially with liquid helium, the degree of cooling by means of adiabatic demagnetization may become quite appreciable, because of both the larger paramagnetic susceptibility and the lower heat capacity of the sample. For example, if chrome alum is magnetized at the normal boiling point of helium (4.2°K; still lower starting temperatures, of order 1°K, are available with liquid helium boiling under reduced pressure), then even with a field strength of only 8000 gauss (such as has actually been used in this type of work by Giauque and MacDougall), the value of $-\Delta S$ according to Eq. (6-100) is 6.64×10^6 ergs/mole, or 0.159 eu/mole; since the molal heat capacity is only of order several tenths cal/mole deg in this temperature range, adiabatic demagnetization may be accompanied by an appreciable decrease in the temperature.

The principles of adiabatic demagnetization of an isotropic paramagnetic crystalline solid to produce temperatures below those attainable with liquid helium were first outlined independently by W. F. Giauque and by P. Debye.[1] The experimental difficulties, which are formidable, were first overcome by W. F. Giauque and D. P. MacDougall at the University of California;[2] they succeeded in attaining a temperature of 0.25°K, starting with $Gd_2(SO_4)_3 \cdot 8H_2O$ magnetized in a field of about 8000 gauss at an initial temperature of about 1.4°K. The method has since been taken up by W. J. deHaas and E. C. Wiersma at the University of Leiden and by N. Kürti, F. Simon, and their associates at Oxford University and at the Academy of Science in Paris; temperatures of order as low as 0.005°K have been reported.[3] In these experiments, the sample is suspended by means of a thread within a tube filled originally with helium gas, which serves as heat exchanger, and surrounded by a jacket containing helium boiling under reduced pressure. The sample tube and jacket lie between the pole pieces of a large electromagnet; field strengths of 8000 to 40,000 gauss have been used by the different investigators. After the sample has been magnetized and has returned to thermal equilibrium at the temperature of the liquid helium boiling in the outer jacket, it is insulated by the withdrawal of the helium gas from its immediate container, and the electromagnet is then switched off. The entire operation takes about twenty minutes. Since the temperatures attained by adiabatic demagnetization run below the range in which any other kind of thermometer has so far been standardized, the temperatures are calculated from measurements of the magnetic susceptibility itself. For this purpose, an induction coil is wound around the tube containing the sample and is put in series with a similar coil wound in the opposite direction but not surrounding the sample; with the circuit completed by means of a

[1] W. F. Giauque, *J. Am. Chem. Soc.*, **49**, 1864–1870 (1927); P. Debye, *Ann. Physik*, **81**, 1154–1160 (1926).

[2] W. F. Giauque and D. P. MacDougall, *Phys. Rev.*, **43**, 768 (1933); *J. Am. Chem. Soc.*, **57**, 1175–1185 (1935).

[3] W. J. deHaas and E. C. Wiersma, *Physica*, **1**, 779–780 (1934); **2**, 81–86, 335–340, 438 (1935); etc.

N. Kürti and F. Simon, *Proc. Roy. Soc.* (*London*), (A)**149**, 152–176 (1935); **151**, 610–623 (1935); N. Kürti, P. Lainé, B. V. Rollin, and F. Simon, *Compt. rend.*, **202**, 1576–1578 (1936); etc.

galvanometer, the two coils serve as the secondary to a primary coil to which an exciting potential is applied. In the absence of the sample, the emfs induced in the two secondary coils would exactly cancel each other, but the presence of the paramagnetic salt within the one coil increases its electromagnetic induction sufficiently so that the galvanometer deflection serves as a measure of the paramagnetic susceptibility.

Having ascertained the state attained by the substance in terms of its paramagnetic susceptibility as thermometric property, one must then correlate this property with the thermodynamic temperature. Curie's law, (6-99), cannot be relied upon at temperatures below 1°K, even when it has been shown to be valid for the particular substance at higher temperatures. The method used by the various investigators has been based on the general thermodynamic relationship

$$T = \left(\frac{d\bar{U}}{d\bar{S}}\right)_{\bar{V},\bar{J}} \tag{6-103}$$

[compare Eq. (6-93)]. The condition of constant $\bar{J}$ applies to the unmagnetized state ($\bar{J} = 0$), provided that the substance has no residual magnetism at zero field strength; there is furthermore no significant difference between the conditions of constant volume and of constant pressure at the extremely low temperatures involved in these measurements. Now, the values of $\bar{S}$ at each low-temperature state attained (specified so far only by the observed value of $\bar{X}$ attained after the adiabatic demagnetization), relative to the value of $\bar{S}$ at the initial unmagnetized state at temperature T_0, are known through Eq. (6-100), since they are equal, respectively, to the corresponding values of $\bar{S}$ in the magnetized states at T_0; each is determined in other words by the value of $\mathcal{H}$ used during the magnetization.[1] The values of $\bar{U}$ may be determined calorimetrically by heating the demagnetized sample back from its lowest attained temperature through the states of intermediate temperatures (each characterized by the value of $\bar{X}$) to the original temperature T_0. Giauque and MacDougall have accomplished this by means of an induction heater; Kürti, Lainé, and Simon used the ingenious method of heating the sample by bombarding it with γ rays from a radium salt.[2] In either case, the

[1] In Eq. (6-100), it is assumed that the substance satisfies Curie's law down to the temperature T_0 at which the magnetization is brought about; if this assumption is not correct, one may go back to Eq. (6-98), using the empirical relationship between $\bar{X}$ and T for the particular substance at the temperature T_0, whatever this relationship may be.

[2] W. F. Giauque and D. P. MacDougall, *Phys. Rev.*, **47**, 885–886 (1935); *J. Am. Chem. Soc.*, **58**, 1032–1037 (1936); *ibid.*, **60**, 376–388 (1938); W. F. Giauque and J. W. Stout, *ibid.*, **60**, 388–393 (1938). N. Kürti, P. Lainé, and F. Simon, *Compt. rend.*, **204**, 675–677, 754–756 (1937).

quantity of energy received by the sample in given time was determined by calibration at around 1°K, where T can be measured on the thermodynamic temperature scale by ultimate reference to the low-pressure helium-gas thermometer (compare Sec. 1-4). Having thus established relative $\bar{U}$ and $\bar{S}$ values for the various thermodynamic states of the substance corresponding to observed $\bar{X}$ values in the region below 1°K attained by means of adiabatic demagnetization, the investigators could then determine the absolute thermodynamic temperature of any state according to Eq. (6-103) as the slope of the $\bar{U}$ vs. $\bar{S}$ relationship for that state.

These thermal measurements served incidentally to establish experimental heat-capacity values in the region below 1°K. If the substance followed the Debye T^3 law [Eq. (3-55)] throughout this region, then one could express the left-hand member of Eq. (6-102) in the form $(a/3)(T^3 - T_0^3) = \frac{1}{3}(\bar{C}_p)_0[(T^3/T_0^3) - 1]$, where $(\bar{C}_p)_0$ represents its heat capacity at the initial temperature T_0. Therefore the ideal relationship between T and $\mathcal{H}$ would have the form

$$T = T_0\left[1 - \frac{3}{2}\frac{\bar{A}}{(\bar{C}_p)_0}\frac{\mathcal{H}^2}{T_0^2}\right]^{\frac{1}{3}} \tag{6-104}$$

Giauque and MacDougall found, however, that the first substance they tested, $Gd_2(SO_4)_3 \cdot 8H_2O$, showed an anomaly in its $\bar{C}_p$ vs. T relationship, the value of $\bar{C}_p$ increasing as the temperature was lowered, from a minimum of 0.10 cal/mole deg at about 5.0°K to more than 1.0 cal/mole deg below 0.5°K.[1] This fact, which prevented the temperature from falling as far as was later observed with other paramagnetic salts, is attributed to the doublet structure of the lowest energy level of the Gd^{+++} ion in the crystalline state; energy is absorbed at extremely low temperatures as ions pass from exclusive occupancy of the lower state (at 0°K) to a distribution between the two states, whose energies are slightly different; at temperatures sufficiently high for this redistribution to have been effected (5°K and higher), the heat capacity then behaves "normally."

We have discussed the thermodynamic theory of magnetization at some length, not only because of its bearing on the attainment of the lowest temperatures so far available, but also because it illustrates in a general way how we may treat a situation in which the state of a homogeneous substance of fixed composition depends on other independent variables besides temperature and pressure. A formally similar treatment may be applied to the polarization of a dielectric substance in an electric field; thus, for a homogeneous isotropic dielectric medium, the work of polarization has the form $d'W' = \mathcal{E}\, d\bar{P}$, where $\mathcal{E}$ is the electric field strength and

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[1] W. F. Giauque and D. P. MacDougall, *Phys. Rev.*, **44**, 235–236 (1933).

$\bar{P}$ the molal intensity of polarization, or induced electric moment per mole. Now, for moderate field strengths, $\bar{P}$ is proportional to $\mathcal{E}$, the proportionality relation having the form

$$\bar{P} = \frac{\bar{V}}{4\pi}(D - 1)\mathcal{E} \qquad (T, p \text{ const}) \tag{6-105}$$

where $\bar{V}$ represents the molal volume and D the dielectric constant. This relationship, analogous to (6-94), has its particular form because of the way in which D is defined; thus $1/D$ represents the factor by which electrostatic forces between free charges in the medium are multiplied as a consequence of the medium's polarizability ($D = 1$ for a vacuum). The entire factor multiplying $\mathcal{E}$ on the right of Eq. (6-105) is known as the molal polarizability; it is strictly analogous to the magnetic susceptibility, but is less commonly used than the dielectric constant, which is obtained directly by experimental measurement. For obvious reasons in terms of atomic-molecular theory, there is no electric analogue of diamagnetism and paramagnetism; the induced electric moment in an isotropic dielectric medium always has the same direction as the electric field, whether it results entirely from the polarization of nonpolar molecules or in part from the orientation of polar molecules against the tendency of their thermal motion to orient them at random.[1] By the same kind of argument that led to Eq. (6-98), we may evidently derive an analogous relationship between the temperature coefficient of the dielectric constant and the rate of change of $\bar{S}$ with $\mathcal{E}$,

$$\frac{\bar{V}}{4\pi}\left[\left(\frac{dD}{dT}\right)_p + (D - 1)\alpha\right] = \frac{d\bar{S}}{d(\mathcal{E}^2/2)_{T,p}} \tag{6-106}$$

We do not have a relationship analogous to Curie's law for dielectrics,[2] but Eq. (6-106), with appropriate experimental data either for the terms on the left or the term on the right, may be used as the foundation for setting up the thermodynamic properties of a homogeneous isotropic dielectric in the presence of an electric field. The internal energy, of course, satisfies the general relationship

$$d\bar{U} = T\,d\bar{S} - p\,d\bar{V} + \mathcal{E}\,d\bar{P} \tag{6-107}$$

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[1] See P. Debye, "Polar Molecules," Reinhold Publishing Corporation, New York, 1929; reprinted by Dover Publications, Inc., New York, 1945.

[2] *Ibid.* Debye has shown that the expression $\bar{V}(D - 1)/(D + 2)$ is independent of temperature for substances consisting of nonpolar molecules, but tends to decrease with increasing temperature for substances consisting of polar molecules. In the gaseous state, where dipole interaction is negligible, the temperature coefficient of this expression depends on the dipole moment of the molecules, whose value may be calculated from such experimental information.

and the "generalized" free energy, $\bar{F} \equiv \bar{U} - T\bar{S} + p\bar{V} - \mathcal{E}\bar{P}$, the relationship

$$d\bar{F} = -\bar{S}\,dT + \bar{V}\,dp - \bar{P}\,d\mathcal{E} \tag{6-108}$$

where, according to Eq. (6-105),

$$\left(\frac{d\bar{F}}{d\mathcal{E}}\right)_{T,p} = -\frac{\bar{V}}{4\pi}(D - 1)\mathcal{E} \tag{6-109}$$

Note that in all these relationships if $\bar{V}$ is expressed in cm³/mole and $\mathcal{E}$ in dynes/esu (1 dyne/esu = 299.776 volts), then energies are expressed in ergs/mole.

General References for Chapter 6

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Problems

6-1. Calculate the change in free energy when 1 mole of an ideal gas is compressed at constant temperature of 0°C from 1 atm to 10 atm. What is the physical significance of this quantity? (Can the change be induced without the expenditure on the gas of energy in nonthermal form?)

6-2. Calculate the change in enthalpy and the change in entropy when 1 mole of an ideal monatomic gas ($\bar{C}_p^\circ = \frac{5}{2}R$) is heated at constant pressure of 1 atm from 0 to 100°C.

Note that the change in free energy cannot be evaluated except with reference to the value assigned to $\bar{H}^\circ$ or to $\bar{S}^\circ$ at some one temperature. Letting $\bar{H}_{273}^\circ$ represent the arbitrary value assigned to $\bar{H}^\circ$ at the temperature 273°K, express $\bar{H}_T^\circ$ as a function of T for the ideal monatomic gas, and calculate the change in the quantity $(\bar{F}_T^\circ - \bar{H}_{273}^\circ)/T$ when the gas is heated from 0 to 100°C at 1 atm.

6-3. For N_2(g), the heat capacity at 1 atm is represented between 300 and 3000°K within ±3 per cent by the empirical equation

$$\bar{C}_p^\circ = 6.50 + 0.00100T$$

[K. K. Kelley, *U.S. Bur. Mines Bull.* 371, (1934)]. Express $\bar{H}_T^\circ - \bar{H}_{300}^\circ$ as a function of T, and calculate the change in the quantity $(\bar{F}_T^\circ - \bar{H}_{300}^\circ)/T$ when N_2(g) is heated at 1 atm from 300 to 2000°K.

6-4. Using the data given in Table 6-1, together with Eq. (6-28), calculate precisely the fugacity coefficient of N_2(g) at 25°C and 100 atm.

6-5. Estimating the temperature coefficient of the second virial coefficient of N_2(g) from the data in Table 6-1, calculate the difference between the actual entropy $\bar{S}$ of N_2(g) at 1 atm and the ideal-gas entropy $\bar{S}^\circ$ at 25°C.

6-6. From gas-density measurements on acetylene by J. Sameshima (Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIa, p. 61, 1931), the following values of $(pV)/(pV)_{0°C,1\,atm}$ have been established, the density at 0°C and 1 atm being 1.173 g/liter:

p, atm	$\frac{(pV)}{(pV)_{0°C,1\,atm}}$	
	0°C	25°C
0.5	1.0057	1.0989
1.0	(1.0000)	1.0937
2.0	0.9891	1.0841
4.0	0.9708	1.0684
6.0	0.9530	1.0531
8.0	0.9360	1.0385
10.0	0.9194	1.0255
12.0	0.9026	1.0139

Determine by graphical extrapolation the limiting value of pV at zero pressure at each temperature, and assuming an approximately linear change of pV with p between 0 and 1 atm, calculate the fugacity coefficient at 1 atm for each temperature. From a plot of $[pV - \lim\limits_{p\to 0}(pV)]$ vs. log p, calculate at each temperature the fugacity coefficient also at 10.0 atm [see Eq. (6-27)].

Assuming to a first order of approximation a linear relationship between ln ν and T over the temperature range under consideration, calculate $(\bar{S}_{T,p} - \bar{S}_T^\circ)$ for $C_2H_2(g)$ at 298.16°K, for both 1 atm and 10 atm pressure.

6-7. The compressibility of n-pentane (l) at high pressures has been studied by P. W. Bridgman (Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIIa, p. 89, 1935), with the following results at 0°C:

Pressure, kg/cm²	Relative Volume
0	(1.0000)
1,000	0.9021
3,000	0.8229
6,000	0.7647
10,000	0.7192

From a plot of V vs. p, determine by graphical integration the free-energy change per unit volume of pentane when the liquid is compressed from 1 atm to 5000 atm and to 10,000 atm (10,332 kg/cm²) at 0°C. The molal volume of liquid pentane being 111.6 ml/mole at 0°C and 1 atm, calculate the free-energy changes per mole of pentane.

6-8. From the following compressibility data for $CO_2(g)$ at 100°C, the standard density at 0°C and 1 atm being 1.9769 g/liter ("International Critical Tables," Vol. III, pp. 3, 11, 1928), calculate by graphical integration the fugacity coefficient at 200 atm, at 600 atm, and at 1000 atm at that temperature. Compare with the results estimated from Fig. 6-3.

$\dfrac{pV}{(pV)_{0^\circ\mathrm{C},1\,\mathrm{atm}}}$ for $CO_2(g)$ at 100°C

p, atm	$\dfrac{pV}{(pV)_{0^\circ\mathrm{C},1\,\mathrm{atm}}}$	p, atm	$\dfrac{pV}{(pV)_{0^\circ\mathrm{C},1\,\mathrm{atm}}}$
50	1.2065	500	1.2005
100	1.0300	600	1.3655
150	0.8780	700	1.5285
200	0.8145	800	1.6890
250	0.8355	900	1.8460
300	0.8900	1000	1.9990
400	1.0385		

6-9. The density of $CH_3NH_2(g)$ has been measured at low pressures at 0°C by J. C. Arthur and W. A. Felsing [*J. Am. Chem. Soc.*, **68**, 1883–1885 (1946)] with the following results:

p, atm	ρ, g/liter
0.2	0.2796
0.5	0.7080
0.8	1.1476

Assuming a linear relationship between $p\bar{V}$ and p over the range 0 to 1 atm, determine graphically the "best" value of the second virial coefficient, and calculate the fugacity coefficient of $CH_3NH_2(g)$ at 0°C and 1 atm.

6-10. (*a*.) Show that for a gas satisfying Berthelot's equation of state (Prob. 3-6), the fugacity coefficient satisfies the equation

$$\ln \nu = \frac{9}{128}\frac{p}{p_c}\frac{T_c}{T}\left(1 - 6\frac{T_c^2}{T^2}\right)$$

Test this equation on $N_2(g)$ at 25°C and 1 atm, $C_2H_2(g)$ at 25°C and 1 atm and 10 atm, and $CH_3NH_2(g)$ at 0°C and 1 atm, comparing with the results of Probs. 6-4, 6-6, and 6-9.

Construct according to this equation a graph of the $\ln \nu$ vs. p/p_c relationship at the reduced temperature $T/T_c = 1.5$, and compare with the results expressed in Fig. 6-3.

(*b*.) Show that for a Berthelot gas,

$$\bar{S}_{T,p} - \bar{S}_T^\circ = -\frac{27}{32}R\frac{p}{p_c}\left(\frac{T_c}{T}\right)$$

Calculate by means of this equation the difference $\bar{S}_{T,1\,\mathrm{atm}} - \bar{S}_T^\circ$ for $N_2(g)$ at 25°C, and compare with the result of Prob. 6-5. Estimate also the difference between $\bar{S}_{T,p}$ and $\bar{S}_T^\circ$ for $C_2H_2(g)$ at 25°C for $p = 1$ atm and $p = 10$ atm, and compare with the results of Prob. 6-6.

6-11. Using the generalized fugacity-coefficient chart (Fig. 6-3) estimate the difference between the actual entropy $\bar{S}_{T,p}$, and the ideal-gas entropy $(\bar{S}_T^\circ - R \ln p)$ for a gas at reduced temperature 1.3 and reduced pressure 5.0 [see Eq. (6-44)].

6-12. The latent heat of vaporization of ethyl chloride has been measured at its normal boiling point, 285.37°K, by J. Gordon and W. F. Giauque [*J. Am. Chem.*

Soc., **70**, 1506–1510 (1948)], using electrical heating. They obtained the mean value $\bar{L}_{lg} = 5892 \pm 6$ cal/mole. They also measured the vapor pressure, obtaining at 1 atm, $dp/dT = 28.591$ mm Hg/deg. Calculate a value of $\bar{L}_{lg}$ from the vapor-pressure data, and compare with the calorimetric value.

Calculate the entropy of vaporization at 285.37°K and 1 atm. Calculate also the correction to the hypothetical ideal-gas state at 1 atm, using Berthelot's equation of state (Prob. 6-10), and thereby determine $\Delta S^\circ_{285.37}$ for the process

$$C_2H_5Cl(l) = C_2H_5Cl(g)$$

6-13. The vapor pressure of methanol has been measured by E. F. Fiock, D. C. Ginnings, and W. B. Holton [*J. Research Natl. Bur. Standards*, **6**, 881–900 (1931)] with the following results:

t, °C	p, atm
0	0.0389
10	0.0713
20	0.1251
25	0.1632
30	0.2109
40	0.3427
50	0.5388

From a plot of log p vs. $1/T$, calculate the value of $\bar{L}_{lg}$ at 25°C, and calculate also the entropy of vaporization at the equilibrium pressure.

Calculate ΔS° and ΔF° at 298.16°K for the hypothetical process

$$CH_3OH(l, 1\text{ atm}) = CH_3OH(g, 1\text{ atm})$$

(the methanol vapor may be treated as an ideal gas at the saturation pressure, which is sufficiently low at the given temperature).

6-14. The vapor pressure of Hg(l) at 400°K is 0.001364 atm, and its latent heat of vaporization at that temperature is $\bar{L}_{lg} = 14{,}368$ cal/mole. The heat capacity of the gas, which is practically entirely monatomic at that temperature and low pressure, has the value $\bar{C}^\circ_p = 4.97$ cal/mole deg, while that of the liquid is 6.61 cal/mole deg from 0°C to the boiling point. Express the latent heat of vaporization and the vapor pressure as functions of T, and compute the vapor pressure of mercury at 298.16°K.

Compute also the values of ΔH°, ΔF°, and ΔS° for the hypothetical process

$$Hg(l, 1\text{ atm}) = Hg(g, 1\text{ atm})$$

at $T = 298.16$°K. [Compare K. K. Kelley, *U.S. Bur. Mines Bull.* 383, pp. 68–69 (1935)].

Use your vapor-pressure equation to calculate p_{Hg} at the normal boiling point of mercury, 630°K. The difference from 1 atm represents $p_{Hg_2}^{''}$ of $Hg_2(g)$ molecules present in the gas phase. Estimate the per cent of the mercury vapor in this state at 630°K and 1 atm.

6-15. The vapor pressures of several of the alkali halides have been measured by B. H. Zimm and J. E. Mayer [*J. Chem. Phys.*, **12**, 362–369 (1944)], using a surface ionization method, in which the concentration of the vapor was measured by complete dissociation and ionization of the alkali metal on the surface of an incandescent tungsten filament, the escaping metal ions being collected and measured electrically. The following (selected) results were obtained between 600 and 1000°K in the case of KCl(c):

T, °K	$-\log p$, atm	$1000/T$ °K
945.1	4.48	1.058
887.2	5.14	1.127
818.3	6.18	1.222
775.2	7.01	1.290
756.9	7.32	1.321
706.7	8.45	1.415
650.2	9.78	1.538
623.8	10.45	1.603

The difference between the molal heat capacities of the gas and the crystalline solid has the approximate value $-2R$ over the temperature range in question ($\frac{9}{2}R$ for the diatomic gas, and $6R$ to $7R$ for the crystalline solid). Plot $[\log p - (\Delta C_p^\circ/R) \log T]$ vs. $1/T$. Noting that according to Eq. (6-73), the slope of this line equals $-[(\bar{L}_{cg})_0 - (\Delta \bar{C}_p^\circ)T_0]/2.303R$, where $(\bar{L}_{cg})_0$ represents the latent heat of sublimation at the temperature T_0, calculate the value of $(\bar{L}_{cg})$ at 800°K, and also express $\log p$ as a function of T over the given range.

Extrapolating to 298.16°K (neglecting departure of the heat capacities from the high-temperature values), calculate $\Delta H^0_{298.16}$ and $\Delta F^0_{298.16}$ for the process

$$\mathrm{KCl(c)} = \mathrm{KCl(g)}$$

What is the corresponding vapor pressure of KCl(c) at that temperature?

6-16. Using the results of the preceding problem, calculate the vapor pressure of KCl(c) at its melting point, 1043°K. The latent heat of fusion at the melting point being 6410 cal/mole, calculate the latent heat of vaporization, and express it as a function of T, using for KCl(l) the heat capacity 16.0 cal/mole deg. Express the vapor pressure of KCl(l) as a function of T, and test whether this equation agrees with the experimental value of the normal boiling point, 1680°K. [Compare K. K. Kelley, *U.S. Bur. Mines Bull.* 383, pp. 85–86 (1935); see also E. F. Fiock and W. H. Rodebush, *J. Am. Chem. Soc.*, **48**, 2522–2528 (1926), who measured directly the vapor pressure of liquid KCl between 1179 and 1378°K.]

6-17. Using the data in the text, calculate $\Delta H^0_{298.16}$ and $\Delta S^0_{298.16}$ for the process

$$\mathrm{S(I,\ monoclinic)} = \mathrm{S(II,\ rhombic)}$$

and show that condition (5-29) is satisfied for the transformation of monoclinic to rhombic sulfur at that temperature, but not for the reverse transformation.

6-18. Using the Mollier diagram for steam presented in Fig. 6-5, estimate the ideal work done per gram of steam in the Rankine cycle, if saturated steam enters the cylinder at 5 atm boiler pressure and leaves at 100°C. What per cent increase in the ideal work is obtained if the steam at 5 atm is superheated to 400°C before it enters the cylinder? What further increase is obtained if the spent steam leaves the cylinder at 50°C? Estimate the percentage of the steam leaving the cylinder in the condensed state under the latter condition.

6-19. Using Callendar's equation of state for steam given in Prob. 3-33, derive an expression for $(d\bar{S}/dp)_T$, and an equation for the entropy of steam relative to $\bar{S}_T^\circ$, its entropy as a hypothetical ideal gas at the same temperature and 1 atm. Using this equation, calculate $(\bar{S}_{T,p} - \bar{S}_T^\circ)$ at 100°C and 1 atm, and also at 300°C and 30 atm.

Derive also according to Callendar's equation an expression for the fugacity coefficient of steam, and calculate its value at the same two sets of conditions. Compare the value at 300°C and 30 atm with that estimated from Fig. 6-2.

6-20. Show how Eq. (6-73) is modified when one takes into account deviation of the vapor phase from ideal-gas behavior in terms of a fugacity coefficient, and using the value of ν for $H_2O(g)$ at 373.16°K and 1 atm given in the text, derive a formula for log p as a function of T. Use this formula to calculate the vapor pressure of water at 25°C, deviation of the vapor phase from ideal-gas behavior being negligible at the low pressure concerned. What assumptions remain involved in your formula that may still introduce error?

6-21. Derive a general expression for the vapor pressure of a liquid satisfying Trouton's law, assuming that the vapor phase satisfies the ideal-gas law, and neglecting the variation of $\bar{L}_{lg}$ itself with temperature; use the normal boiling point as the adjustable parameter in terms of which to fix the integration constant in the equation. Test the equation by computing the vapor pressure of carbon tetrachloride at 60°C, its normal boiling point being 76.75°C. (Look up the experimental value for comparison.)

6-22. The second law of thermodynamics may be applied to thermal radiation, provided that we can devise a thermodynamically reversible means of deriving nonthermal energy from thermal radiation energy, *i.e.*, provided that we have some means of establishing equilibrium between thermal radiation and an ordinary mechanical force. We may accomplish this in principle through the agency of radiation pressure, predicted originally on theoretical grounds by J. C. Maxwell in 1873, and confirmed experimentally by the work of P. Lebedew [*J. Russ. Phys. Chem. Soc.*, **32,** 211–217 (1900); **33,** 53–75 (1901)], and of E. F. Nichols and G. F. Hull [*Phys. Rev.*, **13,** 307–320 (1901)]. The pressure exerted by radiation of energy density, $u = U/V$, has the theoretical value $p = u/3$. Assuming that u inside a black-body enclosure is a function of the temperature only, proportional to the rate per unit area at which radiant energy is being emitted by the walls, prove by means of Eqs. (6-52) and (6-60) (noting that for the case under consideration, $(dU/dV)_T = U/V = u$) that p and u are proportional to the fourth power of the absolute thermodynamic temperature, and so derive the Stefan-Boltzmann black-body radiation law (1-18). (In this thermodynamic derivation due to Boltzmann, the proportionality constant enters as an empirical integration constant; Planck's radiation theory provides a theoretical connection between this constant and other natural constants, from which its value may then be derived.)

CHAPTER 7

THERMODYNAMIC BEHAVIOR OF SOLUTIONS AND HETEROGENEOUS MIXTURES

The general thermodynamic treatment of mixtures of chemical substances was first systematically explored by J. Willard Gibbs in his monumental paper, "On the Equilibrium of Heterogeneous Substances," published originally in the Transactions of the Connecticut Academy, 1876–1878.[1] Gibbs's methods were applied with brilliant success to a variety of chemical problems by W. Ostwald, J. H. van't Hoff, P. Duhem, B. Roozeboom, and other scientists during the latter part of the nineteenth century; this work established the foundations of modern physical chemistry.[2] Distinctive contributions were made during the early part of the twentieth century by W. Nernst, M. Planck, and F. Haber.[3] Haber's work in particular demonstrated the value of precise, systematic thermodynamic data to chemical industry. Modern chemical thermody-

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[1] This great classic appears in "The Collected Works of J. Willard Gibbs," Vol. I, pp. 55–353, Longmans, Green & Co., Inc., New York, 1928.

[2] See, for example, W. Ostwald, "Lehrbuch der allgemeinen Chemie," W. Engelmann, Leipzig, 1893; J. H. van't Hoff, *Z. physik. Chem.*, 1, 481–508 (1887) (a translation of this famous paper appears in *Alembic Club Reprint* 19, published for the Alembic Club by Oliver & Boyd, Ltd., Edinburgh and London, 1929); also, "Zur Bildung der ozeanischen Salzablagerungen," Friedrich Vieweg & Sohn, Brunswick, 1905–1909; P. Duhem, "Le Potentiel thermodynamique et ses applications," Hermann & Cie, Paris, 1886; also, "Traité élémentaire de mécanique chimique," Hermann & Cie, Paris, 1897; B. Roozeboom, "Die heterogenen Gleichgewichte," Friedrich Vieweg & Sohn, Brunswick, 1901–1904.

[3] Summarized in the following works:

W. Nernst, "Theoretische Chemie," 6th ed., F. Enke, Stuttgart, 1909; "Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes," 2d ed., W. Knapp, Halle, 1924, English translation by G. Barr, "The New Heat Theorem," E. P. Dutton & Co., Inc., New York, 1926.

M. Planck, "Vorlesungen über Thermodynamik," Veit, Leipzig, 1897, English translation by A. Ogg, Longmans, Green & Co., Inc., 1926 (reprinted by Dover Publications, New York, 1945); for particular application to thermal radiation, see "Wärmestrahlung," 5th ed., J. A. Barth, Leipzig, 1923.

F. Haber, "Thermodynamik der technischen Gasreactionen," R. Oldenbourg, Munich, 1905, English translation by A. B. Lamb, Longmans, Green & Co., Inc., New York, 1908.

namics has been profoundly influenced by the original work of G. N. Lewis and his associates, whose methods have left a permanent imprint on the very terminology of the subject.[1]

The thermodynamic properties of solutions (homogeneous substances consisting of two or more chemical constituents of definite compositions whose proportions may be continuously varied without the appearance of a new phase) are important not only in themselves, as guides to our understanding of problems arising in connection with distillation, solubility, heat effects on mixing or separating the components, etc., but also because many chemical processes, in the laboratory and in industry, are actually carried out in gaseous or liquid solution. In this chapter, we shall pursue discussion of the equilibrium behavior of solutions in the absence of chemical reactions among the constituents. This study, valuable for certain applications in itself, provides the necessary experimental and theoretical foundation on which the general study of chemical equilibrium for reactions in solution may be based, as will be shown in Chap. 8.

7-1. Thermodynamic Potentials. In the case we have previously been discussing in Chap. 6 of a homogeneous substance whose mass and composition are *fixed*, either by nature or by the conditions of the particular investigation, we have seen that the internal energy for thermodynamically reversible changes of state (changes during which the system is at all successive stages but infinitesimally displaced from a state of equilibrium under the external constraints instantaneously prevailing) satisfies the fundamental equation

$$dU = T\,dS - p\,dV \qquad (W' = 0) \qquad (7\text{-}1\text{-}1)$$

This equation represents a mathematical implication of the first and second laws of thermodynamics, under the supposition that the substance is restricted to changes of state during which the only nonthermal energy exchanged with the surroundings is in the form of mechanical work of expansion or compression, associated with changes in its volume; we reserve for special treatment those cases ($W' \neq 0$) in which the internal energy may be influenced also by the effects of gravity, surfaces bounding the phase in question, electric fields, magnetic fields, etc. In the circumstances, the so-called *variance* of the system is *two*, as we have observed in Sec. 3-1. Equation (7-1-1) is then a complete differential equation representing U as a function of the two independent state-determining varia-

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[1] G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York, 1923.

bles, S and V. By means of suitable transformations, based on experimentally established connections between S and V and other properties of the particular substance, it may be used as the logical starting point in the representation of U as a function of any other pair of independent thermodynamic variables characterizing the state, such as T and p (compare Sec. 6-3), though, in general, such other representations are not as simple in form as Eq. (7-1-1).

Although Eq. (7-1-1) does not explicitly say so, it is to be understood that the internal energy for a substance of given composition (whether fixed by nature, as in the case of a chemical compound or element, or held constant by the terms of the particular investigation, as when one measures the thermodynamic properties of 10 per cent aqueous sucrose solution) depends also on the total mass, but it does so in a special way: other conditions such as temperature and pressure being constant (as well as the composition), the *internal energy is directly proportional to the total mass.* The internal energy is in other words what we have called an *extensive property* of the substance or thermodynamic system. We infer this to be true from the fact that when two or more different samples of the same substance, all alike in composition, are combined at the same temperature and pressure into one, there is no net energy change: the heat of mixing is zero, and the net difference between the volumes of the combined and the separate samples is also zero; consequently the internal energy of the combined samples must be equal to the sum of the internal energies of the separate samples, and therefore must be in proportion to the total mass.[1]

Now, if the composition may be continuously varied, as is the case for solutions, then the internal energy instead of being determined by the entropy, volume, and total mass, may depend explicitly on the composition as well. This is indicated experimentally by a net heat effect (heat of solution) and a net volume change that vary with the proportions in which the components are mixed. In this case, we may represent the change in internal energy for a general reversible change of state, which we shall suppose may include gain or loss of any component and of total mass through exchange with neighboring phases, by means of the equation

$$dU = T\,dS - p\,dV + \phi_1\,dn_1 + \phi_2\,dn_2 + \cdots + \phi_c\,dn_c \qquad (7\text{-}1\text{-}2)$$

where, by definition,

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[1] See, however, footnote 1 on page 72. We are assuming throughout this discussion that surface effects are negligible. Energy is not strictly proportional to mass without this restriction. See also Eq. (6-84).

$$\left.\begin{aligned}\phi_1 &\equiv \left(\frac{dU}{dn_1}\right)_{S,V,n_2,n_3,\ldots,n_c}\\ \phi_2 &\equiv \left(\frac{dU}{dn_2}\right)_{S,V,n_1,n_3,\ldots,n_c}\\ &\cdots\cdots\cdots\cdots\\ \phi_c &\equiv \left(\frac{dU}{dn_c}\right)_{S,V,n_1,n_2,\ldots,n_{c-1}}\end{aligned}\right\} \qquad (7\text{-}1\text{-}3)$$

In these equations, C represents the *number of components* of the phase in question, in the sense in which this expression was introduced in Sec. 3-1. For we may always write formally [compare Eq. (3-12)],

$$\begin{aligned}U &= U(S, V, n_1, n_2, \ldots, n_c)\\ dU &= \left(\frac{dU}{dS}\right)_{V,n_1,n_2,\ldots,n_c} dS + \left(\frac{dU}{dV}\right)_{S,n_1,n_2,\ldots,n_c} dV\\ &\qquad + \phi_1\,dn_1 + \phi_2\,dn_2 + \cdots + \phi_c\,dn_c\end{aligned}$$

where $\phi_1, \phi_2, \ldots, \phi_c$ are defined by Eq. (7-1-3); but from Eq. (7-1-1), which applies to any homogeneous body for a change of state at fixed mass and composition,

$$\left(\frac{dU}{dS}\right)_{V,n_1,n_2,\ldots,n_c} = T \qquad (7\text{-}1\text{-}4a)$$

$$\left(\frac{dU}{dV}\right)_{S,n_1,n_2,\ldots,n_c} = -p \qquad (7\text{-}1\text{-}4b)$$

Therefore Eq. (7-1-2), which is a generalization of Eq. (7-1-1), follows.

The quantities $\phi_1, \phi_2, \ldots, \phi_c$, which were first conceived by Gibbs, are known as *thermodynamic potentials* of the respective components.[1] Their immediate physical significance is precisely as represented by the defining equations, (7-1-3). Thus, suppose one were to measure ΔU, by the experimental operation of measuring $Q - W$, for the process of adding Δn_i moles of component i to the solution, under such conditions that the *total entropy*, the *total volume*, and the *numbers of moles of all the other components* of the solution underwent *no change;* then ϕ_1 would be found by taking $\lim\limits_{n_i \to 0} (\Delta U/\Delta n_i)$ for a series of observations conducted under those conditions. Taking the limit as $\Delta n_i \to 0$ allows for the second-order change in the quantity ϕ_i itself (as well as in all the other thermodynamic potentials) as the composition changes; if one were merely to take

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[1] Gibbs originally used the masses of the components, rather the numbers of moles, as variables defining the total mass and composition; the advantage in chemical applications of using molal units of mass is obvious, provided that all required molecular weights are known, or conventional formula weights agreed upon.

$(\Delta U/\Delta n_i)$ for a *finite* change Δn_i in the amount of component i, subject to constant S, constant V, and constant amounts of all the other components, one would obtain the mean value of ϕ_i between the initial and final compositions, but not the instantaneous value at the given (initial) composition. The quantities $\phi_1, \phi_2, \ldots, \phi_c$ thus have the character of *differential molal internal energies at fixed total entropy, total volume, and composition.* This, however, is not the character most convenient for their experimental establishment, as we shall see presently. One should note that the thermodynamic potentials are *not* equal to the partial molal internal energies $\upsilon_1, \upsilon_2, \ldots, \upsilon_c$ introduced by Eqs. (3-12) and (3-14); those quantities were defined as differential molal internal energies of solution under conditions of *constant temperature and pressure.* No such simple thermodynamic functional relationship as Eq. (7-1-1) exists, however, between the internal energy and the temperature and pressure as state-determining independent variables at fixed composition; the relationship between U and T and p is far more involved [Eq. (3-32)], bringing in specific thermodynamic properties of the substance, and is not well adapted to general theoretical development.

Let us examine some of the properties of the thermodynamic potentials. Experience teaches us that S and V, like U, are extensive properties of the solution; there is neither a net heat effect nor a net volume change when different samples of the same substance, all at the same temperature, pressure, and composition, are combined into one. Therefore if we consider a change in which each of the quantities $n_1, n_2, \ldots, n_c$ is multiplied by a common factor, λ, but without change in the temperature or pressure, then since no change in composition is involved but merely an increase in the total mass of solution by the factor λ, the quantities S, V, and U all likewise increase by the same factor. Equation (7-1-2) thereby implies that the thermodynamic potentials $\phi_1, \phi_2, \ldots, \phi_c$ are themselves *intensive properties* of the solution, varying perhaps with temperature, pressure, and composition, but *independent of the total mass.* In fact, if we let $dn_1 = \lambda n_1$, $dn_2 = \lambda n_2$, . . . , $dn_c = \lambda n_c$ in Eq. (7-1-2) with T and p fixed, then experiment leads us to suppose that $dS = \lambda S$, $dV = \lambda V$, and $dU = \lambda U$; upon substituting these values in Eq. (7-1-2), we draw the conclusion that

$$U = TS - pV + \phi_1 n_1 + \phi_2 n_2 + \cdots + \phi_c n_c \qquad (7\text{-}1\text{-}5)$$

In this integral equation, U may of course include an arbitrary integration constant, whose value is independent of S, V, and $n_1, n_2, \ldots, n_c$.[1]

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[1] The student of differential equations will recognize Eq. (7-1-2), granted the linear dependence of U, S, and V on the total mass at fixed temperature, pressure, and

Now let us compare the general differential of U, as derived from Eq. (7-1-5),

$$dU = T\,dS + S\,dT - p\,dV - V\,dp + \phi_1\,dn_1 + n_1\,d\phi_1 + \phi_2\,dn_2 + n_2\,d\phi_2 + \cdots + \phi_c\,dn_c + n_c\,d\phi_c$$

with Eq. (7-1-2) from which we began; thus

$$S\,dT - V\,dp + n_1\,d\phi_1 + n_2\,d\phi_2 + \cdots + n_c\,d\phi_c = 0 \quad (7\text{-}1\text{-}6)$$

Equation (7-1-6) must therefore likewise be satisfied for all reversible changes of state, including changes during which the entire mass of the homogeneous phase in question may undergo change, as well as the amounts of the individual components present. This equation is the most general form of the *Gibbs-Duhem relation* [compare Eqs. (3-16) and (4-36)]. In particular, for changes taking place in the composition at fixed temperature and pressure:

$$n_1\,d\phi_1 + n_2\,d\phi_2 + \cdots + n_c\,d\phi_c = 0 \quad (T, p \text{ const}) \quad (7\text{-}1\text{-}7)$$

Equation (7-1-7) implies that if at given temperature and pressure, the thermodynamic potentials of all but one of the components have been determined at all compositions, then the thermodynamic potential of the remaining component is also determined, except for an additive integration constant independent of the composition. The existence of some such relationship among the C thermodynamic potentials is of course implied by the fact that while the extensive property U at given S and V or at given T and p depends on as many composition variables as there are components, the intensive properties $\phi_1, \phi_2, \ldots, \phi_c$ are each determined by the composition, independently of the total mass; at given temperature and pressure, there can therefore be only as many independently varying thermodynamic potentials as the number of independent variables required to define the composition, namely, $C - 1$. If we divide Eq. (7-1-7) through by the total number of moles: $n = n_1 + n_2 + \cdots + n_c$, we may express this important relationship entirely in terms of intensive properties of the solution, without reference to the total mass; thus

$$x_1\,d\phi_1 + x_2\,d\phi_2 + \cdots + x_c\,d\phi_c = 0 \quad (T, p \text{ const}) \quad (7\text{-}1\text{-}8)$$

where $x_1, x_2, \ldots, x_c$ represent the respective *mole fractions* of the com-

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composition, as a homogeneous differential equation of first order for U in terms of the independent variables $S, V, n_1, n_2, \ldots, n_c$; Eq. (7-1-5) then follows as a consequence of Euler's theorem for such equations. Compare the general treatment here given to Eq. (7-1-2) with that previously given on a less general basis to Eq. (3-12), Sec. 3-1, and to Eq. (4-34), Sec. 4-5.

ponents. Equation (7-1-8) is particularly useful when applied to a two-component solution, where we have determined by experiment (as we shall presently describe) the value of one thermodynamic potential ϕ_1 at various values of the composition, and wish to calculate the value of the other; thus

$$d\phi_2 = -\frac{x_1}{x_2}\,d\phi_1 = -\frac{x_1}{1-x_1}\,d\phi_1 \qquad (T,\ p \text{ const})$$

$$\phi_2'' - \phi_2' = -\int_{x_1'}^{x_1''} \frac{x_1}{1-x_1}\,d\phi_1 \qquad (T,\ p \text{ const}) \qquad (7\text{-}1\text{-}9)$$

The integral in Eq. (7-1-9) may be evaluated numerically or graphically from the experimental data (*e.g.*, from a plot of x_1/x_2 vs. ϕ_1) to determine ϕ_2 at any one composition relative to its value at any other.

One should note that it is possible by means of an expression such as those of Eqs. (7-1-3) to define formally a thermodynamic potential with respect to *any* chemical constituent of fixed composition present in the solution, whether or not it has been counted as one of the components in the sense of Sec. 3-1. The *number* of components, however, represents the least number of chemical constituents in terms of which the internal energy may be represented completely as a function of the state by means of an equation such as (7-1-2). This number, C, is characteristic of the system under investigation (and its circumstances with respect to possible chemical reactions among the constituents, as noted in Sec. 3-1), but does not depend on which particular constituents are regarded as "the" components. These may be chosen to suit the convenience of the investigator, in the same sense that a chemical analyst might choose to report the aluminum content of a clay in terms of the percentage of Al_2O_3, even though aluminum does not actually exist in the sample in that form, or to report the composition of an aqueous sulfuric acid solution in terms of the percentage of H_2SO_4, disregarding the fact that this compound is undoubtedly ionized in aqueous solution. Now, in an aqueous solution of sulfuric acid, there is nothing to prevent us from defining and measuring thermodynamic potentials with respect to H_2SO_4, H_2O, SO_3 (compare Tables 4-11 and 4-12, where partial molal enthalpies were computed with respect to these three constituents), or even with respect to the ions, H_3O^+, HSO_4^-, and $SO_4^{=}$, after we have introduced certain preliminary conventions to take account of the experimental requirement of electrical neutrality of the solution as a whole (discussed in Sec. 7-4). Obviously, however, all these thermodynamic potentials cannot be unrelated; this system has but two components, on whatever basis they may be selected. Thus, a solution prepared by the addition of 1 mole of H_2SO_4 to 15 moles of H_2O is identical with one prepared by the addition of 1 mole of SO_3 to 16 moles of H_2O (allowing for technical difficulty of getting SO_3 to dissolve directly in the water), or with one prepared by the removal of 15 moles of SO_3 from 16 moles of H_2SO_4 (again allowing for the technical difficulty that would be encountered in the actual carrying out of this operation). The chemical species actually present in the solution may be quite different from the two components in terms of which the composition is in this case defined. It is immaterial for general theoretical purposes which particular two substances are regarded as the components, provided only that their relative amounts completely specify the composition; one could not, for example, regard H_3O^+ and HSO_4^- as the components, because on account of the requirement of electrical neutrality, the amounts of these ions in aqueous sulfuric acid solutions are not independently variable. Thus, while Eqs. (7-1-3) may be applied to define thermodynamic potentials with respect to any individual chemical constituents of the solution, Eqs. (7-1-2) and (7-1-7) apply to any set of C constituents whose amounts in the phase in question are independently variable under the conditions of the particular investigation.

We may obtain further insight into the nature of the thermodynamic potentials by introducing into Eq. (7-1-5) the *Gibbs free-energy* function

$$F \equiv U - TS + pV$$

whose general significance was elaborated in Sec. 5-6. Thus

$$F = n_1\phi_1 + n_2\phi_2 + \cdots + n_c\phi_c \tag{7-1-10}$$

Therefore the quantities $\phi_1, \phi_2, \ldots, \phi_c$ have precisely the values one would ascribe to the *molal free energies* of the components *in solution* if one were to represent the total free energy as a sum of terms contributed by the several components; in general, however, they are *not* equal to the molal free energies of the *pure* components at the same temperature and pressure. If we differentiate Eq. (7-1-10) in the most general manner,

$$dF = n_1\,d\phi_1 + \phi_1\,dn_1 + n_2\,d\phi_2 + \phi_2\,dn_2 + \cdots + n_c\,d\phi_c + \phi_c\,dn_c$$

and introduce Eq. (7-1-6), we then obtain

$$dF = -S\,dT + V\,dp + \phi_1\,dn_1 + \phi_2\,dn_2 + \cdots + \phi_c\,dn_c \tag{7-1-11}$$

Equation (7-1-11) is clearly a generalization for phases of variable composition of Eq. (6-5), which applied to homogeneous substances of fixed composition and mass. From Eq. (7-1-11), it is evident that

$$\left.\begin{aligned}\phi_1 &= \left(\frac{dF}{dn_1}\right)_{T,p,n_2,n_3,\ldots,n_c}\\ \phi_2 &= \left(\frac{dF}{dn_2}\right)_{T,p,n_1,n_3,\ldots,n_c}\\ &\cdots\cdots\cdots\cdots\\ \phi_c &= \left(\frac{dF}{dn_c}\right)_{T,p,n_1,n_2,\ldots,n_{c-1}}\end{aligned}\right\} \qquad (7\text{-}1\text{-}12)$$

In other words, the thermodynamic potentials $\phi_1, \phi_2, \ldots, \phi_c$ are identical with *partial molal free energies* of the respective components, where this expression is applied in the same sense in which partial molal internal energies applied to the quantities defined by Eq. (3-14) and partial molal enthalpies to the quantities defined by Eq. (4-33); they represent the respective increases in the *free energy* of the solution per mole of component added, when the particular component is added to the solution *at constant temperature and pressure* without changing sensibly the composition. We could indeed have started with Eqs. (7-1-11) and (7-1-12) as primary definitions of $\phi_1, \phi_2, \ldots, \phi_c$. From the standpoint of the general logical structure of thermodynamics, however, it is preferable to introduce them by means of Eq. (7-1-2), which relates them fundamentally to the internal-energy function given immediately by the first law of thermodynamics; relationships similar in form to Eqs. (7-1-3) and (7-1-12) may be derived connecting the thermodynamic potentials with the enthalpy at constant entropy and pressure and with the Helmholtz free energy [defined by Eq. (5-49)] at constant temperature and volume.

From the standpoint of experimental procedure, the relationship of the thermodynamic potentials to the Gibbs free-energy function at constant temperature and pressure has proved to be their most useful property, both because of the comparative ease with which constant temperature and pressure may be maintained in laboratory and industrial operations and because of the general equilibrium condition, Eq. (5-61). For let us consider a situation in which our solution is in equilibrium with some other phase; the general equilibrium criterion (5-61) expressed in differential notation has the form

$$dF = 0 \qquad (T, p \text{ const}) \qquad (7\text{-}1\text{-}13)$$

We may state at the outset that the two phases cannot be in equilibrium thermally unless both are at the *same* temperature; otherwise irreversible changes associated with heat exchange between them can take place (as described on page 215, Sec. 5-5); likewise, they cannot be in equilibrium mechanically unless both are at the *same* pressure, in the absence of semipermeable diaphragms or surface forces interfering with the transmission of pressure but not with the exchange of material substances between the two phases. The kind of change to which the general equilibrium condition (7-1-13) applies in this case therefore reduces to one involving the transfer of small amounts of the components from one phase to the other at uniform temperature and pressure, the total quantity of each component between the two phases being constant (we shall discuss in Chap. 8 how the conclusions are modified when the amounts of the components may change through chemical reactions taking place in either phase). The conditions of conservation may be put in the form

$$\left.\begin{aligned} dn_1' &= -dn_1'' \\ dn_2' &= -dn_2'' \\ \cdots&\cdots\cdots \\ dn_c' &= -dn_c'' \end{aligned}\right\} \tag{7-1-14}$$

where $'$ designates quantities belonging to the one phase, and $''$ quantities belonging to the other. Now, according to Eq. (7-1-11), we may write for either phase

$$\left.\begin{aligned} dF' &= \phi_1'\,dn_1' + \phi_2'\,dn_2' + \cdots + \phi_c'\,dn_c' \\ dF'' &= \phi_1''\,dn_1'' + \phi_2''\,dn_2'' + \cdots + \phi_c''\,dn_c'' \end{aligned}\right\} \quad (T,\ p \text{ const})$$

These equations express how the free energy of either phase varies separately with changes in the amounts of the various components present, the temperature and pressure being fixed. Therefore the net free-energy change for both phases corresponding to the virtual exchange of small quantities of the components between them is given by

$$\begin{aligned} dF = dF' + dF'' = \phi_1'\,dn_1' + \phi_2'\,dn_2' + \cdots + \phi_c'\,dn_c' \\ + \phi_1''\,dn_1'' + \phi_2''\,dn_2'' + \cdots + \phi_c''\,dn_c'' \\ (T,\ p \text{ const}) \end{aligned}$$

Introducing the condition for equilibrium (7-1-13), and also the conservation conditions (7-1-14),[1]

$$(\phi_1' - \phi_1'')dn_1' + (\phi_2' - \phi_2'')dn_2' + \cdots + (\phi_c' - \phi_c'')dn_c' = 0 \tag{7-1-15}$$

Since the quantity of each component in the one phase is by hypothesis independently variable, the unconditional equilibrium equation (7-1-15) can be satisfied in general only if

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[1] One may compare the treatment of the present situation to that leading to the Clapeyron-Clausius equation, Eq. (6-68), where it was assumed that the compositions of the two phases were identical, but the general equilibrium condition (5-61) then led to a relation between the equilibrium temperature and pressure for the two phases.

$$\left.\begin{aligned} \phi_1' &= \phi_1'' \\ \phi_2' &= \phi_2'' \\ \cdot\ \cdot\ &\cdot\ \cdot\ \cdot \\ \phi_c' &= \phi_c'' \end{aligned}\right\} \tag{7-1-16}$$

The argument is but slightly modified if the second phase contains certain of the components, but not the others [*e.g.*, as in the case of a saturated solution of KCl in water, in equilibrium with KCl(c), where the crystalline KCl phase would contain no water]; for then we should have $dn_j'' = dn_j' = 0$ for each component, j, that is confined by nature to but a single one of the two phases; but Eqs. (7-1-15) and (7-1-16) would continue to apply to all other components that can coexist in both phases. Thus, *the thermodynamic potential of any component present in two homogeneous phases in equilibrium with each other has the same value in both phases.*

The usefulness of the equilibrium law (7-1-16) becomes further evident when one observes that for the special case of a homogeneous chemical substance of definite composition, since for such a substance, $F_{T,p} = n\bar{F}_{T,p}$, Eq. (7-1-12) defining the thermodynamic potential in general reduces to $\phi = \bar{F}_{T,p}$; *the thermodynamic potential of a pure chemical substance is equal to its molal free energy at the given temperature and pressure.*[1] Therefore equilibrium data between the solution and its pure components, when such equilibrium can be established, serve most directly to relate the thermodynamic potentials in solution to the molal free energies of the respective pure components. For example, the solubility of KCl in water at 25°C and 1 atm (more precisely, in water saturated with air at 1 atm) is 4.81 mole/kg H_2O; therefore ϕ_{KCl} in 4.81 molal aqueous solution at 25°C and 1 atm is equal to $\bar{F}^\circ_{298.16}$ for KCl(c). At the same time, the vapor pressure of this solution at 25°C is 20.021 mm Hg,[2] the equilibrium vapor phase consisting of practically pure water vapor; therefore ϕ_{H_2O} in 4.81 molal aqueous KCl solution at 25°C and 20.021 mm Hg is equal to $\bar{F}_{H_2O(g)}$ at 25°C and 20.021 mm Hg; by the methods of Chap. 6, this quantity is equal approximately to

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[1] For this reason, certain authors have referred to the Gibbs free-energy function $U - TS + pV$ itself as the thermodynamic potential (P. Duhem, "Le Potentiel thermodynamique et ses applications," Hermann & Cie, Paris, 1886; P. S. Epstein, "Textbook of Thermodynamics," John Wiley & Sons, Inc., New York, 1937). Gibbs characteristically never gave a name to this function, to which he referred merely by the symbol ζ. It is useful, however, for us to reserve the expression "thermodynamic potential" generally for the quantities $\phi_1, \phi_2, \ldots, \phi_c$, related to F by means of Eqs. (7-1-12); for the special case of a homogeneous chemical element or compound, whose composition is determined by nature, the value of the thermodynamic potential then reduces to the molal free energy at the given temperature and pressure.

[2] J. N. Pearce and R. D. Snow, *J. Phys. Chem.*, **31**, 231–245 (1927).

$$(\bar{F}^{\circ}_{298.16})_{\mathrm{H_2O(l)}} + RT \ln \frac{20.021 \text{ mm Hg}}{23.756 \text{ mm Hg}} = (\bar{F}^{\circ}_{298.16})_{\mathrm{H_2O(l)}} - 0.1013 \text{ kcal/mole},$$

the approximations consisting of the assumptions that $H_2O(g)$ may be treated as an ideal gas and that the change of $\bar{F}_{\mathrm{H_2O(l)}}$ between 1 atm and the vapor pressure of pure water at the given temperature, 23.756 mm Hg, may be neglected. One readily perceives how from further vapor-pressure measurements at lower KCl concentrations in this particular case (where the equilibrium vapor phase consists essentially of one of the pure components) one could establish experimentally the value of $\phi_{\mathrm{H_2O}}$ as a function of KCl or H_2O concentration and how by the application of Eq. (7-1-9) to these results one could proceed to calculate ϕ_{KCl} through graphical or numerical integration; the integration constant required in order to fix the scale of ϕ_{KCl} values relatively to $\bar{F}^{\circ}_{298.16}$ for pure KCl(c) would be determined by the data for the saturated solution. Details of such calculations will be taken up in later sections of this chapter.

The equilibrium law (7-1-16) may be readily generalized for systems consisting of more than two different homogeneous phases in equilibrium. Thus, equilibrium condition (7-1-13) applied to the virtual exchange of small quantities of the components among the several phases in equilibrium at uniform temperature and pressure takes the form

$$\begin{aligned}\phi_1' \, dn_1' + \phi_2' \, dn_2' + \cdots + \phi_c' \, dn_c' & \\ + \phi_1'' \, dn_1'' + \phi_2'' \, dn_2'' + \cdots + \phi_c'' \, dn_c'' & \\ + \phi_1''' \, dn_1''' + \phi_2''' \, dn_2''' + \cdots + \phi_c''' \, dn_c''' & \\ + \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots & = 0 \qquad (7\text{-}1\text{-}17)\end{aligned}$$

subject to the conservation conditions

$$\left.\begin{aligned} dn_1' + dn_1'' + dn_1''' + \cdots &= 0 \\ dn_2' + dn_2'' + dn_2''' + \cdots &= 0 \\ \cdots\cdots\cdots\cdots\cdots\cdots & \\ dn_c' + dn_c'' + dn_c''' + \cdots &= 0 \end{aligned}\right\} \qquad (7\text{-}1\text{-}18)$$

Equations (7-1-17) and (7-1-18) may be solved generally by means of Lagrange's method of undetermined multipliers. Let us multiply the first of Eqs. (7-1-18) by a constant λ_1, the second by a constant λ_2, . . . , and the Cth by a constant λ_c, whose values are to be subsequently determined, and add the resulting equations to Eq. (7-1-17); thus

$$\begin{aligned}(\phi_1' + \lambda_1)dn_1' + (\phi_1'' + \lambda_1)dn_1'' + (\phi_1''' + \lambda_1)dn_1''' + \cdots & \\ + (\phi_2' + \lambda_2)dn_2' + (\phi_2'' + \lambda_2)dn_2'' + (\phi_2''' + \lambda_2)dn_2''' + \cdots & \\ + \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots & \\ + (\phi_c' + \lambda_c)dn_c' + (\phi_c'' + \lambda_c)dn_c'' + (\phi_c''' + \lambda_c)dn_c''' + \cdots & \\ = 0 \qquad (7\text{-}1\text{-}19)\end{aligned}$$

Equation (7-1-19) represents the unconditional criterion for equilibrium among the different phases at the given temperature and pressure, taking into account the restrictions imposed by Eqs. (7-1-18), which represent conservation of the total mass of each component throughout the system (the more general situation in which chemical reactions may change the masses of the components is to be discussed in Chap. 8). Now, the quantities of any particular component in all but one of the different phases may be varied independently in any arbitrary manner, so that for example it should be possible in Eq. (7-1-19) to assign dn_1'', dn_1''', . . . any values whatever independently of the values assigned to the other *dn's*, the value of dn_1' then being left determinate so as to satisfy the first of conditions (7-1-18). Therefore in order that Eq. (7-1-19) may be satisfied unconditionally, no matter what virtual changes in the distribution of component 1 among the several phases may be considered, it is first of all necessary that

$$\begin{aligned} \phi_1'' + \lambda_1 &= 0 \\ \phi_1''' + \lambda_1 &= 0 \\ \cdots&\cdots \end{aligned}$$

Similarly, for each of the other components, it is necessary that

$$\begin{aligned} \phi_2'' + \lambda_2 &= 0 \\ \phi_2''' + \lambda_2 &= 0 \\ \cdots&\cdots \\ \cdots&\cdots \\ \phi_c'' + \lambda_c &= 0 \\ \phi_c''' + \lambda_c &= 0 \\ \cdots&\cdots \end{aligned}$$

But Eq. (7-1-19) then reduces to

$$(\phi_1' + \lambda_1)dn_1' + (\phi_2' + \lambda_2)dn_2' + \cdots + (\phi_c' + \lambda_c)dn_c' = 0$$

where the variations dn_1', dn_2', . . . , dn_c' are no longer arbitrary, since each is determined in accordance with one of Eqs. (7-1-18), but they are none the less independent of each other. Therefore this equation is satisfied in general only if we assign to the constants λ_1, λ_2, . . . , λ_c, whose values have so far been undetermined, values satisfying the equations

$$\begin{aligned} \phi_1' + \lambda_1 &= 0 \\ \phi_2' + \lambda_2 &= 0 \\ \cdots&\cdots \\ \phi_c' + \lambda_c &= 0 \end{aligned}$$

Thus, the conditions necessary for equilibrium among the various phases are

$$\left.\begin{array}{l}\phi_1' = \phi_1'' = \phi_1''' = \cdots (= -\lambda_1) \\ \phi_2' = \phi_2'' = \phi_2''' = \cdots (= -\lambda_2) \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \phi_c' = \phi_c'' = \phi_c''' = \cdots (= -\lambda_c)\end{array}\right\} \qquad (7\text{-}1\text{-}20)$$

The thermodynamic potential of any component throughout a system in a state of equilibrium necessarily has the same value in each phase in which it may be present. For the reasons previously indicated, this law applies to any chemical constituent of fixed composition present, regardless of whether or not it happens to be convenient for the purpose of the particular investigation to consider it as one of "the" components; for one could always select the components in such a way as to include among them any one individual constituent, together with such others as would then satisfy the requirements of Eq. (7-1-11), on which the proof of Eq. (7-1-20) ultimately depends. Furthermore, the presence of phases in which certain of the components do not appear at all, and in which their thermodynamic potentials are therefore undefined, does not affect the validity of Eqs. (7-1-20) as applied to all phases at equilibrium in which the particular component does appear, as one can easily demonstrate by generalizing the argument previously given in connection with two-phase equilibrium.

The equilibrium law (7-1-20) is a special case of the general thermodynamic proposition, (5-60),

$$(\Delta F)_{T,p} \leqq 0 \qquad (W' = 0)$$

Spontaneous changes (changes taking place in the absence of applied nonthermal energy $-W'$) in a system maintained at constant temperature and pressure tend invariably in a direction such that the total free energy decreases toward an ultimate minimum consistent with the given temperature and pressure. Now, according to Eq. (7-1-10), each component of a homogeneous phase contributes to the free energy of that phase a term of the form $n_i\phi_i$; therefore the net free-energy change associated with a change of state involving solely the transfer of a small quantity Δn_i of component i from one phase to another, not necessarily in equilibrium with it, has the general form

$$\Delta F = \Delta n_i (\phi_i'' - \phi_i')$$

to a first order of approximation, assuming that the quantity Δn_i transferred is sufficiently small so that the thermodynamic potentials ϕ_i' and ϕ_i'' of the particular component in the first and second phases, respectively, are not significantly altered by the attendant changes in compositions. According to (5-60), therefore, any component of a thermodynamic system at constant temperature and pressure tends to move from a phase in which its thermodynamic potential is higher to a phase in which its thermodynamic potential is lower. Thus, we may infer that KCl in aqueous solutions at all concentrations lower than 4.81 moles/kg H_2O at 25°C and 1 atm must have a lower thermodynamic potential than that of pure KCl(c) at the same temperature and pressure, and likewise, at all concentrations higher than 4.81 moles/kg H_2O, its thermodynamic potential in aqueous solution at the given temperature and pressure must be higher than that of pure KCl(c). The thermodynamic potential serves as a measure of the substance's tendency to escape from the phase in question.[1] The analogy between the thermodynamic potential of a chemical substance and the potential functions encountered in mechanics, such as the hydrostatic potential, the gravitational potential, the electrostatic potential, etc., was pointed out by Gibbs, to whom we owe its name. The potentials of mechanics are characteristically determined solely by position with respect to other bodies; the thermodynamic potential of a material substance is determined analogously solely by the thermodynamic state of the phase in question, as represented by its temperature, pressure, and composition. We shall observe in Chap. 8 how the thermodynamic potential measures the tendency of the chemical substance to participate in chemical reactions at constant temperature and pressure, chemical reaction being in this respect a means whereby the substance may disappear from a phase in which its thermodynamic potential is sufficiently high or appear in a phase in which its thermodynamic potential is sufficiently low.

If the number of components has been correctly assigned, then the total free energy of a solution is completely determined, except possibly for an arbitrary additive constant, by the temperature, the pressure, and the quantities of the components present; expressed formally: $F = F(T, p, n_1, n_2, \ldots, n_c)$, where F satisfies the differential equation (7-1-11). The change of the thermodynamic potentials $\phi_1, \phi_2, \ldots, \phi_c$ themselves with composition at given temperature and pressure is described in general by Eq. (7-1-7). We may derive equations for the change of any thermodynamic potential with temperature or pressure at fixed composition by applying to Eq. (7-1-11) Euler's criterion for dF to be a perfect differential in terms of the independent state-determining variables $T, p, n_1, n_2, \ldots, n_c$; thus

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[1] Lewis and Randall, *op. cit.*, coined the perspicuous expression "escaping tendency" in this connection.

$$\left(\frac{d\phi_i}{dT}\right)_{p,n} = -\left(\frac{dS}{dn_i}\right)_{T,p,n'} \qquad (7\text{-}1\text{-}21)$$

$$\left(\frac{d\phi_i}{dp}\right)_{T,n} = \left(\frac{dV}{dn_i}\right)_{T,p,n'} \qquad (7\text{-}1\text{-}22)$$

where for short we have used the subscript n to denote that each of the quantities $n_1, n_2, \ldots, n_c$ is held constant during the one differentiation, and the subscript n' to denote that each of them except the one with respect to which the differentiation is being carried out is held constant in the other. The quantity on the right of Eq. (7-1-21) we recognize as the negative of the *partial molal entropy*, σ_i, of component i, and the quantity on the right of Eq. (7-1-22) as the *partial molal volume*, v_i, of component i,

$$\left(\frac{d\phi_i}{dT}\right)_{p,n} = -\sigma_i \qquad (7\text{-}1\text{-}23)$$

$$\left(\frac{d\phi_i}{dp}\right)_{T,n} = v_i \qquad (7\text{-}1\text{-}24)$$

The partial molal volumes of the components may be evaluated from experimental data for the volume changes on combining the components in various proportions by essentially the same mathematical techniques that were described in Sec. 4-5 for the evaluation of partial molal enthalpies from heats of solution. For liquid and solid solutions generally, the relatively small magnitudes of the partial molal volumes imply that the thermodynamic potentials of the components are relatively insensitive to the pressure, just as the molal free energy of a pure liquid or solid is insensitive to variations in the pressure; for pressure variations of order 1 atm or less, one may ordinarily disregard the effect of pressure on the thermodynamic potentials in liquid or solid solutions (see footnote on page 337, Sec. 7-3).

Equation (7-1-23) may be conveniently transformed by a method similar to that used on Eq. (6-9); thus, by applying the definitions of the partial molal quantities to the general relationship defining F,

$$-S = \frac{F - H}{T}$$

it follows that for a solution

$$-\sigma_i = \frac{\phi_i - \eta_i}{T} \qquad (7\text{-}1\text{-}25)$$

where η_i represents the *partial molal enthalpy* of component i at the given temperature, pressure, and composition, as introduced in Sec. 4-5. Substituting in Eq. (7-1-23) and rearranging terms,

$$\left(\frac{d\phi_i}{dT}\right)_{p,n} - \frac{1}{T}\phi_i = -\frac{\eta_i}{T}$$

This equation reduces to the forms

$$\left[\frac{d(\phi_i/T)}{dT}\right]_{p,n} = -\frac{\eta_i}{T^2} \tag{7-1-26a}$$

or

$$\left[\frac{d(\phi_i/T)}{d(1/T)}\right]_{p,n} = \eta_i \tag{7-1-26b}$$

Thus, the change of any ϕ_i with temperature depends on η_i for the particular component in the same way that the change of $\bar{F}$ for a substance of fixed composition depends on $\bar{H}$ [compare Eqs. (6-12) and (6-13)]; and in the same sense, the change of any ϕ_i with pressure, according to Eq. (7-1-24), depends on v_i in the same way that the change of $\bar{F}$ for a substance of fixed composition depends on $\bar{V}$ [compare Eq. (6-10)]. Equations (7-1-24) and (7-1-23) or (7-1-26) serve when the necessary thermal and equation-of-state data for the solution are available to determine each ϕ_i at other temperatures and pressures, once its value for the particular composition has been established at some standard reference temperature and pressure; conversely, measurement of the temperature or pressure coefficient of any ϕ_i for a particular composition serves as an indirect means of establishing the value of η_i or v_i, respectively.

In the following sections, we take up specific methods of establishing the values of the thermodynamic potentials in various types of solutions important to chemical thermodynamics. One should recognize that from the standpoint of general theory the possibility of change of composition has introduced new variables into the problem, whose effects on the thermodynamic properties cannot be foreseen by purely thermodynamic reasoning. There is no purely thermodynamic connection between the properties of the solution and the properties of the pure components; rather, our objective in the study of solutions must be to establish by experimental observation, guided possibly by empirical or theoretical generalizations of nonthermodynamic origin (analogous for example to the ideal-gas equation of state), how the properties of a particular solution actually are related to the properties of the components and the composition. Thermodynamic reasoning then interrelates the properties in a manner conducive to systematic economy, so that, for example, from measurements of the partial vapor pressure of H_2S in aqueous solution, one can predict the effect of H_2S concentration on the equilibrium state of a chemical reaction involving H_2S in aqueous solution, or from measurements of the vapor pressure of H_2O from aqueous sucrose solutions, one can predict the osmotic pressures of those solutions. Empirical establishment of the values of the thermodynamic potentials $\phi_1, \phi_2, \ldots, \phi_c$ (or of appropriate functions of these fundamental quantities) as functions of the composition at given temperature and pressure, relative to the molal free energies $\bar{F}_1, \bar{F}_2, \ldots, \bar{F}_c$ of the pure components, constitutes the experimental problem whose answer comprehends the general thermodynamic behavior of the solution in the systematically most simple form.

7-2. Gaseous Solutions. In order to establish the values of the thermodynamic potentials of the components in a gas mixture, it would be convenient according to the principle established in Sec. 7-1 if we could determine the conditions under which the respective pure components would be in equilibrium with the mixture; for then the thermodynamic potentials would be equal, respectively, to the molal free energies of the pure components, and we have already seen in Sec. 6-1 how to calculate the molal free energy of a pure gaseous substance (characterized by invariant composition) at various temperatures and pressures relative to its value in some arbitrary reference state. Now, equilibrium with the mixture could be established with respect to any single pure component if we had a semipermeable diaphragm serving as a window of the container which would permit the free transfusion of the one gas but not that of the others. In a few cases, this technically difficult experiment has actually been carried out; thus, by making use of a palladium window, which at temperatures around 300°C is permeable to hydrogen but not to nitrogen, Sir William Ramsay was able to establish equilibrium between pure hydrogen gas on the one side and a mixture of hydrogen with nitrogen (and with certain other gases, such as CO and CO_2, to which palladium is also impermeable at the given temperature and sufficiently low pressures) on the other.[1] Experiments of this nature, while not precise, on account of the slowness with which equilibrium is attained, have afforded direct confirmation in the low-pressure range of the concept proposed originally by John Dalton that to a first approximation, the constituents of a gas mixture behave independently of each other, contributing to the total pressure, for example, terms equal to the pressures each would exert in the absence of the other constituents.[2] Thus, in Ramsay's experiments, the increase of pressure observed on the nitrogen side of the palladium septum upon exposure to pure hydrogen on the other side was

[1] W. Ramsay, *Phil. Mag.*, (5) **38**, 206–218 (1894).

[2] J. Dalton, *Mem. Manchester Lit. & Phil. Soc.*, (2) **1**, 244–258 (1805); this paper appears in *Alembic Club Reprint* 2, published for the Alembic Club by Oliver & Boyd, Ltd., Edinburgh and London, 1923.

found to be approximately equal to the pure hydrogen pressure, so that one is justified in supposing that at sufficiently low total pressures (of order 2 atm or less in Ramsay's experiments), nitrogen and hydrogen in each other's presence continue to exert the same pressures as though the other component were not there. Because of mechanical difficulties, unfortunately, such direct equilibrium measurements have not been feasible at high pressures, where one would surely expect to find that, in general, the increase of total pressure resulting from the presence of the second component would influence the equilibrium pressure of the first.

In most cases, we do not have experimental means by which the true equilibrium pressures of the pure components can be observed directly at all, much less measured precisely, and we are therefore compelled to rely on more or less indirect evidence. Many gas mixtures can be treated with sufficient accuracy, particularly in the low-pressure range, by means of *Dalton's law of partial pressures: Each constituent contributes to the total pressure a partial pressure (Dalton pressure) equal to the pressure it would exert if it alone were present at the given temperature in the volume occupied by the mixture.* We may put Dalton's law in precise mathematical form as follows, bearing in mind that experimental p-V-T data for gases are commonly represented in terms of the compressibility factor $z = p\bar{V}/RT$ (or alternatively in terms of $pV/(pV)_0$, where $(pV)_0$ represents the pressure-volume product of an arbitrary reference quantity of the gas at some standard temperature and pressure, such as 0°C and 1 atm). Let $\bar{V}$ represent the volume per mole of gas *mixture*, $\bar{V} = V/(n_1 + n_2 + \cdots + n_c)$ at the given temperature T and pressure p; then $\bar{V}/y_i$ will represent the volume per mole of component i, where y_i is its mole fraction.[1] In other words, if component i alone were to occupy the volume of the mixture at the given temperature, then its molal volume would be $\bar{V}/y_i$. Let p_i represent the Dalton partial pressure of component i; then, by definition:

$$p_i\left(\frac{\bar{V}}{y_i}\right) = p_i\bar{V}_i$$

where $\bar{V}_i$ is the molal volume of pure component i at temperature T and pressure p_i; thus

$$p_i = \frac{y_i}{\bar{V}}(p_i\bar{V}_i)$$

Multiplying numerator and denominator of the term on the right by p,

$$p_i = y_i p\,\frac{(p_i\bar{V}_i)}{(p\bar{V})} = y_i p\,\frac{z_i(T, p_i)}{z(T, p)} \quad \text{(Dalton } p_i\text{)} \qquad (7\text{-}2\text{-}1)$$

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[1] In this chapter, where we shall have occasion to discuss liquid-vapor equilibrium, we use y_i to denote the mole fraction of component i in the gas phase, retaining x_i to denote its mole fraction in particular in a liquid or a solid phase.

where $z_i(T, p_i)$ represents the compressibility factor of pure component i at T and p_i, and $z(T, p)$ represents the compressibility factor of the mixture at T and p. Equation (7-2-1) may be solved for p_i by means of successive approximations, given the value of z (or of $p\bar{V}$) for the mixture, and experimental data for z_i (or $p_i\bar{V}_i$) at the given temperature expressed as a function of p_i. The experimental test of Dalton's law consists of comparing the sum of the Dalton partial pressures so derived from equation-of-state data for the pure constituents with the actual pressure of the mixture. Table 7-1 presents data for a mixture of hydrogen and nitrogen, selected from the extensive work of E. P. Bartlett and his associates; for a mixture of hydrogen and carbon monoxide, selected from the work of Townend and Bhatt; and for a mixture of argon and ethylene, selected from the work of Masson and Dolley. The Dalton partial pressures satisfying Eq. (7-2-1) are given in the fifth and sixth columns of this table, and their sums in the seventh column; one sees that Dalton's law is quite satisfactory for these gas mixtures at pressures of order 50 atm or less, but at pressures beyond 100 atm, it becomes increasingly unreliable as the total pressure is further increased.

Some gas mixtures, including the H_2-N_2 and the H_2-CO mixtures under the conditions of Table 7-1, show better agreement in the high-pressure range with *Amagat's law of additive volumes:*[1] *The volume occupied by the gas is equal to the sum of the volumes each pure constituent would occupy if it were separately at the temperature and pressure of the mixture.* Amagat's law is equivalent to the supposition that each constituent contributes to the total pressure a term equal to the pressure it would exert if it alone occupied the volume of the mixture, but if its compressibility factor corresponded to the pressure p of the mixture instead of to its own partial pressure. For according to Amagat's law,

$$\bar{V} = y_1\bar{V}_1 + y_2\bar{V}_2 + \cdots + y_c\bar{V}_c$$

where the molal volume of the mixture $\bar{V}$ and the molal volumes of the pure constituents $\bar{V}_1, \bar{V}_2, \ldots, \bar{V}_c$ are all taken at the temperature T and pressure p of the mixture; therefore

$$\begin{aligned} p\bar{V} &= y_1(p\bar{V}_1) + y_2(p\bar{V}_2) + \cdots + y_c(p\bar{V}_c) \\ p &= y_1p\,\frac{(p\bar{V}_1)}{(p\bar{V})} + y_2p\,\frac{(p\bar{V}_2)}{(p\bar{V})} + \cdots + y_cp\,\frac{(p\bar{V}_c)}{(p\bar{V})} \end{aligned}$$

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[1] Named after the French physicist E. H. Amagat who during the latter part of the nineteenth century extended H. V. Regnault's pioneer work on the physical properties of gases to really high pressures (as high as 3000 atm). The law is also known as Leduc's law of partial volumes; see A. Leduc, *Compt. rend.*, **126,** 218–220 (1898).

TABLE 7-1. COMPRESSIBILITIES AND PARTIAL PRESSURES OF GAS MIXTURES

Hydrogen-Nitrogen at 0°C[*]

Observed data				Calculated quantities					
				Dalton's law			Amagat's law		
p, atm	$3H_2:1N_2$, pV	H_2, pV	N_2, pV	p_{H_2}	p_{N_2}	Sum	p_{H_2}	p_{N_2}	Sum
0	0.9995	0.9994	1.0005						
1	(1.0000)	(1.0000)	(1.0000)	0.7500	0.2503	1.0003	0.7500	0.2503	1.0003
50	1.0269	1.0330	0.9846	37.4	12.1	49.5	37.8	12.0	49.8
100	1.0583	1.0639	0.9846	74.3	23.4	97.7	75.5	23.3	98.8
200	1.1278	1.1336	1.0365	146.4	43.6	190.0	151.2	46.1	197.3
400	1.2890	1.2775	1.2557	278	76	354	297.8	97.8	395.6
800	1.6342	1.5665	1.7959	434	121	555	575.2	220.0	795.2
1000	1.8029	1.7107	2.0641	591	139	730	713.3	287.2	1000.5

Hydrogen-Carbon Monoxide at 25°C[†]

Observed data				Calculated quantities					
				Dalton's law			Amagat's law		
p, atm	$2H_2:1CO$, pV	H_2, pV	CO, pV	p_{H_2}	p_{CO}	Sum	p_{H_2}	p_{CO}	Sum
0	1.0909	1.0909	1.0918						
1	1.0915	1.0915	1.0915	0.6667	0.3336	1.0003	0.6667	0.3336	1.0003
100	1.1480	1.1556	1.0838	65.7	31.4	97.1	67.0	31.4	98.4
200	1.2176	1.2245	1.1382	129.0	59.5	188.5	134.5	62.4	196.9
300	1.2968	1.2960	1.2344	187.1	83.5	270.6	199.9	95.2	295.1
400	1.3820	1.3686	1.3565	241	105	346	263.9	130.8	394.7
500	1.4694	1.4411	1.4908	293	124	417	326.8	169.4	496.2
600	1.5560	1.5128	1.6252	340	142	482	389.1	209.2	598.3

Argon-Ethylene at 24.95°C[‡]

p, atm	Observed data			Calculated quantities					
				Dalton's law			Amagat's law		
	50.05 mole % A, pV	A, pV	C_2H_4, pV	p_A	$p_{C_2H_4}$	Sum	p_A	$p_{C_2H_4}$	Sum
50	0.8773	0.9714	0.6467	28.0	24.1	52.1	27.7	18.4	46.1
75	0.8229	0.9619	0.3666	44.4	35.2	79.6	43.9	16.7	60.6
100	0.7758	0.9551	0.3596	62.3	44.8	107.1	61.5	23.2	84.7
125	0.7436	0.9513	0.4081	81.0	52.4	133.4	80.0	34.3	114.3

[*] Compressibility data of E. P. Bartlett, H. L. Cupples, and T. H. Tremearne, *J. Am. Chem. Soc.*, **50**, 1275–1288 (1928). For each gas, $pV = 1.0000$ at 0°C and 1 atm; therefore the compressibility factor ratios appearing in Eqs. (7-2-1) and (7-2-2) for $y_{N_2} = 0.25$ and $y_{H_2} = 0.75$ have been computed as follows:

$$\frac{z_{N_2}}{z} = \frac{1.0005}{0.9995}\,\frac{(pV)\text{ for }N_2}{(pV)\text{ for mixture}};\qquad \frac{z_{H_2}}{z} = \frac{0.9994}{0.9995}\,\frac{(pV)\text{ for }H_2}{(pV)\text{ for mixture}}$$

(the factors 1.0005/0.9995 and 0.9994/0.9995 correct for slight deviations from ideal-gas behavior at standard conditions, 0°C and 1 atm).

[†] Compressibility data of D. T. A. Townend and L. A. Bhatt, *Proc. Roy. Soc.* (*London*), (A)**134**, 502–512 (1931). For each gas, $pV = 1.0000$ at 0°C and 1 atm; the compressibility factor ratios appearing in Eqs. (7-2-1) and (7-2-2) for $y_{CO} = 0.3333$ and $y_{H_2} = 0.6667$ have been computed as follows:

$$\frac{z_{CO}}{z} = \frac{1.0918}{1.0909}\,\frac{(pV)\text{ for CO}}{(pV)\text{ for mixture}};\qquad \frac{z_{H_2}}{z} = \frac{1.0909}{1.0909}\,\frac{(pV)\text{ for }H_2}{(pV)\text{ for mixture}}$$

[‡] Gas-density data of I. Masson and L. G. F. Dolley, *Proc. Roy. Soc.* (*London*), (A)**103**, 524–538 (1923). For each gas, $pV = 1.0000$ at 24.95°C and 1 atm; correction for deviation from ideal-gas behavior at 1 atm has been neglected in the above computations.

We may therefore define Amagat partial pressures by expressions of the form

$$p_i = y_i p \frac{(p\bar{V}_i)}{(p\bar{V})} = y_i p \frac{z_i(T, p)}{z(T, p)} \quad \text{(Amagat } p_i\text{)} \qquad (7\text{-}2\text{-}2)$$

where $z(T, p)$ represents the compressibility factor of the mixture at the temperature T and the pressure p and $z_i(T, p)$ represents the compressibility factor of pure component i at the *same* temperature and pressure. In the eighth and ninth columns of Table 7-1, Amagat partial pressures have been computed according to Eq. (7-2-2) from the experimental data; their sums, given in the last column of the table, show that Amagat's law is in excellent agreement with the data for the H_2-N_2 and the H_2-CO mixtures, even at the highest pressures recorded. That this is not universally true is shown by the comparatively poor agreement in the case of the argon-ethylene mixture.

From the kinetic molecular point of view, Dalton's law corresponds to the supposition that the molecules of each constituent gas behave entirely independently of those of the other constituents, though not necessarily of each other. Amagat's law, on the other hand, corresponds to the supposition that the molecules of all the constituents exert the same effects on each other, including molecules of the same and of different kinds, as they would exert in the pure state at the same total pressure. Now, for the H_2-N_2 and the H_2-CO mixtures represented in Table 7-1, at the respective temperatures 0°C and 25°C, both pure components in either case at pressures exceeding 100 atm are in regions where the compressibility factor is increasing with pressure; in other words, the van der Waals "b" effect (finite molecular dimensions) predominates in this region over the "a" effect (intermolecular attraction). This is evident in Fig. 7-1, where the compressibility factors of H_2, N_2, and the $3H_2$-N_2 mixture have been plotted at 0°C against the pressure; one sees that between 250 atm and 1000 atm, z_{N_2} increases from 1.086 to 2.069, while over the same pressure range, z_{H_2} increases from 1.176 to 1.715. It is therefore not surprising to find that if one were to start with pure N_2 at 0°C and 250 atm, and increase the total pressure by adding hydrogen, the contribution of N_2 to the total pressure would increase, while likewise, the contribution of H_2 to the total pressure of the mixture would be greater than its pressure in the pure state at the temperature and volume of the mixture; in other words, we find that the compressibility of N_2 in the mixture is reduced on account of the finite space occupied by the H_2 molecules to about the same extent to which it would be reduced if one were to compress additional N_2 molecules (instead of the H_2 molecules) into the container until the pressure reached the same value. A similar conclusion may be drawn from Fig. 7-2, where the compressibility factors of H_2, CO, and the $2H_2$:1CO mixture at 25°C have been plotted against pressure. The case of argon-ethylene mixtures is rather different (Fig. 7-3); ethylene at 25°C is still far below its Boyle point, and at pressures up to 80 atm, the effect of intermolecular attraction evidently predominates greatly over the effect of finite molecular size on the compressibility; for argon, on the other hand, the effect of intermolecular attraction at 25°C must be relatively insignificant. In these circumstances, it is not surprising to find that, at least up to 100 atm, the presence of the argon molecules has comparatively little effect on the behavior of the ethylene molecules, as shown by the better agreement of the mixture with Dalton's law rather than with Amagat's law. There is, however, some indication from the trend of the data that at pressures beyond 125 atm, Amagat's law might come to fit the data better than Dalton's law.

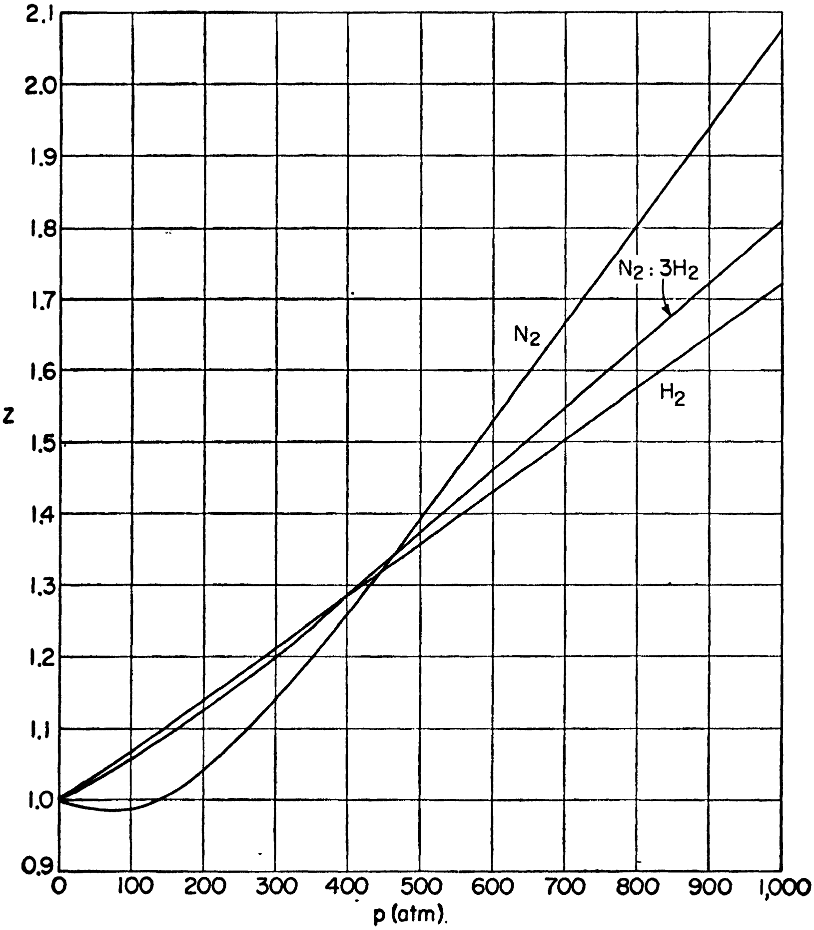

FIG. 7-1. Compressibility factors of N_2, H_2, and N_2:$3H_2$ mixture at 0°C. *(From data of E. P. Bartlett, H. L. Cupples, and T. H. Tremearne.)*

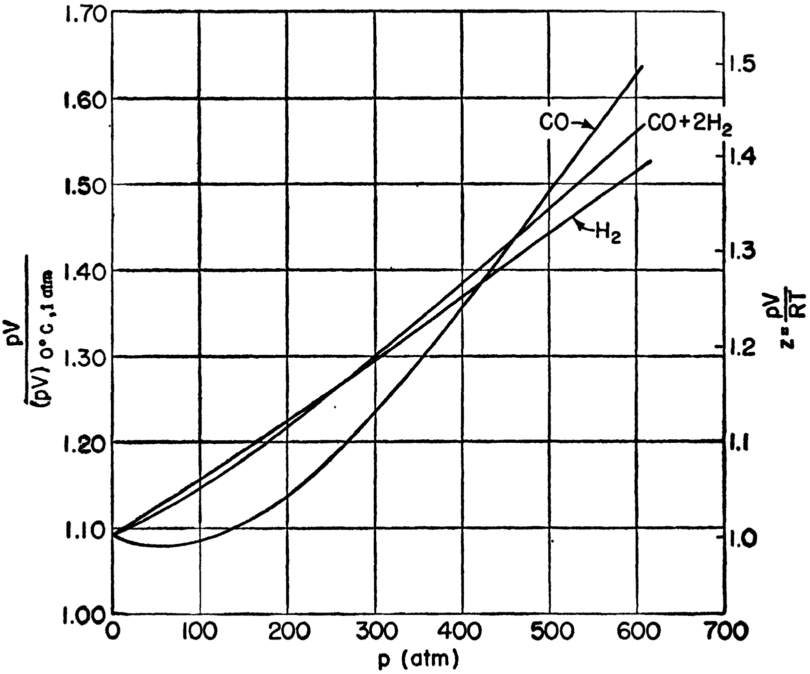

FIG. 7-2. Compressibilities of H_2, CO, and CO:$2H_2$ mixture at 25°C. (*From data of D. T. A. Townend and L. A. Bhatt.*)

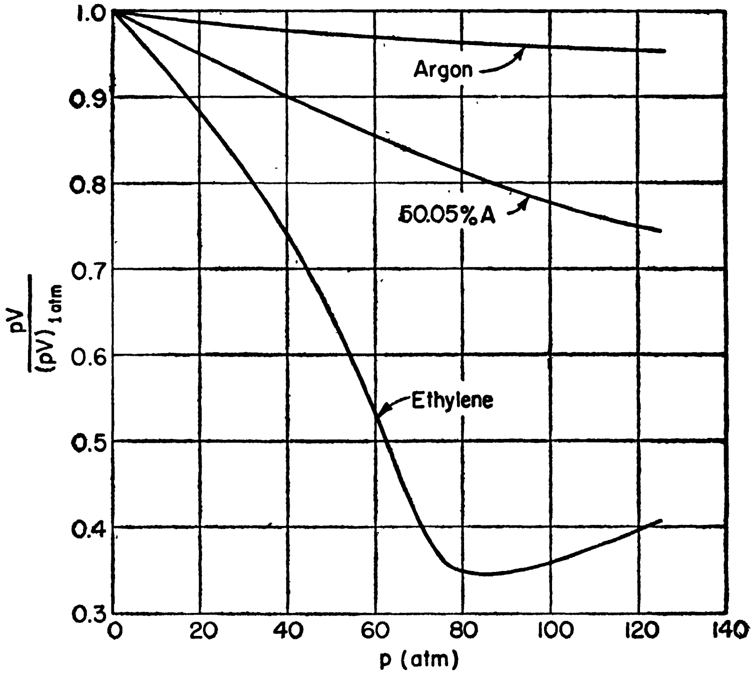

FIG. 7-3. Compressibilities of argon, ethylene, and 50.05 mole per cent argon-ethylene mixture at 24.95°C. (*From data of I. Masson and L. G. F. Dolley.*)

If we had a mixture at moderately high pressure of two gases both well below their Boyle points, so that intermolecular attraction would be a dominant influence over its behavior, then the specific intermolecular attraction between the two different kinds of molecules might be quite different in magnitude from the attractions between like molecules; in such a situation, neither Dalton's law nor Amagat's law could be expected to give a satisfactory description of the behavior at pressures beyond the ideal-gas-law range. H. A. Lorentz carried out an extension of van der Waals' theory to binary gas mixtures,[1] obtaining an equation of state similar in form to van der Waals' original equation, but with constants a and b dependent on the composition in the form (per mole of gas mixture)

$$a = a_{11}y_1^2 + 2a_{12}y_1y_2 + a_{22}y_2^2$$
$$b = b_{11}y_1^2 + 2b_{12}y_1y_2 + b_{22}y_2^2$$

In these equations, a_{11} and b_{11} represent the van der Waals constants of the one pure component gas, and a_{22} and b_{22} the corresponding constants for the other; a_{12} and b_{12} represent additional empirical constants allowing for the mutual interaction between the two different kinds of molecules. Since van der Waals' equation is itself too crude to be of practical value, the form assumed by this extension to binary mixtures is indicative, rather than actually useful. W. B. Kay has shown that the generalized compressibility factor chart shown in Fig. 6-1, based on the theory of corresponding states, may be applied with some degree of satisfaction to gas mixtures, provided that one assigns a *pseudocritical* temperature and pressure for the purpose of computing the reduced temperature and pressure of the mixture; these pseudocritical constants may be estimated by averaging the values for the pure components, in the forms

$$T'_c = y_1(T_c)_1 + y_2(T_c)_2 + \cdots + y_c(T_c)_c$$
$$p'_c = y_1(p_c)_1 + y_2(p_c)_2 + \cdots + y_c(p_c)_c$$

and they are generally lower than the actual critical constants for the mixture; the compressibility factor z of the mixture may then be estimated from the chart as in the case of a pure gas having critical constants equal to the pseudocritical values.[2] Direct experimental p-V-T data for gas mixtures at high pressures are still comparatively scarce, although there is a steadily growing body of such information.[3]

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[1] H. A. Lorentz, *Ann. Physik u. Chem.*, **12,** 127–136 (1881).

[2] W. B. Kay, *Ind. Eng. Chem.*, **28,** 1014–1019 (1936).

[3] Attention is called to the work of B. H. Sage and W. N. Lacey with their associates at California Institute of Technology on hydrocarbon mixtures; for a complete list of the published papers in this important series covering 1934 through March, 1949, see

Now, in the low-pressure ideal-gas range, both Dalton's law (7-2-1) and Amagat's law (7-2-2) reduce to

$$p_i = y_i p \qquad \text{(ideal gas } p_i\text{)} \qquad (7\text{-}2\text{-}3)$$

where, for each component,

$$p_i \equiv \frac{n_i}{V} RT \qquad \text{(ideal gas } p_i\text{)} \qquad (7\text{-}2\text{-}4)$$

If over the pressure range under consideration, the pure components satisfy the ideal-gas law within sufficient accuracy for one's purpose, then their partial pressures in the mixture, whether defined in the Dalton or the Amagat sense, are given by Eq. (7-2-4), where n_i denotes the number of moles of component i present in the volume V of the mixture. Certainly in this case, the partial pressures calculated according to either Eq. (7-2-3) or Eq. (7-2-4) must agree with the pressures at which the respective pure component gases would be in equilibrium with the mixture through hypothetical semipermeable diaphragms appropriate to each gas (as has actually been demonstrated in certain cases by the experiments of Ramsay previously described). Therefore in accordance with the equilibrium principle outlined in Sec. 7-1, together with Eq. (6-17) which relates the molal free energy of a pure ideal gas of fixed composition to its pressure at given temperature, the thermodynamic potential of each component of an ideal-gas mixture at given temperature T must be given by an expression of the form

$$\begin{aligned} \phi_i &= (\bar{F}_{T,p_i})_i = (\bar{F}^\circ_T)_i + RT \ln p_i \\ &= (\bar{F}^\circ_T)_i + RT \ln p + RT \ln y_i \qquad \text{(ideal gas)} \qquad (7\text{-}2\text{-}5) \end{aligned}$$

where $(\bar{F}^\circ_T)_i$ represents the standard molal free energy of pure component i as a gas at the temperature T (and at 1 atm, within the accuracy of the ideal-gas-law approximation).

The total free energy per mole of ideal-gas mixture, in view of Eq. (7-1-10) and Eqs. (7-2-5), is given by

$$\begin{aligned} \bar{F}_{T,p} &= y_1\phi_1 + y_2\phi_2 + \cdots + y_c\phi_c \\ &= y_1[(\bar{F}^\circ_T)_1 + RT \ln p] + y_2[(\bar{F}^\circ_T)_2 + RT \ln p] + \cdots \\ &\quad + y_c[(\bar{F}^\circ_T)_c + RT \ln p] + y_1 RT \ln y_1 + y_2 RT \ln y_2 + \cdots \\ &\qquad + y_c RT \ln y_c \end{aligned}$$

Ind. Eng. Chem., **41**, 474 (1949). Masson and his associates have reported work on oxygen-ethylene, argon-oxygen, argon-hydrogen, and argon-helium mixtures, as well as the argon-ethylene mixtures referred to in Table 7-1 [I. Masson and L. G. F. Dolley, *Proc. Roy. Soc.* (*London*), (A) **103**, 524–538 (1923); C. C. Tanner and I. Masson, *ibid.*, (A) **126**, 268–288 (1930)]. Data for N_2-CH_4 mixtures are given by F. G. Keyes and H. G. Burks, *J. Am. Chem. Soc.*, **50**, 1100–1106 (1928).

This equation may be rearranged in the form

$$\bar{F}_{T,p} - y_1[(\bar{F}^\circ_T)_1 + RT \ln p] - y_2[(\bar{F}^\circ_T)_2 + RT \ln p] - \cdots \\ - y_c[(\bar{F}^\circ_T)_c + RT \ln p] = RT(y_1 \ln y_1 + y_2 \ln y_2 + \cdots \\ + y_c \ln y_c)$$

The expression on the left represents the difference between the free energy of the mixture and the sum of the free energies of the pure component gases, each at the same temperature T and pressure p as the mixture; the expression on the right must therefore correspond to the ideal free energy of mixing, when each pure component is originally at uniform temperature T and pressure p, and the mixture is finally at the same temperature T and pressure p,

$$\Delta \bar{F}_{T,p} = RT(y_1 \ln y_1 + y_2 \ln y_2 + \cdots + y_c \ln y_c) \qquad (7\text{-}2\text{-}6)$$

This ideal-gas free energy of solution is independent of the particular uniform pressure at which the gases are permitted to mix. The entropy of mixing is related to the free energy of mixing in general by the equation

$$\Delta \bar{S} = -\left(\frac{d\Delta \bar{F}}{dT}\right)_{p,n}$$

Therefore over a temperature range in which the gas mixture continues to satisfy the ideal-gas law at the given pressure:

$$\Delta \bar{S}_{T,p} = -R(y_1 \ln y_1 + y_2 \ln y_2 + \cdots + y_c \ln y_c) \qquad (7\text{-}2\text{-}7)$$

This ideal-gas entropy of solution is independent of the particular uniform temperature as well as of the particular uniform pressure at which the mixture and the pure components are compared. Since the mole fractions $y_1, y_2, \ldots, y_c$ are all necessarily positive numbers smaller than 1, the value of $\Delta \bar{S}_{T,p}$ is essentially positive, corresponding to the fact that interdiffusion of the component gases is a thermodynamically irreversible process. The enthalpy of mixing is related to $\Delta \bar{F}_{T,p}$ and $\Delta \bar{S}_{T,p}$ in general by

$$\Delta \bar{H}_{T,p} = \Delta \bar{F}_{T,p} + T\,\Delta \bar{S}_{T,p}$$

Therefore, according to Eqs. (7-2-6) and (7-2-7), the enthalpy of solution in the case of an ideal-gas mixture is zero; in other words, the free diffusion of one gas into another at uniform temperature and pressure is accompanied by no net exchange of thermal energy with the surroundings. If, for example, one conducts a Joule experiment (compare Sec. 3-5) with different gases at the same pressure on either side of the stopcock, instead of with a gas on one side and a vacuum on the other, then when the stopcock is opened the two gases intermix, exchanging no net heat with the surroundings, provided that the original pressure is sufficiently low so that the ideal-gas law is satisfied. One will note that in this experiment, the total entropy increases by the same amount as though each component gas had separately expanded at the given temperature from its initial to the final volume; for if V_1 represents the initial volume of the one gas and V_2 the initial volume of the other, and if V represents their final combined volume $(= V_1 + V_2)$, then for an ideal-gas mixture, $y_1 = V_1/V$ and $y_2 = V_2/V$, whence according to Eq. (7-2-7) the entropy change *per mole of gas mixture* is given by $\Delta\tilde{S} = -R[y_1 \ln (V_1/V) + y_2 \ln (V_2/V)]$; but the terms $-Ry_1 \ln (V_1/V)$ and $-Ry_2 \ln (V_2/V)$ according to Eq. (6-46) represent, respectively, the entropy changes per y_1 mole of component 1 in expanding from V_1 into V and per y_2 mole of component 2 in expanding from V_2 into V. A similar conclusion evidently applies to the mixing of more than two ideal gases.

Equation (7-2-7) raises a significant issue discussed by Gibbs, which gives us further insight into the nature of thermodynamic investigation.[1] Suppose we conduct a Joule experiment such as has just been described, using two different gases at equal initial pressures on either side of the stopcock; then, supposing for concreteness that the two halves of the container have exactly equal volumes, the change of entropy taking place after the connecting stopcock has been opened allowing the gases to interdiffuse is equal to $R \ln 2$ per mole of gas in the mixture. We recognize this calculated value of the entropy change as a measure of deferred "degradation" of energy. Since in this experiment no work is done and no heat is exchanged with the surroundings, there has been no immediate change in the relationship of the system to its surroundings to correspond to the obvious change that has taken place in the state of the gas. Our experience summarized in the second law of thermodynamics leads us, however, to the discovery that if at some future time we wish to separate the two gases, restoring the system to its original state, then this can be accomplished only to the accompaniment of certain inevitable changes in the surroundings, changes equivalent to the conversion of a certain quantity of energy in nonthermal form to energy in thermal form; the entropy change that has taken place measures how large this quantity of energy has to be, in the sense that it will be at least equal to $T^* \Delta S$ ($RT^* \ln 2$ per mole of gas mixture, in the particular example under discussion), where T^* represents the temperature of the coldest part of the surroundings available to receive the expended thermal energy at the time the transaction is completed. Now, suppose we conduct a similar experiment, using instead two samples of the *same* gas at equal pressures on either side of the stopcock. When the stopcock is opened, again no exchange in any form

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[1] Gibbs, *op. cit.*, pp. 165–168.

of energy with the surroundings takes place, but now we say that neither is there a change of entropy. If one could conduct a detailed examination that would distinguish the individual molecules, one would undoubtedly have to conclude that the gas could not be separated again into identically the same two portions without leaving a "permanent" change in the surroundings, just as in the case of the two different gases. It is precisely because we do *not* distinguish such differences in thermodynamic investigation that we assign no entropy change to the self-diffusion of the one gas; we say that the entropy of the two portions when "mixed" is the same as it was before the stopcock was opened, not necessarily to imply that no change whatever has taken place in the gas occupying either half of the container, but in the sense that we are unable to *perceive* any such change by the relatively insensitive methods of thermodynamic experimentation, where we are always observing average properties of huge assemblies of molecules. Quantum mechanics, indeed, goes so far as to deny altogether any distinction between states of a molecular system differing only by the interchange of identical particles (such a distinction, if it existed, would serve of itself as a means of discriminating between the supposedly identical particles). It is therefore meaningless to speak of a hypothetical change that might restore the individual molecules of the gas to the respective halves of the container in which they were originally confined, because no operation exists by which such a state could be distinguished from other states in which the same *numbers* of molecules (regardless of individuality) are present on either side (including the state produced merely by the reclosing of the stopcock at any arbitrary time after it has been opened).

A pertinent question arises in regard to isotopic composition of the chemical elements. Chlorine, for example, consists of Cl^{35} and Cl^{37} in 0.754:0.246 proportion, so that the entropy of the normal isotopic mixture is greater by $-R(0.754 \ln 0.754 + 0.246 \ln 0.246)$ units per gram-atom than the entropy of the separated pure isotopes. Which is the proper reference base for the thermodynamic properties of chlorine and its compounds? It all depends on our purpose. So long as we are dealing exclusively with ordinary physical or chemical transformations that leave the isotopic ratio sensibly unchanged, there is no point in carrying the entropy of isotope mixing, because this term would only cancel out of all calculations; ordinary physical and chemical transformations do not in fact discriminate between the two isotopes, and therefore the existence of the two kinds of isotopes has no bearing on the ordinary thermodynamic properties of chlorine. But in problems of the enrichment of isotopes, or in other situations where the isotopes are distinguished from each other by some significant difference in behavior (*e.g.*, in tracer studies, where the tracer is distinguished either by means of the mass spectrograph or by means of its radioactivity), then the entropy of mixing becomes significant.

At first sight, it may appear strange that the ideal entropy of mixing does not depend in any way on the particular nature of the substances involved. It is just as large for two substances such as the chlorine isotopes, that are all but indistinguishable by ordinary methods of investigation, as for substances that are easily distinguished, such as oxygen and nitrogen. On reflection, however, one realizes that one either *has* a method by which the constituent substances can be distinguished (and which could always be extended in principle to provide a means of separating them), or has not. So long as one has not, the question of a possible separation never arises, and the question of a possible entropy of mixing has no meaning; as soon as one has such a method, then it becomes obvious that a mixture such as the chlorine isotopes is just as thoroughly scrambled, no more nor less, as a mixture in similar relative proportion of oxygen with nitrogen. The entropy of mixing measures precisely this degree of "mixed-up-ness," which is recognized as soon as one has discovered a means of distinguishing the constituents, however slight the distinction may be, and however technically difficult the means of separation.

Equation (7-2-5) contains the answer to our problem of how the thermodynamic potentials of the components are determined in an ideal gas mixture. In a gas mixture at high pressure, outside the ideal-gas range, the partial pressures of the components have no clearly defined significance. As we have noted, the partial pressures defined by Dalton's law are in general not equal to the partial pressures defined by Amagat's law, nor have we reason to believe that either of these partial pressures would be equal to the pressure at which the particular pure component would be in equilibrium with the mixture through a hypothetical selective diaphragm suitable for the purpose. Furthermore, the sums of these three differently defined sets of partial pressures do not necessarily equal the actual total pressure. For thermodynamic purposes, the partial pressures are of no consequence in themselves, however they may be defined, but serve merely as convenient reference bases in relation to the thermodynamic potentials, which are the truly significant and rigorously defined thermodynamic properties of the mixture. It is customary therefore for *formal partial pressures* to be *defined* by means of equations formally identical with (7-2-3):

$$p_i \equiv y_i p \qquad \text{(formal } p_i\text{)} \qquad (7\text{-}2\text{-}8)$$

In the low-pressure range, where the ideal-gas law is applicable, partial pressures so defined are identical with the experimentally determined

Dalton and Amagat partial pressures, and presumably also with the thermodynamic equilibrium pressures of the respective pure components (as conceived through the agency of appropriate selective diaphragms); but at high pressures, they have purely formal significance, bearing no special relation to the behavior of the gas except as conventional forms for representing its composition.[1] The thermodynamic potentials are then conventionally translated into *fugacity coefficients* by means of expressions of the form

$$\begin{aligned}\phi_i &\equiv (\bar{F}^\circ_T)_i + RT \ln p_i\nu_i \\ &\equiv (\bar{F}^\circ_T)_i + RT \ln p + RT \ln y_i + RT \ln \nu_i \qquad (7\text{-}2\text{-}9)\end{aligned}$$

where $(\bar{F}^\circ_T)_i$ represents the standard molal free energy of pure component i as a gas at T and ν_i represents its fugacity coefficient in the mixture, *defined* by Eq. (7-2-9). In view of the ideal limiting form (7-2-5), we may take

$$\lim_{p\to 0} \nu_i = 1 \quad (T, y_1, y_2, \ldots, y_c \text{ const}) \qquad (7\text{-}2\text{-}10)$$

for each component at any composition. The mathematical advantages gained by the introduction of fugacity coefficients for gas mixtures are similar to those gained by the introduction of fugacity coefficients for pure gases (compare Sec. 6-1); they vary much less rapidly with p than the thermodynamic potentials themselves, and in particular remain finite, satisfying Eq. (7-2-10), in the ideal-gas limit as $p \to 0$; furthermore, as we shall see in Chap. 8, they represent factors by which each formal partial pressure must be multiplied in the thermodynamically exact form of the familiar law of mass action for gas reactions. The first three terms on the right of Eq. (7-2-9) represent the "ideal" part of ϕ_i, while the last term represents the effect on ϕ_i of deviation of the gas mixture from ideal limiting behavior, as represented by the ideal-gas law combined with Dalton's law of partial pressures. The different fugacity coefficients at given temperature and pressure vary with composition in ways that are related through the Gibbs-Duhem equation (7-1-8), which assumes the

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[1] One occasionally finds references to Eq. (7-2-8) itself as Dalton's law. This usage is correct only when the compressibility factors of the pure components at the respective pressures $p_1, p_2, \ldots, p_c$ given by Eq. (7-2-8) happen to be equal to the compressibility factor of the mixture at the pressure p [compare Eq. (7-2-1)]. This is generally not the case at high pressures, even for a mixture satisfying Dalton's law in the sense that the sum of the Dalton partial pressures given correctly by Eq. (7-2-1) agrees with the actual total pressure. For kinetic as opposed to equilibrium studies of gases at high pressures, the question of what constitutes the true contribution of each component to the total pressure may be of considerable importance in itself.

form

$$y_1\, d \ln \nu_1 + y_2\, d \ln \nu_2 + \cdots + y_c\, d \ln \nu_c = 0 \quad (T, p \text{ const}) \qquad (7\text{-}2\text{-}11)$$

We may measure the fugacity coefficients (or the equivalent thermodynamic potentials) exactly from detailed equation-of-state data for the mixtures at various compositions and pressures, at the given temperature. Thus, according to the basic equation (7-1-24),

$$\left(\frac{d\phi_i}{dp}\right)_{T,n} = v_i$$

From the partial molal volume v_i of any component, established from the experimental data at any particular composition as a function of the pressure, we could integrate this equation, and thus derive the value of ϕ_i directly at the given composition and various values of the pressure. It is convenient, however, for us to express this relationship in terms of the fugacity coefficient ν_i and the compressibility factor $z \equiv pV/nRT$ of the mixture, both of which vary much less rapidly with p than ϕ_i or v_i; introducing Eq. (7-2-9), which defines ν_i in relation to ϕ_i,

$$\frac{RT}{p} + RT\left(\frac{d \ln \nu_i}{dp}\right)_{T,n} = v_i$$

$$\left(\frac{d \ln \nu_i}{d \ln p}\right)_{T,n} = \frac{pv_i}{RT} - 1 \qquad (7\text{-}2\text{-}12)$$

Now, from the nature of their definitions, the partial molal volumes are related to the molal volume $\bar{V}$ of the mixture at given temperature and pressure by the equation

$$\bar{V} = y_1v_1 + y_2v_2 + \cdots + y_cv_c$$

Therefore

$$\frac{p\bar{V}}{RT} = z = y_1\left(\frac{pv_1}{RT}\right) + y_2\left(\frac{pv_2}{RT}\right) + \cdots + y_c\left(\frac{pv_c}{RT}\right)$$

In other words, the quantities

$$\zeta_i \equiv \frac{pv_i}{RT} \quad (i = 1, 2, \ldots, c) \qquad (7\text{-}2\text{-}13)$$

are related to z in the same way that $v_1, v_2, \ldots, v_c$ are related to $\bar{V}$; we may call them *partial molal compressibility factors.* In the case of a binary mixture, for example, we may calculate their values at given temperature and pressure from experimental values of z expressed as a function of composition by the same graphical techniques that were described in Sec. 4-5 for the calculation of partial molal enthalpies from $\bar{H}$ values for the solution expressed as a function of composition; thus, if we plot z vs. y_2, as in Fig. 7-4 where Bartlett's data for N_2-H_2 mixtures at 0°C are given and Fig. 7-5 where the data of Masson and Dolley for argon-

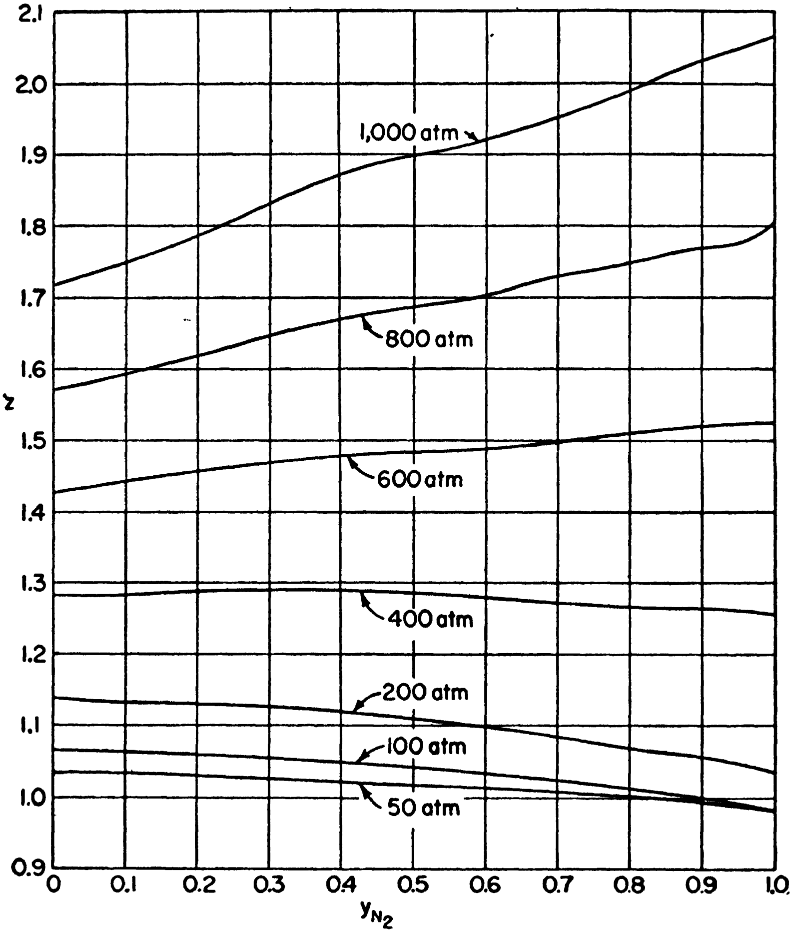

FIG. 7-4. Compressibility factors of N_2-H_2 mixtures for various fixed pressures at 0°C. [*From data of E. P. Bartlett, J. Am. Chem. Soc.*, **49**, 687, 1955 (1927).]

ethylene mixtures at 24.95°C are given, then the tangent to any of these isopiestic curves at a given value of the composition intercepts the $y_2 = 0$ and the $y_2 = 1$ axis, respectively, at the values of ζ_1 and ζ_2 corresponding to the given pressure and composition.[1] Having established the value of

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[1] Where the experimental data have been reported in the form of $pV/(pV)_0$ relative to an arbitrary quantity of gas for which $pV = (pV)_0 = 1.0000$ at some standard reference condition, such as 0°C and 1 atm (as in Table 7-1), then since at any temperature $\lim_{p \to 0} (pV)_T = nRT$, therefore $z = (pV)_T/\lim_{p \to 0}(pV)_T$; one may readily compute the z values by dividing the tabulated values of $pV/(pV)_0$ at the given temperature by the limiting value for $p \to 0$ at the same temperature. The error will generally not

any ζ_i by such means at various values of the pressure for a particular value of the composition, one may then evaluate ν_i at that composition for various values of the pressure by integrating Eq. (7-2-12) in the form

$$\log \nu_i = \int_{p=0}^{p=p} (\zeta_i - 1) d \log p \quad (T, y_1, y_2, \ldots, y_c \text{ const}) \tag{7-2-14}$$

the value of $\log \nu_i$ vanishing at the lower limit of integration, $p = 0$, in accordance with (7-2-10); the value of the integral may be conveniently determined graphically from a plot of the quantity $(\zeta_i - 1)$ vs. $\log p$.

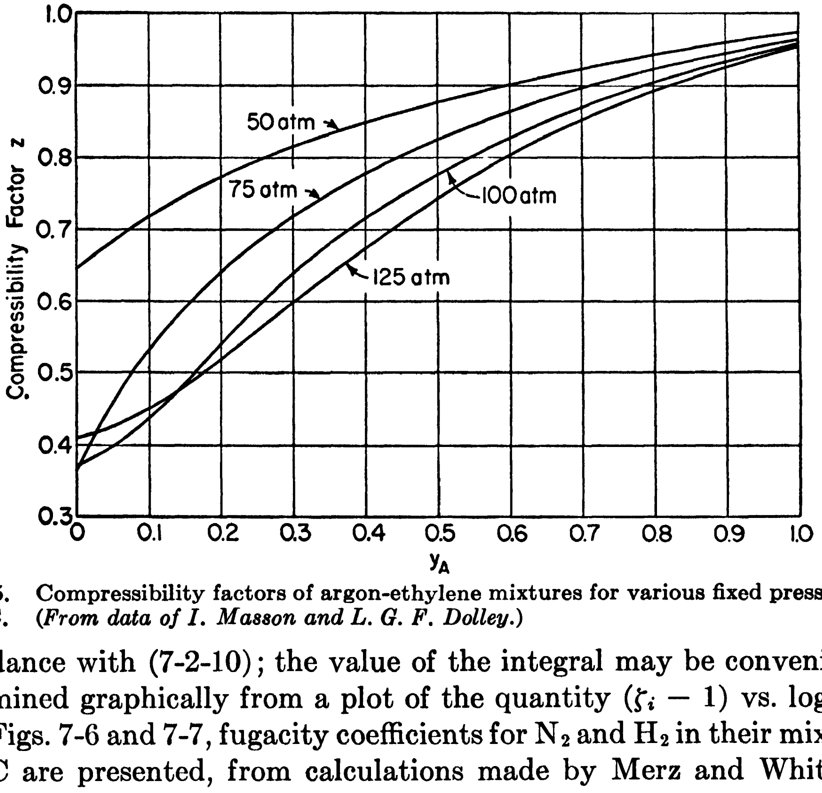

FIG. 7-5. Compressibility factors of argon-ethylene mixtures for various fixed pressures at 24.95°C. (*From data of I. Masson and L. G. F. Dolley.*)

In Figs. 7-6 and 7-7, fugacity coefficients for N_2 and H_2 in their mixtures at 0°C are presented, from calculations made by Merz and Whittaker based on the experimental data of Bartlett summarized in Fig. 7-4;[1] Fig. 7-6 presents the fugacity coefficients for various values of the composition plotted as functions of the pressure; Fig. 7-7 presents the same data plotted at three selected values of the pressure as functions of the composition (*i.e.*, of y_{N_2}). Figures 7-8 and 7-9 present similarly the fugacity coefficients of argon and ethylene in their mixtures at 24.95°C, as

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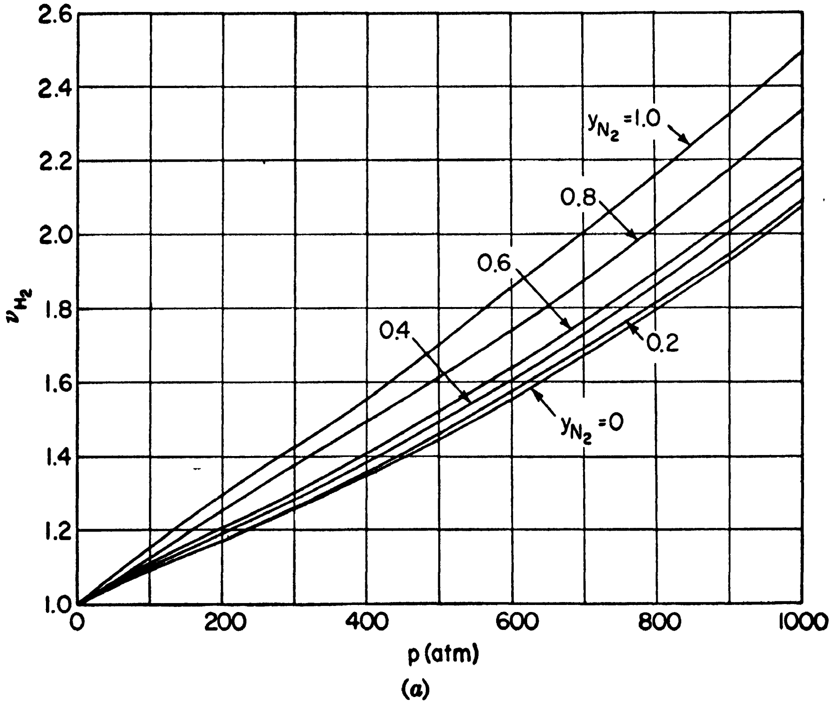
be appreciable if one divides by the value of $pV/(pV)_0$ at 1 atm, in place of the true limiting value as $p \rightarrow 0$ (which would correct for the deviation from ideal-gas behavior at 1 atm itself); thus, if the data are tabulated with $pV/(pV)_0 = 1.0000$ at 0°C and 1 atm, the error will be slight if one takes the tabulated values of $pV/(pV)_0$ themselves as equal to z at 0°C, and of $pV/(pV)_0$ multiplied by 273.16 deg/T for z at other temperatures T.

[1] A. R. Merz and C. W. Whittaker, *J. Am. Chem. Soc.*, **50**, 1522–1526 (1928).



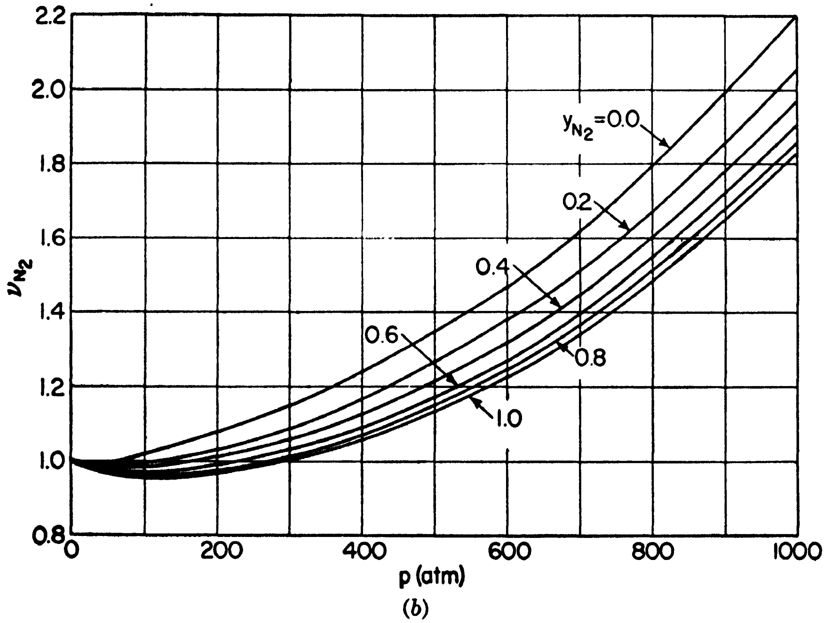


FIG. 7-6. (*a*) Fugacity coefficient of hydrogen in N_2-H_2 mixtures at 0°C. (*b*) Fugacity coefficient of nitrogen in N_2-H_2 mixtures at 0°C. (*As calculated by Merz and Whittaker from measurements of compressibility by Bartlett.*)

calculated by Gibson and Sosnick from the experimental data of Masson and Dolley summarized in Fig. 7-5.[1]

If one has already measured the fugacity coefficients of the pure components, then the precision in the evaluation of the pressure integral required

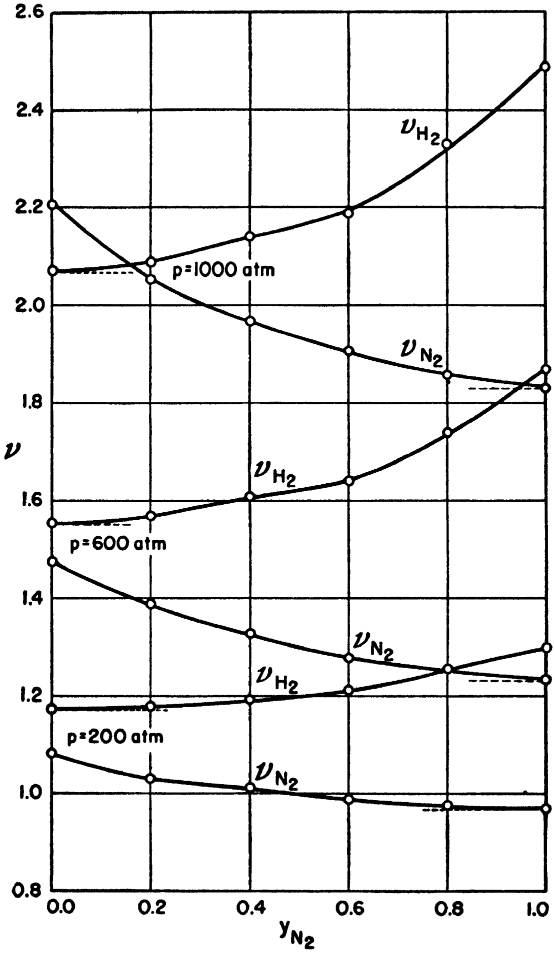


FIG. 7-7. Fugacity coefficients of N_2 and H_2 in their mixtures at 0°C and fixed pressures of 200, 600, and 1000 atm. (*As calculated by Merz and Whittaker from measurements of compressibility by Bartlett.*)

in Eq. (7-2-14) may be increased by the introduction of Eq. (6-29), by which the fugacity coefficients of the pure components are determined; thus, letting ν_i° denote the fugacity coefficient of pure component i at the temperature T and pressure p of the mixture

$$\log \frac{\nu_i}{\nu_i^\circ} = \int_{p=0}^{p=p} (\zeta_i - z_i) d \log p \quad (T, y_1, y_2, \ldots, y_c \text{ const}) \qquad (7\text{-}2\text{-}15)$$

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[1] G. E. Gibson and B. Sosnick, *ibid.*, **49**, 2172–2179 (1927).

This equation enables us to calculate by graphical integration the value of ν_i relative to the fugacity coefficient of the pure component at the same pressure, z_i representing the compressibility factor of the pure component at the pressure p of the mixture; since the difference $(\zeta_i - z_i)$ will generally be smaller than $(\zeta_i - 1)$, the value of the integral appearing in Eq. (7-2-15) will generally be smaller than the value of the integral appearing in Eq. (7-2-14), and the value of ν_i calculated by means of Eq. (7-2-15) will therefore be less sensitive to inaccuracy in the evaluation of the pressure integral, though it will of course be sensitive to error in the original evaluation of ν_i°.[1]

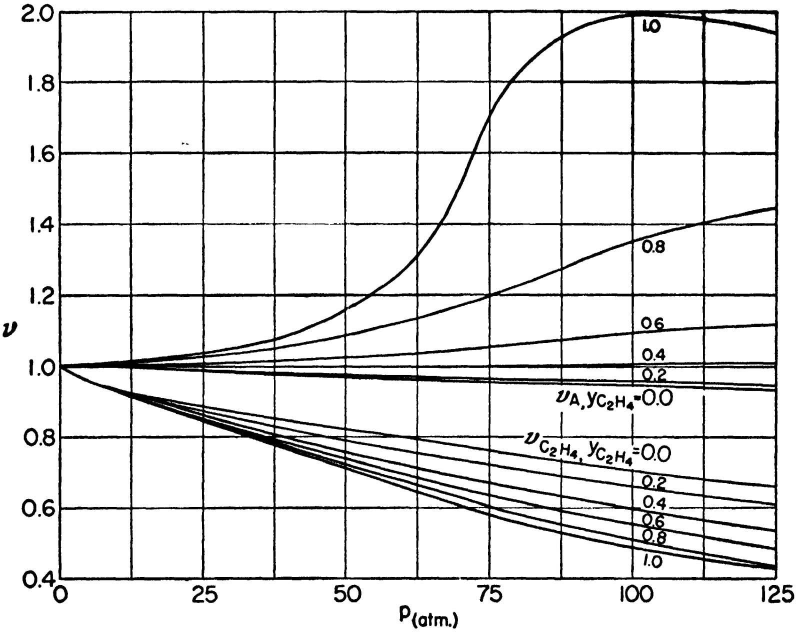

FIG. 7-8. Fugacity coefficients of argon and ethylene in their mixtures at 24.95°C. (*As calculated by Gibson and Sosnick from measurements of compressibility by Masson and Dolley.*)

The exact establishment of fugacity coefficients or the equivalent thermodynamic potentials in gas mixtures at high pressures is evidently a tedious and laborious assignment, even when the mixture contains but two components. The labor of computation and the experimental data required are greatly multiplied when there are more than two components. One will have observed that *p-V-T* data merely for a particular temperature, pressure, and composition are not sufficient to determine the values

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[1] P. Bolshakov, *Acta Physicochim. U.R.S.S.*, **20**, 259–267 (1945), has computed such relative fugacity coefficients for N_2 and H_2 in their mixtures at various temperatures and pressures, using the extended experimental *p-V-T* data of E. P. Bartlett and his associates, and of R. Wiebe and V. L. Gaddy, *J. Am. Chem. Soc.*, **60**, 2300–2303 (1938).

of the fugacity coefficients in that state; one needs such data over the *entire composition range* (at least sufficient to establish the *rate of change* of z with composition over that part of the range in which one is interested), for *all pressures* up to the desired pressure, before one can apply the basic equation (7-2-14). This comes about because we have no generally valid theoretical or empirical principle (necessarily of nonthermodynamic origin) relating the behavior of the mixture to the behavior of the pure components outside the low-pressure ideal-gas range, nor do we have experimental means of applying the equilibrium principle outlined in Sec. 7-1 to measure thermodynamic potentials directly in a gas mixture at high pressure. The growing importance of high-pressure catalytic gas reactions in industry has, however, emphasized the value of such information.

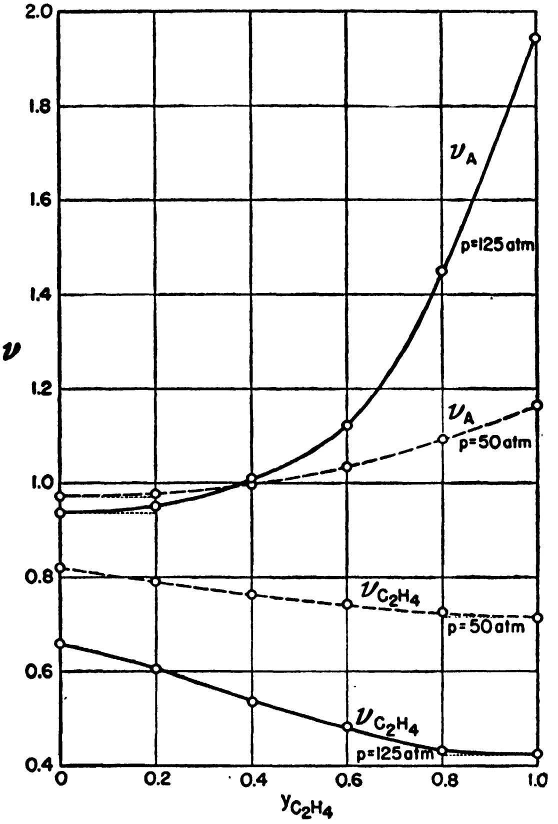

FIG. 7-9. Fugacity coefficients of argon and ethylene in their mixtures at 24.95°C and fixed pressures of 50 and 125 atm. (*As calculated by Gibson and Sosnick from measurements of compressibility by Masson and Dolley.*)

When insufficient experimental p-V-T data are available for a particular mixture of gases to admit of an exact computation of the fugacity coefficients, certain approximate methods may be applied. If, for example, from the limited data at one's command, one can assume that the mixture satisfies Amagat's law at all pressures up to the range in which one is interested, then since this assumption is equivalent to the vanishing of the integrand in Eq. (7-2-15) [compare the discussion leading to Eq. (7-2-2)], one may assign to each component a fugacity coefficient in the mixture equal to its fugacity coefficient in the pure state *at the temperature and pressure of the mixture.* That N_2 and H_2 in their mixtures at 0°C satisfy approximately this law is evident from Fig. 7-4, where z has been plotted against y_{N_2} for several values of the pressure; perfect conformity would call for straight-line relationships in this type of plot. One can even tell from qualitative examination of the form of the curvatures at a particular composition [bearing in mind that the values of ζ_{H_2} and ζ_{N_2} for use in Eq. (7-2-15) are determined by the intercepts, respectively, on the $y_{N_2} = 0$ and the $y_{N_2} = 1$ abscissas of the tangents to these curves at the particular value of the composition], what qualitative relationship the actual values of ν_{H_2} and ν_{N_2} will bear to the respective fugacity coefficients of the pure component gases; thus, at $y_{N_2} = 0.25$, one can see that ζ_{H_2} at all pressures up to 1000 atm is almost identical with z_{H_2} for pure H_2 at the same pressure, whereas ζ_{N_2} at all pressures up to 1000 atm is slightly higher than z_{N_2}; therefore the actual values of ν_{H_2} at that composition must be in close agreement with the values of $\nu^{\circ}_{H_2}$ at the same pressures, whereas the actual values of ν_{N_2} must be slightly higher than the values of $\nu^{\circ}_{N_2}$ at the same pressures. These conclusions are corroborated by actual computation of the fugacity coefficients, as shown in Figs. 7-6 and 7-7, where one sees that even at 1000 atm, the greatest deviation of either fugacity coefficient from that of the corresponding pure component is but 20 per cent.

The approximation we have just considered, *viz.*, the assumption that each component of a gas mixture may be assigned a fugacity coefficient equal to that of the pure component at the temperature and pressure of the mixture, was proposed as a general rule by Lewis and Randall, in the absence at that time of much precise data on gas mixtures at high pressures, though they recognized the need for further theoretical and experimental investigation.[1] The assumption is tenable, however, only for gas mixtures satisfying Amagat's law. Argon-ethylene mixtures at 24.95°C, for example, are far from satisfying Amagat's law, particularly at pressures near 85 atm, where z for pure ethylene passes through a minimum (Fig. 7-5; compare Fig. 7-3). From qualitative examination of Fig. 7-5, one perceives that the values of ζ_A and $\zeta_{C_2H_4}$ at all intermediate compositions are greater than the values of z_A and $z_{C_2H_4}$, respectively, at the same pressures and that therefore the application of Eq. (7-2-15) necessarily

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[1] Lewis and Randall, *op. cit.*, pp. 225–227.

yields values of ν_A and $\nu_{C_2H_4}$ appreciably greater than the respective values of the fugacity coefficients of the pure components at the pressure of the mixture, particularly for A at low concentration in C_2H_4 where the z vs. y_A curves deviate most markedly from the Amagat straight lines. These conclusions are corroborated by actual computation of the fugacity coefficients, plotted in Figs. 7-8 and 7-9; one sees that for argon at low concentration in ethylene, the value of ν_A around 100 atm becomes as much as 100 per cent greater than the value of ν_A° at the same pressure.

Where insufficient data are available for calculating precisely the thermodynamic properties of the pure components themselves, one may use the approximations based on the theory of corresponding states, described in Sec. 6-1. Thus, from the generalized fugacity-coefficient charts, Figs. 6-2 to 6-4, one may estimate the value of ν° for each pure component gas from a knowledge of its critical temperature and pressure. How one would apply such information to estimate fugacity coefficients in a gas mixture would depend on one's surmise concerning the general behavior of the mixture; if one had reason to suppose that Amagat's law applied, one would then read from the charts fugacity coefficients for each component corresponding to the temperature and pressure of the mixture (reduced in accordance with the pure component's own critical temperature and pressure). Newton and Dodge[1] have shown that fugacity coefficients estimated in this way for H_2, N_2, and NH_3 in their equilibrium mixtures are in excellent agreement with experimental observations on the deviation of the ideal law-of-mass-action equilibrium constant K_p from its limiting value at $p \to 0$ (Chap. 8). Much experimental work remains to be done, however, before the thermodynamic properties of gas mixtures at high pressures can be put on a sound theoretical basis.

7-3. Liquid Solutions. *a. General Thermodynamic Theory.* In a liquid solution, according to the general argument advanced in Sec. 7-1, the thermodynamic potential of any component is equal in particular to its thermodynamic potential in the equilibrium vapor phase. We have just studied in Sec. 7-2 how to measure the thermodynamic potentials in gas mixtures; equilibrium data between the solution and its vapor phase therefore constitute a primary experimental means of establishing the thermodynamic potentials in liquid solutions.

Now, in a binary solution, the thermodynamic potentials of the two components in the liquid phase are related to each other through the Gibbs-Duhem equation (7-1-8), so that only one is independently variable; *both* thermodynamic potentials are determined, for example, by the composition at given temperature and pressure. Let us express this relationship symbolically in the form $\phi_2 = \phi_2(\phi_1, T, p)$. The thermody-

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[1] R. H. Newton and B. F. Dodge, *Ind. Eng. Chem.*, **27**, 577–581 (1935).

namic potentials of the two components in the corresponding vapor phase are likewise related to each other through a Gibbs-Duhem equation of the general form (7-1-8), but of course the particular manner in which either potential depends on temperature, pressure, and composition is in general different from that for the liquid phase. Let us express the interdependence of the two vapor-phase thermodynamic potentials symbolically in the form $\phi_2^* = \phi_2^*(\phi_1^*, T^*, p^*)$, where * denotes properties referring to the vapor phase. Therefore the requirement that at equilibrium between the two phases, not only must they be at the same temperature ($T = T^*$ for thermal equilibrium), and at the same pressure ($p = p^*$ for mechanical equilibrium, in the absence of a mechanical barrier between the phases), but also the thermodynamic potential of component 1 in the liquid phase must be equal to the thermodynamic potential of component 1 in the vapor phase ($\phi_1 = \phi_1^*$) and at the same time, the thermodynamic potential of component 2 in the liquid phase must be equal to the thermodynamic potential of component 2 in the vapor phase ($\phi_2 = \phi_2^*$), implies four independent relations among the six otherwise independent thermodynamic variables: T, p, ϕ_1, T^*, p^*, and ϕ_1^*. Hence the equilibrium state is determined by the values of any *two* of these six variables characterizing the states of the two phases. Thus, to each composition and temperature of the liquid phase, there corresponds a unique pressure and composition of the vapor phase at which equilibrium may be maintained; a liquid solution of specified composition has at each temperature not only a characteristic *vapor pressure* but also a characteristic *composition of the equilibrium vapor phase,* which is generally different, however, from that of the liquid, and cannot be computed from it on purely thermodynamic grounds. The extension of the argument to solutions containing more than two components is straightforward, but will be deferred to Sec. 7-6, in which the problem of heterogeneous equilibrium in general is discussed.

b. Liquid-Vapor Equilibrium in General at Uniform Temperature. It is customary, following the extensive original experimental work of Zawidski,[1] to represent the composition of the equilibrium vapor phase of a liquid solution in terms of so-called *partial vapor pressures* of the components, *defined* by

$$p_i \equiv y_i^* p \tag{7-3-1}$$

where p represents the vapor pressure of the solution (at specified temperature and composition), and y_i^* the mole fraction of component i in the equilibrium vapor phase [compare Eq. (7-2-8)]. For a binary liquid solution, the experimentally determined equilibrium data between the liquid and vapor phases at a specified uniform temperature are then con-

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[1] J. von Zawidski, *Z. physik. Chem.*, **35**, 129–203 (1900).

veniently represented by means of a graph of p_1 and p_2 (together with $p = p_1 + p_2$) vs. x_2, the mole fraction of one of the components in the liquid phase. Figure 7-10 presents typical results for several binary systems, plotted in this way. While the values of p and the composition of the equilibrium vapor phase are *fixed* by the temperature and composition of the liquid phase, in the sense that their values are uniquely determined by general thermodynamic laws, there is no general rule by which these uniquely determined values can be calculated from the composition of the liquid phase and the properties of the pure components. Therefore extensive research has been carried out on the direct experimental measurement of liquid-vapor equilibrium conditions for a wide variety of solutions; this information has great practical value in connection with distillation problems. The data presented in Fig. 7-10, while illustrating the variety of relationships encountered, do show certain general regularities whose nature will be discussed at length in Sec. 7-3*c*.

The partial vapor pressures in general have no ulterior physical significance beyond representing in a convenient form the composition of the equilibrium vapor phase; they cannot be directly measured independently of the defining equation (7-3-1). If, however, the equilibrium vapor phase can be regarded as an ideal gas, then in the vapor phase, according to Eq. (7-2-5),

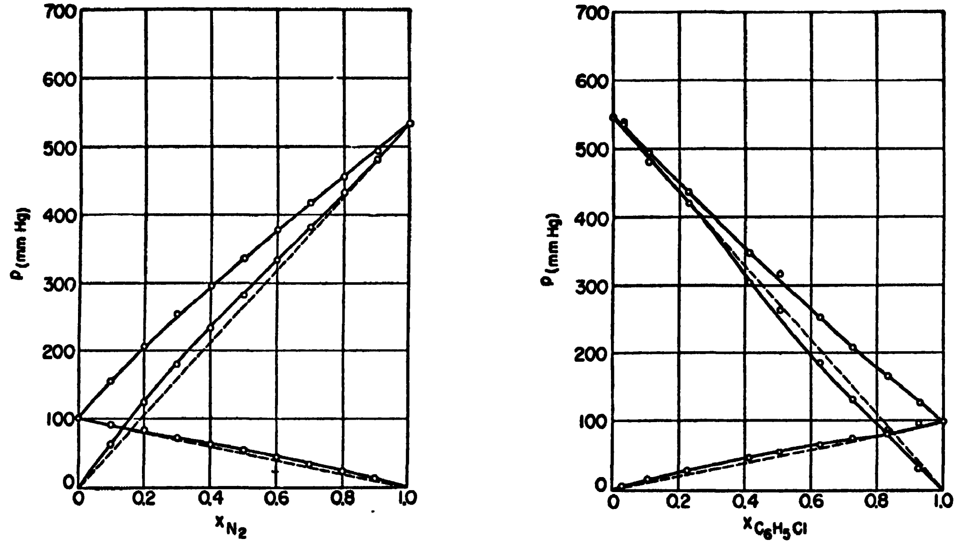
$$\phi_i^* = (\bar{F}_T^\circ)_{i(g)} + RT \ln p_i$$

where $(\bar{F}_T^\circ)_{i(g)}$ represents the standard molal free energy of pure component i as a *gas* at the temperature T. Since by the equilibrium principle developed in Sec. 7-1, $\phi_i = \phi_i^*$, where ϕ_i represents the thermodynamic potential of component i in the liquid phase at temperature T and pressure p (the total equilibrium vapor pressure of the solution), we have here a straightforward connection between thermodynamic potentials in liquid solutions and vapor-pressure data. If the pure component is itself a liquid or a solid at the standard conditions T and 1 atm, then it is convenient for us to replace $(\bar{F}_T^\circ)_{i(g)}$ in terms of $(\bar{F}_T^\circ)_{i(l)}$ or $(\bar{F}_T^\circ)_{i(c)}$, representing the standard molal free energy in the respective normal state; we may do this by taking note that for pure component i in equilibrium with its own pure vapor phase at the temperature T,

$$(\bar{F}_{T,p_i^\circ})_i = (\bar{F}_{T,p_i^\circ})_i^*$$

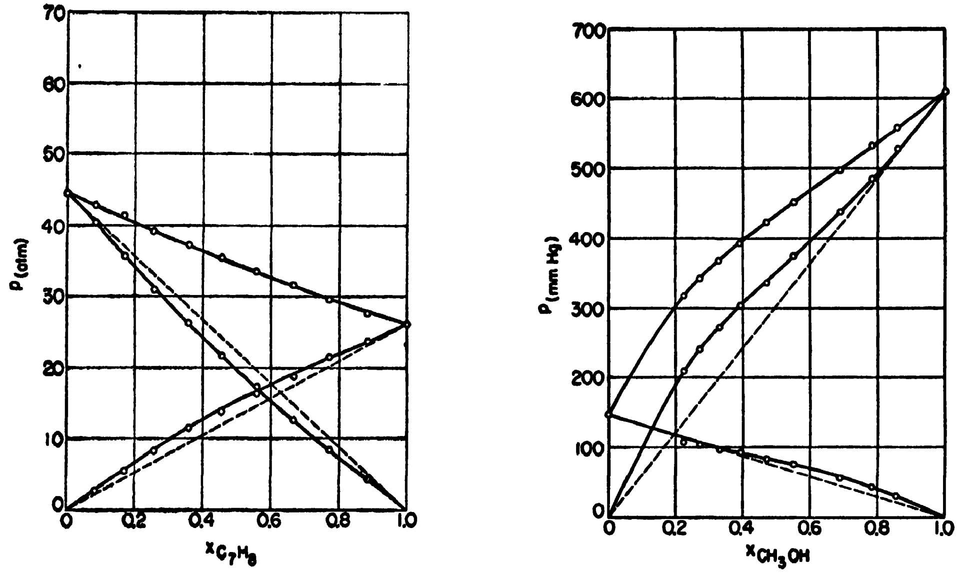
where p_i° represents the vapor pressure of pure component i; therefore, according to Eqs. (6-16) and (6-17),

$$(\bar{F}_T^\circ)_i + \int_{1\ \text{atm}}^{p_i^\circ} V_i\, dp = (\bar{F}_T^\circ)_{i(g)} + RT \ln p_i^\circ$$



(*a*) Oxygen and nitrogen at 74.7°K [*J. K. H. Inglis, Phil. Mag.*, (6) **11**, 640–658 (1906)]; nearly ideal liquid solutions.

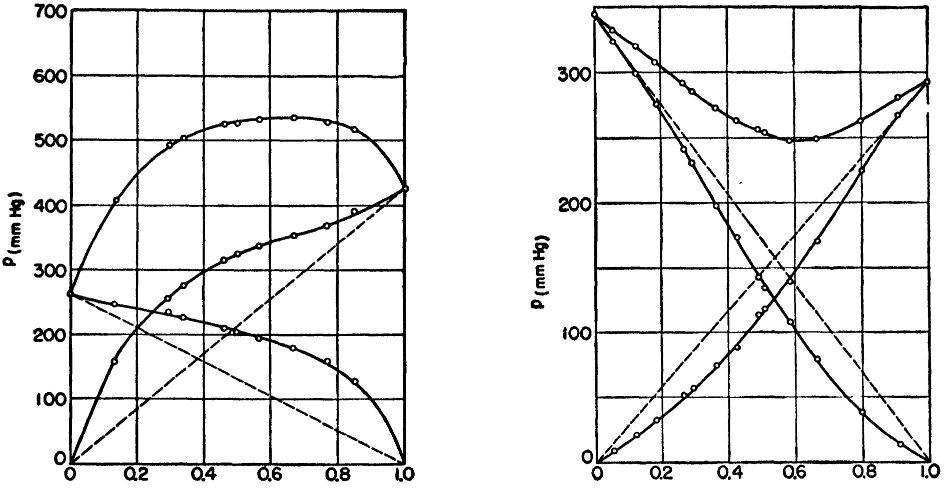
b) Benzene and chlorobenzene at 70°C [*A. R. Martin and B. Collie, J. Chem. Soc.*, 2658–2665 (1932)]; nearly ideal liquid solutions.



(*c*) Benzene and toluene at 280°C [*W. v. Huhn, as reported in Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Suppl.* IIIc, *p.* 2483, 1936]; nearly ideal liquid solutions at high pressures.

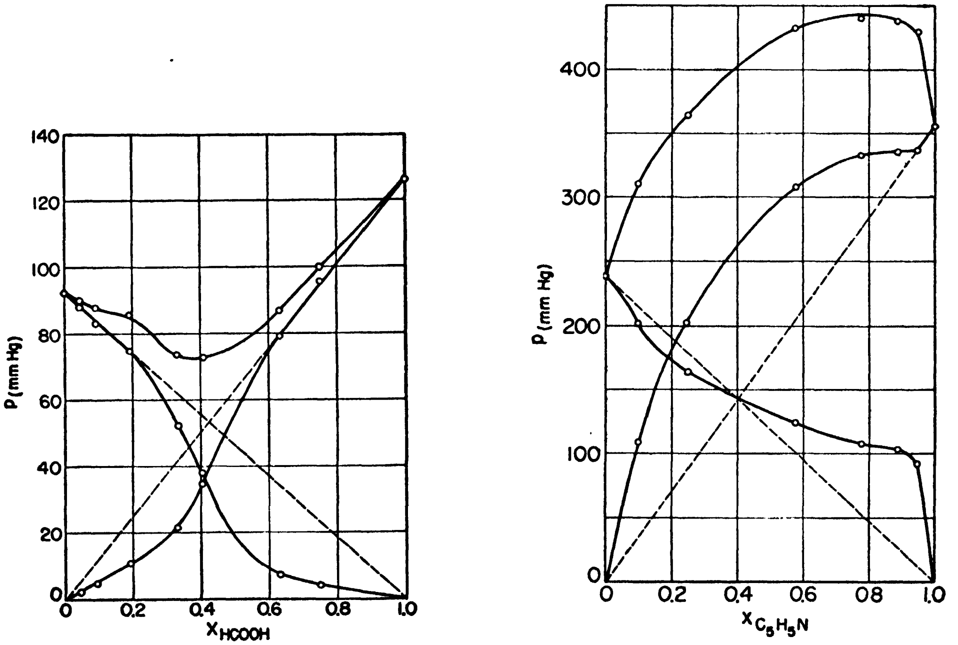
(*d*) Methanol and water at 59.4°C [*M. S. Vrevskii, Z. physik. Chem.*, **81**, 1–29 (1912)]; positive deviations from Raoult's law.

FIG. 7-10. Vapor pressures and partial vapor pressures of binary liquid solutions.



(*e*) Carbon disulfide and acetone at 29.2°C [*J. Hirshberg, as reported in Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Suppl.* IIIc, *p.* 2466, 1936]; large positive deviations from Raoult's law.

(*f*) Chloroform and acetone at 35.17°C [*J. von Zawidski, Z. physik. Chem.*, **35**, 129–203 (1900)]; negative deviations from Raoult's law.



(*g*) Formic acid and water at 50°C [*A. N. Campbell and A. J. R. Campbell, Trans. Faraday Soc.*, **30**, 1109–1114 (1934)]; large negative deviations from Raoult's law, complicated by partial association of HCOOH in the vapor phase.

(*h*) Pyridine and water at 80.05°C [*J. von Zawidski, Z. physik. Chem.*, **35**, 129–203 (1900)]; pathological deviations from ideal behavior.

FIG. 7-10. Vapor pressures and partial vapor pressures of binary liquid solutions (*continued*).

Thus

$$\phi_i = \phi_i^* = (\bar{F}_T^\circ)_i + \int_{1\ \text{atm}}^{p_i^\circ} \bar{V}_i\, dp + RT \ln \frac{p_i}{p_i^\circ}$$

This represents the thermodynamic potential of component i in the liquid solution at temperature T and pressure p; if we wish to represent the value of ϕ_i at T and standard pressure of 1 atm, we may make use of the general thermodynamic relation (7-1-24)

$$(\phi_i)_{T,1\ \text{atm}} = (\phi_i)_{T,p} + \int_p^{1\ \text{atm}} v_i\, dp$$

where v_i stands for the partial molal volume of component i in the liquid solution; thus, finally,

$$\phi_i = (\bar{F}_T^\circ)_i + RT \ln \frac{p_i}{p_i^\circ} + \int_{1\ \text{atm}}^{p_i^\circ} \bar{V}_i\, dp + \int_p^{1\ \text{atm}} v_i\, dp \qquad (7\text{-}3\text{-}2)$$

If we had wished to relate ϕ_i to $\bar{F}_i$ at some other pressure P, we could have done so by replacing the 1 atm limit in the two integrals by P. We may extend Eq. (7-3-2) formally to include components that happen to be gases in the pure state at standard conditions, T and 1 atm, if we adopt the convention that in such cases, $p_i^\circ \equiv 1$ atm, the value of $(\bar{F}_T^\circ)_i$ then referring to the standard molal free energy of the pure gas.

Now, for pressures of order 1 atm or less, the two integrals on the right of Eq. (7-3-2) are generally negligibly small in magnitude; they can certainly be replaced by the approximations $\bar{V}_i(p_i^\circ - 1\ \text{atm})$ and $v_i(1\ \text{atm} - p)$, respectively, in view of the relative incompressibility of liquids and solids, but since $\bar{V}_i$ and v_i are relatively small ($\bar{V}_i$ would be large for a gaseous solute, but in such cases, we have agreed to let p_i° represent 1 atm), the two terms may usually be neglected altogether, except in work of the highest precision. Therefore Eq. (7-3-2) may be used practically in the form

$$\phi_i = (\bar{F}_T^\circ)_i + RT \ln \frac{p_i}{p_i^\circ} \quad \text{(vapor-phase ideal)} \qquad (7\text{-}3\text{-}3)$$

The value of ϕ_i so obtained is not particularly sensitive to the pressure [compare the last term in Eq. (7-3-2)], and may be regarded as sensibly constant for liquid solutions between 0 and 2 atm. The ideal-gas law assumption is usually sufficiently precise for all purposes at vapor pressures not greatly exceeding 1 atm, *i.e.*, at temperatures not greatly above the normal boiling point of the solution (provided that the components do not show obviously "abnormal" behavior, such as the association of acetic acid molecules in the vapor state); but at high pressures, or generally where extra precision is warranted, we may introduce empirically determined fugacity coefficients, as shown in Sec. 7-2. Equation (7-3-2) then takes the general form

$$\phi_i = (\bar{F}^\circ_T)_i + RT \ln \frac{p_i \nu_i}{p_i^\circ \nu_i^\circ} + \int_{1\ \text{atm}}^{p_i^\circ} \bar{V}_i \, dp + \int_{p}^{1\ \text{atm}} v_i \, dp \qquad (7\text{-}3\text{-}4)$$

where ν_i represents the fugacity coefficient of component i in the equilibrium gas phase, and ν_i° its fugacity coefficient as a pure gas at pressure p_i° (its vapor pressure at the temperature T); $\bar{V}_i$ represents the molal volume of the pure component, and v_i represents its partial molal volume in the solution at the given composition. It may be convenient for some purposes to refer ϕ_i to the standard molal free energy of pure component i as a *gas* at the temperature T; in that case, Eq. (7-3-4) may be replaced by its exact equivalent

$$\phi_i = (\bar{F}^\circ_T)_i^* + RT \ln p_i \nu_i \qquad (7\text{-}3\text{-}5)$$

In the case of a binary solution, the Gibbs-Duhem relation in the form (7-1-8)

$$x_1 \, d\phi_1 + x_2 \, d\phi_2 = 0 \qquad (T, p \text{ const}) \qquad (7\text{-}3\text{-}6)$$

when Eq. (7-3-3) is valid for both components, implies a simple connection between the two partial vapor pressures for different compositions at the same temperature; strictly, of course, we cannot vary the composition of the liquid phase at constant temperature without changing also the total equilibrium (vapor) pressure, but since the thermodynamic potentials in liquid solutions are relatively insensitive to changes in the pressure, we may apply (7-3-6) to (7-3-3) over the entire composition range without restriction on the pressure, provided that the difference between the vapor pressures of the components is not extremely large in magnitude. Thus

$$x_1 \, d \ln p_1 + x_2 \, d \ln p_2 = 0 \qquad (T \text{ const}) \qquad (7\text{-}3\text{-}7)$$[1]

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[1] The exact form of Eq. (7-3-7), taking into account the variations of ϕ_1 and ϕ_2 with the total (vapor) pressure, may be derived as follows: for a general change of state at constant temperature (but not necessarily at constant pressure), according to Eq. (7-1-6),

$$x_1 \, d\phi_1 + x_2 \, d\phi_2 = \bar{V} \, dp \qquad (T \text{ const})$$

where $\bar{V}$ represents the volume per mole of liquid solution. Introducing (7-3-3) on the assumption that the equilibrium vapor phase may be treated as an ideal gas,

$$x_1 \, d \ln p_1 + x_2 \, d \ln p_2 = \frac{\bar{V}}{RT} \, dp \qquad (T \text{ const}) \qquad (7\text{-}3\text{-}7a)$$

This represents the generalization of Eq. (7-3-7), to which (7-3-7*a*) reduces if we may assume that the term on the right is negligible in comparison with the other terms, when integrated over the pressure range under consideration. For example, in the system chloroform-acetone at 35.17°C, as studied by Zawidski (Fig. 7-10*f*), $\bar{V}$ is at or, in view of the fact that $d/dx_1 = -d/dx_2$,

$$\left(\frac{dp_1}{dx_1}\right) = \frac{p_1/x_1}{p_2/x_2}\left(\frac{dp_2}{dx_2}\right) \qquad (T \text{ const}) \qquad (7\text{-}3\text{-}8)$$

Relation (7-3-8) is attributed to P. Duhem; its alternative form

$$\left(\frac{d \ln p_1}{d \ln x_1}\right) = \left(\frac{d \ln p_2}{d \ln x_2}\right) \qquad (T \text{ const}) \qquad (7\text{-}3\text{-}8a)$$

is known as the *Duhem-Margules equation.*[1]

Equation (7-3-8) implies a direct connection between the slopes of the two partial vapor-pressure curves at any composition, when the experimental data are plotted as in Fig. 7-10; this connection was first tested and verified in precise detail by the fine experimental work of Zawidski.[2] In Fig. 7-11, similar data for several binary systems have been plotted in the form of log p_1 vs. log x_1 and log p_2 vs. log x_2 (Fig. 7-11*a* corresponds to the same data as in Fig. 7-10*f*); in this kind of plot, according to Eq. (7-3-8*a*), the slopes of the two curves are identical at corresponding values of x_1 and x_2 (*e.g.*, at $x_1 = 0.7$ for the one component and at $x_2 = 0.3$ for the other); in particular, the slopes are equal at $x_1 = x_2 = 0.5$, and the limiting slope of the one curve as $x_1 \to 1$ or as $x_2 \to 1$, respectively, is equal to the limiting slope of the other as $x_2 \to 0$ or as $x_1 \to 0$, respectively.[3]

The same connection may be expressed in terms of the total vapor pressure and the composition of the equilibrium vapor phase by the introduc-

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most 81.5 ml/mole (the value for pure chloroform), and the extreme range of pressures lies between 148 and 345 mm Hg; therefore the value of $(\bar{V}/RT)\Delta p$ over the entire composition range cannot exceed 0.0009. Since each of the terms on the left of (7-3-7*a*) integrated over the entire composition range is of order +1 or −1, respectively, Eq. (7-3-7) is in this case a valid approximation to Eq. (7-3-7*a*) within a precision of 0.1 per cent.

[1] P. Duhem, *Compt. rend.*, **102,** 1449–1451 (1886); M. Margules, *Sitzber. Akad. Wiss. Wien, Math.-Naturw. Klasse,* (2) **104,** 1243–1278 (1895).

[2] Zawidski, *loc. cit.*

[3] One will note that the limiting slopes of the two curves as $x_1 \to 1$ and $x_2 \to 1$, respectively, in Fig. 7-11 are equal, having the common value 1 (the dashed straight lines indicated in the graphs have been so drawn); this empirical fact (Raoult's law) is not a necessary consequence of thermodynamics, and indeed is not universally true, as we shall see in the case of electrolytes. We shall discuss this point at length in Sec. 7-3*c*. If, however, it is a fact that the two slopes in the respective limits $x_1 \to 1$ and $x_2 \to 1$ are both equal to 1, then thermodynamic reasoning through Eq. (7-3-8*a*) implies that the two curves also become parallel with slopes = 1 in the respective limits $x_1 \to 0$ and $x_2 \to 0$; that this is true for the data presented in Fig. 7-11 is confirmed by the corresponding dashed lines shown on the graphs, which have been so drawn.

tion of Eq. (7-3-1) in Eq. (7-3-7) [or more rigorously, within the ideal-gas law approximation, in Eq. (7-3-7*a*)]:

$$x_1\, d\ln y_1^* + x_2\, d\ln y_2^* + d\ln p = 0 \qquad (T \text{ const})$$

Thus, since $x_2 = 1 - x_1$ and $y_2^* = 1 - y_1^*$,

$$\frac{y_1^* - x_1}{y_1^*(1 - y_1^*)}\left(\frac{dy_1^*}{dx_1}\right)_T = \left(\frac{d\ln p}{dx_1}\right)_T \tag{7-3-9}$$

The practical usefulness of (7-3-9) as a quantitative relation is limited, because it involves the three quantities x_1, y_1^*, and p; while at given temperature, only one of these quantities is independently variable, thermodynamics gives no information concerning the relationship between p and x_1, or the relationship between y_1^* and x_1, beyond the interrelationship expressed by Eq. (7-3-9) itself. In principle, if one knew empirically how p varied with x_1 in a given case, one could introduce this information in Eq. (7-3-9) and solve for y_1^* as a function of x_1, although since the variables of this differential equation are not generally separable, one could not always express the result in simple analytical form. In particular, if one

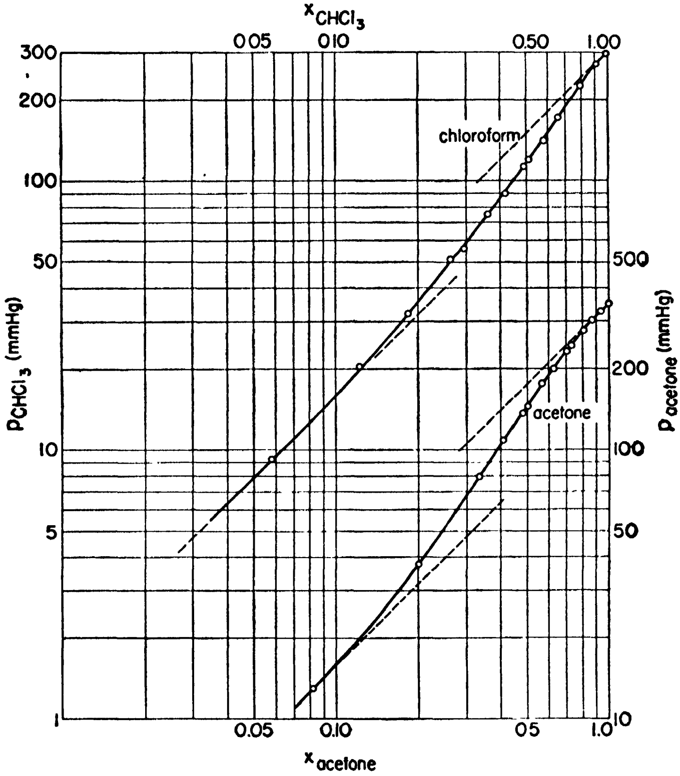

FIG. 7-11*a*. Log p_1 vs. log x_1 and log p_2 vs. log x_2 for solutions of acetone and chloroform at 35.17°*C*. [*J. von Zawidski, Z. physik. Chem.*, **35**, 129–203 (1900).]

has measured the value of y_1^* empirically for a given value of x_1, and also knows from empirical measurement how p varies with x_1 at that composition and temperature, one may apply Eq. (7-3-9) to calculate the effect of

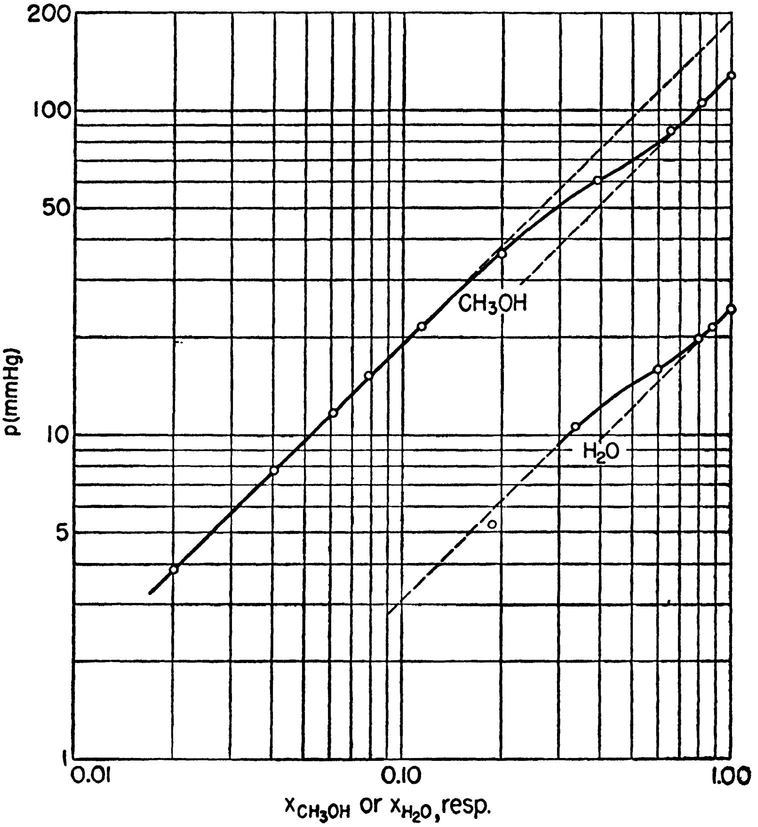

FIG. 7-11*b*. Log p_1 vs. log x_1 and log p_2 vs. log x_2 for solutions of methanol and water at 25°C. [*J. A. V. Butler, D. W. Thomson, and W. H. Maclennan, J. Chem. Soc.*, 674–686 (1933).]

a small change in the liquid composition on the composition of the equilibrium vapor phase

$$\Delta y_1^* = \left[\frac{y_1^*(1 - y_1^*)}{y_1^* - x_1}\,\frac{1}{p}\left(\frac{dp}{dx_1}\right)_T\right]\Delta x_1 \quad (T \text{ const}; \Delta x_1 \to 0) \qquad (7\text{-}3\text{-}9a)$$

Now, the expression $(dy_1^*/dx_1)_T$ occurring in Eq. (7-3-9) is necessarily confined by nature to nonnegative values (positive or zero); a situation in which decrease in the concentration of the given component in the liquid phase resulted in increase of its relative concentration in the equilibrium vapor phase would surely be unstable, since the loss of that component to the vapor phase would then be self-sustaining. The two factors in the denominator of the left-hand member of Eq. (7-3-9) are likewise essentially positive numbers. Therefore the sign of the expression $(y_1^* - x_1)$

is determined by the sign of $(d \ln p/dx_1)_T$, or, what amounts to the same thing, by the sign of $(dp/dx_1)_T$. Thus if at given temperature and composition p tends to increase with x_1, then the equilibrium vapor phase cannot be poorer with respect to component 1 than the liquid phase; if on the other hand p tends to decrease with x_1, then the equilibrium vapor phase cannot be richer with respect to component 1 than the liquid phase. This well-known constant-temperature distillation rule of Konowalow[1] is thus embodied in quantitative form in Eq. (7-3-9). Furthermore, if p

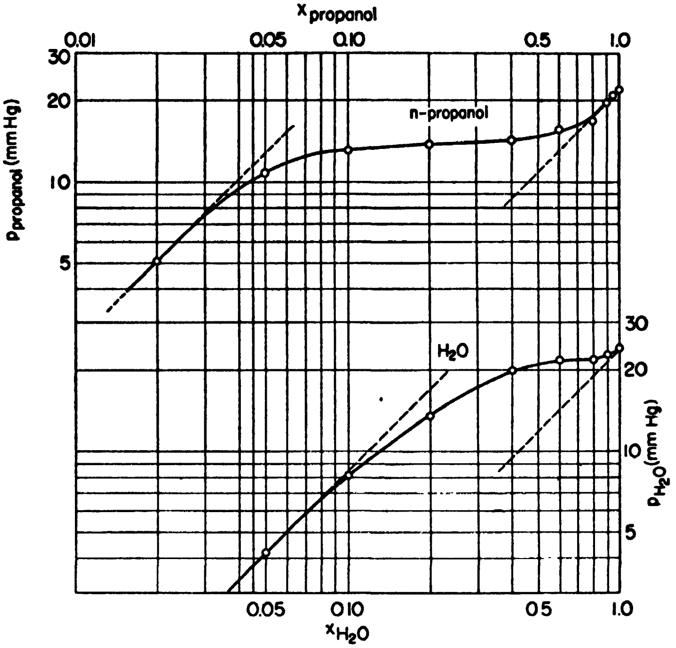

FIG. 7-11c. Log p_1 vs. log x_1 and log p_2 vs. log x_2 for solutions of *n*-propanol and water at 25°C. [*J. A. V. Butler, D. W. Thomson, and W. H. Maclennan, J. Chem. Soc.*, 674–686 (1933).]

passes through either a maximum or a minimum with change in the composition of the liquid phase, then at the extremum, according to Eq. (7-3-9), either $y_1^* = x_1$, or $(dy_1^*/dx_1)_T = 0$. The latter situation arises when there is a halt in the vapor-pressure-composition relationship (not necessarily a maximum or a minimum, though a maximum is common in this situation), associated with the separation of the liquid into two mutually saturated liquid phases, *i.e.*, when the two components show limited miscibility at the given temperature. The situation $y_1^* = x_1$ arises of course in the case of ordinary *azeotropic mixtures*, where a maximum or a minimum exists in the vapor-pressure-composition relationship for a homogeneous liquid phase (Figs. 7-10*e* to *h*); the equilibrium vapor

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[1] D. Konowalow, *Ann. Physik u. Chem.*, **14**, 34–52 (1881).

phase corresponding to the liquid having the maximum or the minimum vapor pressure has the same composition as the liquid phase. For liquid pairs forming an azeotropic mixture with *maximum* vapor pressure, then since p increases with x_1 so long as x_1 is below the azeotropic composition but decreases with x_1 when x_1 is above the azeotropic composition, it follows from Eq. (7-3-9) that $y_1^* > x_1$ so long as x_1 is below the azeotropic composition, but $y_1^* < x_1$ when x_1 exceeds the azeotropic composition. In other words, the plot of y_1^* vs. x_1 has the general form shown in Fig. 7-12*a*, where the data for CS_2-acetone solutions presented in Fig. 7-10*e* have been replotted; in this diagram, the azeotropic composition evidently corresponds to the point at which the curve crosses the 45 deg line representing equal liquid and vapor compositions (the dashed line drawn in the graph). On the other hand, for liquid pairs forming an azeotropic mixture with *minimum* vapor pressure, by similar reasoning, $y_1^* < x_1$ so long as x_1 is below the azeotropic composition, but $y_1^* > x_1$ when x_1 exceeds the azeotropic composition; the plot of y_1^* vs. x_1 has the general form of Fig. 7-12*b*, where the data for $CHCl_3$-acetone solutions presented in Fig. 7-10*f* have been replotted. When the vapor pressures for all compositions lie between those of the pure components, so that neither a maximum nor a minimum appears in the vapor-pressure-composition relationship, then all values of y_1^* in a plot such as those of Fig. 7-12 lie either above or below the 45 deg line, depending on whether p increases or decreases continually with x_1, the composition in terms of the particular component, 1.

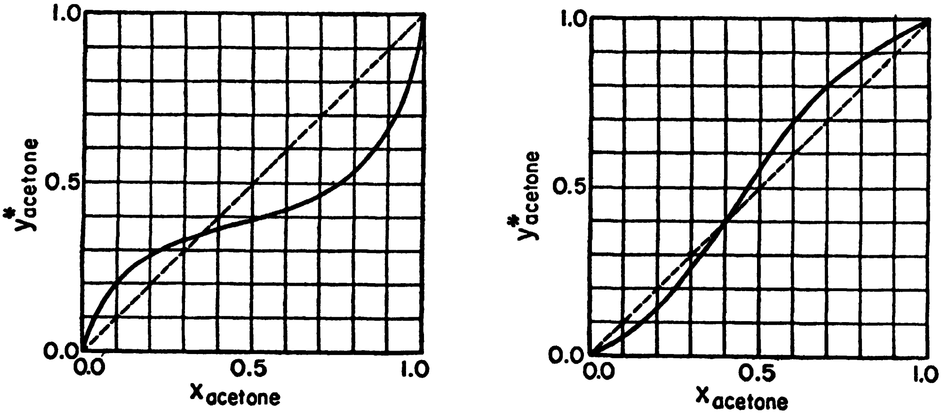

FIG. 7-12. Equilibrium vapor vs. liquid composition. (*a*) Carbon disulfide-acetone solutions at 29.2°C, showing an azeotrope with maximum vapor pressure. (*J. Hirshberg, as reported in Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Suppl.* IIIc, p. 2466, 1936.) (*b*) Chloroform-acetone solutions at 35.17°C, showing an azeotrope with minimum vapor pressure. [*J. von Zawidski, Z. physik. Chem.*, **35**, 129–203 (1900).]

A companion equation for the relation between the compositions of liquid and equilibrium vapor phases and the boiling point at constant pressure may be derived as follows. For equilibrium between the liquid and vapor phases of a binary solution at constant pressure, conditions (7-1-16) must apply at each liquid composition and its corresponding equilibrium temperature, or boiling point under the given pressure. Therefore for a change from one composition to another slightly different one, the change in boiling point is determined by the conditions

$$\left.\begin{aligned} d\phi_1 &= d\phi_1^* \\ d\phi_2 &= d\phi_2^* \end{aligned}\right\} \qquad (p \text{ const})$$

In view of Eq. (7-1-26*a*), which we shall want to use, we may put these general equilibrium conditions in the more convenient form

$$\left.\begin{aligned} d\left(\frac{\phi_1}{T}\right) &= d\left(\frac{\phi_1^*}{T}\right) \\ d\left(\frac{\phi_2}{T}\right) &= d\left(\frac{\phi_2^*}{T}\right) \end{aligned}\right\} \qquad (p \text{ const}) \qquad (7\text{-}3\text{-}10)$$

This procedure is legitimate, since the temperatures of the two phases are equal to each other in all equilibrium states throughout. Now, we may write in general,

$$d\left(\frac{\phi_1}{T}\right) = \left[\frac{d(\phi_1/T)}{dT}\right]_{p,x_1} dT + \left[\frac{d(\phi_1/T)}{dx_1}\right]_{T,p} dx_1 \qquad (p \text{ const})$$

where for a binary solution, only one of the two mole fractions x_1 and x_2 has been considered as composition variable determining the values of the intensive properties ϕ_1/T and ϕ_2/T. Introducing Eq. (7-1-26*a*), this equation assumes the form

$$d\left(\frac{\phi_1}{T}\right) = -\frac{\eta_1}{T^2}\,dT + \left[\frac{d(\phi_1/T)}{dx_1}\right]_{T,p} dx_1 \qquad (p \text{ const})$$

Similarly,

$$d\left(\frac{\phi_1^*}{T}\right) = -\frac{\eta_1^*}{T^2}\,dT + \left[\frac{d(\phi_1^*/T)}{dy_1}\right]_{T,p} dy_1 \qquad (p \text{ const})$$

which, in view of Eq. (7-2-5), we may put in the form

$$d\left(\frac{\phi_1^*}{T}\right) = -\frac{\eta_1^*}{T^2}\,dT + \frac{R}{y_1}\,dy_1 \qquad (p \text{ const})$$

assuming that we may treat the equilibrium vapor phase as an ideal gas. Introducing now the general equilibrium condition (7-3-10),

$$\frac{\eta_1^* - \eta_1}{T^2}\left(\frac{dT}{dx_1}\right)_p = \frac{R}{y_1^*}\left(\frac{dy_1^*}{dx_1}\right)_p - \left[\frac{d(\phi_1/T)}{dx_1}\right]_{T,p} \qquad (7\text{-}3\text{-}11)$$

A corresponding equation in terms of component 2 is derived from the second of conditions (7-3-10), which, in view of the fact that $x_2 = 1 - x_1$ and $y_2^* = 1 - y_1^*$, we may put in the form

$$\frac{\eta_2^* - \eta_2}{T^2}\left(\frac{dT}{dx_1}\right)_p = -\frac{R}{1 - y_1^*}\left(\frac{dy_1^*}{dx_1}\right)_p - \left[\frac{d(\phi_2/T)}{dx_1}\right]_{T,p} \qquad (7\text{-}3\text{-}12)$$

If we multiply Eq. (7-3-11) by x_1 and Eq. (7-3-12) by x_2, and add the resulting equations, then, according to the Gibbs-Duhem equation (7-1-8), the contributions of the last terms on the right of Eqs. (7-3-11) and (7-3-12) cancel each other, leaving

$$\frac{x_1(\eta_1^* - \eta_1) + x_2(\eta_2^* - \eta_2)}{T^2}\left(\frac{dT}{dx_1}\right)_p = R\,\frac{x_1 - y_1^*}{y_1^*(1 - y_1^*)}\left(\frac{dy_1^*}{dx_1}\right)_p$$

The expressions $(\eta_1^* - \eta_1)$ and $(\eta_2^* - \eta_2)$ evidently represent partial molal heats of vaporization of the respective components, and the entire numerator of the factor on the left of this equation represents the total latent heat of vaporization per mole of solution, corresponding to the particular liquid composition and equilibrium temperature; let us designate this quantity for short by the symbol $\bar{L}_{lg}$; thus

$$\left(\frac{dT}{dx_1}\right)_p = \frac{RT^2}{\bar{L}_{lg}}\,\frac{(x_1 - y_1^*)}{y_1^*(1 - y_1^*)}\left(\frac{dy_1^*}{dx_1}\right)_p \qquad (7\text{-}3\text{-}13)$$

Equation (7-3-13) is the counterpart to Eq. (7-3-9), and is thermodynamically exact within the ideal-gas-law approximation for the equilibrium vapor phase. Its practical utility is limited, however, because it involves too many quantities whose relationships to each other can be established independently only through empirical measurement; it is perhaps most useful for the purpose of calculating latent heats of vaporization of solutions from precise T-y_1^*-x_1 experimental data. One may easily derive Konowalow's rule for constant-pressure distillation, bearing in mind that $(dy_1^*/dx_1)_p$ is necessarily confined to nonnegative values (otherwise the distillation would be self-sustaining): if the boiling point rises with increase in the value of x_1, then y_1^* cannot be greater than x_1, whereas if the boiling point falls with increase in the value of x_1, then y_1^* cannot be less than x_1. Furthermore, one sees that if T goes through either a minimum or a maximum with change in the value of x_1, then at the extremum either $y_1^* = x_1$ (as in the case of an azeotropic mixture) or $(dy_1^*/dx_1)_p = 0$ (as may happen if the liquid phase separates into two mutually saturated liquids over part of the composition range, corresponding to limited miscibility of the components at the given pressure).

c. Raoult's Law: the Ideal Dilute Solution. While Eq. (7-3-3), or its generalizations that take into account deviation from the ideal-gas law of the equilibrium vapor phase, always enables one to determine thermodynamic potentials in liquid or solid solutions accurately from measurements of the vapor pressure and the composition of the equilibrium vapor phase, we should like if possible to relate them directly to the composition of the phase in question. In general, such relations can never be established by purely thermodynamic reasoning. Thermodynamics consists essentially of a system of differential equations; the functions on which these equations operate can be established only through empirical observation, guided perhaps by theoretical generalizations of nonthermodynamic origin.

While no relation of a universal form has been discovered between the vapor pressure and the composition of a liquid solution valid over the entire composition range (as one can well understand by observing the wide variety of relationships shown by the data assembled in Fig. 7-10), many solutions do show a certain type of regularity when the concentrations of all but one of the components are sufficiently small. Let subscript 1 denote the *solvent*, or component present at relatively high concentration; then *at sufficiently low solute concentration*

$$p_1 = x_1 p_1^\circ \qquad (T \text{ const}; x_1 \rightarrow 1) \qquad (7\text{-}3\text{-}14)$$

where p_1° represents the vapor pressure of the pure solvent. This empirical limiting law for the so-called *ideal dilute solution* has come to be known as *Raoult's law*.[1] An important class of apparent exceptions, noted by Raoult, and incorporated by Arrhenius as one of the bases of his

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[1] F. M. Raoult, *Compt. rend.*, **103**, 1125–1127 (1886); *Z. physik. Chem.*, **2**, 353–373 (1888). Raoult experimented originally with the lowering of the vapor pressure of a volatile solvent resulting from the presence of a nonvolatile solute at various concentrations. In this special case, the directly observed vapor pressure of the solution is the same as the partial vapor pressure of the solvent. From extensive measurements with solutes of known molecular weights, Raoult established the generality of the law

$$\frac{\Delta p_1}{p_1^\circ} = \frac{p_1^\circ - p_1}{p_1^\circ} = x_2 \qquad (T \text{ const}; x_2 \rightarrow 0) \qquad (7\text{-}3\text{-}14a)$$

which for binary solutions is equivalent to (7-3-14). He then applied this empirical relation to measure the molecular weights of solutes such as the sugars, to which Avogadro's method based on density in the gaseous state could not be applied. The importance of this work to the systematic development of chemistry cannot be overemphasized.

ionization theory,[1] consists of the electrolytes, which we shall discuss in Sec. 7-4.

Raoult's law implies that the limiting slopes of the partial vapor-pressure curves plotted in Fig. 7-10 as the mole fractions of the respective components approach 1 are the same as those of the straight lines connecting the vapor pressures of the pure components with the corresponding origins (the dashed lines shown on the graphs). In these binary liquid solutions, in which the components are miscible over the entire composition range, the distinction between solvent and solute is purely formal, depending merely on which end of the composition range one wishes to consider. One sees in Fig. 7-10 that even though the shapes of the complete partial vapor-pressure curves vary widely, nevertheless Raoult's law is satisfied by each component as its own mole fraction approaches sufficiently close to 1. The same point is illustrated in Fig. 7-11, where Raoult's law implies that the limiting slopes of the log p_i vs. log x_i graphs equal 1 as $x_i \rightarrow 1$. Other apparent exceptions to Raoult's limiting law besides the electrolytes have been recognized, such as the behavior of acetic acid and of benzoic acid dissolved in benzene, the behavior of acetic acid dissolved in water, etc. Generally, these have received rational explanations in terms of polymerization of the solute, reaction of the solute with the solvent, or other unusual behavior affecting the true mole fractions of the components. Indeed, the very extent of deviation from Raoult's law in such cases has commonly been used to reveal the true nature of the solution, and the kinds of chemical species present. We may regard the law as having a sound though not completely general empirical foundation.

Over the ideal dilute-solution range, however wide it may happen to be in a particular case, the thermodynamic potential of the *solvent* must be given according to Eqs. (7-3-3) and (7-3-14) by

$$\phi_1 = (\bar{F}_T^\circ)_1 + RT \ln x_1 \quad (T \text{ const}; x_1 \rightarrow 1) \quad (7\text{-}3\text{-}15)$$

assuming that the pressure is sufficiently close to 1 atm so that one may use $(\bar{F}_T^\circ)_1$ as the molal free energy of the pure solvent at the given temperature and pressure [otherwise one must use $(\bar{F}_{T,p})_1$, related to $(\bar{F}_T^\circ)_1$ by Eq. (6-16)]. Equation (7-3-15) constitutes in fact a thermodynamic generalization of Raoult's law, for we may suppose in the absence of sufficient reason to the contrary that this equation continues to represent the ideal limiting behavior at low solute concentration for a solvent whose vapor pressure at the given temperature happens to be too low to be measured precisely. This supposition may of course be confirmed by

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[1] S. Arrhenius, *Z. physik. Chem.*, **1**, 631–648 (1887).

experimental test of the thermodynamic implications of Eq. (7-3-15), assumed as an empirical principle, as we shall see in subsequent sections of this chapter.

Now, in the case of a binary solution, according to the Gibbs-Duhem equation (7-1-8), the thermodynamic potential of the *solute* is related to that of the *solvent* by

$$d\phi_2 = -\frac{x_1}{x_2}\,d\phi_1 \qquad (T, p \text{ const})$$

Therefore over the ideal dilute range in which the thermodynamic potential of the *solvent* is given by Eq. (7-3-15), the thermodynamic potential of the *solute* satisfies the equation

$$\begin{aligned} d\phi_2 &= -RT\frac{dx_1}{x_2} \\ &= RT\,d\ln x_2 \\ \phi_2 &= \phi_2^\circ + RT\ln x_2 \quad (T \text{ const}; x_2 \to 0) \qquad (7\text{-}3\text{-}16) \end{aligned}$$

In Eq. (7-3-16), ϕ_2° represents an integration constant, by hypothesis independent of x_2, but in general *not* equal to the standard molal free energy of the pure solute. Its value at given temperature and pressure[1] depends on the particular solute and solvent, and can be determined only by empirical measurement of ϕ_2 at some composition x_2 falling within the ideal dilute range; more precisely, its value may be established as the limit

$$\phi_2^\circ = \lim_{x_2 \to 0} (\phi_2 - RT\ln x_2) \qquad (7\text{-}3\text{-}17)$$

from a series of measurements of ϕ_2 at low values of x_2.

If the solute happens to be sufficiently volatile for its partial vapor pressure to be measured in the equilibrium vapor phase (*i.e.*, for its concentration to be measured in the equilibrium vapor phase, or distillate), then Eq. (7-3-3), which applies to *any* volatile component within the precision of the ideal-gas-law approximation, constitutes a direct independent means of measuring ϕ_2. Comparing with the ideal limiting law (7-3-16), we may draw the conclusion

$$p_2 = k_2x_2 \quad (T \text{ const}; x_2 \to 0) \qquad (7\text{-}3\text{-}18)$$

where the proportionality constant k_2 is related to ϕ_2° by means of the equation

$$\phi_2^\circ = (\bar{F}_T^\circ)_2 + RT\ln\frac{k_2}{p_2^\circ} \qquad (T \text{ const}) \qquad (7\text{-}3\text{-}19)$$

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[1] Taken to be 1 atm unless otherwise specified; we have seen that the thermodynamic properties of liquid solutions are not particularly sensitive to changes in the pressure.

Equation (7-3-18), known as *Henry's law*,[1] necessarily applies to the solute over the composition range in which the solvent satisfies Raoult's law (7-3-14). This conclusion implies that in Fig. 7-10, so long as the partial vapor-pressure curve of the one component coincides with the Raoult straight line as its mole fraction approaches 1, the partial vapor pressure of the other component approaches 0 also along a straight line, whose slope ($=k_2$), however, has no necessary connection with that of the Raoult line for that component. Measurement of k_2 by the application of Eq. (7-3-18) to experimental liquid-vapor equilibrium data constitutes a straightforward method of relating the integration constant ϕ_2° of Eq. (7-3-16) to the thermodynamic properties of the pure solute through Eq. (7-3-19); there is no general connection of a purely thermodynamic nature between ϕ_2° and $(\bar{F}_T^\circ)_2$. For example, from the data for chloroform-acetone solutions at 35.17°C presented in Figs. 7-10*f* and 7-11*a*, one concludes that for dilute solutions of acetone in chloroform,

$$k_2 = \lim_{x_2 \to 0} p_2/x_2 = 193 \text{ mm Hg}$$

Since at the given temperature, $p^\circ_{\text{acetone}} = 345$ mm Hg, therefore

$$\phi^\circ_{\text{acetone (in CHCl}_3)} - \bar{F}^\circ_{\text{acetone}} = RT \ln (193 \text{ mm Hg}/345 \text{ mm Hg}) = -356 \text{ cal/mole}$$

Similarly, for dilute solutions of chloroform in acetone,

$$\phi^\circ_{\text{CHCl}_3\text{(in acetone)}} - \bar{F}^\circ_{\text{CHCl}_3} = RT \ln (156 \text{ mm Hg}/293 \text{ mm Hg}) = -387 \text{ cal/mole}$$

On the other hand, for dilute solutions of *n*-propanol in water at 25°C, according to the data presented in Fig. 7-11*c*, $k_2 = 260$ mm Hg, whence,

$$\phi^\circ_{n\text{-propanol (aq)}} - \bar{F}^\circ_{n\text{-propanol}} = RT \ln (263 \text{ mm Hg}/21.76 \text{ mm Hg}) = 1470 \text{ cal/mole}$$

Equation (7-3-16) is, however, more general than Eq. (7-3-18), because it applies equally well to solutes insufficiently volatile under the given conditions of investigation for their concentrations in the equilibrium

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[1] Named after William Henry, who in 1803 first stated the empirical law that the solubility of a gas in a liquid with which it undergoes no chemical reaction is approximately proportional to the pressure of the gas. Equation (7-3-18) is of course more general than Henry's original law. Since at low solute concentrations, the mole fraction x_2 for a given solute and solvent is approximately proportional to other concentration measures, such as the molality m_2 and the molar concentration C_2, Henry's law (7-3-18) may be expressed in the equivalent forms $p_2 = k_2'm_2$ or $p_2 = k_2''C_2$, where the proportionality constants k_2' and k_2'' differ from but are numerically related to k_2; see Sec. 7-3*g*.

vapor phase to be measured. We may therefore regard Eq. (7-3-16) as a thermodynamic generalization of Henry's law for the solute, in the same sense as we may regard Eq. (7-3-15) as a thermodynamic generalization of Raoult's law for the solvent. Other methods of measuring ϕ_2 relatively to $(\bar{F}_T)_2$, when the solute happens not to be volatile, will be discussed later.

As we have previously mentioned, Eq. (7-3-15) represents an empirical law, which cannot be inferred from purely thermodynamic principles. Equation (7-3-16) is, however, a logically entailed consequence of (7-3-15), derived by means of the Gibbs-Duhem relation. Equations (7-3-15) and (7-3-16) together, provided that one has measured the value of ϕ_2° for each individual case, constitute empirically a complete thermodynamic description of most binary liquid solutions (excluding electrolytes, which require further empirical study, as shown in Sec. 7-4) when the concentration of either component is sufficiently low. Applying to them the general thermodynamic relation (7-1-26*b*),

$$\eta_1 = \left[\frac{d(\phi_1/T)}{d(1/T)}\right]_{p,n} = \left[\frac{d((\bar{F}_T^\circ)_1/T)}{d(1/T)}\right]_p$$

$$\eta_2 = \left[\frac{d(\phi_2/T)}{d(1/T)}\right]_{p,n} = \left[\frac{d(\phi_2^\circ/T)}{d(1/T)}\right]_p$$

one finds that the partial molal enthalpies in the ideal dilute range are given by

$$\lim_{x_1\to 1} \eta_1 = (\bar{H}_T^\circ)_1; \qquad \lim_{x_2\to 0} \eta_2 = (\Phi_h^\circ)_2 = \left[\frac{d(\phi_2^\circ/T)}{d(1/T)}\right]_p \tag{7-3-20}$$

Thus, over the composition range in which the solvent satisfies approximately Raoult's law, its partial molal enthalpy in solution is equal within the same order of approximation to its standard molal enthalpy as a pure liquid (or solid, as the case may be), at the given temperature; but the partial molal enthalpy of the solute over the same range assumes a constant value, determined by the temperature coefficient of ϕ_2°. Recalling Eq. (4-30), one sees that the total molal heat of solution of component 2 as solute in component 1 as solvent is given by

$$\bar{Q}_s^\circ = (\bar{H}_T^\circ)_2 - \left[\frac{d(\phi_2^\circ/T)}{d(1/T)}\right]_p \qquad (T,\ p\ \text{const}) \tag{7-3-21}$$

$$= \left[\frac{d((\bar{F}_T^\circ)_2 - \phi_2^\circ)/T}{d(1/T)}\right]_p \qquad (T,\ p\ \text{const}) \tag{7-3-22}$$

These equations serve either to establish the temperature coefficient of the quantity ϕ_2° from calorimetric heat-of-solution data, or to establish

$\bar{Q}_s^\circ$ indirectly from equilibrium data (*e.g.*, vapor pressure data) obtained for the solution at various temperatures. Of course, in the case of a binary solution consisting of two liquids miscible over the entire composition range, the value of $\bar{Q}_s^\circ$ for component 2 in component 1 differs in general from the value of $\bar{Q}_s^\circ$ for component 1 in component 2, even though both are computed from essentially the same set of basic measurements (by extrapolations in opposite directions of thermal data obtained for the mixing of the two components in various finite proportions).

Similarly, by application of the thermodynamic relation (7-1-24) to the general forms of Raoult's and Henry's laws,

$$\left.\begin{aligned} \phi_1 &= (\bar{F}_{T,p})_1 + RT \ln x_1 \\ \phi_2 &= \phi_2^\circ + RT \ln x_2 \end{aligned}\right\} \quad (T,\ p \text{ const};\ x_2 \rightarrow 0) \qquad (7\text{-}3\text{-}23)$$

which we may suppose apply at pressures other than 1 atm, we obtain

$$v_1 = \left(\frac{d\phi_1}{dp}\right)_{T,n} = \left(\frac{d\bar{F}_1}{dp}\right)_T$$
$$v_2 = \left(\frac{d\phi_2}{dp}\right)_{T,n} = \left(\frac{d\phi_2^\circ}{dp}\right)_T$$

Therefore the partial molal volumes in the ideal dilute range are given by

$$\lim_{x_1 \rightarrow 1} v_1 = \bar{V}_1; \qquad \lim_{x_2 \rightarrow 0} v_2 = \left(\frac{d\phi_2^\circ}{dp}\right)_T \qquad (7\text{-}3\text{-}24)$$

Over the composition range in which the solvent satisfies Raoult's law, in the general sense of Eq. (7-3-23), its partial molal volume in solution is equal to its molal volume in the pure state at the same temperature and pressure; but the partial molal volume of the solute over the same composition range has a constant value, in general *not* equal to the molal volume of the pure solute. There will thus be a net volume change on mixing the components, whose limiting value per mole of solute in the ideal dilute-solution range is represented by $\left(\frac{d\phi_2^\circ}{dp}\right)_T - \bar{V}_2$. Since, as we have already noted, the value of v_2 in liquid or solid solutions is numerically small, even when the pure solute is itself a gas, the value of ϕ_2° is relatively insensitive to small changes in the pressure, of order 1 atm; but Eq. (7-3-24) may always be used to calculate precisely the pressure effect.

While Eqs. (7-3-15) and (7-3-16) correctly describe the behavior of most binary solutions at sufficiently low concentrations of either component, provided that the solute is not an electrolyte in the given solvent and that no other unusual chemical effect tends to alter the significance of the conventional mole-fraction composition measures, the extent of the ideal dilute-solution range (which of course is not sharply defined) depends altogether on the particular pair of components present. In the majority of cases, one would be justified in assuming that the ideal dilute-solution laws apply without significant error when $x_2 \leqq 0.02$ (compare Fig. 7-10); the noteworthy fact is that in this range, the thermodynamic potential and other partial molal properties attributed to the *solvent* do not depend at all on the nature of the solute but only on its molecular concentration; on the other hand, the corresponding properties of the *solute,* while satisfying uniform laws with regard to the effect of concentration, each involve specific constants (ϕ_2°, Φ_h°, etc.) that vary from one solvent to another. In many cases, one will observe significant departure from ideal dilute behavior at solute concentrations as low as $x_2 = 0.1$. There are certain liquid pairs, however, that conform closely to Raoult's law over the entire composition range (compare Fig. 7-10*a* to *c*). In such cases, it necessarily follows from the Gibbs-Duhem relation that if one component satisfies Raoult's law (more or less approximately) over the entire composition range, then the other component must likewise satisfy Raoult's law over the entire composition range; *i.e.*, the value of the integration constant ϕ_2° in Eq. (7-3-16) for the "solute" in this special case must be equal to $(\bar{F}_T^\circ)_2$. Experience indicates that we are most likely to encounter such ideal behavior over the entire composition range when the two components happen to consist of molecules showing close structural similarity, particularly with regard to degree of polarity and molecular size. Thus, solutions practically ideal over the entire composition range are formed by the following liquid pairs (among many others that have been studied): D_2O and H_2O,[1] O_2 and N_2,[2] benzene and toluene,[3] benzene and chlorobenzene,[4] *n*-hexane and *n*-heptane,[5] ethyl bromide and ethyl iodide,[5] ethylene bromide and propylene bromide.[6]

A general appreciation of the factors influencing the ideality or the nonideality of liquid solutions may be derived from the molecular theory of their structure, which is of course beyond the scope of thermodynamics proper.[7] The behavior of molecules in the liquid state is strongly influ-

[1] G. N. Lewis and W. T. Hanson, *J. Am. Chem. Soc.*, **56,** 1000–1001 (1934).

[2] J. K. H. Inglis, *Phil. Mag.*, (6) **11,** 640–658 (1906); see Fig. 7-10*a*.

[3] G. C. Schmidt, *Z. physik. Chem.*, **99,** 71–86 (1921); also W. von Huhn, Dissertation, Munich, 1931 (see Fig. 7-10*c*).

[4] A. R. Martin and B. Collie, *J. Chem. Soc.*, 2658–2665 (1932); see Fig. 7-10*b*.

[5] C. P. Smyth and E. W. Engel, *J. Am. Chem. Soc.*, **51,** 2646–2660 (1929).

[6] Zawidski, *loc. cit.*

[7] An excellent comprehensive discussion of the theory of solutions is given by J. H. Hildebrand and R. L. Scott, "The Solubility of Non-electrolytes," 3d ed., Reinhold Publishing Corporation, New York, 1950.

enced by van der Waals' attractive forces, whose origin appears to be electrostatic, whether arising from the interaction of permanent electric dipoles existing in the molecules or of temporary dipoles induced by mutual polarization of neighboring molecules. In the ideal dilute solution, we may suppose that solute molecules are thinly dispersed throughout a medium essentially like the pure solvent, in that the neighbors of a given molecule of either kind are predominantly solvent molecules. The effect of the solute in this range is therefore primarily one of pure dilution, without specific influence on the behavior of the solvent molecules. No specific property of the solute enters Eqs. (7-3-14) and (7-3-15); it is noteworthy that in the ideal dilute range, the partial vapor pressure of the solvent is lowered to the same extent by a volatile as by a nonvolatile solute at the same molecular concentration. From the standpoint of the solute, however, the situation in the ideal dilute range is in general different from that encountered in the pure solute; the behavior of the solute molecules is determined by the interaction between solute and solvent molecules, which may be quite different from the interaction between the solute molecules themselves in the pure state. Thus, we find that while p_2 increases in direct proportion to x_2 over the ideal dilute range, the proportionality factor, k_2 in Eq. (7-3-18), is in general unrelated to the vapor pressure of pure component 2, and varies from one solvent to another. If the van der Waals attraction between solute and solvent molecules tends to be weaker than the normal attraction between solute molecules in the pure state, resulting in a relatively higher potential energy of intermolecular attraction per solute molecule in the solution as compared with the pure state, then we can expect that p_2 will increase with x_2 more rapidly than one would be led to expect from its vapor pressure in the pure state; that is, k_2 in Eq. (7-3-18) will be greater than p_2°, or what amounts to the same thing, ϕ_2° in Eq. (7-3-16) will exceed $(\bar{F}_T^\circ)_2$. This type of behavior, so-called *positive deviation from Raoult's law* (compare Fig. 7-10*d*, *e*, *h*), is likely to be encountered when there is a marked difference in the polarities of the two kinds of molecules, as when one dissolves a polar solute in a nonpolar solvent (*e.g.*, acetone in CS_2, *n*-butanol in CCl_4, ethanol in *n*-heptane, etc.). *Negative deviation from Raoult's law* (compare Fig. 7-10*f*, *g*) may imply that van der Waals' attraction between solute and solvent molecules is stronger than the normal attraction between solute molecules in the pure state; in some such cases, there is clear evidence of a tendency for actual chemical reaction to take place between the solute and solvent (*e.g.*, NH_3 in H_2O). It may also be a consequence, however, of the influence of the shapes and relative sizes of the molecules on the degree of order with which they may pack in the liquid state; this effect has been observed particularly in solutions of high polymers.[1] Positive deviation from Raoult's law is, however, far more common than negative deviation (if one reserves for special consideration the behavior of electrolytes). If it happens that both solute and solvent molecules are nonpolar, or if they are both polar and have similar general shapes and sizes, so that Van der Waals' forces between the different kinds of molecules are approximately the same in character as the forces between like molecules, then conditions are most favorable for the formation of solutions ideal over the entire composition range.

The difference, $\phi_2^\circ - (\bar{F}_T^\circ)_2$, serves as a measure of the influences we have been discussing. If the solute is similar to the solvent in molecular configuration and polarizability, we may expect a zero or at most a small positive value for this difference; if the solute and solvent differ considerably in molecular configuration, particularly when one type of molecule is strongly polar (as indicated by a comparatively large dipole moment) and the other nonpolar, then we may expect a relatively large positive value for this difference; in those relatively uncommon cases in which solute and solvent are exceptionally strongly attracted to each other, possibly with a tendency toward compound formation, or in which the two kinds of molecules differ considerably in size, then the difference may be negative in value.

Since in sufficiently dilute solution, the particular nature of the solute appears to have no effect on the thermodynamic potential of the solvent, we should expect that if several independent solutes were present, each at a sufficiently low concentration, then the solvent would continue to satisfy the empirical law (7-3-15); or what amounts to approximately the same thing, the partial vapor pressure of the solvent would decrease according to the empirical generalization

$$\frac{p_1^\circ - p_1}{p_1^\circ} = x_2 + x_3 + \cdots \qquad (T \text{ const}; x_2, x_3, \cdots \to 0) \qquad (7\text{-}3\text{-}25)$$

This equation and its thermodynamic implications (*e.g.*, effect on the boiling point, freezing point, etc., as we shall show later) have been tested experimentally and found to be generally correct. Now, according to the general Gibbs-Duhem equation in the form (7-1-8)

$$x_2\,d\phi_2 + x_3\,d\phi_3 + \cdots = -x_1\,d\phi_1 \qquad (T, p \text{ const})$$

which if the solvent satisfies Raoult's law in the form (7-3-15), reduces to

$$\begin{aligned} x_2\,d\phi_2 + x_3\,d\phi_3 + \cdots &= -RT\,dx_1 \\ &= RT(dx_2 + dx_3 + \cdots) \qquad (T \text{ const}; x_1 \to 1) \end{aligned} \qquad (7\text{-}3\text{-}26)$$

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[1] Hildebrand and Scott, *op. cit.*, Chaps. VI and XX.

Equation (7-3-26) is not sufficient to enable us to separate in a rigorous manner the effects of the different composition variables x_2, x_3, . . . on the thermodynamic potentials ϕ_2, ϕ_3, ... It seems reasonable for us to suppose, however, that at sufficiently low total solute concentration, in the absence of specific chemical reactions among the solutes masking their true concentrations, the behavior of each solute will be independent of the presence of the others, and will be essentially the same as though it alone were present in the solvent at the same concentration. In other words, let us suppose that in sufficiently dilute solution in the given solvent, ϕ_2 does not depend explicitly on x_3, x_4, . . . , but only on x_2, and ϕ_3 likewise does not depend explicitly on x_2, x_4, . . . , but only on x_3, . . . ; then we may separate terms in Eq. (7-3-26) that depend, respectively, only on x_2, on x_3, . . . , and thus draw the conclusions

$$\left.\begin{aligned} \phi_2 &= \phi_2^\circ + RT\ln x_2 \\ \phi_3 &= \phi_3^\circ + RT\ln x_3 \\ &\cdots\cdots\cdots\cdots \end{aligned}\right\} \quad (T \text{ const}; x_2, x_3, \ldots \to 0) \qquad (7\text{-}3\text{-}27)$$

where by supposition, the constants ϕ_2°, ϕ_3°, . . . have the same values one would obtain for the respective solutes dissolved separately in the same solvent. The essential correctness of this idea is substantiated by equilibrium data for chemical reactions taking place in dilute solution in a given solvent, as we shall see in Chap. 8.

If we have a third component dissolved at relatively low concentration in a liquid (or solid) medium consisting of two other components at relatively high concentrations, then presumably ϕ_3 for the third component (the "solute") may satisfy an equation of the form (7-3-27), but with ϕ_3° a "constant" dependent on the relative proportions of the other two components. In other words, the medium consisting of the other two components in fixed relative proportion may be regarded as itself the "solvent"; but the value of ϕ_3° in this case will in general not be simply related to the ϕ_3° values obtained for component 3 as solute in the other two components separately as solvents. This problem of the thermodynamics of solutions in "mixed" solvents is technically important, but too complex for further discussion here.

d. The Ideal Concentrated Solution. While the properties of ideal concentrated solutions have limited practical value, there is considerable interest in the ideal solution as a theoretical concept, and as a reference base from which to study the properties of real solutions. Whereas real binary solutions satisfy the limiting Eqs. (7-3-15) and (7-3-16) in the ideal dilute range only, with ϕ_2° an empirical constant whose value cannot be deduced by purely thermodynamic means from the properties of the pure solute, we may define ideal concentrated solutions as solutions satisfying at all temperatures, pressures, and compositions the pair of equations

$$\left.\begin{aligned} \phi_1 &= (\bar{F}_{T,p})_1 + RT \ln x_1 \\ \phi_2 &= (\bar{F}_{T,p})_2 + RT \ln x_2 \end{aligned}\right\} \qquad (7\text{-}3\text{-}28)$$

The thermodynamic potentials of the components are in other words completely defined by the molal free energies $(\bar{F}_{T,p})_1$ and $(\bar{F}_{T,p})_2$ of the pure components at the particular temperature and pressure, together with the composition. Comparing with Eq. (7-2-5), one perceives that a binary ideal-gas solution essentially satisfies Eqs. (7-3-28). In applying Eqs. (7-3-28) to liquid or solid solutions, the terms $(\bar{F}_{T,p})_1$ and $(\bar{F}_{T,p})_2$ refer, however, to the two pure components in the liquid state, or in the solid state, as the case may be, just as in Eq. (7-2-5) the corresponding terms $((\bar{F}_T^\circ)_i + RT \ln p)$ refer to the gaseous state; obviously, there must be a limit to the composition range over which the solution exists unless both components in the pure state are in similar states of aggregation (gas, liquid, or crystalline solid). For a liquid or a solid solution satisfying Eqs. (7-3-28), if we may assume that the equilibrium vapor phase satisfies the ideal-gas law and that the changes of $(\bar{F}_{T,p})_1$ and $(\bar{F}_{T,p})_2$ with pressure between the vapor pressures of the pure components may be neglected, then these equations are equivalent to

$$\left.\begin{aligned} p_1 &= x_1 p_1^\circ; \qquad p_2 = x_2 p_2^\circ \\ p &= p_1 + p_2 = x_1 p_1^\circ + x_2 p_2^\circ \\ y_1^* &= \frac{x_1 p_1^\circ}{x_1 p_1^\circ + x_2 p_2^\circ}; \qquad y_2^* = \frac{x_2 p_2^\circ}{x_1 p_1^\circ + x_2 p_2^\circ} \end{aligned}\right\} \quad (T \text{ const}) \qquad (7\text{-}3\text{-}29)$$

for all compositions.

By the same argument that led to Eqs. (7-3-20) and (7-3-24), we may easily show that for a solution satisfying Eqs. (7-3-28)

$$\left.\begin{aligned} \eta_1 &= (\bar{H}_{T,p})_1; \qquad \eta_2 = (\bar{H}_{T,p})_2 \\ v_1 &= (\bar{V}_{T,p})_1; \qquad v_2 = (\bar{V}_{T,p})_2 \end{aligned}\right\} \qquad (7\text{-}3\text{-}30)$$

The partial molal enthalpies and the partial molal volumes are equal, respectively, to the molal enthalpies and the molal volumes of the pure components at the same temperature and pressure. Therefore for an ideal concentrated solution, the heat of solution and the net volume change on mixing the components in any proportion are both zero.

Just as in the case of an ideal-gas mixture, the free energy of solution per mole of solution formed, given in general by the expression

$$\Delta\bar{F} = x_1\phi_1 + x_2\phi_2 - x_1(\bar{F}_{T,p})_1 - x_2(\bar{F}_{T,p})_2 \quad (T, p \text{ const})$$

assumes the ideal form

$$\Delta\bar{F} = RT(x_1 \ln x_1 + x_2 \ln x_2) \quad (T, p \text{ const}) \quad (7\text{-}3\text{-}31)$$

Likewise, the entropy of solution per mole of solution formed, given in general by

$$\Delta\bar{S} = \frac{\Delta\bar{H} - \Delta\bar{F}}{T} \qquad (T, p \text{ const})$$

assumes the ideal form (since $\Delta\bar{H} = 0$)

$$\Delta\bar{S} = -R(x_1 \ln x_1 + x_2 \ln x_2) \quad (T, p \text{ const}) \quad (7\text{-}3\text{-}32)$$

Equation (7-3-32) and the corresponding identical equation for ideal-gas mixtures, Eq. (7-2-7), have a simple interpretation in terms of molecular statistical theory (which we shall discuss in detail in Chap. 10). Let us suppose that in 1 mole of ideal solution, there are N_0 completely equivalent places occupied by x_1N_0 molecules of component 1 and x_2N_0 molecules of component 2; in an ideal gas, each place is considered to be equivalent because intermolecular forces between the molecules at the comparatively large intermolecular distances involved are supposed to be completely negligible; in an ideal liquid or solid solution, each place is equivalent not because intermolecular forces are negligible, but because we suppose that the forces between neighboring molecules are similar, regardless of which type of molecule happens to occupy the adjacent positions. Now, if the N_0 places are filled completely at random, then corresponding to any composition x_1, x_2 there will be a certain number Ω of different ways in which the places could be filled, all of which are presumably equally likely if the distribution is governed by chance; there is of course no means of finding out which particular way prevails at any instant, in view of the relative coarseness of the methods of thermodynamic investigation, but all are equivalent. The number of ways of filling N_0 different places so that x_1N_0 are occupied by the one kind of molecule, and x_2N_0 by the other, is given by

$$\Omega = \frac{N_0!}{(x_1N_0)!(x_2N_0)!}$$

Let us take logarithms, for mathematical convenience; thus

$$\ln \Omega = \ln N_0! - \ln (x_1N_0)! - \ln (x_2N_0)!$$

Since the number N_0 (Avogadro's number) is enormous, we may without significant error apply Stirling's approximation

$$\ln N! \sim N \ln N - N \qquad (N \text{ large})$$

Therefore

$$\begin{aligned}\ln \Omega &= N_0 \ln N_0 - N_0 - (x_1N_0) \ln (x_1N_0) + x_1N_0 - (x_2N_0) \ln (x_2N_0) \\ &\qquad + x_2N_0 \\ &= -N_0(x_1 \ln x_1 + x_2 \ln x_2)\end{aligned}$$

(in view of the fact that $x_1 + x_2 = 1$). Comparing with Eq. (7-3-32), one sees that $\Delta\bar{S}$ is proportional to the logarithm of the total number of ways in which the two kinds of molecules may be distributed among the N_0 equivalent places:

$$\Delta\bar{S} = \frac{R}{N_0} \ln \Omega \tag{7-3-33}$$

In molecular statistical theory, we interpret this identification to mean that the value of $\Delta\bar{S}$ given by Eq. (7-3-32) corresponds simply to complete randomization when the two components are mixed. The irreversibility of the solution process measured by the value of $\Delta\bar{S}$ is thus a statistical effect, representing the unlikelihood that if chance alone rules, the solution will ever separate again into the two pure components. Such a separation would be equivalent to a configuration in which all x_1N_0 molecules of Type 1 occupied, say, the first x_1N_0 positions, while all x_2N_0 molecules of Type 2 occupied the remaining positions, *i.e.*, to a particular one of the various ways in which the places could be occupied by both kinds of molecules; the chance of such an event, $1 : \Omega$, is given according to Eq. (7-3-33) by the number $\exp\left(-\frac{N_0}{R}\Delta\bar{S}\right)$, which for a 50 mole per cent solution assumes the vanishingly small value $e^{-4.2\times 10^{23}}$. Equation (7-3-33) is a special case of a general relation between entropy and probability postulated by L. Boltzmann.

In real solutions, the entropy of solution may have a value different from that represented by Eq. (7-3-32); in such cases, other influences are present besides purely random intermixture of the component molecules.[1] On the other hand, we may have completely random dispersion of the molecules, but interaction energy that results in failure of the solution to be ideal in other respects. J. H. Hildebrand has proposed to call such solutions, satisfying Eq. (7-3-32) but not necessarily satisfying Eqs.

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[1] This is particularly the case for solutions of high polymers, where some degree of order [corresponding to an entropy of solution smaller than the ideal value given by Eq. (7-3-32)] may exist even in quite dilute solutions as a result of certain preferred orientations of the macromolecules with respect to each other. For a treatment of this important subject, see A. R. Miller, "The Theory of Solutions of High Polymers," Oxford University Press, London, 1948; see also Hildebrand and Scott, *op. cit.*, Chap. XX.

(7-3-28), "regular" solutions.[1] Equation (7-3-31) represents likewise the free energy of purely random mixing; the value of $-\Delta\bar{F}$ given by Eq. (7-3-31) represents the least quantity of energy in principle that must be expended on the solution in nonthermal form, other than work of compression, in order to separate the components at the fixed temperature T and pressure p in the absence of specific interaction between them. If specific effects beyond those of purely random mixing are present, as is generally true of nonideal solutions, then $\Delta\bar{F}$ differs from the ideal value given by Eq. (7-3-31), and the difference is called the *excess free energy of solution.*[2] It is the object of theories of solution to derive the value of this quantity from suitable assumptions concerning the sources of deviation from ideal behavior.

Solutions ideal at high solute concentrations need not be confined to liquid pairs, or solid pairs, but may include solutions of solids in liquids whose molecules are structurally similar, such as naphthalene in benzene. The difference from ordinary ideal behavior is that beyond a certain fixed proportion of solute to solvent at given temperature and pressure, the solute separates out of solution as a solid phase. The condition for equilibrium between the pure crystalline solute and the saturated solution is given in general by

$$\phi_2 = (\bar{F}_{T,p})_{2(c)}$$

which in the case of the ideal concentrated solution [Eqs. (7-3-28)] assumes the form

$$(\bar{F}_{T,p})_{2(l)} + RT \ln x_2^* = (\bar{F}_{T,p})_{2(c)} \quad \text{(ideal soln)} \qquad (7\text{-}3\text{-}34)$$

where x_2^* represents the solubility at T and p. We must evidently interpret the term $(\bar{F}_{T,p})_{2(l)}$ introduced by Eqs. (7-3-28) as the molal free energy of pure component 2 in the form of a supercooled liquid at the given temperature and pressure. Since both $(\bar{F}_{T,p})_{2(l)}$ and $(\bar{F}_{T,p})_{2(c)}$ are properties of the pure solute, independent of the particular solvent, Eq. (7-3-34) implies that the solubility of the particular solid in any liquid solvent with which it happens to form ideal concentrated solutions is the same, when expressed in terms of x_2, at the same temperature and pressure throughout. Since furthermore we have observed that in nonideal solutions, positive deviations from Raoult's law are much more common than negative deviations (particularly when one excludes known cases of chemical interaction between the components, dissociation of the solute, etc.), we may expect ϕ_2 in the nonideal saturated solution to be generally larger

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[1] J. H. Hildebrand, *J. Am. Chem. Soc.*, **51,** 66–80 (1929); see also Hildebrand and Scott, *op. cit.* The same concept has been discussed from a somewhat different point of view by E. A. Guggenheim, *Proc. Roy. Soc.* (*London*), (A) **148,** 304–312 (1935).

[2] G. Scatchard and W. J. Hamer, *J. Am. Chem. Soc.*, **57,** 1805–1809 (1935).

than the ideal value given by Eq. (7-3-34), and x_2^* therefore to be generally smaller than the ideal value. These ideas are substantiated by experiment; thus, in Table 7-2, one sees that the solubility of naphthalene at 25°C and 1 atm in many solvents is practically uniform, between the values: $x_2^* = 0.28$ to 0.32, but for several others, the solubility is considerably less than the ideal value.

By applying Eq. (6-12) to Eq. (7-3-34), we may derive an expression for the effect of temperature on the ideal solubility

$$\left(\frac{d\ln x_2^*}{dT}\right)_p = \frac{(\bar{H}_{T,p})_{2(l)} - (\bar{H}_{T,p})_{2(c)}}{RT^2}$$

The numerator of the right-hand term is simply the latent heat of fusion of pure component 2; thus

$$\left(\frac{d\ln x_2^*}{dT}\right)_p = \frac{(\bar{L}_{cl})_2}{RT^2} \qquad \text{(ideal soln)} \qquad (7\text{-}3\text{-}35)$$

The latent heat of fusion varies generally with temperature, according to an equation analogous to Eq. (6-72). One would find it difficult to determine $\bar{C}_p$ precisely for the supercooled liquid at temperatures well below the normal freezing point. Over a sufficiently small range of temperatures, however, we may integrate Eq. (7-3-35), treating $(\bar{L}_{cl})_2$ as constant; thus, starting from the normal freezing point of pure component 2, T_2°, where by supposition $x_2^* = 1$ in the liquid phase:

$$\log x_2^* = -\frac{(\bar{L}_{cl})_2}{2.303R}\left(\frac{1}{T} - \frac{1}{T_2^\circ}\right) \qquad \text{(ideal soln)} \qquad (7\text{-}3\text{-}36)$$

TABLE 7-2. SOLUBILITY OF NAPHTHALENE IN VARIOUS SOLVENTS AT 25°C*

Solvent	x_2^*
Chloroform	0.331
Chlorobenzene	0.317
Ethylene chloride	0.317
Pyridine	0.314
Ethylene bromide	0.311
Nitrobenzene	0.298
Benzene	0.296
Toluene	0.286
Carbon tetrachloride	0.260
Ethyl ether	0.242
Acetone	0.224
Hexane	0.125

* Solubilities are taken from the "International Critical Tables," Vol. IV, McGraw-Hill Book Company, Inc., New York, 1928; $\bar{L}_{cl}$ for naphthalene is taken from the critical review by G. S. Parks and H. M. Huffman, *Ind. Eng. Chem.*, **23**, 1138–1139 (1931).

The ideal solubility according to Eq. (7-3-36), with $\bar{L}_{cl} = 4610$ cal/mole at the normal melting point, 80°C, is $x_2^* = 0.298$; a slightly higher value is obtained if one attempts to take account of the change of $\bar{L}_{cl}$ with temperature.

Table 7-2 includes the ideal value of x_2^* for naphthalene at 25°C, as derived from Eq. (7-3-36); one sees that it is in good agreement with the group of higher experimental values of x_2^*. Clearly, the effect of temperature on the ideal solubility of the given solid is merely the obverse aspect of the lowering of its freezing point by the presence of component 1 as ideal "solute" in the liquid phase; *any* ideal solute at the same concentration, $1 - x_2^*$, would produce the same lowering of the freezing point. The freezing out of either pure component and the solubility of that component in the liquid phase at the given temperature are but two ways of looking at the same equilibrium state; we shall discuss the freezing points of liquid solutions generally in Sec. 7-5.

By applying Eq. (6-10) to Eq. (7-3-34), we may readily derive an equation analogous to (7-3-35) for the effect of pressure on the ideal solubility at constant temperature.

We may comment briefly on the relation between the boiling point and the composition of a binary liquid solution ideal over the entire composition range. According to (7-3-29),

$$x_1p_1^\circ + x_2p_2^\circ = p \qquad (T \text{ const}) \qquad (7\text{-}3\text{-}37)$$

For a change in composition at fixed total pressure (*e.g.*, atmospheric pressure), the equilibrium temperature between the liquid and vapor phases must therefore satisfy the relationship

$$p_1^\circ\left(\frac{dx_1}{dT}\right)_p + x_1\left(\frac{dp_1^\circ}{dT}\right) + p_2^\circ\left(\frac{dx_2}{dT}\right)_p + x_2\left(\frac{dp_2^\circ}{dT}\right) = 0$$

Thus

$$(p_1^\circ - p_2^\circ)\left(\frac{dx_1}{dT}\right)_p = -x_1\left(\frac{dp_1^\circ}{dT}\right) - x_2\left(\frac{dp_2^\circ}{dT}\right)$$

The Clausius-Clapeyron equation (6-69) may be introduced, with appropriate assumptions, in the two terms on the right

$$(p_1^\circ - p_2^\circ)\left(\frac{dx_1}{dT}\right)_p = -\frac{1}{RT^2}[x_1p_1^\circ(\bar{L}_{lg})_1 + x_2p_2^\circ(\bar{L}_{lg})_2]$$

where $(\bar{L}_{lg})_1$ and $(\bar{L}_{lg})_2$ represent the molal latent heats of vaporization of the respective pure components. Thus

$$\left(\frac{dT}{dx_1}\right)_p = RT^2\frac{(p_2^\circ - p_1^\circ)}{x_1p_1^\circ(\bar{L}_{lg})_1 + x_2p_2^\circ(\bar{L}_{lg})_2} \qquad (7\text{-}3\text{-}38)$$

Equation (7-3-38) represents a special case of Eq. (7-3-13). The equation as it stands is not particularly useful, because the vapor pressures and heats of vaporization of the pure components vary in complex ways with the temperature; therefore the equation cannot be readily integrated. A more practical approach to the construction of the boiling point vs. composition relation is to solve Eq. (7-3-37) for x_1 (noting that $x_2 = 1 - x_1$), at various values of T intermediate between the boiling points T_1 and T_2 of the pure components at the given pressure p, using the experimental or calculated values of p_1° and p_2° at each temperature; in this way, the entire T vs. x_1 relationship can be constructed for an ideal liquid pair, from knowledge of the vapor pressure vs. temperature relationships for both pure components. Equation (7-3-38) may be conveniently applied, however, to the calculation of the terminal slopes (as $x_1 \rightarrow 0$ and as $x_1 \rightarrow 1$, respectively) of the T vs. x_1 curve; thus

$$\left.\begin{aligned} \lim_{x_1\rightarrow 0}\left(\frac{dT}{dx_1}\right)_p &= \frac{RT_2^2}{(\bar{L}_{lg})_2}\,\frac{(p - p_1^\circ)}{p} \\ \lim_{x_1\rightarrow 1}\left(\frac{dT}{dx_1}\right)_p &= \frac{RT_1^2}{(\bar{L}_{lg})_1}\,\frac{(p_2^\circ - p)}{p} = -\lim_{x_2\rightarrow 0}\left(\frac{dT}{dx_2}\right)_p \end{aligned}\right\} \qquad (7\text{-}3\text{-}39)$$

These equations may be used to estimate the effect of a small concentration of either component on the boiling point. For example, CCl_4 boils at 76.6°C (349.8°K) under normal atmospheric pressure, and its molal latent heat of vaporization is 7283 cal/mole; the vapor pressure of $TiCl_4$ at the same temperature is 120 mm Hg; therefore in $TiCl_4$-CCl_4 solutions

$$\begin{aligned} &\lim_{x_{TiCl_4}\rightarrow 0}\left(\frac{dT}{dx_{TiCl_4}}\right)_{1\text{ atm}} \\ &\qquad = \frac{1.987\text{ cal/mole deg }(349.8\text{ deg})^2}{7283\text{ cal/mole}}\;\frac{(760 - 120)\text{ mm Hg}}{760\quad\text{mm Hg}} \\ &\qquad = 28.2\text{ deg} \end{aligned}$$

The actual boiling point of a solution containing 9.76 mole per cent $TiCl_4$ in CCl_4, as measured by N. Nasu,[1] is 79.2°C, in good agreement with the calculated increase of 0.0976 × 28.2 deg = 2.75 deg as estimated from the theoretical terminal slope of the T vs. x_1 relationship. It should be emphasized that the limiting equations (7-3-39) do *not* apply unless the two components form solutions ideal over the entire composition range.

e. Thermodynamic Description of Nonideal Solutions; the Activity Functions. The pair of equations (7-3-28), with their thermodynamic implications, tells us all we need to know concerning the behavior of a binary liquid solution ideal over the entire composition range; in this special case, the thermodynamic properties are completely determined by the properties of the pure components and the composition. For solu-

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[1] N. Nasu, as reported in Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIIc, p. 2478, 1936.

tions that are not ideal in this sense, it is necessary for us to determine ϕ_1 and ϕ_2 at various compositions by empirical measurement. There is no known theoretical connection of general validity relating the thermodynamically significant properties ϕ_1 and ϕ_2 to the composition. Even in the ideal dilute range, where the value of ϕ_1 for the solvent is determined completely by the properties of the pure solvent and the composition [Eq. (7-3-15)], it is still necessary for us to measure ϕ_2 empirically at at least one composition in order to establish the value of the constant ϕ_2° [Eq. (7-3-16)].

In view of the ideal forms empirically relating ϕ_1 and ϕ_2 to the composition in special cases, Eqs. (7-3-28) in the case of solutions ideal over the entire composition range, and Eqs. (7-3-15) and (7-3-16) more generally for solutions sufficiently dilute with respect to either component, it is convenient for us to express thermodynamic data for real solutions in terms of functions of the thermodynamic potentials related to them by definition in the same way that the concentrations of the components are related empirically in the ideal limits. Thus, these functions, known as *activities* of the respective components, are defined generically by the equations

$$\left.\begin{aligned} d\phi_1 &\equiv RT\,d\ln a_1 \\ d\phi_2 &\equiv RT\,d\ln a_2 \\ &\cdots\cdots\cdots\cdots \\ d\phi_c &\equiv RT\,d\ln a_c \end{aligned}\right\} \quad (T,\,p \text{ const}) \qquad (7\text{-}3\text{-}40)$$

They were first introduced in thermodynamic investigation by G. N. Lewis;[1] they bear to the thermodynamic potentials in liquid (or solid) solution a relationship similar to that between the fugacity and the molal free energy of a gas. According to the Gibbs-Duhem relation (7-1-8), the activities of the various components must satisfy the general condition

$$x_1\,d\ln a_1 + x_2\,d\ln a_2 + \cdots + x_c\,d\ln a_c = 0 \quad (T,\,p \text{ const}) \qquad (7\text{-}3\text{-}41)$$

Since the behavior of the ideal concentrated solution, as represented by Eqs. (7-3-28), is rather different from that of the ideal dilute solution, as represented by Eqs. (7-3-15) and (7-3-16), in that the properties of the former are completely determined in terms of the properties of the pure components down to the values of the integration constants [the terms $(\bar{F}_{T,p})_1$ and $(\bar{F}_{T,p})_2$] whereas the properties of the latter involve the empirical integration constant ϕ_2°, the assignment of absolute numerical values to the activities [*i.e.*, the assignment of integration constants to the inte-

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[1] G. N. Lewis, *Proc. Am. Acad. Arts Sci.*, **43**, 259–293 (1907); *Z. physik. Chem.*, **61**, 129–165 (1907); see also Lewis and Randall, *op. cit.*

gral form of Eqs. (7-3-40)] is subject entirely to our convenience, depending on whether we choose to regard (7-3-28) as the ideal form at all compositions, or whether we choose to regard Eqs. (7-3-15) and (7-3-16) as the ideal limit, as actually attained in the sufficiently dilute range. The former choice has proved to be the more useful for the study of liquid-vapor equilibrium in general for binary and multicomponent liquid solutions, where each component in turn satisfies Raoult's law (7-3-15) as its own mole fraction approaches 1. The latter choice is the more useful when one wishes to correlate the thermodynamic properties of various solutes in a common solvent (*e.g.*, aqueous solutions, solutions in the solvent methanol, etc.), where at sufficiently low concentrations all solutes satisfy the same limiting law (7-3-16) (of course with different values of ϕ_2°). We shall discuss these two problems separately in Secs. 7-3*f* and 7-3*g*.

f. Activity Coefficients in the Study of Liquid-Vapor Equilibrium. Suppose we assign numerical values to the activities in accordance with the integral equations

$$\left.\begin{aligned} \phi_1 &= (\bar{F}_{T,p})_1 + RT \ln a_1 \\ \phi_2 &= (\bar{F}_{T,p})_2 + RT \ln a_2 \\ &\cdots\cdots\cdots\cdots\cdots \\ \phi_c &= (\bar{F}_{T,p})_c + RT \ln a_c \end{aligned}\right\} \quad (T,\ p \text{ const}) \qquad (7\text{-}3\text{-}42)$$

In these equations, $(\bar{F}_{T,p})_1$, $(\bar{F}_{T,p})_2$, . . . , $(\bar{F}_{T,p})_c$ stand, respectively, for the molal free energies of the pure components as liquids (or as solids, if we are dealing with a solid solution) at the temperature and pressure of the solution. Over the comparatively small pressure ranges one is likely to encounter in the study of liquid-vapor equilibrium at temperatures not greatly exceeding the normal boiling point of the solution, $(\bar{F}_{T,p})_i$ for any pure component, i, may be replaced by the standard value $(\bar{F}_T^\circ)_i$ at 1 atm without significant error; furthermore, by the application of (7-1-24) and (6-10) to (7-3-42),

$$\left(\frac{d \ln a_i}{dp}\right)_{T,n} = \frac{v_i - (\bar{V}_{T,p})_i}{RT} \qquad (7\text{-}3\text{-}43)$$

one sees that in view of the relatively small numerical value of the difference between the partial molal volume v_i in liquid solution and the molal volume $(\bar{V}_{T,p})_i$ of the pure liquid component, the activities themselves in liquid solutions can be only slightly sensitive to variations in the pressure; at any rate, one can always correct all data to a common standard pressure by the application of Eq. (7-3-43). In the following discussion, we shall suppose that such pressure correction may be neglected, and that Eq. (7-3-42) refers to data at essentially 1 atm pressure.

For activities defined in accordance with the convention (7-3-42), it is then generally empirically true that for each component

$$\lim_{x_i \to 1} a_i = x_i \quad (T, p \text{ const}; i = 1, 2, \ldots, c) \quad (7\text{-}3\text{-}44)$$

This statement merely represents Raoult's law in the respective ideal dilute-solution limits as each component in turn is regarded as the "solvent." For the ideal concentrated solution, of course, a_i would equal x_i for each component at *all* compositions [compare Eqs. (7-3-42) and (7-3-28)]. The apparent exceptions to (7-3-44) (*e.g.*, electrolytes, benzoic acid in benzene, etc.) usually have a more or less definite chemical significance.

If the pressure under consideration is sufficiently low so that the equilibrium vapor phase satisfies the ideal-gas law with sufficient accuracy for our purpose, then from comparison of (7-3-42) with (7-3-3), which applies to any component whether the liquid solution is ideal or not,

$$a_i = \frac{p_i}{p_i^\circ} = \frac{y_i^* p}{p_i^\circ} \quad (T, p \text{ const}; i = 1, 2, \ldots, c) \quad (7\text{-}3\text{-}45)$$

By this relationship, any activity may be calculated directly from the vapor pressure and equilibrium vapor composition of the solution; the calculation is rigorous, within experimental error and the precision of the ideal-gas law assumption. If the vapor phase fails to satisfy the ideal-gas law, then we may replace Eq. (7-3-45) by

$$a_i = \frac{y_i^* p}{p_i^\circ} \frac{\nu_i}{\nu_i^\circ} \quad (T, p \text{ const}; i = 1, 2, \ldots, c) \quad (7\text{-}3\text{-}46)$$

where ν_i represents the fugacity coefficient of component i in the equilibrium vapor at the pressure p (as determined by the methods of Sec. 7-2), and ν_i° represents the fugacity coefficient of pure component i in the gaseous state at its own vapor pressure p_i° at the given temperature T. We shall assume hereafter that the equilibrium vapor phase may be treated approximately as an ideal gas, for pressures of order 1 atm or less, bearing in mind, however, that at higher pressures, or where higher precision is warranted, the equations that follow may be readily generalized by the use of Eq. (7-3-46) throughout in place of Eq. (7-3-45).

It is convenient for us to introduce *activity coefficients*, defined in this case by

$$\gamma_i \equiv \frac{a_i}{x_i} \quad (T, p \text{ const}; i = 1, 2, \ldots, c) \quad (7\text{-}3\text{-}47)$$

Equations (7-3-42) then take the form

$$\left.\begin{aligned} \phi_1 &= (\bar{F}_{T,p})_1 + RT \ln x_1 + RT \ln \gamma_1 \\ \phi_2 &= (\bar{F}_{T,p})_2 + RT \ln x_2 + RT \ln \gamma_2 \\ &\cdots\cdots\cdots\cdots\cdots\cdots \\ \phi_c &= (\bar{F}_{T,p})_c + RT \ln x_c + RT \ln \gamma_c \end{aligned}\right\} \quad (T,\ p \text{ const}) \qquad (7\text{-}3\text{-}48)$$

These equations themselves may be taken as *defining* the quantities $\gamma_1, \gamma_2, \ldots, \gamma_c$. In terms of direct experimental data, according to Eq. (7-3-45),

$$\gamma_i = \frac{p_i}{x_i p_i^\circ} = \frac{y_i^* p}{x_i p_i^\circ} \quad (T,\ p \text{ const};\ i = 1, 2, \ldots, c) \qquad (7\text{-}3\text{-}49)$$

In the ideal dilute range, with the particular component i regarded as solvent, Eq. (7-3-44) is equivalent to

$$\lim_{x_i \to 1} \gamma_i = 1 \quad (T,\ p \text{ const};\ i = 1, 2, \ldots, c) \qquad (7\text{-}3\text{-}50)$$

The deviation of γ_i from 1 outside this range measures the extent to which this component deviates from ideal behavior, with Raoult's law taken as the norm. At the other end of the composition scale, by comparison of Eq. (7-3-49) with Eq. (7-3-18),

$$\lim_{x_i \to 0} \gamma_i = \frac{k_i}{p_i^\circ} \quad (T,\ p \text{ const};\ i = 1, 2, \ldots, c) \qquad (7\text{-}3\text{-}51)$$

where k_i represents the mole fraction Henry's law constant for component i as solute in ideal dilute solution; in a binary solution, the value of k_i for either component depends only on the temperature, but in a solution containing several components, the value of k_i for component i may vary also with the relative proportions of the other components.

The activity coefficients of the different components at given temperature and pressure are related through the Gibbs-Duhem equation, which assumes the form [compare Eq. (7-3-41)]

$$x_1\, d \ln \gamma_1 + x_2\, d \ln \gamma_2 + \cdots + x_c\, d \ln \gamma_c = 0 \quad (T,\ p \text{ const}) \qquad (7\text{-}3\text{-}52)$$

In the case of a binary solution, Eq. (7-3-52) implies that if one of the activity coefficients has been measured over the entire composition range, such as through the application of Eq. (7-3-49) to liquid-vapor equilibrium data, then the other may be determined by numerical or graphical integration of the data in the form

$$\ln \gamma_2 = -\int_{x_1=0}^{x_1=x_1} \frac{x_1}{1 - x_1}\, d \ln \gamma_1 \quad (T,\ p \text{ const}) \qquad (7\text{-}3\text{-}53)$$

condition (7-3-50) being used to fix the value of the implied integration constant.

From experimental liquid-vapor equilibrium data, in the form of p, y_1, y_2, . . . , y_c measured for various liquid compositions (x_1, x_2, . . . , x_c) at the given temperature, one may construct a table of γ_1, γ_2, . . . , γ_c values for the various compositions, and thus characterize completely the exact thermodynamic properties of the solution through Eqs. (7-3-48), which constitute generalizations of the ideal equations, (7-3-28). Figure 7-13 shows, for example, graphic plots of log γ_1 and log γ_2 vs. x_2 for several representative binary liquid solutions, computed from data previously presented in Figs. 7-10 and 7-11. This procedure results in no new information that could not have been represented directly in terms of the experimentally determined values of ϕ_1, ϕ_2, . . . , ϕ_c themselves; but the mathematical convenience with which the empirical data may be represented when in the form of comparatively small deviations from an ideal standard of behavior is manifest. A particular advantage is that the value of γ_i remains finite as $x_i \rightarrow 0$ [Eq. (7-3-51)], whereas the value of ϕ_i approaches $-\infty$.

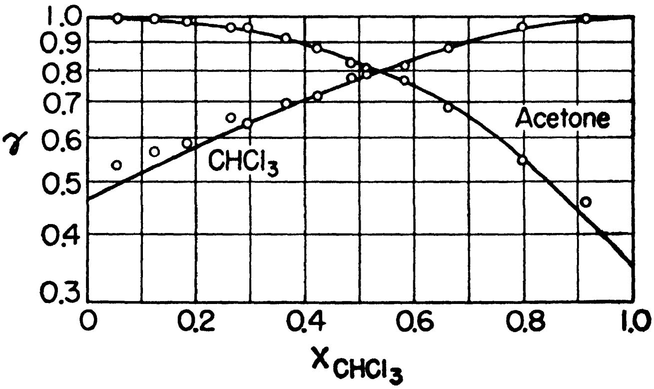

FIG. 7-13*a*. Activity coefficients in acetone-chloroform solutions at 35.17°C [*from vapor pressure data of J. von Zawidski, Z. physik. Chem.*, **35**, 129–203 (1900)]; solid curves represent van Laar equations with $A_1 = -0.46$ and $A_2 = -0.34$.

It would be even more useful, however, if we could discover empirical rules or generalizations that would guide us in setting up activity coefficient values over the entire composition range from measurements conducted at but a few compositions. Such empirical equations of state, containing a small number of parameters adjusted to fit each individual case, would serve as second-order approximations to the actual data, beyond the first-order approximation represented by Eqs. (7-3-28) ($\gamma_1 = \gamma_2 = \cdots = \gamma_c = 1$), which is valid only when the solution is practically ideal over the entire composition range. Any such system of

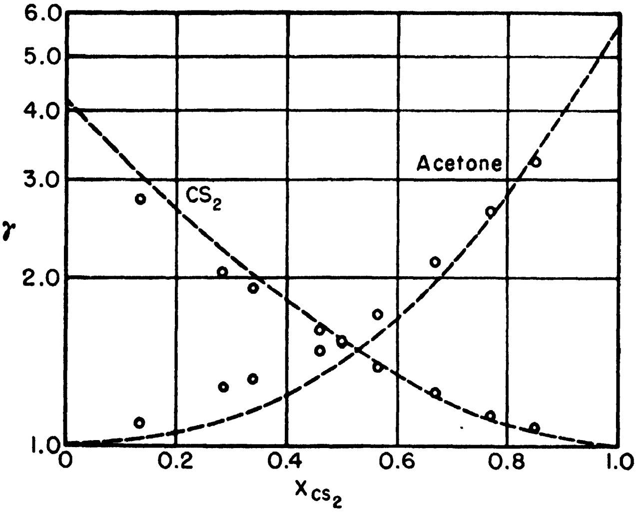

FIG. 7-13*b*. Activity coefficients in acetone-carbon disulfide solutions at 29.2°C (*from vapor pressure data of J. Hirshberg, as reported in Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed, Suppl.* IIIc, p. 2466, 1936); dashed curves represent van Laar equations with $A_1 = 0.76$ and $A_2 = 0.62$.

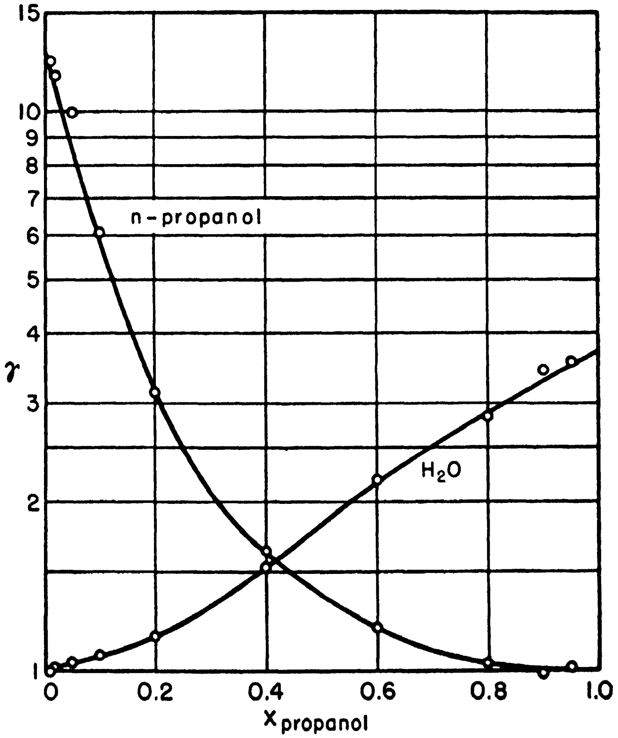

FIG. 7-13*c*. Activity coefficients in *n*-propanol–water solutions at 25°C [*from vapor pressure data of J. A. V. Butler, D. W. Thomson, and W. H. Maclennan, J. Chem. Soc.*, 674–686 (1933)]; solid curves represent van Laar equations with $A_1 = 0.57$ and $A_2 = 1.11$.

empirical equations must of course satisfy reciprocal symmetry relations of a form imposed by Eq. (7-3-52). This problem was first investigated by M. Margules, but its status has recently been critically reviewed by H. C. Carlson and A. P. Colburn, and by K. Wohl, who have developed several valuable practical applications.[1] Perhaps the most convenient set of empirical equations for binary solutions is one proposed originally by J. J. van Laar,[2] as revised by Carlson and Colburn,

$$\left.\begin{aligned} \log \gamma_1 &= \frac{A_1}{\left(1 + \dfrac{A_1 x_1}{A_2 x_2}\right)^2} \\ \log \gamma_2 &= \frac{A_2}{\left(1 + \dfrac{A_2 x_2}{A_1 x_1}\right)^2} \end{aligned}\right\} \qquad (7\text{-}3\text{-}54)$$

The constants A_1 and A_2 are characteristic of the particular liquid pair at the given temperature. Rearranging terms,

$$\left.\begin{aligned} A_1 &= \left(1 + \frac{x_2 \log \gamma_2}{x_1 \log \gamma_1}\right)^2 \log \gamma_1 \\ A_2 &= \left(1 + \frac{x_1 \log \gamma_1}{x_2 \log \gamma_2}\right)^2 \log \gamma_2 \end{aligned}\right\} \qquad (7\text{-}3\text{-}55)$$

In the form (7-3-55), the van Laar constants A_1 and A_2 may be readily calculated from measurements of γ_1 and γ_2 at any one liquid composition [*e.g.*, from liquid-vapor equilibrium data through Eq. (7-3-49)]; then, if the van Laar equations fit the data sufficiently well, Eqs. (7-3-54) may be used to calculate γ_1 and γ_2 approximately at other compositions. The values of γ_1 and γ_2 so obtained permit one by implication to calculate the vapor pressure and composition of the equilibrium vapor phase for other liquid compositions than the one used in determining the values of A_1 and A_2; Eqs. (7-3-54), in other words, happen to be a comparatively simple form for expressing what would otherwise be an extremely complicated empirical connection between the liquid and equilibrium vapor compositions. The curves drawn in Fig. 7-13 have actually been constructed by means of Eqs. (7-3-54), using appropriate values of A_1 and A_2 as indicated on the graphs; for *n*-propanol-water (Fig. 7-13*c*), the fit is particularly good, considering how far from ideal these solutions are in the intermediate composition range (compare Fig. 7-11*c*); for acetone-CS_2 (Fig. 7-13*b*), the van Laar equations cannot be made to fit the data much better

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[1] Margules, *loc. cit.*; H. C. Carlson and A. P. Colburn, *Ind. Eng. Chem.*, **34,** 581–589 (1942); K. Wohl, *Trans. Am. Inst. Chem. Eng.*, **42,** 215–249 (1946).

[2] J. J. van Laar, *Z. physik. Chem.*, **72,** 723–751 (1910); **83,** 599–608 (1913).

than the dashed curves indicate, but the agreement is not bad. Other empirical equations are discussed by Carlson and Colburn, which fit the data better in certain cases, but the van Laar equations appear to be the simplest in application.

The estimation of A_1 and A_2 is particularly simple if the two liquids happen to form an azeotropic mixture, for in this case, an independent analysis of the composition of the equilibrium vapor phase at the azeotropic liquid composition is not required; in fact, according to (7-3-49), $\gamma_1 = p_m/p_1^\circ$ and $\gamma_2 = p_m/p_2^\circ$ (within the ideal-gas-law approximation) at the azeotropic composition, p_m representing the azeotropic pressure (maximum or minimum, as the case may be), and p_1° and p_2° the vapor pressures of the pure components at the same temperature. If the determination of A_1 and A_2 by this method is to be precise, the azeotropic composition should not be too close to either end of the composition range.

One can easily see from Eq. (7-3-54) that

$$\left.\begin{aligned} A_1 &= \lim_{x_1\to 0} \log \gamma_1 \\ A_2 &= \lim_{x_2\to 0} \log \gamma_2 \end{aligned}\right\} \qquad (7\text{-}3\text{-}56)$$

Therefore the van Laar constants may be estimated also from precise data in the dilute composition ranges [see, for example, Eq. (7-3-51)]. As shown by Carlson and Colburn,[1] this need not necessarily call for actual measurement of the equilibrium vapor composition, for in the ideal dilute limit, $x_1 \to 0$, one may assume that component 2 (the "solvent" in this range) satisfies Raoult's law, $p_2 = x_2 p_2^\circ$, while in the other ideal dilute limit, $x_2 \to 0$, one may assume that component 1 satisfies Raoult's law, $p_1 = x_1 p_1^\circ$. Therefore one may replace Eq. (7-3-49) (which is exact within the ideal-gas-law approximation for the equilibrium vapor phase) by the approximations

$$\left.\begin{aligned} \lim_{x_1\to 0} \gamma_1 &= \frac{p - x_2 p_2^\circ}{x_1 p_1^\circ} \\ \lim_{x_2\to 0} \gamma_2 &= \frac{p - x_1 p_1^\circ}{x_2 p_2^\circ} \end{aligned}\right\} \qquad (7\text{-}3\text{-}57)$$

From precise measurements of the vapor pressure p for compositions near both ends of the composition range, one may thus estimate by means of Eqs. (7-3-57) the terminal values of γ_1 and γ_2, and, by taking their logarithms, determine A_1 and A_2 in accordance with Eqs. (7-3-56).

The general effect of temperature on the activity coefficients may be deduced by the application of Eqs. (7-1-26a) and (6-12) to (7-3-48),

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[1] Carlson and Colburn, *loc. cit.*

$$\left(\frac{d \ln \gamma_i}{dT}\right)_{p,n} = \frac{(\bar{H}_{T,p})_i - \eta_i}{RT^2} \tag{7-3-58}$$

The numerator of the term on the right of Eq. (7-3-58) evidently represents the differential or partial molal heat of solution of component i, the heat evolved per mole of component i at constant temperature and pressure when the pure component is dissolved in a relatively large quantity of the solution, so that the composition (and with it, the value of η_i itself) undergoes no significant change. A knowledge of the value of this quantity for each component is important in the operation of extractive distillation columns, and other continuous-flow methods of separating the components. It may be derived from straightforward calorimetric measurements, as in Sec. 4-5; but Eq. (7-3-58), which we may rearrange in the form

$$\eta_i - (\bar{H}_{T,p})_i = 2.303R\left[\frac{d \log \gamma_i}{d(1/T)}\right]_{p,n} \tag{7-3-59}$$

provides a means of determining it from equilibrium data obtained at several temperatures, expressed in the form of activity-coefficient values for the given composition to which η_i refers.[1]

If we apply Eq. (7-3-59) to the terminal values of log γ_1 and log γ_2 of a binary solution satisfying the van Laar equations, then, in view of Eqs. (7-3-56), we obtain equations for the temperature coefficients of A_1 and A_2 in terms of thermal data; since the difference $(\bar{H}_{T,p})_i - \eta_i$ becomes equal in the limit $x_i \rightarrow 0$ to the total molal heat of solution of component i in the other component, as defined in Sec. 4-5, therefore

$$\left.\begin{aligned} -(\bar{Q}_s^\circ)_1 &= 2.303R\left[\frac{dA_1}{d(1/T)}\right]_p \\ -(\bar{Q}_s^\circ)_2 &= 2.303R\left[\frac{dA_2}{d(1/T)}\right]_p \end{aligned}\right\} \tag{7-3-60}$$

where $(\bar{Q}_s^\circ)_1$ and $(\bar{Q}_s^\circ)_2$ represent, respectively, the total molal heat of solution of component 1 in component 2 as solvent, and the total molal heat of solution of component 2 in component 1 as solvent. According to Carlson and Colburn, the values of $(\bar{Q}_s^\circ)$ for organic liquid pairs run as high as 2000 cal/mole, and for mixtures of various alcohols with water, as high as 5000 cal/mole. Unfortunately, most of the direct calorimetric data for solutions have been obtained only at room temperature, and there are indications that differential heats of solution may change quite

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[1] See, for example, T. S. Mertes and A. P. Colburn, *Ind. Eng. Chem.*, **39**, 787–796 (1947).

rapidly with temperature.[1] Over a sufficiently narrow range of temperature, however, we may treat the activity coefficients at given composition as approximately constant; thus, if $(\bar{H}_i - \eta_i)$ in Eq. (7-3-58) were of order 1000 cal/mole, a change of 10 deg in T around 298°K would be accompanied by a change of order 2.5 per cent in γ_i.

Empirical equations of state for ternary liquid solutions have been analyzed by K. Wohl; an example of their use is found in a recent paper by Gerster, Mertes, and Colburn.[2]

Essentially the same method outlined in this section for the empirical representation of the thermodynamic potentials in liquid solutions as functions of the composition is applied also to solid solutions, with the difference of course that the reference states of the pure components are taken to be the crystalline solid rather than the liquid states of aggregation. Thus, activity coefficients in binary solid solutions are commonly defined by the equations

$$\left.\begin{aligned} \phi_1 &= (\bar{F}_{T,p})_{1(s)} + RT \ln x_1 + RT \ln \gamma_1 \\ \phi_2 &= (\bar{F}_{T,p})_{2(s)} + RT \ln x_2 + RT \ln \gamma_2 \end{aligned}\right\} \quad (T, p \text{ const}) \qquad (7\text{-}3\text{-}61)$$

From such data as are available, a generalization of Raoult's law apparently applies, in that the results satisfy empirically the limiting laws

$$\lim_{x_1 \to 1} \gamma_1 = 1; \qquad \lim_{x_2 \to 1} \gamma_2 = 1 \quad (T, p \text{ const}) \qquad (7\text{-}3\text{-}62)$$

Most of the experimental data are based on emf measurements of cells with solid-solution alloys as electrodes, according to the theory to be developed in Chap. 9. Figure 7-14 presents activity coefficients satisfying Eqs. (7-3-61) for Au-Ag solid solutions at 200°C, as obtained by A. Wachter from such emf measurements.[3] One could presumably measure ϕ_1 and ϕ_2 in solid solutions relatively to their corresponding values in the equilibrium liquid state by precise freezing-point measurements, including analysis of both the solid and equilibrium liquid phases; few solid solutions are sufficiently volatile for their thermodynamic properties to be evaluated from vapor-pressure data, such as by means of Eq. (7-3-49). One could also measure ϕ_1 and ϕ_2 in binary solid solutions relatively to

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[1] The change is represented formally by the equation

$$\left[\frac{d(\bar{H}_i - \eta_i)}{dT}\right]_p = (\bar{C}_p)_i - (\gamma_p)_i$$

Compare Eq. (4-45), where $(\gamma_p)_i$ represents the partial molal heat capacity of component i in the solution.

[2] K. Wohl, *Trans. Am. Inst. Chem. Eng.*, **42**, 215–249 (1946); J. A. Gerster, T. S. Mertes, and A. P. Colburn, *Ind. Eng. Chem.*, **39**, 787–804 (1947).

[3] A. Wachter, *J. Am. Chem. Soc.*, **54**, 4609–4617 (1932).

their corresponding values in a suitable liquid solvent from solubility data; the solubilities of the two components in the liquid solvent would have to be comparatively low, as otherwise the analysis of the thermodynamic properties of the resulting ternary liquid solution would present formidable technical difficulties.

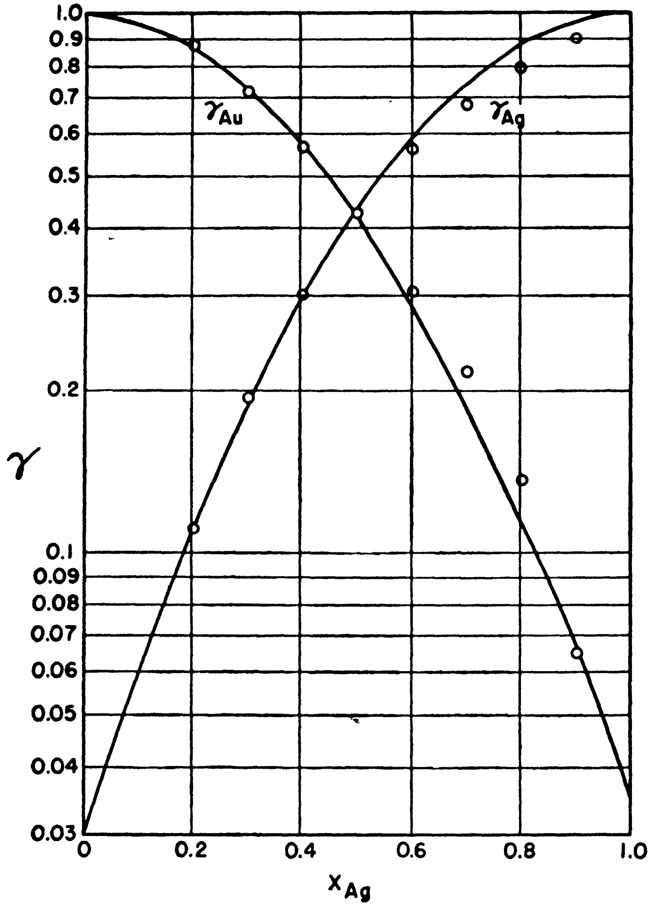

FIG. 7-14. Activity coefficients in gold-silver solid solutions at 200°C (*from emf data of A. Wachter*); the curves have been drawn according to van Laar's equations (7-3-54), with $A_1 = -1.45$ and $A_2 = -1.52$.

g. Activity Coefficients for the Correlation of Thermodynamic Data in a Particular Solvent. When one wishes to compare the behaviors of different solutes in a common solvent, then activities and activity coefficients set up according to the convention represented by Eqs. (7-3-42) and (7-3-48) are in general not particularly satisfactory. In sufficiently dilute solution, where each solute tends to satisfy empirically the same limiting law (7-3-16) (each of course with a different characteristic value of ϕ_2°), this significant fact is obscured when the data are represented in terms of activity coefficients defined by Eq. (7-3-48), because each solute, with the exception of those forming ideal concentrated solutions with the given solvent, then has a different terminal value of γ_2 in that range. Furthermore, if the pure solute happens to be a solid or a gas at the temperature and pressure under consideration, then we may have difficulty in assigning correctly the value of $(\bar{F}_{T,p})_2$, which in the application of Eq. (7-3-48) to liquid solutions, should represent the molal free energy of the pure solute in the liquid state.[1] If, however, we assign numerical values to the activities of the solvent and the solute (confining our attention for the moment to binary liquid solutions) in accordance with the equations

$$\left.\begin{aligned} \phi_1 &\equiv (\bar{F}_{T,p})_1 + RT \ln a_1 \\ \phi_2 &\equiv \phi_2^\circ + RT \ln a_2^\circ \end{aligned}\right\} \quad (T,\, p \text{ const}) \qquad (7\text{-}3\text{-}63)$$

where, by hypothesis, ϕ_2° is defined in accordance with the convention

$$\lim_{x_2 \to 0} a_2^\circ = x_2 \qquad (T,\, p \text{ const}) \qquad (7\text{-}3\text{-}64)$$

then in the ideal dilute range, so long as the solvent satisfies Raoult's law (as represented by the empirical condition $a_1 = x_1$), the activity a_2° of *any solute* at given concentration has the same value, namely, x_2. According to such a scheme of representation, the differences in the values of ϕ_2 for different solutes are thrown into the empirical constants ϕ_2° [so-called standard free energies of formation *in solution in the given solvent*, relative to the particular convention (7-3-64)], but in sufficiently dilute solution, the specific effect of concentration is given by the same law (7-3-16) for all solutes. That the expression

$$\lim_{x_2 \to 0} (\phi_2 - RT \ln x_2) = \phi_2^\circ \quad (T,\, p \text{ const}) \qquad (7\text{-}3\text{-}65)$$

used in the definition of ϕ_2° actually converges to a finite limit is implied by the empirical observation that the solvent in the ideal dilute range satisfies Raoult's law (7-3-15), as shown in Sec. 7-3*c*; Eq. (7-3-64) is equivalent to Henry's law (7-3-16) for the solute.

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[1] For a solid solute, one could write for the saturated solution at the given temperature and pressure

$$(\bar{F}_{T,p})_{2(0)} = (\bar{F}_{T,p})_2 + RT \ln x_2^* + RT \ln \gamma_2^*$$

and thus relate $(\bar{F}_{T,p})_2$ for the hypothetical supercooled liquid state to $(\bar{F}_{T,p})_{2(0)}$ for the pure solid solute, provided that one had independent means of measuring γ_2^* for the saturated liquid solution; for a solute that happened to form ideal concentrated solutions with the solvent, one could set $\gamma_2^* = 1$ [compare Eq. (7-3-34)], but in general this is not the case.

Let us introduce activity coefficients defined by

$$\gamma_1 \equiv \frac{a_1}{x_1}; \qquad \gamma_2^\circ \equiv \frac{a_2^\circ}{x_2} \tag{7-3-66}$$

Then Eqs. (7-3-63) take the form

$$\left.\begin{aligned} \phi_1 &\equiv (\bar{F}_{T,p})_1 + RT \ln x_1 + RT \ln \gamma_1 \\ \phi_2 &\equiv \phi_2^\circ + RT \ln x_2 + RT \ln \gamma_2^\circ \end{aligned}\right\} \quad (T,\ p \text{ const}) \tag{7-3-67}$$

where

$$\left.\begin{aligned} \lim_{x_2 \to 0} \gamma_1 &= 1 \\ \lim_{x_2 \to 0} \gamma_2^\circ &= 1 \end{aligned}\right\} \quad (T,\ p \text{ const}) \tag{7-3-68}$$

The first of Eqs. (7-3-68) is valid if the solvent satisfies Raoult's law in the ideal dilute-solution limit; the second then follows as a consequence of the first, combined with the definitions. Thus, the activity coefficient of the *solvent* is defined precisely as before [Eq. (7-3-48)], and its deviation from 1 measures the extent to which the solvent deviates from ideal behavior as represented by *Raoult's law;* but the activity coefficient γ_2° of the *solute* is now defined in such a way that its deviation from 1 measures the extent to which the solute deviates from ideal behavior *as a solute in dilute solution in the given solvent, i.e.,* ideal behavior as represented by *Henry's law,* rather than by Raoult's law. In other words, we are using the ideal dilute solution, instead of the ideal concentrated solution, as the standard of behavior for both solvent *and* solute. It should be emphasized that this treatment does not alter in the slightest respect the fundamental thermodynamic relations connecting ϕ_1 and ϕ_2 directly to the experimental data used in their measurement; it affects merely the formal method of expressing ϕ_1 and ϕ_2 as functions of the composition, to which they bear no a priori relation given by thermodynamics.

By comparing Eq. (7-3-67) defining γ_2° with Eq. (7-3-48), which defined γ_2, we may easily derive the connection between these alternative scales for representing the same experimental information,

$$\gamma_2^\circ = \gamma_2 \exp \frac{(F_{T,p})_{2(l)} - \phi_2^\circ}{RT} \tag{7-3-69}$$

Since the values of $(\bar{F}_{T,p})_{2(l)}$ (the standard molal free energy of pure component 2 as a *liquid* at the given temperature and pressure) and ϕ_2° are independent of the composition, it follows that over the entire composition range, γ_2° is directly proportional to γ_2; in fact, if we introduce Eq. (7-3-19) (assuming that the equilibrium gas phase may be treated as an ideal gas), and also take into consideration Eq. (7-3-51), then

$$\gamma_2^\circ = \gamma_2 \frac{p_2^\circ}{k_2} = \frac{\gamma_2}{\lim\limits_{x_2 \to 0} \gamma_2} \qquad (T, p \text{ const}) \qquad (7\text{-}3\text{-}70)$$

In Table 7-3, both kinds of activity coefficients are given for solutions of *n*-propanol in water, as computed from the partial-vapor-pressure data in Fig. 7-11*c* (see also Fig. 7-13*c*). The activity and activity coefficient of the solvent may be determined from vapor-pressure data exactly as before [Eqs. (7-3-45), (7-3-46), and (7-3-49)]; these equations are particularly simple to apply if the solute happens to be insignificantly volatile compared with the solvent, because then an analysis of the equilibrium vapor phase is not necessary. If the solute is sufficiently volatile, then its own activity coefficient may be computed directly from measurement of its partial vapor pressure, in accordance with the relation [compare Eqs. (7-3-49) and (7-3-70)],

$$\gamma_2^\circ = \frac{p_2}{k_2 x_2} = \frac{y_2^* p/x_2}{\lim\limits_{x_2 \to 0} (y_2^* p/x_2)} \qquad (T \text{ const}) \qquad (7\text{-}3\text{-}71)$$

One will note that a single measurement of p_2 at the particular composition x_2 in which one is interested is not sufficient; one must also carry out sufficient measurements in the dilute-solution range to establish essentially the value of the Henry's law constant k_2; for this purpose, the analysis of the equilibrium vapor phase is not strictly necessary, for as one approaches

TABLE 7-3. PARTIAL VAPOR PRESSURES AND ACTIVITY COEFFICIENTS IN *n*-PROPANOL–WATER SOLUTIONS AT 25°C*

$x_{n\text{-propanol}}$	p_{H_2O}, mm Hg	p_{propanol}, mm Hg	γ_1, H_2O	γ_2	γ_2°
0	23.76	.....	(1.00)	(12.9)	(1.00)
0.0100	23.4	2.68	0.99	12.3	0.954
0.0200	23.5	5.05	1.01	11.6	0.900
0.0500	23.2	10.8	1.03	9.92	0.769
0.1000	22.7	13.2	1.06	6.05	0.469
0.2000	21.8	13.6	1.15	3.12	0.242
0.4000	21.7	14.2	1.52	1.63	0.126
0.6000	19.9	15.5	2.10	1.19	0.092
0.8000	13.4	17.8	2.82	1.02	0.079
0.9000	8.13	19.4	3.42	0.99	0.077
0.9500	4.20	20.8	3.54	1.01	0.078
1.0000	.....	21.76	(3.71)	(1.00)	(0.077_5)

* Data of J. A. V. Butler, D. W. Thomson, and W. H. Maclennan, *J. Chem. Soc.*, 674–686 (1933).

the region in which the solvent may be presumed to satisfy Raoult's law,

$$k_2 = \lim_{x_2 \to 0} \frac{p - x_1 p_1^\circ}{x_2} \qquad (T \text{ const}) \qquad (7\text{-}3\text{-}72)$$

[compare Eqs. (7-3-57)]. While the vapor-pressure method thus constitutes a simple primary means of establishing activity coefficients (or fundamentally, the thermodynamic potentials themselves), other methods are commonly employed, because of the experimental difficulty of measuring vapor pressures and equilibrium vapor compositions with sufficient precision; several of these methods are discussed in Secs. 7-5 and 7-6, whereas special methods available for electrolytes, based on electrochemical measurements, are discussed in Chap. 9.

Since ln γ_2° and ln γ_2 differ merely by an integration constant independent of composition, it follows that γ_2° and γ_1 are related through a Gibbs-Duhem differential equation of precisely the same form as that of Eq. (7-3-52) relating γ_2 and γ_1:

$$x_1\, d \ln \gamma_1 + x_2\, d \ln \gamma_2^\circ = 0 \qquad (T, p \text{ const})$$

Values of γ_2° may therefore be computed from experimental values of γ_1 by means of numerical or graphical integration, in the form

$$\ln \gamma_2^\circ = -\int_{x_2=0}^{x_2=x_2} \frac{x_1}{x_2}\, d \ln \gamma_1 \qquad (7\text{-}3\text{-}73)$$

Equation (7-3-73) differs from Eq. (7-3-53) for γ_2 merely in that the integration extends from the opposite end of the composition scale.

The relationship between ϕ_2° and the molal free energy of the pure solute may be established experimentally in one of several ways, depending on the nature of the solute. Thus, if the pure solute is a volatile liquid or solid with vapor pressure p_2° at the given temperature, then by comparison of the defining equation (7-3-67) with the thermodynamic equation (7-3-3)[1]

$$\phi_2 \equiv \phi_2^\circ + RT \ln x_2 \gamma_2^\circ = (\bar{F}_T^\circ)_2 + RT \ln \frac{p_2}{p_2^\circ}$$

Introducing (7-3-71),

$$\phi_2^\circ = (\bar{F}_T^\circ)_2 + RT \ln \frac{k_2}{p_2^\circ} \qquad (7\text{-}3\text{-}74)$$

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[1] Exact within the ideal-gas law approximation for the equilibrium vapor phase, neglecting corrections for deviation of the pressure from 1 atm; the generalization and the kind of data required to implement it when these approximations are inadequate are obvious from previous discussion [see Eq. (7-3-4)].

Thus, the difference between ϕ_2° and $(\bar{F}_T^\circ)_2$ may be determined from experimental establishment of the Henry's law constant $k_2 = \lim_{x_2 \to 0} (p_2/x_2)$ for the solute in the particular solvent, together with its own vapor pressure; $(\bar{F}_T^\circ)_2$ here represents the standard molal free energy of the pure solute in the liquid or solid state, as the case may be [compare Eq. (7-3-19)]; the equation may be applied also to a gaseous solute, provided that one formally lets $p_2^\circ = 1$ atm [or whatever pressure to which the standard free-energy value $(\bar{F}_T^\circ)_2$ for the pure gas refers; see the statement following Eq. (7-3-3)]. If the solute happens to be a liquid miscible with the solvent over the entire composition range, then taking Eq. (7-3-67) in the limit as $x_2 \to 1$,

$$\lim_{x_2 \to 1} \phi_2 = (\bar{F}_{T,p})_2 = \phi_2^\circ + RT \lim_{x_2 \to 1} \ln \gamma_2^\circ$$

Therefore

$$\phi_2^\circ = (\bar{F}_{T,p})_2 - RT \lim_{x_2 \to 1} \ln \gamma_2^\circ \tag{7-3-75}$$

We may thus relate ϕ_2° to $(\bar{F}_{T,p})_2$ for the pure liquid solute by experimental establishment of the terminal value of $\ln \gamma_2^\circ$; for example, for *n*-propanol in H_2O, from the data presented in Table 7-3,

$$\phi^\circ_{n\text{-propanol(aq)}} - (\bar{F}^\circ_{298.16})_{n\text{-propanol}} = -RT \ln (0.0775) = 1514 \text{ cal/mole}$$

Equation (7-3-75) is of course exactly equivalent to Eq. (7-3-69), since at the $x_2 \to 1$ end of the composition scale, component 2 (the "solute") presumably conforms to Raoult's law, $\gamma_2 \to 1$. If the pure solute happens to be a solid that forms a saturated liquid solution of composition x_2^* with the particular solvent at the given temperature, then provided that the phase in equilibrium with the saturated solution is actually the pure crystalline solute, and not a solid solution or compound with the solvent,

$$(\bar{F}_T^\circ)_{2(c)} = (\phi_2)_{\text{satd soln}} = \phi_2^\circ + RT \ln x_2^* + RT \ln (\gamma_2^\circ)^*$$

Therefore

$$\phi_2^\circ = (\bar{F}_T^\circ)_{2(c)} - RT \ln x_2^* - RT \ln (\gamma_2^\circ)^* \tag{7-3-76}$$

[compare Eq. (7-3-34), which is a special case of (7-3-76)]. We may thus relate ϕ_2° to $(\bar{F}_T^\circ)_2$ for the pure solid solute by experimental establishment of the value of γ_2° in the saturated solution; it may be possible to do this, for example, from measurements of a_1 or γ_1 for the solvent [see Eq. (7-3-49)], followed by numerical or graphical integration of the data in the form of Eq. (7-3-73) from $x_2 = 0$ up to $x_2 = x_2^*$. This method could be applied also to a slightly soluble liquid solute, provided that the solvent is not sufficiently soluble in the liquid "solute" phase to affect its thermodynamic potential significantly. The value of the constant ϕ_2° may be determined also from chemical equilibrium data for certain types of reactions taking place in the solvent, as we shall see in Chap. 8.

Besides the activity scale a_2° defined by Eqs. (7-3-63) and (7-3-64), there are two other related activity scales in common use also based on a reference state for the solute in ideal dilute solution in the given solvent, but differing in the composition measures employed. One is tied to the *molality* of the solute as composition measure, and the other to the *molarity*, or its molar concentration by volume. It is indeed unfortunate that so many different ways of representing essentially the same kind of information have become accepted, because this complexity of conventions, which results merely from the different methods that have been found convenient for representing the composition for various purposes, has nothing to do with the underlying thermodynamic principles, which are basically simple enough.

The *molality* of the solute, m_2, is defined as the *number of moles of solute per kilogram of solvent;* therefore the exact relationship between m_2 and x_2 in a given solvent of formula weight $\bar{M}_1$ is

$$x_2 = \frac{m_2}{m_2 + \dfrac{1000 \text{ g/kg}}{\bar{M}_1}} \tag{7-3-77}$$

For aqueous solutions in particular,

$$x_2 = \frac{m_2}{m_2 + 55.51 \text{ moles/kg H}_2\text{O}} \tag{7-3-77a}$$

Now, in sufficiently dilute solution, where the ideal dilute-solution laws, Eqs. (7-3-15) and (7-3-16), presumably apply, m_2 becomes small in comparison with the other term in the denominator of (7-3-77); in this region, therefore, x_2 is practically proportional to m_2:

$$\lim_{m_2 \to 0} x_2 = m_2 \frac{\bar{M}_1}{1000 \text{ g/kg}} \tag{7-3-78}$$

In water as solvent, for example, the value of x_2 for a 1m solution given by the approximation represented by the right-hand member of (7-3-78) exceeds the exact value given by (7-3-77) by 1.8 per cent, and for a 0.1m solution, the difference is only 0.2 per cent. Therefore the ideal limiting law (7-3-16) for the solute may be equally well put in the form

$$\phi_2 = \phi_2' + RT \ln m_2 \quad (T, p \text{ const}; m_2 \to 0) \tag{7-3-79}$$

where the empirical integration constant ϕ_2' is related to ϕ_2° defined in Eqs. (7-3-63) and (7-3-64) by

$$\phi_2' = \phi_2^\circ - RT \ln \frac{1000 \text{ g/kg}}{\bar{M}_1} \tag{7-3-80}$$

If corresponding to the ideal limiting form (7-3-79) we now define the activity and the activity coefficient of the solute by the equations

$$\begin{aligned} \phi_2 &\equiv \phi_2' + RT \ln a_2' && (T, p \text{ const}) \quad (7\text{-}3\text{-}81) \\ &\equiv \phi_2' + RT \ln m_2 + RT \ln \gamma_2' && (T, p \text{ const}) \quad (7\text{-}3\text{-}82) \end{aligned}$$

then these definitions of the quantities a_2' and γ_2' are tantamount to letting

$$\lim_{m_2 \to 0} a_2' = m_2; \qquad \lim_{m_2 \to 0} \gamma_2' = 1 \quad (T, p \text{ const}) \tag{7-3-83}$$

The value of the constant ϕ_2' may be determined directly from experimentally determined values of ϕ_2 (precisely the same experimental data required for the determination of ϕ_2°, but expressed now in terms of m_2 as composition measure, instead of x_2) in the form

$$\phi_2' = \lim_{m_2 \to 0} (\phi_2 - RT \ln m_2) \tag{7-3-84}$$

Thus, while ϕ_2' and ϕ_2° are formally interrelated through Eq. (7-3-80), we may determine ϕ_2' directly from the experimental data, without explicitly calculating ϕ_2° first.

The values of a_2' are evidently directly proportional to the values of a_2° over the entire composition range

$$a_2' = a_2^\circ \frac{1000 \text{ g/kg}}{\bar{M}_1} \tag{7-3-85}$$

but the relation between the molal activity coefficient γ_2' and the mole-fraction activity coefficient γ_2° is more complex, varying with the composition,[1]

$$\gamma_2' = \gamma_2^\circ \frac{1}{1 + \dfrac{m_2 \bar{M}_1}{1000 \text{ g/kg}}} = \gamma_2^\circ x_1 \tag{7-3-86}$$

The definition of the activity a_1 of the *solvent* remains unaffected by this maneuver

$$\phi_1 = (\bar{F}_{T,p})_1 + RT \ln a_1 \quad (T, p \text{ const}) \tag{7-3-87}$$

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[1] D. A. MacInnes, in "The Principles of Electrochemistry," Chap. VI, Reinhold Publishing Corporation, New York, 1939, calls the activity coefficient here designated by γ_2° and defined by Eqs. (7-3-66) and (7-3-67) a "rational" activity coefficient, as distinguished from γ_2', the molal activity coefficient. The latter is more widely used, particularly for representing the thermodynamic properties of aqueous solutions. The distinction may become important, however, in solvents of relatively high molecular weights, where even in quite dilute solutions, γ_2' may differ significantly from γ_2°. MacInnes uses f for our γ_2°, γ for our γ_2', and *f* for our γ_2'' [Eqs. (7-3-102) and (7-3-103)].

but in this case, one generally does not attempt to define an activity coefficient for the solvent. The relation of a_1 to experimentally determined properties of the solution, such as the partial vapor pressure of the solvent [Eq. (7-3-45) or Eq. (7-3-46)], remains of course precisely the same as before.

One may readily derive relations between a_2' or γ_2' and the experimentally determined properties of the solution. Thus, if the solute is sufficiently volatile so that its own partial vapor pressure can be measured with precision, then

$$\gamma_2' = \frac{p_2}{k_2' m_2} = \frac{y_2^* p / m_2}{\lim\limits_{m_2 \to 0} (y_2^* p / m_2)} \qquad (T \text{ const}) \qquad (7\text{-}3\text{-}88)$$

[compare Eq. (7-3-71)]. Here, k_2' represents the *molal* Henry's law constant; for if it is true that $p_2 = k_2 x_2$ in the ideal dilute range [Eq. (7-3-18)], then this relationship may certainly be expressed in the form $p_2 = k_2' m_2$, where the relationship between k_2' and k_2 is determined by Eq. (7-3-78). Equation (7-3-88) is based on the supposition that the equilibrium vapor phase may be treated as an ideal gas; the generalization, taking into account the fugacity coefficient of the solute in the vapor phase, is evident.

Whether the solute is volatile or not, its activity a_2' may be computed by integration of the Gibbs-Duhem equation from experimentally determined values of the activity a_1 of the solvent; since $\ln a_2'$, $\ln a_2^\circ$, and $\ln a_2$ differ from each other merely by constants independent of the composition, this equation [compare Eq. (7-3-41)] assumes the form

$$\frac{1000 \text{ g/kg}}{\bar{M}_1} d \ln a_1 + m_2 \, d \ln a_2' = 0 \qquad (T, p \text{ const}) \qquad (7\text{-}3\text{-}89)$$

Since $a_2' = m_2 \gamma_2'$, Eq. (7-3-89) may be rearranged in the form

$$d \ln \gamma_2' = -\frac{1}{m_2} \left(\frac{1000 \text{ g/kg}}{\bar{M}_1} d \ln a_1 + dm_2 \right)$$

whence, from integration by parts between $m_2 = 0$ ($\gamma_2' = 1$) and $m_2 = m_2$,

$$\ln \gamma_2' = -\left(\frac{1000 \text{ g/kg}}{\bar{M}_1} \frac{\ln a_1}{m_2} + 1 \right) - \int_0^{m_2} \frac{\left(\frac{1000 \text{ g/kg}}{\bar{M}_1} \frac{\ln a_1}{m_2} + 1 \right)}{m_2} dm_2 \qquad (7\text{-}3\text{-}90)$$

TABLE 7-4. SOLVENT ACTIVITY a_1 AND SOLUTE ACTIVITY COEFFICIENT γ_2' IN AQUEOUS SUCROSE SOLUTIONS AT 25°C*

m_2, moles/kg	$\frac{\Delta p_1}{m_2 p_1^\circ}$, kg/mole	$\frac{\Delta p_1}{p_1^\circ}$	a_1	$\frac{\ln a_1}{m_2}$	$\left(\frac{55.51 \ln a_1}{m_2} + 1\right)$	$\frac{\left(\frac{55.51 \ln a_1}{m_2} + 1\right)}{m_2}$	$\int_0^{m_2} \frac{\left(\frac{55.51 \ln a_1}{m_2} + 1\right)}{m_2} dm_2$	$\ln \gamma_2'$	γ_2'
0	(0.01802)†	(0)	1.00000	(−0.01802)	(0)	....	(0)	(0)	1.000
0.2	0.01796	0.00359	0.99641	−0.01799	+0.0014	+0.0070	(−0.0018)	(0.0004)	1.000
0.4	0.01821	0.00728	0.99272	−0.01828	−0.0147	−0.0368	−0.0068	0.0215	1.022
0.6	0.01848	0.01109	0.98891	−0.01858	−0.0314	−0.0523	−0.0156	0.0470	1.048
0.8	0.01881	0.01505	0.98495	−0.01895	−0.0519	−0.0649	−0.0272	0.0791	1.083
1.0	0.01936	0.01936	0.98064	−0.01955	−0.0852	−0.0852	−0.0406	0.1258	1.134
1.2	0.01959	0.02351	0.97649	−0.01983	−0.1008	−0.0840	−0.0572	0.1580	1.171
1.4	0.01985	0.02779	0.97221	−0.02014	−0.1180	−0.0843	−0.0746	0.1926	1.212
2.0	0.0209	0.0418	0.9582	−0.0214	−0.188	−0.094	−0.130	0.318	1.374
3.0	0.0223	0.0669	0.9331	−0.0231	−0.282	−0.094	−0.224	0.506	1.659
4.0	0.0235	0.0940	0.9060	−0.0247	−0.371	−0.093	−0.318	0.689	1.992
5.0	0.0245	0.1225	0.8775	−0.0261	−0.449	−0.090	−0.410	0.859	2.361
6.0	0.0250	0.1500	0.850	−0.0271	−0.504	−0.084	−0.498	1.002	2.724
6.18 (satd)	(0.0252)‡	0.1557	0.844	−0.0274	−0.521	−0.084	−0.513	1.034	2.812

* Vapor-pressure data, 0 to 1.4*m*, from D. A. Sinclair, *J. Phys. Chem.*, **37**, 495–504 (1933); at higher concentrations, the "International Critical Tables," Vol. III, p. 293, McGraw-Hill Book Company, Inc., New York, 1928.

† Ideal limiting value $\left(= \frac{\bar{M}_1}{1000} \text{ g/kg}\right)$.

‡ Estimated by extrapolation.

As shown by Lewis and Randall,[1] the integral in Eq. (7-3-90) converges rapidly at low solute concentrations, and may be evaluated graphically with ease from a comparatively rough plot of its integrand vs. m_2. In Table 7-4, a_1 and γ_2' are given for solutions of sucrose in water at 25°C, as derived from vapor-pressure measurements; the data from 0 to 1.4*m* are taken from work of D. A. Sinclair, while the data at the higher concentrations represent older work, as reported in the "International Critical Tables" by J. C. W. Frazer, R. K. Taylor, and A. Grollman. The a_1 values have been calculated by means of Eq. (7-3-45), which in the case of a nonvolatile solute assumes the form $a_1 = 1 - (\Delta p_1/p_1^\circ)$, and the γ_2' values have then been calculated by means of Eq. (7-3-90); Fig. 7-15 shows the graph of $\left(55.51 \dfrac{\ln a_1}{m_2} + 1\right)\Big/ m_2$ vs. m_2 used in computing the integral in Eq. (7-3-90).

The value of the constant ϕ_2' defined by Eq. (7-3-84) is known as the *standard molal free energy of formation in solution*, of the particular solute, component 2, in the given solvent, component 1. It represents the thermodynamic potential of the solute in a hypothetical ideal dilute solution at 1*m* concentration in the given solvent; *i.e.*, it represents what the value of ϕ_2 would be at 1*m* concentration if the solute continued to satisfy the ideal limiting law (7-3-79) up to that concentration. The effect of temperature on ϕ_2' may be derived by the application of (7-1-26*b*) to (7-3-82);

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[1] Lewis and Randall, *op. cit.*, pp. 273–275. They have shown that in many cases, the expression $\left(\dfrac{1000\ \text{g/kg}}{\bar{M}_1} \dfrac{\ln a_1}{m_2} + 1\right)$ turns out empirically to be approximately proportional to m_2 in dilute solutions, in which event the entire Eq. (7-3-90) reduces to

$$\ln \gamma_2' \sim -2\left(\frac{1000\ \text{g/kg}}{\bar{M}_1} \frac{\ln a_1}{m_2} + 1\right) \tag{7-3-90a}$$

One may compute $(\ln a_1)/m_2$ directly from precise measurements of the lowering of the solvent's vapor pressure (among other experimental methods) by means of the series approximation

$$\frac{\ln a_1}{m_2} = -\frac{\Delta p_1}{m_2 p_1^\circ}\left[1 + \frac{1}{2}\left(\frac{\Delta p_1}{p_1^\circ}\right) + \frac{1}{3}\left(\frac{\Delta p_1}{p_1^\circ}\right)^2 + \cdots\right] \tag{7-3-90b}$$

where in sufficiently dilute solution (not necessarily ideal), only the first, or the first two terms of the series need be taken into consideration; in Eq. (7-3-90*b*), it is assumed that the equilibrium vapor phase may be treated as an ideal gas; otherwise the series approximation is exact, if one uses a number of terms consistent with the precision of the experimental data. It is actually in the form of the expression $\Delta p_1/m_2 p_1^\circ$ that vapor-pressure data for solutions of nonvolatile solutes are generally tabulated; see, for example, the "International Critical Tables," Vol. III, pp. 292–300, McGraw-Hill Book Company, Inc., New York, 1928.

in view of (7-3-83) and (4-37),

$$\left[\frac{d(\phi_2'/T)}{d(1/T)}\right]_p = \lim_{m_2\to 0} \eta_2 = \Phi_h^\circ \qquad (7\text{-}3\text{-}91)$$

where $\Phi_h^\circ = \bar{H}_2^\circ - \bar{Q}_s^\circ$ [see Eq. (4-30)]; the same equation is evidently satisfied by ϕ_2° in place of ϕ_2', since ϕ_2'/T and ϕ_2°/T differ merely by a constant [Eq. (7-3-80)]. Likewise, the effect of pressure on ϕ_2' may be derived by the application of (7-1-24) to (7-3-82),

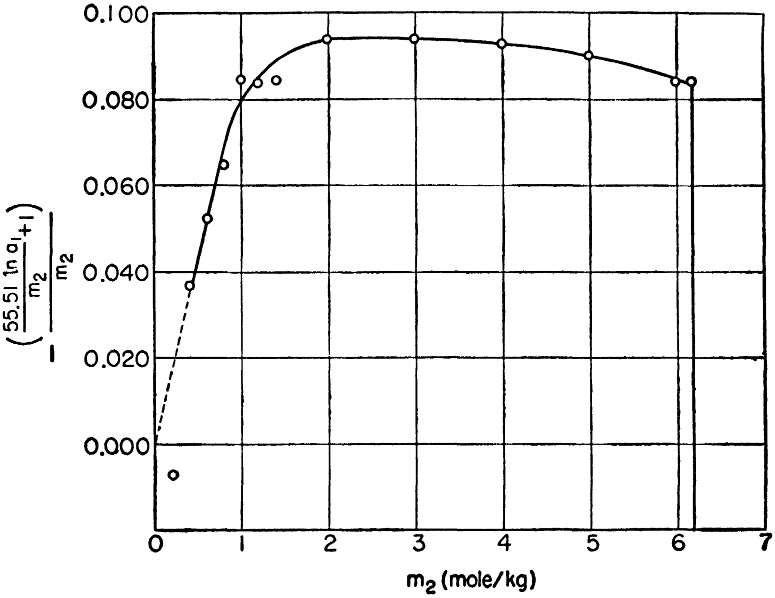

FIG. 7-15. Plot of the quantity $\left(\frac{55.51 \ln a_1}{m_2} + 1\right) \Big/ m_2$ vs. m_2 for solutions of sucrose in water at 25°C (data of Table 7-4). The area enclosed by the curve above the 0.000 ordinate between the $m_2 = 0$ and the $m_2 = m_2$ abscissas represents the value of the integral in Eq. (7-3-90) for the evaluation of $\ln \gamma_2'$ from experimentally established values of a_1.

$$\left(\frac{d\phi_2'}{dp}\right)_T = \lim_{m_2\to 0} v_2 = \Phi_v^\circ \qquad (7\text{-}3\text{-}92)$$

where Φ_v° represents the limiting apparent molal volume of the solute at infinite dilution in the given solvent, defined in a manner analogous to the definition of Φ_h°; since Φ_v° is generally relatively small in magnitude for liquid solutions, we may ordinarily neglect the effect of pressure on ϕ_2' for pressure variations of order 1 atm. The effect of temperature on γ_2' itself at given composition is evidently given by

$$\left(\frac{d\ln\gamma_2'}{dT}\right)_{p,n} = \frac{1}{R}\left[\frac{d(\phi_2-\phi_2')/T}{dT}\right]_{p,n} = \frac{1}{RT^2}(\Phi_h^\circ - \eta_2) \qquad (7\text{-}3\text{-}93)$$

The quantity $\phi_2' - (\bar{F}_T^\circ)_2$, relating ϕ_2' to the standard molal free energy of the pure solute, and representing the *standard free energy of solution* of component 2 in component 1 relatively to the convention represented by Eqs. (7-3-82) and (7-3-83), may be measured by essentially the same methods described for the measurement of ϕ_2° relatively to $(\bar{F}_T^\circ)_2$. If the pure solute happens to be a volatile liquid or solid with vapor pressure p_2° at the given temperature, then

$$\phi_2' = (\bar{F}_T^\circ)_2 + RT \ln \frac{k_2'}{p_2^\circ} \tag{7-3-94}$$

where k_2' represents the molal Henry's law constant: $k_2' = \lim_{m_2 \to 0} (p_2/m_2)$ [compare Eq. (7-3-74)]. This equation may be applied also to a gaseous solute, if one formally sets $p_2^\circ = 1$ atm [or any other standard pressure to which the term $(\bar{F}_T^\circ)_2$ then refers]. For example, the solubility of H_2S at a partial pressure of 1 atm in water at 25°C is 0.102 mole/kg;[1] since the solution at this low concentration is known to satisfy Henry's law closely, and since the deviation of H_2S from ideal-gas behavior is negligible at the given pressure, we may take $k_2' = 1$ atm/0.102 mole/kg, and hence,

$$\begin{aligned} H_2S(g) = H_2S(aq); \quad \Delta F_{298.16}^\circ = \phi_{H_2S(aq)}' - \bar{F}_{H_2S(g)}^\circ &= -RT \ln 0.102 \\ &= 1350 \text{ cal/mole} \end{aligned}$$

This quantity represents what the change in free energy *would be* if 1 mole of $H_2S(g)$ at an original pressure of 1 atm were to be dissolved in water in a hypothetical ideal dilute solution at $1m$ concentration (at that *actual* concentration, the solution would probably deviate to some extent from the ideal dilute-solution laws); having found in this way the value of ϕ_2', we may then calculate the value of ϕ_2 at other concentrations approximately by means of Eq. (7-3-39), or exactly, with the aid of additional experimental information, by means of Eq. (7-3-82). If the pure solute happens to be a solid, whose solubility in the given solvent at the temperature T and pressure p is represented by m_2^*, then evidently

$$\phi_2' = (\bar{F}_{T,p})_{2(c)} - RT \ln m_2^*(\gamma_2')^* \tag{7-3-95}$$

[compare Eq. (7-3-76)]. Thus, from the data for aqueous sucrose solutions presented in Table 7-4:

$$\begin{aligned} C_{12}H_{22}O_{11}(c) = C_{12}H_{22}O_{11}(aq); \quad \Delta F_{298.16}^\circ &= \phi_{\text{sucrose(aq)}} - \bar{F}_{\text{sucrose(c)}}^\circ \\ &= -RT \ln (6.12)(2.81) \\ &= -1686 \text{ cal/mol} \end{aligned}$$

This quantity, too, represents what the change in free energy would be if 1 mole of crystalline sucrose were to be dissolved in a hypothetical ideal

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[1] As quoted by Lewis and Randall, *op. cit.*, p. 543. (See also Prob. 7-12.)

dilute solution at finite concentration $1m$; one sees in Table 7-4 that at an actual concentration of $1m$, this solute deviates from ideal dilute-solution behavior [as represented by Eq. (7-3-79)] to the extent of 13 per cent; *i.e.*, its activity satisfying Eq. (7-3-81) is 13 per cent higher than its molal concentration. One will note that in this case, where the thermodynamic properties of the solute have been calculated from those of the solvent (as given by vapor-pressure measurements) through integration of the Gibbs-Duhem equation, it is not sufficient for the determination of $\phi_2' - (\bar{F}_T^\circ)_2$ to measure the vapor pressure of the solvent merely for the saturated solution; while we know that $\phi_2 = (\bar{F}_T^\circ)_2$ in the saturated solution, it is necessary for us to have a_1 data over the entire composition range, down to the Raoult-Henry law region, in order for us to evaluate the extent of deviation from those laws in the saturated solution, as represented by the value of $(\gamma_2')^*$. It is also necessary for us to know in applying Eq. (7-3-95) that the equilibrium solid phase consists of the pure solute, and not a solid solution or a compound between the supposed solute and the solvent.

According to the scheme represented by Eqs. (7-3-82) and (7-3-83), we thus set up in the given solvent a standard state for each solute represented by a hypothetical ideal dilute solution conforming to Raoult's and Henry's laws, with the solute assigned a standard concentration of 1 mole/kg of solvent; the specific effect of concentration on the solute's thermodynamic potential is then represented empirically in terms of the activity coefficient γ_2', whose value is to be determined by appropriate experiments over the composition range with which one is concerned. We thus conceive of a separation of ϕ, artificial but none the less useful, into three contributing terms: a term ϕ_2' *constant* for the particular solute in the particular solvent at given temperature and pressure, differing from the molal free energy of the pure solute by a characteristic amount, the so-called "standard free energy of solution";[1] a general term $RT \ln m_2$, representing the *ideal* (modified Henry's law) effect of the solute's *concentration;* and a term of the form $RT \ln \gamma_2'$, representing specifically the effect of *deviation from the ideal dilute-solution laws* [as represented by Eq. (7-3-79)] at finite solute concentrations.

The molality would appear to be a rather capricious choice for representing the composition, when we have seen that the mole fraction is more

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[1] For a liquid solute that happened to form solutions ideal over the entire composition range with the liquid solvent, the difference would degenerate to

$$-RT \ln \frac{(1000\ \text{g/kg})}{\bar{M}_1}$$

a formal quantity depending merely on our choice of composition measure; compare Eq. (7-3-80).

immediately related to the physical properties of the solution (as shown particularly by the behavior of those solutions that happen to be ideal in the sense of Raoult's law for both components over the entire composition range). It was introduced at a time when the empirical laws of dilute solutions were first being established; Raoult originally expressed his concentrations, for example, in terms of grams of solute per 100 g of solvent. Such a measure has clear advantages from the point of view of precision over the otherwise convenient volumetric measures (*e.g.*, grams of solute per 100 ml of solution, moles of solute per liter of solution, etc.), in that the composition of a liquid solution can be determined by weight more precisely than by volume, and is at the same time independent of temperature. Randall has called attention to these advantages.[1] When we base the composition on the mole fractions, however, it is always necessary for us to assume some particular formula for the solvent; in the case of a solvent such as water, we are by no means sure of the actual molecular configuration in the liquid state, and in the case of a solvent such as acetic acid, the situation is worse, because even in the vapor state both monomeric and dimeric molecules are known to be present. When we represent the composition in terms of the molality of the solute (or other proportional measure based on the same general principle), we are relieved of the necessity of assigning a physically significant molecular weight to the solvent; indeed, as the empirical limiting form (7-3-79) shows, the molecular weight of the solvent is quite immaterial for the representation of the dependence of ϕ_2 on the solute's concentration over the ideal dilute range. Even in an equation such as (7-3-90), the value assigned to $\bar{M}_1$ has purely formal significance. Furthermore, in the case of an electrolytic solute, such as NaCl, the values assigned to the mole fractions of both solute and solvent at high solute concentrations are influenced by one's decision whether or not to count the ions as independent solutes; when we compute the so-called *stoichiometric molality*, however, we merely adopt the definite convention that the number of "moles" of solute is determined in accordance with its conventional formula weight, the formula being explicitly stated when necessary (*e.g.*, 58.454 for NaCl). The empirical relation between ϕ_2 and m_2 in the ideal dilute-solution limit is then of course different for an electrolyte from that for a nonelectrolyte, but it continues to have a quite simple form, as we shall see in Sec. 7-4. One should realize that the value of ϕ_2 does not depend in any way on the real or assumed structure of the substance to which it refers. The fundamental definitions (7-1-3) imply of course that we have in mind for each substance a definite unit of mass, represented generally in relation to its conventional chemical formula; the actual

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[1] M. Randall, *Trans. Faraday Soc.*, **23**, 498–502 (1927).

numerical magnitude of ϕ_2 will be proportional to the size of this unit assigned to the particular component, but we could equally well measure physically significant ϕ_2 values with respect to a quite arbitrary or capricious formula for the substance. It is only when we come to consider essentially nonthermodynamic generalizations such as are represented by Eqs. (7-3-16) and (7-3-79) that the advantage of assigning "proper" formula weights becomes evident; for these laws are correct only when we assign to each solute a formula weight that in general agrees empirically with its ordinary chemical formula weight, as deduced from other evidence. Raoult's law was used originally, of course, precisely to determine such chemical formula weights, or molecular weights, of solutes in solution, particularly of substances such as the sugars, whose molecular weights could not be determined by other methods available at the time. The generalization has to be modified in the case of electrolytes, as shown originally by Arrhenius; in certain special cases, the chemical formula of the substance in solution has to be modified (benzoic acid dissolved in benzene; formaldehyde dissolved in water, etc.).

At any rate, most of the thermodynamic data for aqueous solutions, and much of the data for other solvents as well, will be found in the chemical literature of recent years expressed in terms of the molal activity coefficient, that we have here represented by the symbol γ_2' defined by Eqs. (7-3-82) and (7-3-83) (modified for electrolytes, as we shall show in Sec. 7-4). The mole-fraction activity coefficient that we have represented by the symbol γ_2° in Eqs. (7-3-67) and (7-3-68) is in fact seldom employed, despite its theoretical simplicity. On the other hand, the mole-fraction activity coefficients γ_1 and γ_2 based on the pure (liquid) components as respective states of reference [Eqs. (7-3-48)], are used extensively in the correlation of liquid-vapor equilibrium data, as we have described in Sec. 7-3*f*; and analogously defined mole-fraction activity coefficients based on the pure solid components are used in the description of the thermodynamic properties of solid solutions, as mentioned in connection with Eqs. (7-3-61). In certain cases, it may be convenient for one to define activity coefficients in liquid solutions with respect to some special standard state; for example, if one of the components happens to be a solid in the pure state at the temperature and pressure under consideration, and if one lacks sufficient data in the dilute-solution range to carry out precisely the extrapolation required for establishment of the standard state in ideal dilute solution, then it may be convenient to represent ϕ_2 in the form

$$\phi_2 = (\bar{F}_{T,p})_{2(c)} + RT \ln x_2 + RT \ln \gamma_2,$$

but under the convention $a_2^* = x_2^* \gamma_2^* = 1$ in the *saturated* solution [where according to general theory, $\phi_2 = (\bar{F}_{T,p})_{2(c)}$]. Such a procedure introduces no complication, so long as the reference state is always clearly specified.[1]

Finally, for certain purposes it is desirable for us to be able to represent the thermodynamic potential of the solute as a function of its *volume concentration.* Activity coefficients are seldom tabulated in this form, on account of the relatively poor precision with which the solute concentration may be established experimentally by volume, as compared with its establishment by weight; however, it is useful for us to know how to relate ϕ_2 to the molar concentration by volume, when we have available the necessary thermodynamic data expressed according to custom in some other form, as in terms of ϕ_2' and γ_2'. The *molarity* of the solute, C_2, is defined as the *number of moles of solute per liter of solution.* Thus

$$C_2 = \frac{n_2}{V} \text{ (1000 ml/liter)} \tag{7-3-96}$$

where V represents the volume (in milliliters) of solution containing n_2 moles of solute. The molarity of a given solution evidently varies in general with temperature (and also slightly with pressure, generally understood to be 1 atm unless otherwise specified). In sufficiently dilute solution, however, it becomes proportional to m_2, and therefore also to x_2 [in view of Eq. (7-3-78)]; thus, the exact relation between C_2 and m_2 at all concentrations is

$$m_2 = \frac{C_2}{\rho - \dfrac{C_2\bar{M}_2}{1000 \text{ g/kg}}} \tag{7-3-97}$$

where ρ represents the density of the solution and $\bar{M}_2$ the molecular weight or formula weight of the solute; therefore,

$$\lim_{C_2 \to 0} m_2 = \frac{C_2}{\rho_1} \tag{7-3-98}$$

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[1] In the correlation of liquid-vapor equilibrium data for nonideal solutions according to the methods of Sec. 7-3*f*, we may have occasion to deal with a liquid solution one of whose components in the pure state is a gas at the temperature and pressure under consideration. In this event, it is convenient for us to retain Eqs. (7-3-48), but with the term $(\bar{F}_{T,p})_2$ for the particular component referring to it in a hypothetical liquid state; the value of this constant is defined through extrapolation of the experimental data, in the form $\lim_{x_2 \to 1} (\phi_2 - RT \ln x_2 - RT \ln \gamma_2) = (\bar{F}_{T,p})_2$. The relation between the constant $(\bar{F}_{T,p})_2$ and the standard molal free energy of the pure gas, $(\bar{F}_T^\circ)_{2(g)}$, may then be established experimentally in the usual way, through the relation $\phi_2 = \phi_2^*$ for any liquid composition at which the value of γ_2 in the liquid phase has been determined, and also p_2 (that is, y_2^*p) and ν_2 in the equilibrium vapor phase; compare Eq. (7-2-9) for the gas phase.

where ρ_1 represents the density of the pure solvent at the given temperature and pressure. Thus, in the ideal dilute range, the value of ϕ_2 satisfies the empirical limiting law [Henry's law, Eq. (7-3-16), expressed merely in a different composition measure]:

$$\phi_2 = \phi_2'' + RT \ln C_2 \quad (T, p \text{ const}; C_2 \to 0) \qquad (7\text{-}3\text{-}99)$$

where, by definition,

$$\phi_2'' = \phi_2' - RT \ln \rho_1 \qquad (7\text{-}3\text{-}100)$$

We could therefore conveniently define a *molar activity function* a_2'', and a corresponding *molar activity coefficient* γ_2'' for the solute, in accordance with the equations

$$\begin{aligned} \phi_2 &\equiv \phi_2'' + RT \ln a_2'' && (T, p \text{ const}) \qquad (7\text{-}3\text{-}101)\\ &\equiv \phi_2'' + RT \ln C_2 + RT \ln \gamma_2'' && (T, p \text{ const}) \qquad (7\text{-}3\text{-}102) \end{aligned}$$

which in the ideal dilute limit, where the solvent satisfied empirically Raoult's law (7-3-15), would satisfy the conditions

$$\lim_{C_2 \to 0} a_2'' = C_2; \qquad \lim_{C_2 \to 0} \gamma_2'' = 1 \qquad (7\text{-}3\text{-}103)$$

One readily sees that

$$a_2'' = a_2' \exp \frac{\phi_2' - \phi_2''}{RT} = a_2' \rho_1 \qquad (7\text{-}3\text{-}104)$$

so that over the entire composition range, the value of a_2'' would be directly proportional to a_2', and hence also to a_2° and a_2 as previously defined. The relation between γ_2'' and γ_2', however, would be more complex, varying with composition according to the equations

$$\gamma_2'' = \gamma_2' \rho_1 \left[\frac{1}{\rho - \dfrac{C_2 \bar{M}_2}{1000 \text{ ml/l}}} \right] = \gamma_2' \frac{\rho_1}{\rho} \left[1 + \frac{m_2 \bar{M}_2}{1000 \text{ g/kg}} \right] \qquad (7\text{-}3\text{-}105)$$

Thus, in sufficiently dilute solution (not necessarily ideal), γ_2'' would become identical with γ_2', but this identity would in general not be maintained at high solute concentrations.

Equations (7-3-100) and (7-3-105) permit us to translate ϕ_2' and γ_2' values, as ordinarily presented in thermodynamic tables (with m_2 as composition measure), into ϕ_2'' and γ_2'' values, and so by means of Eq. (7-3-102) to represent ϕ_2 accurately as an empirical function of C_2. It should be emphasized that no new information is created in this way, but merely a rearrangement of the experimental information already at hand. In *aqueous solutions*, since the value of ρ_1 is so close to 1 g/ml at room temperature (within 0.3 per cent at 25°C), we may generally use ϕ_2' values in place of ϕ_2'' directly, without significant error except in work of the highest precision; likewise, in sufficiently dilute solution, we may use γ_2' values in place of γ_2'', but one should bear in mind the exact connection, Eq. (7-3-105), at higher solute concentrations.

Let us now summarize the results of this long discussion of the mechanics of relating the thermodynamic potential of the solute, in solution in a given solvent, to its concentration. There are three general methods in use for representing the composition of a liquid solution: the mole fraction of the solute x_2, the molality m_2, and the molar concentration C_2. It is an empirical fact that in sufficiently dilute solution, the thermodynamic potential of the solute ϕ_2 may be represented by any of the following formulas:

$$\begin{aligned} \phi_2 &= \phi_2^\circ + RT \ln x_2 \qquad (T,\, p \text{ const};\, x_2 \to 0) \qquad &(7\text{-}3\text{-}106a)\\ &= \phi_2' + RT \ln m_2 \qquad (T,\, p \text{ const};\, m_2 \to 0) \qquad &(7\text{-}3\text{-}106b)\\ &= \phi_2'' + RT \ln C_2 \qquad (T,\, p \text{ const};\, C_2 \to 0) \qquad &(7\text{-}3\text{-}106c)\end{aligned}$$

where the empirical constants ϕ_2°, ϕ_2', and ϕ_2'' are interrelated through Eqs. (7-3-80) and (7-3-100). These equations are implied by Raoult's empirical vapor-pressure law (7-3-14) for the solvent, but follow more generally from Eq. (7-3-15), which probably applies even to solvents whose volatilities are too low for Raoult's vapor-pressure law to be put to direct experimental test. Exceptions noted are electrolytic solutes as a class (to be discussed in Sec. 7-4) and certain special cases where other types of dissociation, association, or chemical reaction between solute and solvent are known or believed to take place. Equations retaining the general form of Eqs. (7-3-106) may be set up outside the ideal dilute region if one introduces appropriately defined *activity coefficients* as measures of deviation from ideal dilute-solution behavior:

$$\begin{aligned} \phi_2 &= \phi_2^\circ + RT \ln x_2\gamma_2^\circ \qquad (T,\, p \text{ const}) \qquad &(7\text{-}3\text{-}107a)\\ &= \phi_2' + RT \ln m_2\gamma_2' \qquad (T,\, p \text{ const}) \qquad &(7\text{-}3\text{-}107b)\\ &= \phi_2'' + RT \ln C_2\gamma_2'' \qquad (T,\, p \text{ const}) \qquad &(7\text{-}3\text{-}107c)\end{aligned}$$

These equations are entirely equivalent. The solute activity coefficients, of which γ_2' is the one most commonly in use, are merely convenient empirical measures describing how ϕ_2 varies actually with solute concentration, as determined in each individual case by experimental measurements of various interrelated kinds; the ideal equations (7-3-106) are in general valid only in the low-concentration limit. The value of ϕ_2° represents what the standard molal free energy of the pure (liquid) solute would be if the solute's thermodynamic potential showed the same dependence on composition over the entire composition range that it actually shows in the ideal dilute solution; the value of ϕ_2' represents the thermodynamic potential of the solute in a hypothetical ideal dilute solution at formal concentration, 1 mole/kg of solvent; the value of ϕ_2'' represents the thermodynamic potential of the solute in a hypothetical ideal dilute solution at formal concentration, 1 mole/liter. No general theoretical law has been discovered relating the actual value of ϕ_2 to the composition at high solute concentrations, except in the special case of ideal concentrated solutions.

The problem of several solutes in solution in a given solvent is extremely complex, because of the greater number of composition variables involved. In sufficiently dilute solution, we may suppose that each solute satisfies independently a law of the form of (7-3-106), where for example the ϕ_2' value for each solute is the same as in a binary solution with the given solvent [compare Eqs. (7-3-27)]. Most of the experimental work at higher solute concentrations has been done with electrolytes, in order to test the theoretical dilute solution laws proposed by Debye and Hückel (see Sec. 7-4).

7-4. Solutions of Electrolytes. An electrolyte, such as KCl dissolved in water, consists of at least two different kinds of charged material particles or *ions*, in this case K^+ and Cl^- (undoubtedly hydrated to some extent). The migrations of these ions in opposite directions in an electric field, superimposed on their ordinary random thermal motion, is supposed to account for the electrical conductivity, which is thus fundamentally different in character from the purely electronic type of conductivity that occurs in metals. The charge on an individual ion is always some fixed multiple of the electron charge, but the numbers of ions of opposite sign are always so related that the solution as a whole is electrically neutral. For this reason, a single electrolyte, such as KCl, counts as but one component toward determining the variance of the phase in question, inasmuch as the concentrations of the two ions are not independently variable; for the same reason, a mixture of NaCl and KCl counts as two components, and a mixture of NaCl and KNO_3 also as two, but a mixture of NaCl, KNO_3, and KCl in arbitrary proportions counts as three. Because of this basic fact, the theory of ionization in solution was slow in gaining recognition.

Many electrolytes, including KCl itself, apparently consist of ions in the pure crystalline state, and also in the pure liquid state, as well as in solution. Others, however, such as HCl, apparently give rise to ions only through reaction with a suitable solvent (or possibly with other solutes that may be present). Thus, KCl is an electrolyte in any liquid medium that will dissolve it, as well as in the pure liquid state, whereas HCl is an electrolyte in certain media, including water and liquid ammonia, but a nonelectrolyte in others, such as benzene, and in the pure liquid state. We speak of "strong" electrolytes and "weak" electrolytes; strong electrolytes are substances that in the particular liquid medium under investigation are apparently entirely in the form of ions, showing relatively high electrical conductivity in relation to their concentration; weak electrolytes are substances that are apparently only partially in the ionized state. There may evidently be various degrees of "weakness."[1] Thus, KCl in any liquid medium is a strong electrolyte, and so is $BaSO_4$, even though its solubility in the particular solvent water happens to be low; H_2S and NH_3 on the other hand are weak electrolytes in water; HCl is a strong electrolyte in water (at least at sufficiently low concentrations, say below 6*m*), but in glacial acetic acid it is a weak electrolyte, and in benzene it is a nonelectrolyte. In this section, we shall be concerned primarily with developing methods of treating the thermodynamic properties of strong electrolytes in solution; we shall discuss weak electrolytes in relation to the general theory of chemical equilibrium, in Chap. 8.

In general thermodynamic theory, we define the thermodynamic potential of an electrolyte in precisely the same way as for a nonelectrolyte, *viz.*, through the equivalent relations (7-1-3) or (7-1-12),

$$\phi_2 \equiv \left(\frac{dU}{dn_2}\right)_{S,V,n'} = \left(\frac{dF}{dn_2}\right)_{T,p,n'} \tag{7-4-1}$$

If, for example, we can measure by how much the free energy of the solution changes per "mole" of electrolytic solute added (determined in relation to the conventional formula weight, *e.g.*, 74.553 for KCl) when that solute is introduced into the solution at constant temperature and pressure on such a scale that the composition of the solution is not significantly altered, then we have directly established the value of ϕ_2. According to the theory developed in the preceding sections of this chapter, measurement of the vapor pressure and composition of the equilibrium vapor phase for various liquid compositions gives us essentially this information (among other more precise methods to be discussed later). The problem is simplified generally by the fact that most electrolytic solutes are relatively involatile at ordinary temperatures compared with the solvent, so that the equilibrium vapor phase consists practically of the pure solvent. Thus, in principle, we can measure ϕ_{KCl} in aqueous solution by first measuring ϕ_{H_2O} from measurement of the vapor pressure ($p = p_{H_2O}$ in this case) at various solute concentrations according to Eqs. (7-3-3) or (7-3-4) and then integrating the Gibbs-Duhem equation (7-1-7). If we express Eq.

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[1] The situation may be complicated in certain cases because of complex ion formation; *e.g.*, CdI_4^{-} between Cd^{++} and I^-, $HgCl_4^{-}$ between Hg^{++} and Cl^-. This has the effect of reducing the apparent degree of ionization of such electrolytes as CdI_2 and $HgCl_2$ in solution.

(7-1-7) in terms of the molality of the solute as composition measure, according to custom for solutions of electrolytes,

$$\frac{1000\ \mathrm{g/kg}}{\bar{M}_1}\, d\phi_1 + m_2\, d\phi_2 = 0 \quad (T,\ p\ \text{const}) \qquad (7\text{-}4\text{-}2)$$

therefore

$$\phi_2 = \text{const} - \frac{1000\ \mathrm{g/kg}}{\bar{M}_1} \int \frac{1}{m_2}\, d\phi_1 \qquad (T,\ p\ \text{const})$$

We may eliminate the integration constant from this equation by integrating down from the value of m_2 corresponding to the saturated solution, m_2^*, where $\phi_2 = (\bar{F}_{T,p})_2$ for the pure solute; thus[1]

$$\phi_2 = (\bar{F}_{T,p})_2 - \frac{1000\ \mathrm{g/kg}}{\bar{M}_1} \int_{m_2 = m_2^*}^{m_2 = m_2} \frac{1}{m_2}\, d\phi_1 \quad (T,\ p\ \text{const}) \qquad (7\text{-}4\text{-}3)$$

We may express Eq. (7-4-3) directly in terms of vapor-pressure data by means of Eq. (7-3-3), assuming that the vapor phase may be treated as an ideal gas, and neglecting the effect of small variations in the pressure on $(\bar{F}_{T,p})_2$; thus

$$\phi_2 = (\bar{F}_T^\circ)_2 - \frac{1000\ \mathrm{g/kg}}{\bar{M}_1} RT \int_{m_2 = m_2^*}^{m_2 = m_2} \frac{1}{m_2}\, d \ln \frac{p_1}{p_1^\circ} \qquad (7\text{-}4\text{-}4)$$

Equation (7-4-4) constitutes in fact an important though not the most precise method of determining ϕ_2 for a nonvolatile solute, whether or not it happens to be an electrolyte. The data in Table 7-5 illustrate its application to the determination of ϕ_{KCl} in aqueous KCl solutions at 25°C,

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[1] The value of $(\bar{F}_{T,p})_2$ in Eq. (7-4-3) corresponds of course to the solute phase actually in equilibrium with the saturated solution. For example, in an aqueous solution saturated with $CuSO_4 \cdot 5H_2O$, one could say that $\phi_{\mathrm{CuSO_4\cdot 5H_2O}} = \bar{F}^\circ_{\mathrm{CuSO_4\cdot 5H_2O(c)}} = \phi_2^* + 5\phi_1^*$, where ϕ_2^* and ϕ_1^* stand, respectively, for the thermodynamic potentials of $CuSO_4$ as solute and H_2O as solvent in the saturated solution, since presumably the reaction $CuSO_4 \cdot 5H_2O(aq) = CuSO_4(aq) + 5H_2O$ in the liquid phase is in a state of equilibrium; in this case, one would therefore substitute $\bar{F}^\circ_{\mathrm{CuSO_4\cdot 5H_2O(c)}} - 5\phi_1^*$ in place of $(\bar{F}_{T,p})_2$ (at $p = 1$ atm) in Eq. (7-4-3). The relation between $\bar{F}^\circ_{\mathrm{CuSO_4\cdot 5H_2O(c)}}$ and $\bar{F}^\circ_{\mathrm{CuSO_4(c)}}$ may be established by methods discussed in Chap. 8. In the case of a gaseous solute such as HCl, Eq. (7-4-3) is correct, provided that we substitute for $(\bar{F}_{T,p})_2$ the thermodynamic potential of HCl in the gas phase in equilibrium with the liquid solution at solute concentration m_2; for example, if one may treat the equilibrium vapor phase as an ideal gas, then we may replace $(\bar{F}_{T,p})_2$ by $\bar{F}^\circ_{\mathrm{HCl(g)}}$, provided that m_2^* stands for the HCl molality in a solution for which $p_{\mathrm{HCl}} = 1$ atm; in this case, of course, we must use the partial vapor pressure of H_2O instead of the total vapor pressure in computing $\phi_{\mathrm{H_2O}}$ according to Eq. (7-3-3). For a liquid solute such as HNO_3 miscible with the solvent over the entire composition range, we may replace $(\bar{F}_{T,p})_2$ by $\bar{F}^\circ_{\mathrm{HNO_3(l)}}$, provided that we let $m_2^* \rightarrow \infty$.

TABLE 7-5. THERMODYNAMIC POTENTIAL OF KCl IN AQUEOUS SOLUTIONS AT 25°C FROM VAPOR-PRESSURE DATA FOR THE SOLVENT*

m_2, moles/kg	p_1, mm Hg	a_{H_2O}	$\log a_{H_2O}$	$\int_{4.81}^{m_2} \frac{1}{m_2}\, d \log a_1$	$\phi_{KCl} - \bar{F}^\circ_{KCl(c)}$, cal/mole	$RT \ln m_2$, cal/mole	$[\phi_2 - \bar{F}^\circ_{KCl(c)}] - RT \ln m_2$, cal/mole	$[\phi_2 - \bar{F}^\circ_{KCl(c)}] - 2RT \ln m_2$, cal/mole
0	23.752	1.00000	0.00000	....	$-\infty$	$-\infty$	......	(−1207)
0.2	23.597	0.99348	−0.00280	0.04420	−3347	−954	−2393	−1439
0.4	23.448	0.98721	−0.00560	0.03487	−2641	−543	−2098	−1555
0.6	23.296	0.98081	−0.00842	0.03095	−2344	−303	−2041	−1738
0.8	23.150	0.97466	−0.01115	0.02713	−2055	−132	−1923	−1791
1.0	23.017	0.96906	−0.01365	0.02432	−1842	0	−1842	−1842
1.5	22.620	0.95235	−0.02071	0.01827	−1384	240	−1624	−1864
2.0	22.243	0.93647	−0.02851	0.01404	−1063	411	−1474	−1885
2.5	21.877	0.92107	−0.03571	0.01080	−818	543	−1361	−1904
3.0	21.497	0.90507	−0.04332	0.00801	−607	651	−1258	−1909
3.5	21.089	0.88789	−0.05578	0.00568	−430	742	−1172	−1914
4.0	20.696	0.87134	−0.05981	0.00330	−250	821	−1071	−1892
4.81 (satd)	20.021	0.84292	−0.07422	0	0	847	−847	−1694

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* Vapor-pressure data of J. N. Pearce and R. D. Snow, *J. Phys. Chem.*, **31**, 231–245 (1927). The limiting value of $[\phi_2 - \bar{F}^\circ_{KCl(c)}] - 2RT \ln m_2$ has been derived with the help of data from other sources.

from vapor-pressure measurements by Pearce and Snow;[1] Fig. 7-16 shows $1/m_2$ plotted against log (p_1/p_1°) (one could just as well use log p_1 itself, since p_1° is constant), from which the integral required in Eq. (7-4-4) has been computed by graphical integration, column (5); the values of ϕ_{KCl} relative to $\bar{F}^\circ_{\text{KCl(c)}}$ are tabulated in column (6). Thus, in 1*m* solution, the thermodynamic potential of KCl is lower than the standard molal free energy of pure KCl(c) by 1842 cal/mole,

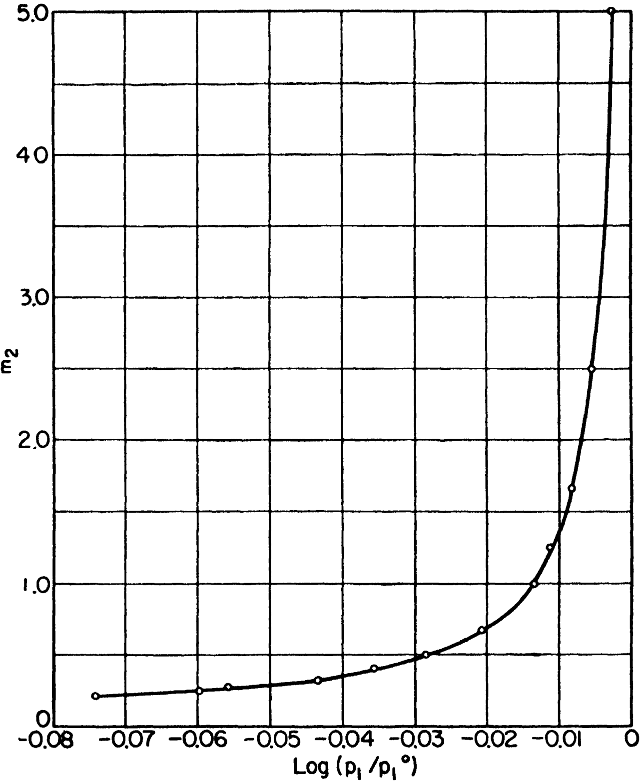

Fig. 7-16. Plot of $1/m_2$ vs. log (p_1/p_1°) for aqueous KCl solutions at 25°C. [*Vapor pressure data of J. N. Pearce and R. D. Snow, J. Phys. Chem.*, **31**, 231–245 (1927).]

$$\text{KCl(c)} = \text{KCl}(1m, \text{aq}) \qquad \Delta F_{298.16} = \phi_{\text{KCl}} - \bar{F}^\circ_{\text{KCl(c)}} = -1842 \text{ cal/mole}$$

The method cannot be applied at solute concentrations much below 0.2*m* because of experimental difficulty in measuring the vapor pressures with sufficient precision.[2]

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[1] Pearce and Snow, *loc. cit.*

[2] In Eq. (7-4-2), there is nothing to suggest what the value of $\bar{M}_1$ should be; we could use for water the formula $(H_2O)_2$, or for that matter, any arbitrary formula unrelated to the composition, so long as we used it consistently. Equation (7-3-3), however, is based ultimately on the ideal-gas law, and is correct only if one assigns to

We have so far introduced no new concepts. We measure ϕ_2 experimentally for electrolytes according to essentially the same theory as for nonelectrolytes. In so far as ϕ_2 is related to other observable properties of the system through purely thermodynamic equations [Eq. (7-4-4) involves also the nonthermodynamic ideal-gas approximation, which may be removed by the experimental methods described in Sec. 7-2, without reference to the properties of the liquid solution], electrolytes cannot be distinguished in any way from nonelectrolytes. It is when we compare such observed values of ϕ_2, empirically determined, with the ideal limiting law (7-3-79) (or its congeners in terms of other composition measures) that the difference becomes manifest. For instead of satisfying (7-3-39), which we may put conveniently in the form

$$\lim_{m_2 \to 0} \left[\frac{d(\phi_2/RT)}{d \ln m_2} \right]_{T,p} = 1 \quad \text{(nonelectrolytes)} \qquad (7\text{-}4\text{-}5)$$

the thermodynamic potential of a 1:1 electrolyte such as KCl in sufficiently dilute aqueous solution conforms to the rule

$$\lim_{m_2 \to 0} \left[\frac{d(\phi_2/RT)}{d \ln m_2} \right]_{T,p} = 2 \quad \text{(1:1 electrolyte)} \qquad (7\text{-}4\text{-}6)$$

The limiting law (7-4-6) is demonstrated most precisely by electrochemical methods of measuring ϕ_2 discussed in Chap. 9, which may be carried on at electrolyte concentrations well below 0.1m, or by the freezing-point method discussed in Sec. 7-5; but it is shown approximately by the vapor-pressure data in Table 7-5. Thus, Fig. 7-17 shows that when one plots $\phi_2 - RT \ln m_2$ against m_2 for aqueous KCl solutions [column (8), Table 7-5], the resulting curve fails to approach a finite limit as $m_2 \to 0$, but when one plots $\phi_2 - 2RT \ln m_2$ [column (9), Table 7-5], the results converge. Expressed in terms of the solvent's partial vapor pressure through Eq. (7-4-2) and (7-3-3), Eq. (7-4-5) (Henry's law for the solute) is equivalent to

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the solvent a molecular weight appropriate to its behavior in the gaseous state at the given temperature and pressure. Therefore in Eq. (7-4-4), one must use for $\bar{M}_1$ the solvent's molecular weight in the gaseous state as derived according to Avogadro's hypothesis, *e.g.*, 18.016 g/mole for water. No speculation or commitment is involved concerning the significance of $\bar{M}_1$ in the liquid state. It is impossible by purely thermodynamic reasoning to find out anything concerning $\bar{M}_1$ or $\bar{M}_2$, which are essentially extrathermodynamic concepts. $\bar{M}_2$ values for nonelectrolytes in liquid solution are established ultimately in accordance with the empirical generalization known as Raoult's law, the values so obtained being generally consistent with purely chemical evidence based on chemical analysis, and with other types of physical evidence. Arrhenius's great contribution, as we shall presently see, was the reconciliation of Raoult's law with the behavior of electrolytes.

$$\lim_{m_2 \to 0} \left(\frac{d \ln p_1}{dm_2} \right)_T = - \frac{\bar{M}_1}{1000 \text{ g/kg}}$$

or if Δp_1 represents the lowering of the solvent's vapor pressure associated with the solute concentration m_2:

$$\lim_{m_2 \to 0} \frac{\Delta p_1}{m_2} = \frac{\bar{M}_1}{1000 \text{ g/kg}} p_1^\circ \quad \text{(nonelectrolytes)} \qquad (7\text{-}4\text{-}7)$$

This of course represents Raoult's law for the solvent in the form (7-3-14*a*), with m_2 as composition measure in place of x_2 [see Eq. (7-3-78)]. Equation (7-4-6) then implies that the 1:1 electrolyte tends in the $m_2 \to 0$ limit to lower the solvent's vapor pressure *twice* as much as a nonelectrolyte at the same molal concentration.

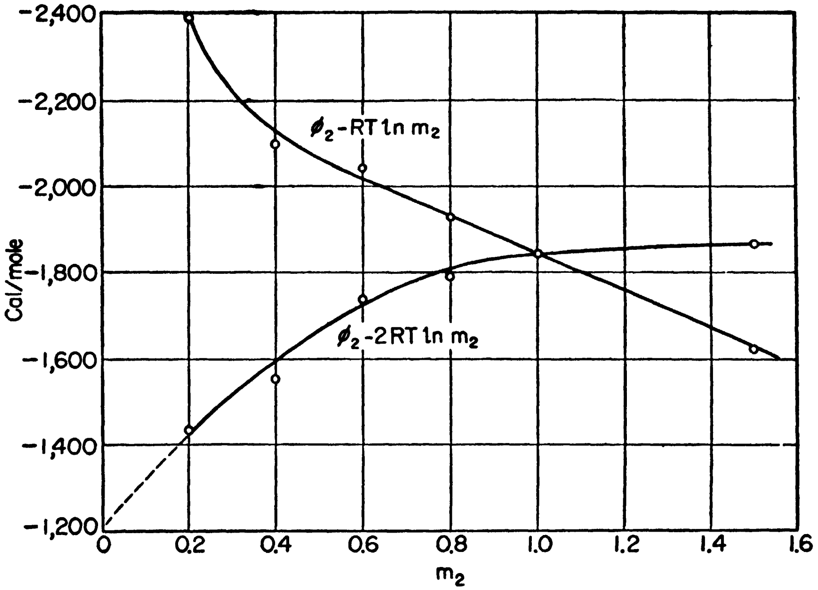

FIG. 7-17. Thermodynamic potential ϕ_2 of KCl in aqueous solutions at 25°C, relative to that of KCl(c).

Recognition of the fact that electrolytic conductivity of liquid solutions is invariably associated with "abnormal" dependence of other physical properties on the composition, viewed from the standpoint afforded by the empirical laws established for nonelectrolytes, was of course the brilliant achievement of Svante Arrhenius, who invented the concept of ions in solution to correlate both groups of effects.[1] The theory of ioniza-

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[1] S. Arrhenius, *Z. physik. Chem.*, **1**, 631–648 (1887); this paper has been translated in *Alembic Club Reprint* 19, published for the Alembic Club by Oliver & Boyd, Ltd., Edinburgh and London, 1929. The evidence and reasoning that led Arrhenius to propose the ionization theory is delightfully recounted in his Gibbs Address, *J. Am. Chem. Soc.*, **34**, 353–364 (1912); see also his Faraday Lecture, *J. Chem. Soc.*, **105**, 1414–1426 (1914).

tion is outside the scope of thermodynamics proper, in that it can be introduced only by *ad hoc* assumptions of a special nature which have nothing to do with the laws of thermodynamics. In this respect, however, its logical status is not greatly different from that of the ideal-gas law, or of Raoult's law, although it is less general in the sense that many complex situations arise calling for special treatment unpredictable by general theory (*e.g.*, hydrolysis of Bi^{+++} salts, complex ion formation between Hg^{++} and Cl^-, etc.). Modern evidence, particularly derived from the X-ray analysis of crystalline solids and the electronic theory of valence, leaves little doubt concerning its essential correctness and value. Therefore it has been worth while to adapt our methods of describing the relations between the thermodynamic properties and the composition, including modification of our concept of the ideal dilute solution, to take account of this important class of solutions.

The essential point of Arrhenius's theory is the *additivity of ionic properties;* in sufficiently dilute solution, the different kinds of ions present behave to a first order of approximation as independent solutes. Apparent exceptions to this rule may arise when complex ion formation or chemical reaction with the solvent takes place, but, in general, the concept of the independent behavior of the different kinds of ions is substantiated by a wealth of chemical and physical evidence. In place of the ideal dilute-solution law (7-3-79), we should expect therefore that the thermodynamic potential of a 1:1 electrolyte like KCl in aqueous solution would satisfy a limiting law of the form

$$\phi_{KCl} = \phi'_{K^+(aq)} + RT \ln m_{K^+} + \phi'_{Cl^-(aq)} + RT \ln m_{Cl^-} \quad (T, p \text{ const}; m_2 \rightarrow 0) \tag{7-4-8}$$

or, since in this case $m_{K^+} = m_{Cl^-} = m_2$, where m_2 represents the formal solute molality,

$$\phi_{KCl} = \phi'_{K^+(aq)} + \phi'_{Cl^-(aq)} + 2RT \ln m_2 \quad (T, p \text{ const}; m_2 \rightarrow 0) \tag{7-4-9}$$

Equation (7-4-9) follows in fact from integration of the empirical limiting law (7-4-6), though one should take note at the outset that the extent of the ideal dilute region over which Eq. (7-4-9) serves as a good approximation is much smaller, for reasons to be discussed presently, than would be typical for a nonelectrolyte (in Table 7-5, the deviation of $\phi_2 - 2RT \ln m_2$ from the ideal limiting value at $m_2 \rightarrow 0$ amounts to 20 per cent at $m_2 = 0.2$ mole/kg; it is much greater for electrolytes whose ions bear multiple charges). The separate terms of the integration constant, $\phi'_{K^+(aq)} + \phi'_{Cl^-(aq)}$, cannot be independently evaluated, but their sum, which we may represent also by the symbol $\phi'_{KCl(aq)}$, is established in a straightforward manner by extrapolation of the experimental ϕ_2 data in the form

$$\lim_{m_2 \to 0} (\phi_2 - 2RT \ln m_2) = \phi'_2 = \phi'_+ + \phi'_- \quad \text{(1:1 electrolyte)} \qquad (7\text{-}4\text{-}10)$$

The generalization of the ideal dilute-solution law (7-4-8) for a strong electrolyte having the type formula $A_{\zeta_+}B_{\zeta_-}$, giving rise to ζ_+ moles of positively charged A ions and ζ_- moles of negatively charged B ions per "mole" (gram-formula-weight) of solute, should evidently have the form

$$\phi_{A_{\zeta_+}B_{\zeta_-}} = \zeta_+[\phi'_A + RT \ln m_A] + \zeta_-[\phi'_B + RT \ln m_B] \quad (T, p \text{ const}; m_2 \to 0) \qquad (7\text{-}4\text{-}11)$$

or, since in this case $m_A = \zeta_+ m_2$ and $m_B = \zeta_- m_2$,

$$\phi_{A_{\zeta_+}B_{\zeta_-}} = \zeta_+\phi'_A + \zeta_-\phi'_B + \zeta RT \ln m_2 + RT \ln \zeta_+^{\zeta_+}\zeta_-^{\zeta_-} \quad (T, p \text{ const}; m_2 \to 0) \qquad (7\text{-}4\text{-}12)$$

where $\zeta = \zeta_+ + \zeta_-$ represents the total number of ions corresponding to the chemical formula of the compound. For example, in the case of $\text{Ca(NO}_3)_2$ in water,

$$\phi_{\text{Ca(NO}_3)_2} = \phi'_{\text{Ca}^{++}(\text{aq})} + 2\phi'_{\text{NO}_3^-(\text{aq})} + 3RT \ln m_2 + RT \ln 4$$

Thus, we assume that each ion represented in the formula contributes ideally a term of the form $RT \ln m_2$ to the composition-dependent part of the solute's thermodynamic potential at the given temperature and pressure. The last term in Eq. (7-4-12) is a constant for the particular electrolyte, depending on its charge type [it is zero for a 1:1 electrolyte like KCl, and a 2:2 electrolyte like CuSO_4, but it is equal to $RT \ln 4$ for a 2:1 electrolyte like $\text{Ca(NO}_3)_2$]; it has purely formal significance, bringing (7-4-12) in accord with (7-4-11), for experimentally, one would be unable to distinguish it from the rest of the constant part of ϕ_2 in (7-4-12), here defined in general by

$$\zeta_+\phi'_A + \zeta_-\phi'_B = \lim_{m_2 \to 0} (\phi_2 - \zeta RT \ln m_2 - RT \ln \zeta_+^{\zeta_+}\zeta_-^{\zeta_-}) \qquad (7\text{-}4\text{-}13)$$

Whether or not an equation having the form of (7-4-13) is actually satisfied by a given electrolyte (in the sense that the expression on the right actually approaches a finite limit as $m_2 \to 0$) remains to be tested by experiment in individual cases. It is apparently satisfied by most of the common strong electrolytes in aqueous solution. In such cases, the concept of Eqs. (7-4-11) and (7-4-12) as the ideal limiting forms in sufficiently dilute solution is well worth while. As we have already noted, however, deviation from ideal behavior in this sense is generally significant at solute concentrations much lower than in the case of nonelectrolytes, so that one may seldom use Eqs. (7-4-11) or (7-4-12) at finite solute concentrations except for the roughest kind of approximation. Furthermore, complexities arising from specific chemical reactions of the ions in dilute solution are much more common than similar complexities in the case of nonelectrolytes. For example, many ions (Bi^{+++}, Fe^{+++}, $S^{=}$, $CO_3^{=}$, etc.) show hydrolytic reactions with water in dilute aqueous solution that may interfere with the applicability of (7-4-13) in the ideal dilute-solution limit; we also have such difficulties to negotiate as partial secondary ionization in the case of aqueous H_2SO_4, complex ion formation in the case of $HgCl_2$, etc. Some of these difficulties may be handled by extension of the theory to include equilibrium in chemical reactions, as we shall see in Chap. 8; in many cases, however, it is by no means easy to discover a rigorous and unequivocal method of interpreting the experimental data. These difficulties, it should be noted, are entirely extrathermodynamic in character, having to do with the success or failure of (7-4-11) or (7-4-12) as empirical limiting laws relating ϕ_2 to the composition in sufficiently dilute solution; there is no difficulty whatever, beyond the purely experimental, in *measuring* ϕ_2 by means of such relations as (7-4-3) or (7-4-4) and their thermodynamic implications, without regard to the form of the dependence of ϕ_2 on the composition.

While Eq. (7-4-13) constitutes a set of directions for measuring the empirical integration constant $\zeta_+\phi'_A + \zeta_-\phi'_B$ appearing in Eq. (7-4-12) [compare Eq. (7-3-84) for nonelectrolytes], where that equation is the correct limiting form, there is no method for determining independently the contributions of the two ions, that is, ϕ'_A and ϕ'_B. To be able to do so would imply that one knew of some operation whereby a solution containing only the one type of ion could be prepared; in view of the empirical fact that solutions of electrolytes are always electrically neutral, no such operation is known, according to presently available experimental techniques. Nevertheless, the additivity hypothesis for ions in sufficiently dilute solution implies that ϕ' values for individual ions in a particular solvent have real physical significance, in the sense that when recombined in the form $\zeta_+\phi'_A + \zeta_-\phi'_B$, they reproduce exactly the ϕ'_2 value for any strong electrolyte $A_{\zeta_+}B_{\zeta_-}$ in that solvent, regardless of the particular anion with which a given cation is combined. The crux of Arrhenius's theory, in so far as it bears on the thermodynamic properties of strong electrolytes in dilute solution, is the experimental fact that in a particular solvent such as water, the ϕ'_2 values of KCl and NaCl [as determined by the application of Eq. (7-4-10) to experimentally determined ϕ_2 values] differ by the same amount as the ϕ'_2 values of KNO_3 and $NaNO_3$, and by the same amount as the ϕ'_2 values of KBr and NaBr, etc.; likewise, the ϕ'_2 values of

KCl and KNO_3 differ by the same amount as the ϕ_2' values of NaCl and $NaNO_3$, etc. The former difference measures experimentally $\phi'_{K^+(aq)} - \phi'_{Na^+(aq)}$, and the latter difference measures $\phi'_{Cl^-(aq)} - \phi'_{NO_3^-(aq)}$. In other words, a self-consistent set of constants for the various ions in the particular solvent may be obtained by difference from the experimental ϕ_2' values for strong electrolytes after we have once assigned an arbitrary value to any single species of ion. By general agreement, the standard ion chosen for this purpose has been H^+, to which has been assigned the conventional value

$$\phi'_{H^+(aq)} \equiv 0 \tag{7-4-14}$$

This applies at standard conditions of 25°C and 1 atm, but it is generally convenient to retain the same convention for other temperatures and pressures. A similar convention would be required in each different solvent, but comparatively few data are available for nonaqueous solvents. Thus, one determines $\phi'_{Cl^-(aq)}$ by equating it to $\phi'_{HCl(aq)}$, as found by the application of Eq. (7-4-10) to experimental measurements of ϕ_2 in aqueous HCl solutions; in a similar manner, the values of ϕ' for the anions of other strong acids in aqueous solution may be directly determined. Having determined the value of $\phi'_{Cl^-(aq)}$ in this manner relatively to the convention represented by (7-4-14), one may then determine $\phi'_{K^+(aq)}$ by difference, from the experimentally established value of $\phi'_{KCl(aq)}$ given by the application of (7-4-10) to ϕ_2 data for aqueous KCl solutions, etc. Since $\phi'_{K^+(aq)}$ may be determined independently from experimental ϕ_2 data for HNO_3 and KNO_3 aqueous solutions, or from experimental ϕ_2 data for HBr and KBr aqueous solutions, etc., such independent sources of information serve as cross checks on the self-consistency of the ionic ϕ' values. The ϕ' values established in this way are known as *standard free energies of formation of the ions in solution* in the particular solvent; representative values are included in Appendix 2.[1] The electrochemical methods discussed in Chap. 9 constitute a particularly valuable source of ϕ_2 data for the establishment of ionic ϕ' constants.

In order to represent the thermodynamic potential of an electrolyte in solution as a function of the composition outside the ideal dilute range, it is appropriate for us to extend the methods outlined in Sec. 7-3*g*. Thus, taking (7-4-11) as the ideal limiting form, we may in principle introduce ionic activities and ionic activity coefficients by means of the defining

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[1] The most comprehensive collection of such data for ions in aqueous solution is by W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, 1938. More recent data will be included in the critical compilation by the National Bureau of Standards under the editorship of F. D. Rossini, "Selected Values of Chemical Thermodynamic Properties."

equations

$$\begin{aligned} \phi_{A_{\zeta_+}B_{\zeta_-}} &\equiv \zeta_+(\phi'_A + RT \ln a_+) + \zeta_-(\phi'_B + RT \ln a_-) && \text{(7-4-15)} \\ &\equiv \zeta_+(\phi'_A + RT \ln m_A + RT \ln \gamma_+) \\ &\qquad + \zeta_-(\phi'_B + RT \ln m_B + RT \ln \gamma_-) && \text{(7-4-16)} \end{aligned}$$

where

$$\gamma_+ = \frac{a_+}{m_+}; \qquad \gamma_- = \frac{a_-}{m_-} \tag{7-4-17}$$

The definitions (7-4-15) and (7-4-16), which correspond formally to the assignment of thermodynamic potentials ϕ_A and ϕ_B

$$\left.\begin{aligned} \phi_A &= \phi'_A + RT \ln a_A = \phi'_A + RT \ln m_A + RT \ln \gamma_A \\ \phi_B &= \phi'_B + RT \ln a_B = \phi'_B + RT \ln m_B + RT \ln \gamma_B \end{aligned}\right\} \tag{7-4-18}$$

to the individual ions A and B, are, however, insufficient to permit one actually to measure a_+ and a_-, or γ_+ and γ_-, independently of each other. This is of course a matter of principle, inasmuch as there is at present no known operation whereby a liquid solution of an electrolyte may be prepared containing an excess of cationic over anionic charge, or of anionic over cationic charge; the possibility of preparing such a solution would be a necessary condition for the experimental study of the contributions of the individual ionic species to the thermodynamic properties of the solution. We may, however, rewrite (7-4-15) and (7-4-16) in the more compact forms:

$$\begin{aligned} \phi_{A_{\zeta_+}B_{\zeta_-}} &= \zeta_+\phi'_A + \zeta_-\phi'_B + RT \ln a_+^{\zeta_+}a_-^{\zeta_-} && \text{(7-4-19)} \\ &= \zeta_+\phi'_A + \zeta_-\phi'_B + RT \ln m_A^{\zeta_+}m_B^{\zeta_-} + RT \ln \gamma_+^{\zeta_+}\gamma_-^{\zeta_-} && \text{(7-4-20)} \end{aligned}$$

If no other electrolyte is present in the solution besides the one electrolyte $A_{\zeta_+}B_{\zeta_-}$, then $m_A = \zeta_+m_2$ and $m_B = \zeta_-m_2$, where m_2 represents the formal molality; thus

$$\phi_{A_{\zeta_+}B_{\zeta_-}} = \zeta_+\phi'_A + \zeta_-\phi'_B + \zeta\, RT \ln m_2 + RT \ln \gamma_+^{\zeta_+}\gamma_-^{\zeta_-} + RT \ln \zeta_+^{\zeta_+}\zeta_-^{\zeta_-} \tag{7-4-21}$$

Equation (7-4-21) represents the generalization of (7-4-12). Now, whereas the individual ionic activity coefficients γ_+ and γ_- have only a formal existence and cannot be measured independently of each other, the product $\gamma_+^{\zeta_+}\gamma_-^{\zeta_-}$ is evidently directly measurable, since all the other terms entering (7-4-21) are measurable. The quantity

$$\gamma_\pm = (\gamma_+^{\zeta_+}\gamma_-^{\zeta_-})^{1/\zeta} \tag{7-4-22}$$

is known as the *mean ionic activity coefficient* of the electrolyte. It represents the geometric mean of the hypothetical individual ionic activity coefficients, or in other words, what their common value would be if they were equal. In terms of Eq. (7-4-21),

$$\phi_{A_{\zeta_+}B_{\zeta_-}} = \zeta_+\phi'_A + \zeta_-\phi'_B + \zeta RT \ln m_2 + \zeta \; RT \ln \gamma_\pm + RT \ln \zeta_+^{\zeta_+}\zeta_-^{\zeta_-} \tag{7-4-23}$$

an equation we may take as defining $\gamma_\pm$ directly in experimental terms; for since the constant part of $\phi_{A_{\zeta_+}B_{\zeta_-}}$ or ϕ_2 is determined by Eq. (7-4-13) (assuming that our analysis of the electrolyte's behavior is justified empirically by the convergence of the expression on the right of that equation, which represents Henry's law for strong electrolytes), we may express (7-4-23) in the equivalent form

$$\zeta RT \ln \gamma_\pm = (\phi_2 - \zeta RT \ln m_2) - \lim_{m_2 \to 0} (\phi_2 - \zeta RT \ln m_2) \tag{7-4-24}$$

from which we may compute $\gamma_\pm$ readily from empirical measurements of ϕ_2 as a function of m_2. It has become customary to tabulate the thermodynamic properties of real solutions of electrolytes in terms of ionic ϕ' values and the associated $\gamma_\pm$ values so defined; the ϕ' values are of course constants for the particular ions in the given solvent, at the given temperature and pressure; by representing $\gamma_\pm$ empirically as a function of m_2 for the particular electrolyte, we have then completed the description of its thermodynamic behavior. Comparing Eq. (7-4-23) with (7-4-12), one sees that ϕ_2 is related to $m_2\gamma_\pm$ at finite solute concentrations according to the same form by which it is related to m_2 in the ideal dilute-solution limit; in other words, $m_2\gamma_\pm$ is numerically equal to the molality at which the solute would have the same thermodynamic potential if it continued to satisfy the ideal dilute-solution law as a completely ionized strong electrolyte at the finite concentration m_2. The deviation of $\gamma_\pm$ from 1 measures the extent to which ϕ_2 deviates from the ideal value in this sense.

This procedure for representing ϕ_2 as a function of m_2 in the case of an electrolytic solute does not affect our conventional method of representing ϕ_1 for the solvent in terms of the activity function a_1, which we continue to define exactly as in Eq. (7-3-87),

$$\phi_1 \equiv (F_{T,p})_1 + RT \ln a_1 \tag{7-4-25}$$

Thus, a_1 may be obtained directly from the solvent's partial vapor pressure through Eqs. (7-3-45) or (7-3-46), just as in the case of a nonelectrolyte, though of course a_1 now varies with m_2 in a different way in the ideal dilute-solution limit. We may put the Gibbs-Duhem relation (7-4-2) in the form

$$\frac{1000 \text{ g/kg}}{\bar{M}_1} d \ln a_1 + \zeta \, dm_2 + \zeta m_2 \, d \ln \gamma_\pm = 0 \tag{7-4-26}$$

or

$$d \ln \gamma_{\pm} = -\frac{1000 \text{ g/kg}}{\bar{M}_1} \frac{1}{\zeta m_2} d \ln a_1 - \frac{dm_2}{m_2}$$

This equation may be integrated in a manner analogous to that leading to Eq. (7-3-90):

$$\ln \gamma_{\pm} = -\left(\frac{1000 \text{ g/kg}}{\bar{M}_1} \frac{\ln a_1}{\zeta m_2} + 1\right) - \int_0^{m_2} \frac{\left(\frac{1000 \text{ g/kg}}{\bar{M}_1} \frac{\ln a_1}{\zeta m_2} + 1\right)}{m_2} dm_2 \qquad (7\text{-}4\text{-}27)$$

Equation (7-4-27) thus enables us to compute $\gamma_{\pm}$ from experimental measurements of a_1 for the solvent, such as one may obtain from vapor-pressure data, and other methods to be considered in Sec. 7-5. It is of course precisely equivalent in content to Eq. (7-4-3), except that in (7-4-27), one is operating from the opposite end of the composition scale. If the range of the experimental data permit, one may evaluate the integral in Eq. (7-4-27) over the entire composition range up to m_2^* corresponding to the saturated solution; in this way, one may measure $\gamma_{\pm}^*$ for the saturated solution, where $\phi_2 = (\bar{F}_{T,p})_2$ (within the limitations mentioned in the footnote on page 393), and thus relate the constant $\zeta_+\phi'_A + \zeta_-\phi'_B$ appearing in Eq. (7-4-23) to the standard molal free energy of the pure solute, entirely from direct experimental measurements of a_1.

Figure 7-18 shows experimental values of $\gamma_{\pm}$ plotted against m_2 for typical strong electrolytes in aqueous solution. Some of these results are based on vapor-pressure measurements, essentially according to the method just described; others are based on the related freezing-point method, to be described in Sec. 7-5, while still others come from emf measurements (Chap. 9). One sees that there is marked but systematic deviation from ideal behavior (as strong electrolytes with completely independent ions), even at concentrations well below $0.1m$. In general, the deviation at low solute concentrations is negative, [that is, ϕ_2 increases with m_2 less rapidly than one would expect from the ideal Henry's law equation (7-4-12)] and tends to be more extreme the greater the numbers of charges on the ions concerned; thus, a 2:2 electrolyte like $CuSO_4$ deviates more markedly from ideal behavior at concentrations below $0.1m$ than a 2:1 electrolyte like $CaCl_2$, and this in turn deviates to a considerably greater extent than a 1:1 electrolyte like KCl. These facts are satisfactorily explained by the interionic attraction theory of Debye and Hückel.

The idea that one may account for the deviations of electrolytes from ideal behavior in dilute solution simply in terms of the electrostatic

Coulomb forces between the ions was first proposed by S. R. Milner,[1] but he was unable to overcome the mathematical difficulties in the way of obtaining a quantitative solution to the problem. These difficulties were overcome, within certain limitations, by P. Debye and E. Hückel in 1923.[2]

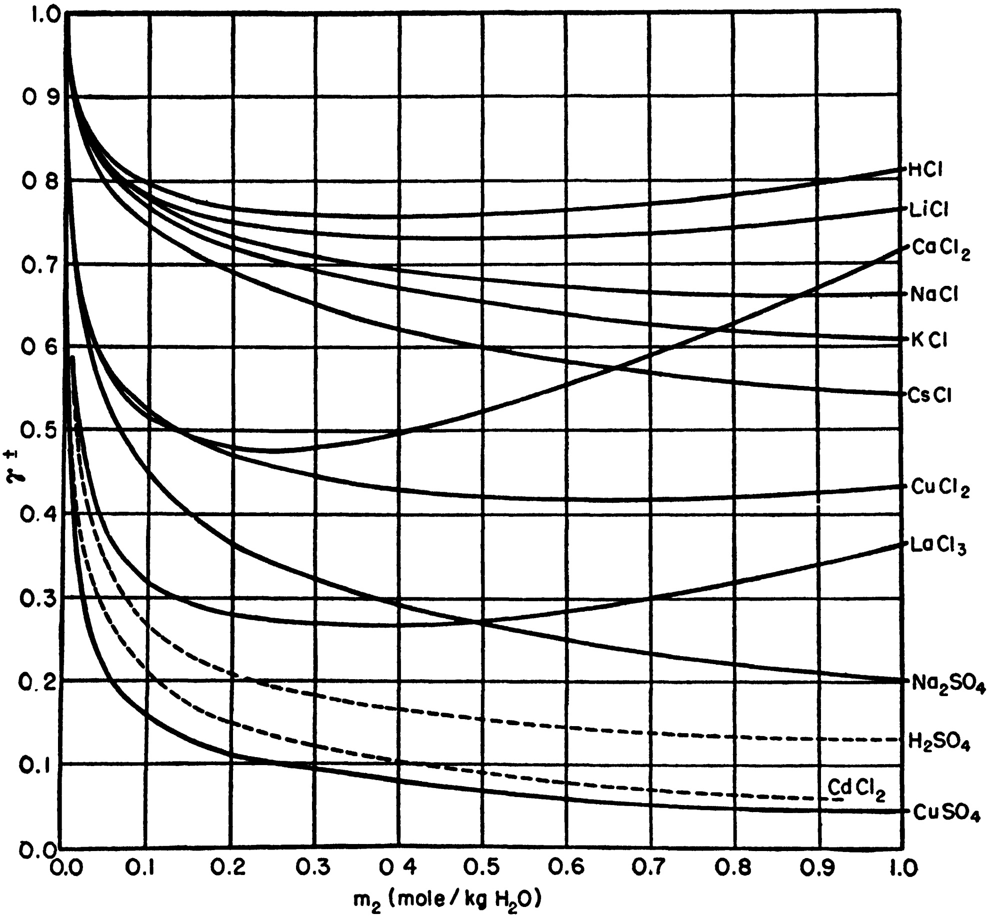

FIG. 7-18. Mean ionic activity coefficients of strong electrolytes in aqueous solutions at 25°C. (*From data compiled by W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York,* 1938.)

Since their theory has been discussed in detail elsewhere and is essentially extrathermodynamic in nature, we shall not reproduce its formal derivation here. The argument runs as follows: ions in solution are supposed to be in random thermal motion, but because of their charges, the neigh-

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[1] S. R. Milner, *Phil. Mag.*, (6) **23**, 551–578 (1912); **25**, 742–751 (1913).

[2] P. Debye and E. Hückel, *Physik. Z.*, **24**, 185–206 (1923). For detailed discussion, see R. H. Fowler, "Statistical Mechanics," 2d ed., Chaps. VIII and XIII, Cambridge University Press, New York, 1936, and MacInnes, *op. cit.*, Chap. VII.

borhood immediately surrounding an ion of a particular species will be richer on the average in ions of opposite sign than in ions of the same sign, even though throughout the solution as a whole the total number of positive ionic charge units and the total number of negative ionic charge units are equal.[1] As a consequence, each ion is subject to an average net electrostatic attraction by all the other ions, which depends on the product of their charges and the mean distance between ions; the latter quantity, in turn, depends on the concentration of the electrolyte. The ion's potential energy in the solution is therefore lower than would be the case if it bore no charge; consequently, the thermodynamic potential of the ion, which measures the theoretically least quantity of nonthermal energy per mole required to transfer it from the solution to some conventional standard state at the same temperature and pressure, is correspondingly more negative than it would be for otherwise identical uncharged solute particles at the same concentration. In concentrated solutions, this comparatively simple picture is no doubt inadequate, because even nonelectrolytes then show deviation from dilute-solution behavior. One would have to take into account the sizes, shapes, and polarizabilities of the ions, as well as their specific interactions with each other and with the solvent; no comprehensive theory for concentrated solutions as yet exists. But in sufficiently dilute solutions, we may ascribe the entire deviation for strong electrolytes to the effect of electrostatic interionic attraction associated with the ionic charges. Debye and Hückel succeeded in overcoming the formidable mathematical difficulties arising in the solution of this essentially statistical molecular problem by introducing certain approximations that presumably become valid at sufficiently low ionic concentrations (the exact range of validity being dependent on the particular solvent and the size of the ions concerned). Their limiting law for a strong electrolyte consisting of two ions bearing, respectively, z_+ and z_- units of charge (multiples of the electron charge e), in a solution whose *ionic strength* is represented by μ, assumes the form

$$-\log \gamma''_{\pm} = z_+z_-A\sqrt{\mu} \qquad (\mu \to 0) \qquad (7\text{-}4\text{-}28)$$

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[1] A similar geometrical situation exists in the ionic crystalline state, where in the case of NaCl, for example, each Na^+ ion has six equivalent Cl^- ions as nearest neighbors, closer than the nearest Na^+ ions, and each Cl^- ion likewise has six equivalent Na^+ ions as nearest neighbors; a sphere of several ionic diameters radius drawn about any ion as center would include more ions of the opposite kind than ions of the same kind, the disproportion decreasing, of course, as the radius of the sphere is increased. The regular permanent order that exists in the crystalline state would, however, be absent in liquid solution, but the tendency for such order to be set up, in opposition to the disruptive random thermal motion, is treated statistically as the foundation on which the interionic attraction theory is based.

where A is a universal constant for the particular solvent at given temperature, having the theoretical value

$$A = \frac{1}{2.3026} \frac{e^3 N_0^2}{(DRT)^{3/2}} \left(\frac{2\pi}{1000 \text{ cm}^3/\text{liter}} \right)^{1/2} \tag{7-4-29}$$

D representing the dielectric constant of the medium (*i.e.*, of the pure solvent, in sufficiently dilute solutions).[1] The ionic strength is a concentration measure defined by

$$\mu = \tfrac{1}{2} \sum_i z_i^2 C_i \tag{7-4-30}$$

the sum extending over all ionic species present; it is thus a peculiar concentration measure in which each ionic species is weighted in proportion to the square of its charge. This weighting takes theoretical account of the fact that a multiply charged ion at given interionic distance (the mean distances being determined inversely by the concentration) contributes more to the net interionic attraction than a singly charged ion.[2] Equation (7-4-28) implies no restriction on the number of electrolytes that may be present (contributing to μ) besides the one to which the equation is applied, but in the case of a single electrolytic solute, the value of μ is related to the formal molar concentration C_2 as follows:

Charge type	Examples	$\frac{\mu}{C_2}$ in solutions containing only the one strong electrolyte
1:1	KCl	1
2:1 or 1:2	$CaCl_2$, Na_2SO_4	3
2:2	$CuSO_4$	4
3:1 or 1:3	$La(NO_3)_3$, $K_3Fe(CN)_6$	6
3:2 or 2:3	$In_2(SO_4)_3$	15
etc.		

The value of the constant A for water at various temperatures is as follows:[3]

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[1] See footnote on page 408.

[2] It is interesting to note that Lewis and Randall had called attention to the empirical dependence of $\gamma_\pm$ on μ, particularly in mixtures of electrolytes in dilute solution, before the Debye-Hückel theory was announced; Lewis and Randall, *op. cit.*, pp. 373–374.

[3] These values are based on the dielectric constant measurements of J. Wyman, *Phys. Rev.*, **35**, 623–634 (1930), which may be represented by the empirical equation

$$D = 78.54[1 - 0.00460(t - 25) + 0.0000088(t - 25)^2]$$

The values used for the natural constants are as follows: $e = 4.8024 \times 10^{-10}$ esu; $N_0 = 6.0228 \times 10^{23}$ mole^{-1}; $R = 8.3144 \times 10^7$ ergs/mole deg; $T = t + 273.16$ deg.

Temperature, °C	A for H_2O, $(\text{mole/liter})^{-1/2}$
0	0.4895
25	0.5091
100	0.6149

Thus, the Debye-Hückel limiting law (7-4-28) in water at 25°C has the form

$$-\log \gamma''_{\pm} = 0.5091\, z_+z_- \sqrt{\mu} \quad (\mu \rightarrow 0 \text{ in } H_2O \text{ at } 25°\text{C}) \qquad (7\text{-}4\text{-}31)$$

For solutions of single electrolytes of various charge types, this limiting equation in extremely dilute aqueous solutions at 25°C assumes the forms

$$\left.\begin{aligned} -\log \gamma''_{\pm} &= 0.5091 \sqrt{C_2} \text{ (1:1 electrolyte)} \\ &= 1.7636 \sqrt{C_2} \text{ (2:1 or 1:2 electrolyte)} \\ &= 4.073 \sqrt{C_2} \text{ (2:2 electrolyte)} \\ &= 3.741 \sqrt{C_2} \text{ (3:1 or 1:3 electrolyte)} \\ &\cdots\cdots\cdots\cdots\cdots\cdots \end{aligned}\right\} \begin{aligned} &(C_2 \rightarrow 0 \\ &\text{ in water} \\ &\text{ at } 25°\text{C}) \end{aligned} \qquad (7\text{-}4\text{-}31a)$$

It is easy to see from these theoretical equations why strong electrolytes, particularly of the higher charge types, show marked deviation from ideal behavior [which would be represented by $\gamma''_{\pm} = 1$ in Eq. (7-4-23)], even at concentrations as low as $0.01M$. At that, water happens to have an exceptionally high dielectric constant; in a nonaqueous medium having a lower dielectric constant, the value of A given by Eq. (7-4-29) would be larger, reflecting the stronger influence of interionic attraction at given mean interionic separation, and significant deviation from the hypothetical ideal dilute-solution behavior as completely independent ions would show up at still lower ionic concentrations. The failure of Henry's law at low solute concentrations had long been a stumbling block in the development of the theory of strong electrolytes, from the time of Arrhenius's original contribution; the outstanding merit of the Debye-Hückel theory has been the reconciliation of this failure of Henry's law with assumed properties of the ions no more complicated than their charges and Coulomb's inverse-square law of force.

The numerical coefficients appearing in Eq. (7-4-31a) represent according to the Debye-Hückel theory the terminal slopes of the $-\log \gamma''_{\pm}$ vs. $\sqrt{C_2}$ relationships for strong electrolytes in aqueous solution at 25°C. In Fig. 7-19, $\log \gamma_{\pm}$ has been plotted against $\sqrt{m_2}$ for electrolytes of various charge types (compare Fig. 7-18);[1] the dashed lines correspond to the

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[1] The Debye-Hückel formula (7-4-28) gives technically the value of the molar concentration activity coefficient, which to be consistent with the terminology for nonelectrolytes introduced in Sec. 7-3g we have represented by the symbol $\gamma''_{\pm}$; the

asymptotic straight lines predicted by Eqs. (7-4-31*a*). One sees that the agreement of theory with experiment is indeed excellent, though the practical range of usefulness of Eqs. (7-4-31*a*), or, more generally, the parent equation (7-4-28), is confined to exceedingly dilute solutions. These equations have proved valuable, however, in the extrapolation of experimental ϕ_2 or $\gamma_\pm$ data at low solute concentrations, below the region in which precise measurements are feasible. If, for example, one can measure ϕ_2 down to some concentration m_2 at which Eq. (7-4-28) is valid, then substitution in Eq. (7-4-24) permits one to evaluate $\lim_{m_2 \to 0} (\phi_2 - \zeta RT \ln m_2)$

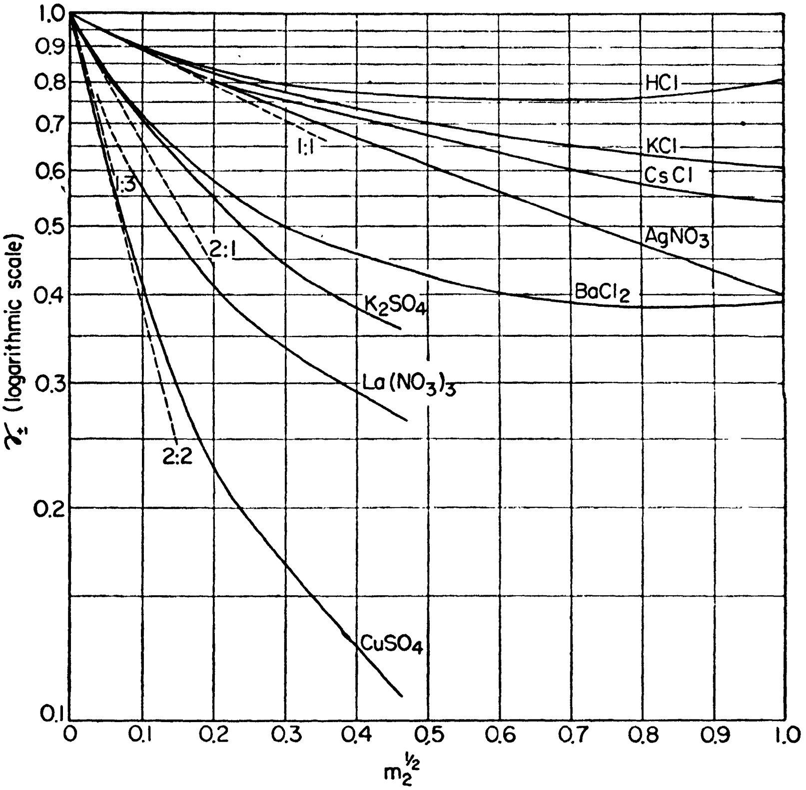

FIG. 7-19. Plot of log $\gamma_\pm$ vs. $m_2^{1/2}$ for electrolytes in aqueous solutions at 25°C; dashed lines drawn with Debye-Hückel limiting slopes, Eqs. (7-4-31*a*).

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mean ionic activity coefficient $\gamma_\pm$ defined by Eq. (7-4-23) is a *molal* activity coefficient, which by analogy with Eq. (7-3-82) we might have represented by the symbol $\gamma'_\pm$. We have omitted the distinguishing ′ sign to simplify the notation, on the ground that no other kind of activity coefficient for electrolytes is in common use, at least for aqueous solutions. In dilute solutions, of course, to which the Debye-Hückel limiting law (7-4-28) may be applied, the distinction between $\gamma''_\pm$ and $\gamma'_\pm$ (that is, $\gamma_\pm$) is of no practical consequence [compare Eq. (7-3-105)], and in dilute aqueous solutions particularly, $C_2 \sim m_2$; for nonaqueous solutions, one would have to replace C_2 by $\rho_1 m_2$ in the dilute range [compare Eq. (7-3-98)].

precisely, without the uncertainty inherent in graphic methods of extrapolation, and thus to determine the important constant for the electrolyte in the given solvent, $\phi'_2 = \zeta_+\phi'_A + \zeta_-\phi'_B$. Or, if one wishes to use the graphic method, the form of Eq. (7-4-28) suggests that $(\phi_2 - \zeta RT \ln m_2)$ be plotted against $\sqrt{\mu}$, rather than any other function of the concentration, since the graph then tends to approach linearity as $\mu \rightarrow 0$.

Equation (7-4-28) is itself the limiting form of the more general equation derived by Debye and Hückel

$$-\log \gamma''_\pm = z_+z_- A \sqrt{\mu} \frac{1}{1 + Bd_i \sqrt{\mu}} \qquad (\mu \rightarrow 0) \qquad (7\text{-}4\text{-}32)$$

where according to the theory, d_i represents the mean ionic "diameter," or distance of closest approach between the particular pair of ions in the solution, and B is another universal constant for the solvent at the given temperature, having the form

$$B = \left(\frac{8\pi e^2 N_0^2}{DRT} \frac{1}{1000 \text{ cm}^3/\text{liter}}\right)^{1/2} \qquad (7\text{-}4\text{-}33)$$

The value of B for water at various temperatures is as follows:

Temperature, °C	B for H_2O, cm^{-1} $(\text{mole/liter})^{-1/2}$
0	0.3244×10^8
25	0.3286×10^8
100	0.3500×10^8

There are at present no satisfactory methods of measuring d_i independently in solution; the ions are no doubt generally solvated to some extent, and their apparent diameters in solution may bear little relation to their diameters in crystalline compounds, as deduced from X-ray crystallography. Therefore d_i is treated practically as an empirical constant for the particular electrolyte in the given solvent, whose value has to be determined from at least one measurement of $\gamma''_\pm$ at some concentration in the dilute range [but not so dilute that Eq. (7-4-32) reduces practically to Eq. (7-4-28)]; the theory is supported obliquely by the fact that empirical d_i values so obtained, at least in aqueous solutions, are of the proper order of magnitude to represent mean ionic diameters (*e.g.*, 5×10^{-8} cm). Equation (7-4-32) may be rearranged for sufficiently small values of μ in a convenient form proposed by D. I. Hitchcock;[1] the factor $1/(1 + Bd_i \sqrt{\mu})$ may be expanded as the series

$$\frac{1}{1 + Bd_i \sqrt{\mu}} = 1 - Bd_i \sqrt{\mu} + B^2 d_i^2 \mu - \cdots$$

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[1] D. I. Hitchcock, *J. Am. Chem. Soc.*, **50**, 2076–2079 (1928).

in which at sufficiently low values of μ, only the first two terms need be retained (the coefficient Bd_i being of order 1); thus, Eq. (7-4-32) assumes the approximate form

$$-\log \gamma_{\pm}'' = z_+z_-A\sqrt{\mu} - B'\mu \quad (\mu \to 0) \qquad (7\text{-}4\text{-}34)$$

which may be regarded as the second-order approximation to the first-order Debye-Hückel approximation (7-4-28). The constant B' is theoretically equal to $z_+z_-ABd_i$, but since d_i has to be determined empirically anyhow, we may regard B' itself in Eq. (7-4-34) as an empirical constant for the particular electrolyte in the particular solvent, A being a property only of the solvent. By means of the single empirical constant B', Eq. (7-4-34) may be fitted to the data for aqueous solutions of most strong 1:1 or 2:1 electrolytes at ionic strengths up to $\mu = 0.1$; at higher concentrations, specific interionic effects neglected in the theory become important, and also the simplifying approximations introduced in the derivation of Eq. (7-4-32) become invalid. Qualitatively, it is noteworthy that while the first term on the right of Eq. (7-4-34), which represents essentially the effect of interionic attraction for point charges (*i.e.*, for ions at mean interionic distances large compared with their diameters), results in a tendency for $\gamma_{\pm}$ to decrease with increasing ionic concentration, the second term, which represents essentially the effect of the finite sizes of the ions, results in an over-all tendency for $\gamma_{\pm}$ to decrease less and less rapidly as the concentration is increased; thus, the graphs of $\log \gamma_{\pm}$ vs. $\sqrt{m_2}$ (and of $\gamma_{\pm}$ vs. m_2) all show positive curvatures over the dilute-solution range.

A serious theoretical limitation to the method originally presented by Debye and Hückel is that in order to obtain a solution in simple mathematical form, they were compelled to make assumptions equivalent to

$$d_i > \frac{z_+z_-e^2N_0}{2DRT} \qquad (7\text{-}4\text{-}35)$$

which for water as solvent at 25°C reduces to

$$d_i > z_+z_-\,4.372 \times 10^{-8}\,\text{cm}$$

This implies that Eqs. (7-4-32) and (7-4-28) are restricted to the larger ions and to the lower charge types. An even more drastic restriction arising from the same source is that in a medium whose dielectric constant is much lower than that of water (which happens to have an exceptionally high dielectric constant, 78.54 at 25°C), condition (7-4-35) may fail to be satisfied even by the largest ions. The elimination of this assumption has been successfully undertaken by H. Müller, and by T. H. Gronwall and his associates, but the resulting equations for $\gamma_{\pm}$ are unfortunately complex and unwieldy.[1] There are furthermore other physical difficulties standing in the way of attempts to refine the theory from the same general line of approach. Thus, no account is taken of statistical fluctuations in the charge distribution about a given ion; furthermore, the shapes, probable orientations, and polarizabilities of the more complex ions no doubt influence their behavior at the higher concentrations; there is also the question of the significance of the dielectric constant in a medium containing an appreciable concentration of mobile ions. Some of these difficulties, and the attempts to overcome them, have been reviewed by Fowler.[2] Meanwhile, the Debye-Hückel theory has given us not only the simple quantitative limiting laws (7-4-32) and (7-4-28), which have been verified experimentally for the simpler strong electrolytes in aqueous solution, but also general insight into the nature of the regularities that attend the deviations of electrolytic solutes from ideal behavior in dilute solution. It has met with similar success in describing the effect of concentration on the conductivities of electrolytes in dilute solution, but this subject is outside the scope of thermodynamics. An important field of application of Eqs. (7-4-32) or (7-4-28) consists of the thermodynamic behavior of the ionic constituents in solutions of weak electrolytes, as we shall note in Chap. 8.

We may define a mean ionic activity coefficient $\gamma_\pm$ by means of Eqs. (7-4-23) or (7-4-24), and proceed accordingly to measure it, on the basis of a quite incorrect concept of how the electrolyte is really ionized at concentrations outside the extremely dilute range. The value of ϕ_2, which is essentially what one actually measures, is of course related directly to physical properties of the solution by means of thermodynamic equations quite independent of assumptions concerning the ultimate structure of the solute [compare, for example, Eq. (7-4-4), which is based on the supposition that the equilibrium vapor phase satisfies empirically the ideal-gas law, but involves no assumptions concerning the thermodynamic properties of the liquid solution itself]. But when we attempt to fit ϕ_2 to the *composition* by means of an equation such as (7-4-23), which represents a generalization of the hypothetical empirical limiting law (7-4-12), then it is necessary for us to assume a particular mode of ionization, *i.e.*, essentially to select the value of ζ. For the simpler strong electrolytes, such as KCl, $CaCl_2$, $CuSO_4$, etc., the choice presents no difficulty; but in

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[1] H. Müller, *Physik. Z.*, **28**, 324–333 (1927); **29**, 78–82 (1928); T. H. Gronwall, *Proc. Nat. Acad. Arts Sci.*, **13**, 198–202 (1927); T. H. Gronwall, V. K. LaMer, and K. Sandved, *Physik. Z.*, **29**, 358–393 (1928); V. K. LaMer, T. H. Gronwall, and L. J. Greiff, *J. Phys. Chem.*, **35**, 2245–2288 (1931).

[2] Fowler, *op. cit.*, Chap. XIII; see also R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Chap. IX, Cambridge University Press, New York, 1939.

the case of H_2SO_4, for example, the picture is obscured by the fact that secondary ionization is by no means complete, even at the lowest solute concentrations feasible for experimental operations (of order $m_2 = 0.0005$ mole/kg).[1] Here, the Debye-Hückel generalization is of great value in calling immediate attention to the existence of such irregularities (which fall outside the scope of purely thermodynamic reasoning) and in suggesting quantitative methods for dealing with them. Thus, when one treats H_2SO_4 as though it were a 1:2 electrolyte at finite concentrations in water [by setting ζ in Eq. (7-4-24) equal to 3], then $\gamma_\pm$ runs significantly below the values typical of other true 1:2 electrolytes, such as Na_2SO_4 (Fig. 7-18). By ascribing to the true mean ionic activity coefficient of H^+ and $SO_4^=$ in the solution a value equal to that of other 1:2 electrolytes at the same ionic strength, and to the mean ionic activity coefficient of H^+ and HSO_4^- a value equal to that of other 1:1 electrolytes, Sherrill and Noyes were able to infer the extent to which secondary ionization, $HSO_4^- = H^+ + SO_4^=$, must actually take place, assuming that primary ionization in dilute solution is practically complete. Hamer later measured the secondary ionization constant directly, and showed that secondary ionization is by no means complete, even in quite dilute sulfuric acid solutions.[2] Likewise, the values of $\gamma_\pm$ for $CdCl_2$, $CdBr_2$, and CdI_2 solutions in water, calculated on the supposition that these substances are 2:1 electrolytes, run far below the values for other 2:1 electrolytes (Fig. 7-18), evidence either that these compounds are incompletely ionized or, as appears more likely from other evidence, that Cd^{++} tends to form complex ions with Cl^-, Br^-, and I^- at sufficiently high halide-ion concentrations.[3] Purely thermodynamic reasoning, in the absence of generalizations essentially extrathermodynamic in nature concerning the behavior of electrolytes, would of course be incapable of suggesting such ideas. At the same time, one must recognize that such ideas are bound to include an element of speculation, whereas the direct interconnections between the properties of the solution that are based on thermodynamic relationships are independent of the supposed structure of the substance under consideration; thus, ϕ_2 of H_2SO_4 in aqueous sulfuric acid solutions is

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[1] M. S. Sherrill and A. A. Noyes, *J. Am. Chem. Soc.*, **48**, 1861–1873 (1926); W. J. Hamer, *ibid.*, **57**, 9–15 (1935); H. S. Harned and W. J. Hamer, *ibid.*, 27–33.

[2] W. J. Hamer, *ibid.*, **56**, 860–864 (1934); he obtained for the secondary ionization constant: $K_2 = 0.0122$ at 25°C, essentially by a potentiometric determination of pH in $NaHSO_4$-Na_2SO_4 "buffer" solutions. The unusual circumstance in sulfuric acid solutions is that the relatively high ionic strength resulting from primary ionization produces a strong primary "salt" effect on the secondary ionization at all finite concentrations; see W. J. Hamer, *ibid.*, **57**, 9–15 (1935).

[3] $CdSO_4$ behaves as a "normal" 2:2 electrolyte, with a mean ionic activity coefficient closely paralleling that of $CuSO_4$ at the same concentration.

defined by straightforward experimental operations that take no cognizance of the state of ionization, or of the concentration itself except as a state-determining variable (like T and p) on which the value of ϕ_2 happens to depend.

In Eqs. (7-4-15) to (7-4-17), we formally introduced the idea of individual ion activities and activity coefficients, even though we found it necessary to point out that only mean ionic activities and mean ionic activity coefficients, such as appear in Eqs. (7-4-19) to (7-4-24), are susceptible to experimental measurement. In order to measure individual ionic activity coefficients, we should have to conceive some method of preparing a solution containing only the one ion, unaccompanied by others, or at least, containing an excess of positive or negative ionic charge. At present, we do not know how to set up such an experiment; when we attempt to add to or remove from the solution the ion in which we are interested, we are constrained to add or remove a proportional quantity of some other ion of opposite charge, and there is no way in which we can disentangle the separate contributions of the two kinds of ions to the thermodynamic properties of the electrolyte outside the ideal dilute region. It is nevertheless convenient for us to use the concept of individual ionic activity coefficients for theoretical purposes, particularly when we are dealing with mixtures of several electrolytes, in which the concentrations of individual cations and anions may be varied independently of each other within the requirement of over-all electrical neutrality. Provided that we observe certain precautions in the interpretation of such quantities, no harm will be done. The basic requirement is that in any equation connecting individual ionic activity coefficients (or activities) with measurable properties of the solution, they must appear recombined in forms that do not conflict with the condition of electrical neutrality of the solution as a whole. In other words, while individual ionic activities and ionic activity coefficients corresponding to an equation such as (7-4-18) have only paper significance, their combinations for any pair of ions in the solution in the forms $a_+^{\zeta_+}a_-^{\zeta_-}$ and $\gamma_+^{\zeta_+}\gamma_-^{\zeta_-}$, where z_+ and z_- denote the respective ionic charges and $\zeta_+z_+ + \zeta_-z_- = 0$, do have real physical significance, in the sense that they can be measured in principle in terms of observable properties of the solution.[1] For example, the activity coefficient of a singly charged cation such as Na^+ and the activity coefficient of a singly charged anion such as Cl^- do not individually have physical significance in solution in a given medium, but an expression of the form $\gamma_{Na^+}\gamma_{Cl^-}$, where both activity coefficients refer to the same solvent, does have physical significance; in the same sense, an

[1] See P. B. Taylor, *J. Phys. Chem.*, **31**, 1478–1500 (1927); E. A. Guggenheim, *ibid.*, **33**, 842–849 (1929).

expression of the form $\gamma_{\text{Ca}^{++}}\gamma^2_{\text{Cl}^-}$ has physical significance and can in principle be measured for a solution in which both ions are present, but no operation is at present known whereby we could measure $\gamma_{\text{Ca}^{++}}$ or γ_{Cl^-} separately. The mean ionic activity coefficient (7-4-22) has of course the proper form in relation to the hypothetical individual ionic activity coefficients to be measurable. Furthermore, expressions of the forms $\gamma_{\text{Cu}^{++}}/\gamma_{\text{Zn}^{++}}$ and $\gamma_{\text{Cu}^{++}}/\gamma^2_{\text{Ag}^+}$, such as turn up in the theory of equilibrium in ionic reactions and in the theory of galvanic cells (Chap. 9), have real physical significance, and can be measured, because they are equivalent actually to expressions such as $\gamma_{\text{Cu}^{++}}\gamma_{\text{SO}_4^-}/\gamma_{\text{Zn}^{++}}\gamma_{\text{SO}_4^-}$ (if $SO_4^=$ happens to be the particular anion present) or $\gamma_{\text{Cu}^{++}}\gamma^2_{\text{NO}_3^-}/\gamma^2_{\text{Ag}^+}\gamma^2_{\text{NO}_3^-}$ (if in this case NO_3^- represents the particular anion, some anion necessarily being present at a concentration equivalent to that of the cations); the numerator and the denominator of each of these expressions, from which one may cancel out the hypothetical anion contribution if both cations are present in the same solution, are both measurable properties of the solution. On the other hand, an expression of the form $\gamma_{\text{Cu}^{++}}/\gamma_{\text{Ag}^+}$ could not be measured. In this connection, it should be noted that one cannot measure such a quantity as a_{H^+} without making unverifiable assumptions concerning the activity coefficient of the accompanying anion; this fact has a bearing on the interpretation of potentiometric measurements of "pH" at high ionic concentrations and in nonaqueous media (Chap. 9); in dilute solutions, one generally assumes either tacitly or openly that the activity coefficients of the cation and the anion are equal [*i.e.*, each equal to the mean ionic activity coefficient; compare (7-4-22)].[1] This discussion has merely taken cognizance of the fact that a given ion cannot enter or leave the liquid phase in question without the accompaniment of an electrically equivalent number of some kind of ion having opposite charge.

We are now in a position to restate the thermodynamic condition for equilibrium between a crystalline electrolyte and its saturated solution, in a form which in special cases reduces to the *solubility product principle.* For in general, without regard to the actual solubility of the electrolyte, or the possible presence of other ions in the solution, we may write as the condition for equilibrium at fixed temperature and pressure

$$A_{\zeta_+}B_{\zeta_-}(\text{c}) = \zeta_+A + \zeta_-B; \qquad \Delta F_{T,1\,\text{atm}} = \zeta_+\phi_A + \zeta_-\phi_B - (\bar{F}^\circ_T)_{A_{\zeta_+}B_{\zeta_-}(\text{c})}$$
$$= \phi_{A_{\zeta_+}B_{\zeta_-}} - (\bar{F}^\circ_T)_{A_{\zeta_+}B_{\zeta_-}(\text{c})} = 0$$

Introducing (7-4-20),

$$\zeta_+\phi'_A + \zeta_-\phi'_B + RT \ln (m_A^{\zeta_+}m_B^{\zeta_-})(\gamma_+^{\zeta_+}\gamma_-^{\zeta_-}) - (\bar{F}^\circ_T)_{A_{\zeta_+}B_{\zeta_-}(\text{c})} = 0$$

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[1] Note the discussion of indicator "acidity functions" given by L P. Hammett, *J. Am. Chem. Soc.*, **50**, 2666–2673 (1928).

Therefore in the solution in equilibrium with the pure crystalline ionic compound, $A_{\zeta_+}B_{\zeta_-}(c)$, we have

$$(m_A^{\zeta_+}m_B^{\zeta_-})(\gamma_+^{\zeta_+}\gamma_-^{\zeta_-}) = \exp \frac{(\bar{F}_T^\circ)_{A_{\zeta_+}B_{\zeta_-}(c)} - \zeta_+\phi'_A - \zeta_-\phi'_B}{RT} = K'_s \tag{7-4-36}$$

The constant K'_s at given temperature and pressure (ordinarily 1 atm), having the form

$$RT \ln K'_s \equiv (\bar{F}_T^\circ)_{A_{\zeta_+}B_{\zeta_-}(c)} - \zeta_+\phi'_A - \zeta_-\phi'_B \tag{7-4-37}$$

we may call the *thermodynamic solubility product* of the electrolyte in the given medium. In view of (7-4-22), we may express (7-4-36) in the form

$$(m_A^{\zeta_+}m_B^{\zeta_-})\gamma_\pm^{\zeta} = K'_s \tag{7-4-38}$$

where $\gamma_\pm$ represents the mean ionic activity coefficient of the particular pair of ions A and B in the saturated solution.

Condition (7-4-38) applies to the saturated equilibrium solution for *any* electrolyte, regardless of its solubility, and regardless of any other ions that may be present in the solution.[1] For rather soluble electrolytes, the hitch in its application is the measurement of $\gamma_\pm$. If we are dealing with solutions containing only the single electrolyte $A_{\zeta_+}B_{\zeta_-}$, then we may measure $\gamma_\pm$ independently by straightforward experimental operations [*e.g.*, by application of Eq. (7-4-27) to activity data for the solvent]; since in that case we may usually assume that $m_A = \zeta_+m_2^*$ and $m_B = \zeta_-m_2^*$, where m_2^* represents the stoichiometric solute molality in the saturated solution, the measurement of the solubility m_2^* and the independent measurement of $\gamma_\pm$ serve to determine the value of the constant K'_s, and so through Eq. (7-4-37) to determine the value of $\zeta_+\phi'_A + \zeta_-\phi'_B$ relatively to the value of $(\bar{F}_T^\circ)_{A_{\zeta_+}B_{\zeta_-}(c)}$.[2] This idea is in no respect different from that expressed in the discussion following Eq. (7-4-27). If the electrolyte is appreciably soluble, however, one can make no general theoretical pre-

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[1] Recall, however, the footnote on page 393 concerning the interpretation of K_s° according to (7-4-37), if the equilibrium crystalline phase happens to be solvated, or if its composition differs in any other way from that of a simple compound of the two ions concerned.

[2] This assumption is not always sound. One must be on guard against the possibility of reaction of either or both ions with the solvent (*e.g.*, hydrolysis), or with each other (complex ion formation), for then m_A may be quite different from ζ_+m_2 and m_B from ζ_-m_2. See, for example, the critical analysis by I. M. Kolthoff, *J. Phys. Chem.*, **35**, 2711–2721 (1931), of metal sulfide solubility data. One must also be certain that equilibrium has been established, which may take a long time in the case of some of the less soluble compounds (*e.g.*, NiS, CoS).

Table 7-6. Solubility of AgCl in Aqueous Solutions of Electrolytes at 25°C*

Electrolyte added	Concentration, moles/liter	C_{AgCl}, moles/liter	$\mu^{1/2}$
None	0	1.273×10^{-5}	0.00358
KNO_3	0.00001280	1.280	0.00506
	0.0002609	1.301	0.01665
	0.0005090	1.311	0.02285
	0.004972	1.385	0.07061
	0.009931	1.427	0.09972
	0.013695	1.453	0.11708
	0.016431	1.469	0.12825
	0.020064	1.488	0.14175
	0.027376	1.516	0.16500
	0.033760	1.537	0.18378
	0.040144	1.552	0.20040
$Ba(NO_3)_2$	0.00000640	1.280	0.00566
	0.00003615	1.291	0.01102
	0.00021108	1.309	0.02542
	0.0007064	1.339	0.04618
	0.001499	1.372	0.06716
	0.003083	1.421	0.09624
	0.004402	1.450	0.11602
	0.005600	1.467	0.12967
	0.008396	1.503	0.15875
	0.011193	1.526	0.18328
	0.01399	1.542	0.20490
$La(NO_3)_3$	0.00000427	1.280	0.00620
	0.00007626	1.305	0.02169
	0.0001438	1.317	0.02960
	0.0005780	1.367	0.05910
	0.001155	1.404	0.08333
	0.001660	1.432	0.09988
	0.002807	1.477	0.12984
	0.003826	1.505	0.15157
	0.005100	1.538	0.17498
	0.006629	1.563	0.19947

* Data of S. Popoff and E. W. Neumann, *J. Phys. Chem.*, **34**, 1853–1860 (1930); E. W. Neumann, *J. Am. Chem. Soc.*, **54**, 2195–2207 (1932).

diction concerning how $\gamma_\pm$ may be affected by the presence of other electrolytes; for as one sees in Fig. 7-18, there is little regularity in the effect of ionic concentration on $\gamma_\pm$ even for single electrolytes, at concentrations of order $1m$ and higher. Therefore the usefulness of condition (7-4-38) is extremely limited in the case of a moderately or highly soluble electrolyte.

In fact, one can perhaps use this equation best for the purpose of measuring $\gamma_\pm$ as affected by the presence of other electrolytes, from measurements of how they affect the solubility, the value of K'_s having been previously established from independent measurements of m_2^* and $\gamma_\pm$ in the saturated solution of the single pure electrolyte.

If the solubility of the electrolyte is sufficiently slight, however, then the ionic strength of the solution is almost entirely determined by the concentrations of other electrolytes that may be present, and this in turn is then the primary factor determining the value of $\gamma_\pm$. If to a first order of approximation we assume that at sufficiently low total electrolyte concentration $\gamma_\pm \sim 1$, then Eq. (7-4-38) reduces to the familiar solubility product principle. More generally, we may express (7-4-38) for aqueous solutions in the form

$$C_A^{\zeta_+} C_B^{\zeta_-} = K_s = \frac{K''_s}{\gamma''^{\zeta}_{\pm}} \tag{7-4-39}$$

where K''_s and $\gamma''_\pm$ have approximately the same significance as before,[1] but K_s represents the ordinary or stoichiometric solubility product, which we see therefore is only approximately constant; its value varies with $\gamma''_\pm$, which is determined primarily by the total ionic strength of the solution. We have seen in Figs. 7-18 and 7-19 that the value of $\gamma''_\pm$ for any electrolyte decreases with increasing electrolyte concentration over the dilute range (up to at least 0.5m in most cases), the decreases representing largely the general effect of increasing interionic attraction. Therefore we should expect that in dilute solution, the value of K_s would tend to increase as the total electrolyte concentration is increased. This is indeed actually the case, as shown, for example, by the solubility data for AgCl in aqueous solutions containing various electrolytes, presented in Table 7-6, from work of Popoff and Neumann.[2] In cases such as this, where the added electrolyte has no ion in common with the slightly soluble electrolyte under investigation, the value of K_s is given by $\zeta_+^{\zeta_+}\zeta_-^{\zeta_-}(C_2^*)^{\zeta}$ [*i.e.*, in the case of AgCl, simply by $(C_2^*)^2$], where C_2^* represents the molar solubility.[3]

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[1] See, however, Eqs. (7-3-97), (7-3-100), and (7-3-105).

[2] S. Popoff and E. W. Neumann, *J. Phys. Chem.*, **34**, 1853–1860 (1930); E. W. Neumann, *J. Am. Chem. Soc.*, **54**, 2195–2207 (1932); a nephelometric method was used.

[3] See, however, footnote 2 on page 416 concerning possible reactions of the ions with the solvent, or with each other. As a matter of fact, at sufficiently high Cl^- concentration, the formation of complex ions between Ag^+ and Cl^- results in a much higher solubility of AgCl than one would predict from Eq. (7-4-39) on the assumption that all the silver in solution were present as free Ag^+. A. Pinkus and N. Berkolaïko, *J. chim. phys.*, **27**, 364–385 (1930), have shown that in the presence of KCl, the solu-

Equation (7-4-39) permits us to measure directly from solubility data the mean ionic activity coefficient $\gamma_\pm$ of the slightly soluble electrolyte in the presence of other electrolytes. It thereby provides a sensitive means of testing the Debye-Hückel limiting law in this case, if the solubility can be measured with sufficient precision. In water at 25°C, making use of the Debye-Hückel limiting law in the form (7-4-31), we may put Eq. (7-4-39) in the approximate limiting form

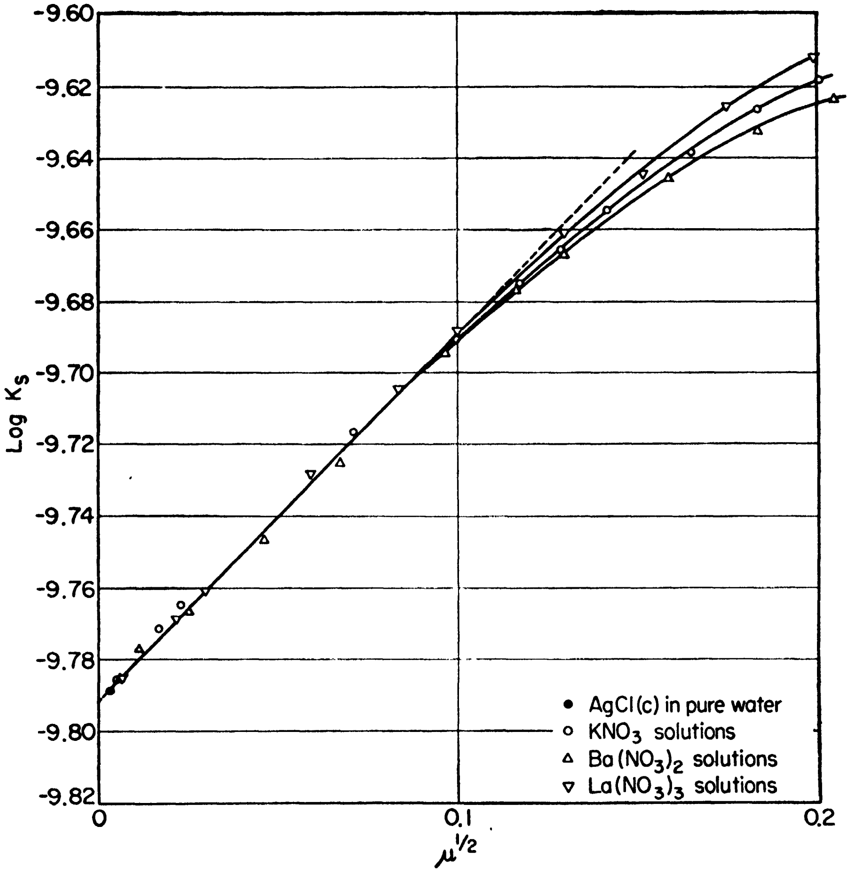

FIG. **7-20.** Plot of log K_s vs. $\mu^{1/2}$ for AgCl in solutions of electrolytes at 25°C [*solubility data of S. Popoff and E. W. Neumann, J. Phys. Chem.*, **34**, 1853–1860 (1930)]; straight line drawn with Debye-Hückel limiting slope, 1.0182.

$$\log K_s = \log K_s'' + \zeta(0.5091\, z_+ z_- \mu^{1/2}) \qquad (\mu \to 0 \text{ in } H_2O \text{ at } 25°C) \qquad (7\text{-}4\text{-}40)$$

Therefore if we plot log K_s vs. $\mu^{1/2}$, the data should approach log K_s'' as $\mu \to 0$ along a straight line having slope 0.5091 $z_+ z_- \zeta$ (1.0182 in the case of a 1:1 electrolyte such as AgCl). In Fig. 7-20, the data from Table 7-6

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bility of AgCl goes through a minimum at about 0.02*M* KCl, and thereafter increases with further increase in the KCl concentration; they estimate that at 0.0001*M* KCl, half the silver is already in forms other than Ag^+ ion.

have been plotted in this form; the straight line in the plot has been drawn with the theoretical Debye-Hückel limiting slope. While the data cover a wide variation in concentrations and charge types of the electrolytes added, one can see that there is general agreement with the Debye-Hückel theory.[1]

The data in Table 7-6 and Fig. 7-20 lead to the conclusion:

$$\mathrm{AgCl(c)} = \mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)}; \qquad \log K'_s = -9.791 \quad (T = 298.16°\mathrm{K})$$

If we substitute in Eq. (7-4-37), we may express this experimental result in the form

$$\phi'_{\mathrm{Ag^+(aq)}} + \phi'_{\mathrm{Cl^-(aq)}} - (\bar{F}^\circ_{298.16})_{\mathrm{AgCl(c)}} = -RT \ln K'_s = 5801 \text{ cal}$$

If any two of the quantities on the left have been established independently, then the measurement of K'_s in this case serves to determine the third; in this sense, precise solubility product data constitute an important experimental method of relating the standard free energies of formation of the ions in solution to the standard molal free energies of their pure compounds. Conversely, since the quantities $(\bar{F}^\circ_T)_{A_{\zeta_+}B_{\zeta_-}(c)}$, ϕ'_A, and ϕ'_B are in principle all independently measurable [*e.g.*, we may determine $\phi'_{\mathrm{Ag^+(aq)}}$ in principle from experimental ϕ_2 data for $AgNO_3$(aq) and for HNO_3(aq) solutions by means of Eqs. (7-4-13) and (7-4-14), and we may similarly determine $\phi'_{\mathrm{Cl^-(aq)}}$ from ϕ_2 data for HCl (aq) solutions], we may predict the value of K'_s, and with the aid of the Debye-Hückel approximation (7-4-40) the corresponding solubility of the slightly soluble electrolyte, from thermodynamic data that are obtainable from other experimental sources.

Finally, we may use the Debye-Hückel limiting law conveniently for the precise extrapolation of thermal data in dilute solutions of electrolytes. For, in general, applying the thermodynamic relation (7-1-26*b*) to (7-4-23), which essentially defines $\gamma_\pm$,

$$\eta_2 - \eta_2^\circ = \zeta R \left[\frac{d \ln \gamma_\pm}{d(1/T)}\right]_p \tag{7-4-41}$$

[compare Eq. (7-3-93) for nonelectrolytes]. This equation permits us to calculate the temperature coefficient of $\gamma_\pm$ for given composition from experimental heat-of-dilution data expressed in terms of $\eta_2 - \eta_2^\circ$. In sufficiently dilute solution, however, we may introduce the Debye-Hückel

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[1] Neumann has called attention, however, to small but apparently systematic deviations, which are more prominent when sulfates (not included in Table 7-6 or Fig. 7-20) instead of the nitrates are used as the added electrolyte.

approximation (7-4-28),

$$\begin{aligned}\eta_2 - \eta_2^\circ &= -2.3026\zeta R z_+ z_- \mu^{1/2}\left[\frac{dA}{d(1/T)}\right]_p \\ &= -\frac{3}{2}\,2.3026\zeta R T z_+ z_- A \mu^{1/2}\left[1 + \frac{T}{D}\left(\frac{dD}{dT}\right)_p\right] \qquad (7\text{-}4\text{-}42)\end{aligned}$$

Now in water at 25°C, from the data of Wyman (see footnote 3 page 407), $D = 78.54$; $\dfrac{1}{D}\left(\dfrac{dD}{dT}\right)_p = -0.00460$. Therefore Eq. (7-4-42) reduces to

$$\eta_2 - \eta_2^\circ = 774\,\frac{z_+ z_- \zeta}{2}\,\mu^{1/2} \quad (\mu \to 0 \text{ in } H_2O \text{ at } 25°C) \qquad (7\text{-}4\text{-}43)$$

or in particular for a 1:1 electrolyte

$$\eta_2 - \eta_2^\circ = 774\, m_2^{1/2} \text{ cal/mole} \quad (1{:}1 \text{ electrolyte}) \qquad (7\text{-}4\text{-}43a)$$

The partial molal enthalpy of the solvent is related to that of the solute by a general Gibbs-Duhem equation, which we may put in the form

$$\frac{1000 \text{ g/kg}}{\bar{M}_1}\, d\eta_1 + m_2\, d\eta_2 = 0$$

Introducing (7-4-43*a*) in the case of a dilute solution of a 1:1 electrolyte in water at 25°C, and integrating from $m_2 = 0$,

$$\begin{aligned}\eta_1 - \bar{H}_1^\circ &= -\frac{1}{3}\,\frac{774 \text{ cal/mole}}{55.51 \text{ moles/kg}}\, m_2^{3/2} \\ &= -4.65 m_2^{3/2} \text{ cal/mole } H_2O \quad (1{:}1 \text{ electrolyte}) \qquad (7\text{-}4\text{-}43b)\end{aligned}$$

The theoretical limiting expressions (7-4-43*a*) and (7-4-43*b*) may be put in terms of the apparent molal enthalpy of the solute, Φ_h; thus, from (4-28) and (4-35),

$$\begin{aligned}m_2\Phi_h &= 55.51 \text{ (moles/kg } H_2O)\eta_1 + m_2\eta_2 - 55.51 \text{ (moles/kg } H_2O)\bar{H}_1^\circ \\ &= 55.51(\eta_1 - \bar{H}_1^\circ) + m_2\eta_2\end{aligned}$$

Introducing (7-4-43*a*) and (7-4-43*b*),

$$\begin{aligned}\Phi_h - \Phi_h^\circ &= \tfrac{2}{3}\, 774 m_2^{1/2} \text{ cal/mole solute} \\ &= 516 m_2^{1/2} \text{ cal/mole solute } (1{:}1 \text{ electrolyte}; \\ &\qquad\qquad m_2 \to 0 \text{ in } H_2O \text{ at } 25°C) \qquad (7\text{-}4\text{-}43c)\end{aligned}$$

Since $(\Phi_h - \Phi_h^\circ)$ simply measures $-(\bar{Q}_s - \bar{Q}_s^\circ)$, where $\bar{Q}_s$ represents the experimentally determined integral molal heat of solution, introduced in Sec. 4-5 [see Eq. (4-31)], therefore $\bar{Q}_s$ itself when plotted against $m_2^{1/2}$ should approach $\bar{Q}_s^\circ$ along a straight line as $m_2 \to 0$, with theoretical slope

-516 (Q_s being expressed in cal/mole solute, and m_2 in mole solute/kg H_2O). This theoretical result, given by the Debye-Hückel approximation, has been useful for the precise extrapolation of thermal data in dilute solutions to find $\bar{Q}_s^\circ$ or the equivalent Φ_H° for the particular electrolyte.[1] Corresponding limiting forms for electrolytes of higher charge types may be derived by replacing μ in Eq. (7-4-43) by the appropriate multiple of m_2 (m_2 and C_2 being practically equal in dilute aqueous solutions).

7-5. The Colligative Properties of Liquid Solutions. It is well known that certain physical properties of liquid solutions are interrelated, in the sense that without regard to the particular solute or its concentration, the value of any one of these properties may be estimated under certain conditions with a high degree of accuracy from the observed value of any one of the others. The properties so interrelated are known as the *colligative properties* of the solution; they include the *vapor-pressure depression* and *boiling-point elevation* associated with the presence of a relatively nonvolatile solute, the *freezing-point depression* associated with the presence of a solute that does not enter into solid solution or solid compound formation with the solvent, and the *osmotic pressure.* These properties have been commonly used in approximate forms for the purpose of estimating the molecular weight of the solute, since it turns out that in sufficiently dilute solution, each is proportional to the molal concentration of the solute; but when the molecular weight of the solute is already known, they may be used more precisely to measure thermodynamic potentials or activity coefficients outside the ideal dilute range.

The colligative properties have in common the establishment of equilibrium between the liquid solution and the *pure solvent,* in some one of its phases. Thus, the basic thermodynamic requirements may be summarized as follows:

$$\left.\begin{array}{lll}\phi_1 = \bar{F}_{1(g)} & & \text{(Vapor pressure and boiling-point equilibrium)} \\ \phi_1'' = \bar{F}_{1(l)} & & \text{(Osmotic equilibrium)} \\ \phi_1 = \bar{F}_{1(c)} & & \text{(Freezing-point equilibrium)}\end{array}\right\} \quad (7\text{-}5\text{-}1)$$

Since $\bar{F}_{1(g)}$, $\bar{F}_{1(l)}$, and $\bar{F}_{1(c)}$ are properties solely of the pure solvent, the conditions under which ϕ_1 will satisfy, respectively, the three equations (7-5-1) must be closely interrelated. The interrelationships will depend on the particular solute and its concentration [assuming that the solute satisfies the general requirements implied, respectively, by conditions (7-5-1)] only to the extent that since the different colligative properties are normally measured at different temperatures and pressures, one must

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[1] See, for example, F. D. Rossini, *J. Research Natl. Bur. Standards,* **6,** 791–806 (1931).

take into account the effect of the solute on the variation of ϕ_1 with temperature and pressure; this effect tends to disappear as the solute concentration is decreased, but in certain situations it may remain quite small at solute concentrations well beyond the ideal dilute range, as we shall presently see. Let us review separately the different equilibrium situations represented by Eqs. (7-5-1).

a. Vapor-pressure Depression and Boiling-point Elevation. In measuring the vapor pressure or the boiling point of a solution containing a *relatively nonvolatile solute,* we are essentially measuring equilibrium conditions between the liquid solution and the *pure solvent* in the gaseous state. The thermodynamic conditions for equilibrium are therefore represented by the first of Eqs. (7-5-1),

$$\phi_1 = \bar{F}_{1(g)} \tag{7-5-2}$$

These conditions are much simpler, both theoretically and experimentally, than the corresponding conditions $\phi_1 = \phi_1^*$ and $\phi_2 = \phi_2^*$, when the solute also is appreciably volatile, such as we considered in general in Sec. 7-3; the term on the right of (7-5-2) is a property solely of the pure solvent, varying with temperature and pressure according to the equations developed in Sec. 6-1, whereas ϕ_1^* and ϕ_2^* when the solute is volatile depend on the composition of the equilibrium vapor phase, which then has to be analyzed empirically, in view of the lack of any general relationship between the liquid and vapor compositions (other than the formal one implied by the conditions $\phi_1 = \phi_1^*$ and $\phi_2 = \phi_2^*$ themselves).

Thus, the vapor-pressure depression associated with the presence of a nonvolatile solute represents the amount by which the pressure of the pure solvent vapor has to be lowered in order that its molal free energy at the given temperature may remain equal to the thermodynamic potential of the solvent in the solution; it measures primarily therefore the lowering of the solvent's thermodynamic potential. Now, for a shift in the equilibrium conditions resulting from a small change in the composition of the liquid phase at the given temperature, according to (7-5-2),

$$d\phi_1 = (d\phi_1)_{T,p} + \left(\frac{d\phi_1}{dp}\right)_{T,n} dp = d\bar{F}_{1(g)} \qquad (T \text{ const})$$

where $(d\phi_1)_{T,p}$ represents the explicit change of ϕ_1 with the change in composition, and the following term represents the change of ϕ_1 associated with the change in the equilibrium pressure. Introducing (6-10) and (7-1-24),

$$(d\phi_1)_{T,p} = (\bar{V}_{1(g)} - v_1)dp \qquad (T \text{ const}) \tag{7-5-3}$$

The only way in which this relationship depends on the specific properties of the solution is through the term v_1, the partial molal volume of the solvent in the liquid phase; but at vapor pressures of order 1 atm or less, we may neglect this term altogether in comparison with $\bar{V}_{1(g)}$ (this assumption might not be warranted, however, at high pressures approaching the critical state). If we assume furthermore that at moderate pressures, the pure solvent vapor may be treated as an ideal gas, then (7-5-3) may be put in the form

$$(d\phi_1)_{T,p} = RT\,d\ln p \qquad (T\text{ const})$$

which integrates to

$$\phi_1 = (\bar{F}_{T,p_1^\circ})_{1(l)} + RT\ln\frac{p}{p_1^\circ} \qquad (T\text{ const})$$

since in the limit as $x_1 \rightarrow 1$, ϕ_1 approaches the molal free energy of the pure liquid solvent at its own vapor pressure, p_1°. For vapor pressures not greatly in excess of 1 atm, we may generally replace $(\bar{F}_{T,p_1^\circ})_{1(l)}$ by the standard molal free energy, $(\bar{F}_T^\circ)_{1(l)}$, without significant error [the error would have the magnitude, $\int_{1\text{ atm}}^{p_1^\circ} \bar{V}_{1(l)}\,dp$, but would be partially canceled by the error introduced when we dropped v_1 from Eq. (7-5-3) in comparison with $\bar{V}_{1(g)}$; compare Eq. (7-3-2)]; thus

$$\phi_1 = (\bar{F}_T^\circ)_{1(l)} + RT\ln\frac{p}{p_1^\circ} \qquad (T\text{ const}) \qquad (7\text{-}5\text{-}4)$$

This equation applies quite independently of the nature of the solute or its concentration, within the restrictions we have noted; there may even be several different solutes present, provided that they are all relatively nonvolatile. The error introduced by the assumption that the solvent vapor satisfies the ideal-gas law is in most cases inappreciable at pressures below 1 atm, and in any event, a correction for nonideality may be introduced in the form of fugacity coefficients, derived by the methods outlined in Sec. 6-1. Equation (7-5-4) differs from the more general equation (7-3-3) only in that for nonvolatile solutes, we have replaced the partial vapor pressure of the solvent by the directly measured vapor pressure of the solution.

Equation (7-5-4), which we may put in the equivalent form

$$\phi_1 - (\bar{F}_T^\circ)_{1(l)} = RT\ln\left(1 - \frac{\Delta p}{p_1^\circ}\right) \qquad (T\text{ const}) \qquad (7\text{-}5\text{-}4a)$$

where $\Delta p \equiv p_1^\circ - p$ represents the vapor-pressure depression, thus permits us to measure ϕ_1 relatively to $(\bar{F}_T^\circ)_{1(l)}$ directly from vapor-pressure-depression measurements, without regard to the particular nature of the solute. For a binary solution, from ϕ_1 values so derived, we may calculate ϕ_2 values by integrating the Gibbs-Duhem equation [*e.g.*, in the form (7-1-9)]; this of course calls for a knowledge of the solute's concentration.

Now, in sufficiently dilute solutions, we have Raoult's empirical generalization (7-3-14*a*), which for nonelectrolytes assumes the form

$$\frac{\Delta p}{p_1^\circ} = x_2 \qquad (T \text{ const}; x_2 \to 0) \qquad (7\text{-}5\text{-}5)$$

If m_2 represents the molality of the solute, this law may be expressed in the approximate form [compare Eq. (7-3-78)]

$$\frac{\Delta p}{m_2 p_1^\circ} = \frac{\bar{M}_1}{1000 \text{ g/kg}} \qquad (T \text{ const}; m_2 \to 0) \qquad (7\text{-}5\text{-}6)$$

Vapor-pressure-depression data are commonly expressed in terms of $\Delta p/m_2p_1^\circ$ at given values of m_2.[1] Historically, Raoult's law constituted one of the first methods for determining the molecular weights of nonvolatile substances; the vapor-pressure method is not particularly precise for this purpose, because at low solute concentrations, where the generalization (7-5-5) or (7-5-6) is valid, Δp is a small difference, not easily measured with precision, whereas at higher solute concentrations, where Δp can be measured more precisely, the ideal limiting law fails. In the ideal dilute range, Eq. (7-5-5) or Eq. (7-5-6) when substituted in Eq. (7-5-4*a*) permits us to calculate the precise value of the thermodynamic property $\phi_1 - (\bar{F}_T^\circ)_{1(l)}$ simply from the composition. Outside the ideal dilute range, however, $\Delta p/p_1^\circ$ continues to measure the true thermodynamic properties, and thus serves as an experimental means of relating them empirically to the composition. This empirical relationship in the case of the solute is represented conveniently in terms of the activity coefficient γ_2' for nonelectrolytes [Eq. (7-3-82)] or $\gamma_\pm$ for electrolytes [Eq. (7-4-23)]. Application of the Gibbs-Duhem equation has given us, respectively, Eqs. (7-3-90) and (7-4-27) for these quantities in terms of $(\ln a_1)/m_2$, which in view of (7-5-4*a*) and the definition (7-3-87) or (7-4-25) of a_1, we may compute readily from the vapor-pressure depression data in the form

$$\begin{aligned} \frac{\ln a_1}{m_2} &= \frac{1}{m_2} \ln \left(1 - \frac{\Delta p}{p_1^\circ}\right) \\ &= -\frac{\Delta p}{m_2 p_1^\circ}\left[1 + \frac{1}{2}\left(\frac{\Delta p}{p_1^\circ}\right) + \frac{1}{3}\left(\frac{\Delta p}{p_1^\circ}\right)^2 + \cdots\right] \qquad (7\text{-}5\text{-}7) \end{aligned}$$

By evaluating the integral in Eq. (7-3-90) or in Eq. (7-4-27) graphically for values of m_2 up to the saturated solution, we may relate the constant

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[1] It was in this form that Raoult actually first stated his vapor-pressure law; *i.e.*, he showed that with solutes of known molecular weights, $\Delta p/m_2p_1^\circ$ in dilute solution was a constant for the given solvent [F. M. Raoult, *Compt. rend.*, **103**, 1125–1127 (1886)].

ϕ_2' in Eq. (7-3-82) for a nonelectrolyte or the constant $\phi_2' = \zeta_+\phi_A' + \zeta_-\phi_B'$ in Eq. (7-4-23) for an electrolyte $A_{\zeta_+}B_{\zeta_-}$, to the standard molal free energy of the pure solute, as we have already shown in the preceding sections.

If we have measured the activity coefficient of the solute from some other experimental source, then if we combine the appropriate equation (7-3-107) or (7-4-23) for ϕ_2 with Eq. (7-5-4) for ϕ_1 in the general Gibbs-Duhem equation (7-1-7), we may express the exact relation between the vapor pressure and the solute concentration (within the scope of the ideal-gas-law approximation for the solvent vapor) in the forms

$$\left(\frac{d\ln p}{dx_2}\right)_T = -\frac{1}{1-x_2}\left[1 + x_2\left(\frac{d\ln\gamma_2^\circ}{dx_2}\right)_{T,p}\right] \tag{7-5-8a}$$

$$\left(\frac{d\ln p}{dm_2}\right)_T = -\frac{\bar{M}_1}{1000\text{ g/kg}}\left[1 + m_2\left(\frac{d\ln\gamma_2'}{dm_2}\right)_{T,p}\right] \tag{7-5-8b}$$

$$\left(\frac{d\ln p}{dm_2}\right)_T = -\frac{\bar{M}_1\zeta}{1000\text{ g/kg}}\left[1 + m_2\left(\frac{d\ln\gamma_\pm}{dm_2}\right)_{T,p}\right] \tag{7-5-8c}$$

If the activity coefficient of the solute were expressed empirically as an analytic function of the concentration, we could express the appropriate relationship (7-5-8) in integral form; the first term on the right of Eq. (7-5-8*a*) or Eq. (7-5-8*b*) when integrated leads in dilute solution to the ideal limiting form, (7-5-5) or (7-5-6), respectively. It is instructive for us to introduce the Debye-Hückel limiting law for log $\gamma_\pm$ in Eq. (7-5-8*c*); using the expressions (7-4-31*a*) for water at 25°C, and assuming as an approximation in dilute solution that $C_2 \sim m_2$

$$\lim_{m_2\to 0}\left[1 + m_2\left(\frac{d\ln\gamma_\pm}{dm_2}\right)_{T,p}\right] = 1 - \frac{2.303}{2}A'm_2^{1/2}$$

where A' represents the appropriate charge-type factor listed in Eq. (7-4-31*a*) (including the factor for converting m_2 to ionic strength). Substituting in Eq. (7-5-8*c*) and integrating,

$$\ln\frac{p}{p_1^\circ} = -\frac{\bar{M}_1\zeta}{1000\text{ g/kg}}\left(m_2 - \frac{2.303}{3}A'm_2^{3/2}\right)$$

or at sufficiently small values of Δp

$$\frac{\Delta p}{m_2 p_1^\circ} = \frac{\bar{M}_1\zeta}{1000\text{ g/kg}}\left(1 - \frac{2.303}{3}A'm_2^{1/2}\right) \quad (T\text{ const};\ m_2 \to 0) \tag{7-5-8d}$$

The first term on the right represents the ideal Raoult's law result for a strong electrolyte [the expression on the right of Eq. (7-5-6), multiplied by ζ]; the second term represents the first-order effect of interionic attraction. One sees that at $m_2 = 0.01$ mole/kg, the interionic-attraction effect accounts for a deviation of -4 per cent from the ideal value of Δp for a 1:1 electrolyte, but -31 per cent from the ideal value for a 2:2 electrolyte (ζ having the same value, 2, in both of these cases); for a nonaqueous solvent having a dielectric constant lower than that of water, the deviations would tend to be even greater. For aqueous solutions, one cannot measure the vapor-pressure depression precisely at concentrations much below $0.1m$, because it becomes too small in relation to experimental error. Therefore over the entire concentration range in which significant vapor-pressure data may be obtained, the electrolytes of higher charge types depart greatly from ideal dilute-solution behavior, as shown by the data for typical solutes presented in Fig. 7-21. This fact seriously

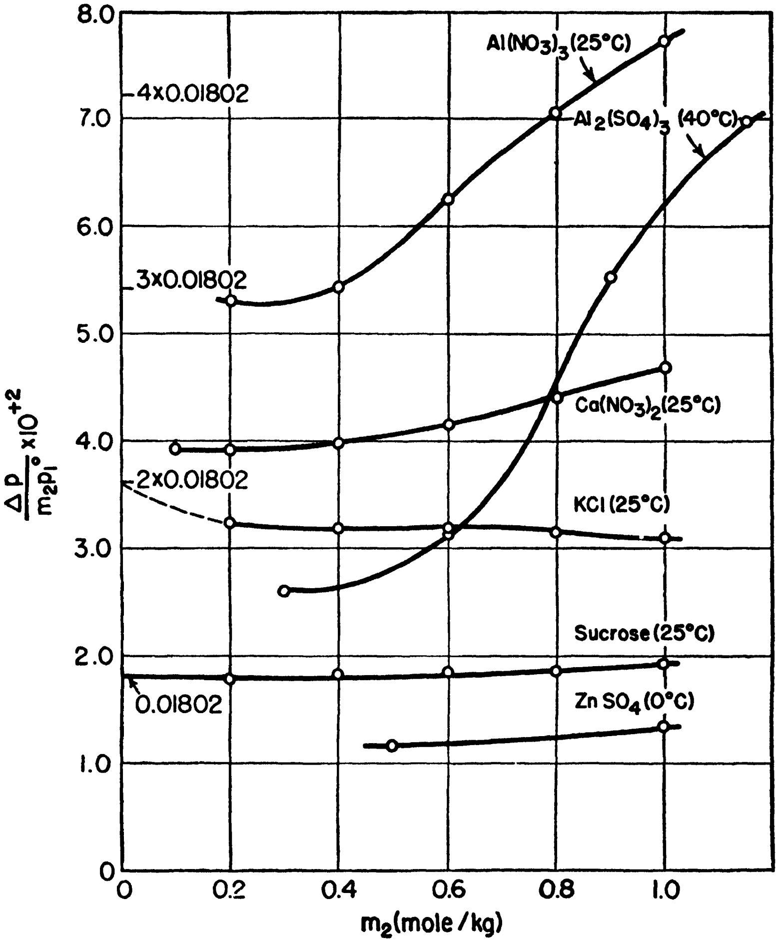

FIG. 7-21. Vapor-pressure depressions for aqueous solutions of various nonvolatile solutes. (*Data from "International Critical Tables," Vol.* 3, 1928, *McGraw-Hill Book Company, Inc., and from Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Suppl.* IIIc, 1936.)

retarded the development of the theory of strong electrolytes from the time of Arrhenius' original discovery until its significance was made clear by the work of Debye and Hückel. We do not mean to imply that the Debye-Hückel limiting law may be applied in a quantitative sense even at the lowest ionic concentrations for which precise vapor-pressure-depression data may be obtained, but the interionic-attraction hypothesis goes far to account for the apparent confusion evident in the vapor-pressure results for electrolytes at concentrations one would ordinarily regard as quite low if one did not have the point of view provided by the theory. Thus, while vapor-pressure data for solutions of electrolytes are quite satisfactory for extending basic free-energy data to high solute concentrations, and are particularly satisfactory for the establishment of the thermodynamic potential of the solvent, they are not capable of sufficient precision for the complete establishment of the solute's activity coefficient, which calls for an extrapolation to zero concentration [the lower limit of the integral in Eq. (7-4-27)].

Let us turn now to the boiling point of a solution containing a relatively nonvolatile solute. We may maintain the general equilibrium condition (7-5-2) not only by lowering the pressure of the pure solvent vapor at the given temperature, in order to make up for the lowering of ϕ_1 associated with the presence of the solute, but also by raising the temperature at the given pressure. For according to Eq. (6-12), the decrease (algebraic) of $\bar{F}_{1(g)}$ with increasing temperature is in proportion to $\bar{H}_{1(g)}$, while according to Eq. (7-1-26*a*), the decrease of ϕ_1 with increasing temperature is in proportion to η_1; since $\bar{H}_{1(g)}$ is bound to exceed η_1 [their difference, $\lambda_1 = \bar{H}_{1(g)} - \eta_1$, representing the partial molal latent heat of vaporization of the solvent from the solution], there must be some temperature above the boiling point of the pure solvent at which ϕ_1 overtakes $\bar{F}_{1(g)}$. In order to derive the boiling-point law, it is convenient for us to express condition (7-5-2) in the form

$$\frac{\phi_1}{T} = \frac{\bar{F}_{1(g)}}{T} \tag{7-5-9}$$

an entirely proper procedure, since for all equilibrium states of the two phases, their temperatures will be equal. For a small change in the composition of the liquid phase at the given pressure, we may write

$$d\left(\frac{\phi_1}{T}\right) = d\left(\frac{\phi_1}{T}\right)_{T,p} + \left[\frac{d(\phi_1/T)}{dT}\right]_{p,n} dT = d\left(\frac{\bar{F}_{1(g)}}{T}\right) \quad (p \text{ const})$$

where as before, $d(\phi_1/T)_{T,p}$ stands for the explicit change of (ϕ_1/T) with the change in composition, and now the following term stands for the change in (ϕ_1/T) associated with the accompanying change in the equilibrium temperature. Thus, introducing (6-12) and (7-1-26*a*),

$$d\left(\frac{\phi_1}{T}\right)_{T,p} = -\frac{\bar{H}_{1(g)} - \eta_1}{T^2}\,dT$$

$$= -\frac{\lambda_1}{T^2}\,dT \qquad (p \text{ const}) \qquad (7\text{-}5\text{-}10)$$

i.e.,

$$\left[\frac{d(\phi_1/T)}{dx_1}\right]_{T,p} = -\frac{\lambda_1}{T^2}\left(\frac{dT}{dx_1}\right)_p \qquad (7\text{-}5\text{-}11)$$

If we may assume that the pure solvent vapor satisfies approximately the ideal-gas law, then ϕ_1 at constant temperature, say at T_B°, the boiling point of the pure solvent, satisfies Eq. (7-5-4); therefore[1]

$$\left(\frac{d \ln p_1}{dx_1}\right)_T = -\frac{\lambda_1}{RT^2}\left(\frac{dT}{dx_1}\right)_p \qquad (7\text{-}5\text{-}12)$$

If we integrate (7-5-12) down from $x_1 = 1$, where the pure solvent is at its own boiling point, T_B°, at the given pressure p_1°, then we may obtain a relationship between the boiling-point elevation at the pressure p_1° and the vapor-pressure depression at the temperature T_B°:

$$\int_{T_B^\circ}^{T_B^\circ + \Delta T_B} \frac{\lambda_1}{RT^2}\,dT = -\ln\frac{p}{p_1^\circ} = -\ln\left(1 - \frac{\Delta p}{p_1^\circ}\right) \qquad (7\text{-}5\text{-}13)$$

This relationship depends on the particular nature of the solution only to the extent that η_1 depends on the particular solute and its concentration [the value of $\lambda_1 = \eta_1 - \bar{H}_{1(g)}$ evidently approaches $(\bar{L}_{lg})_1$ as $x_1 \to 1$]. The extent of this dependence is indicated in a general way by the magnitude of the heat of dilution down to infinitely dilute solution, and may be quite small even when the solution deviates considerably from ideal dilute behavior. Thus, Table 4-11 has shown that in 1*m* H_2SO_4, for example, η_1 differs from $\bar{H}^\circ_{H_2O(l)}$ (at 25°C) by only -5 cal/mole; this happens

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[1] It may seem odd for us to be replacing ϕ_1 in Eq. (7-5-11) by an expression that apparently varies with pressure, in view of the fact that p is to be regarded as constant in the derivatives represented in (7-5-11). Actually, of course, ϕ_1 is quite insensitive to explicit changes in the pressure, so that the condition of constant pressure on the left-hand member of (7-5-11) hardly needs to be explicitly stated; but the *vapor pressure* varies with composition in a manner related to that by which ϕ_1 varies with composition, *i.e.*, according to (7-5-4) when the solvent vapor satisfies the ideal-gas law. Therefore over pressure ranges sufficiently small so that the explicit variation of ϕ_1 with pressure, as given by Eq. (7-1-24), need not be taken into account, we may replace the change of ϕ_1 with composition at constant temperature by the equal change of $RT \ln p_1$ with composition at the same temperature, p_1 being equal to the total vapor pressure when as in the case under consideration, the solute is nonvolatile.

actually to be a rather extreme example of dependence, and in many other cases, λ_1 will remain practically equal to $(\bar{L}_{lg})_1$ at even higher solute concentrations. Equation (7-5-13) then relates ΔT_B to Δp in a manner practically independent of the particular solute and its concentration, provided only that it is not significantly volatile.

If we are dealing with an ideal solution satisfying Eq. (7-5-5), we have seen that the condition $\eta_1 = \bar{H}_{1(l)}$ is necessarily satisfied [Eq. (7-3-20)], and Eq. (7-5-13) then takes the form

$$\int_{T_B{}^\circ}^{T_B{}^\circ+\Delta T_B} \frac{(\bar{L}_{lg})_1}{RT^2}\,dT = -\ln(1 - x_2) \qquad \text{(ideal soln)} \qquad (7\text{-}5\text{-}14)$$

At sufficiently small values of x_2 and ΔT_B, this equation may be put in the approximate limiting form

$$\Delta T_B = \frac{R(T_B^\circ)^2}{(\bar{L}_{lg})_1}\,x_2 \qquad (x_2 \to 0) \qquad (7\text{-}5\text{-}15)$$

Equation (7-5-15) represents Raoult's well-known boiling-point law; the factor

$$k_B \equiv \frac{R(T_B^\circ)^2}{(\bar{L}_{lg})_1} \qquad (7\text{-}5\text{-}16)$$

is a property of the pure solvent known as its *mole-fraction boiling-point constant;* thus, its value for water (at 1 atm) is 28.9 deg, and for benzene, 33.6 deg. The equivalent relationship expressed in terms of the molality of the solute [compare Eq. (7-3-78)] is

$$\left.\begin{aligned} T_B &= k_B' m_2 \qquad (m_2 \to 0) \\ k_B' &\equiv k_B \frac{\bar{M}_1}{1000\text{ g/kg}} \end{aligned}\right\} \qquad (7\text{-}5\text{-}17)$$

where k_B' is known as the *molal boiling-point constant;* its value for water is 0.521 deg kg/mole. Equations (7-5-14), (7-5-15), and (7-5-17) apply of course only to ideal solutions of nonelectrolytes.

In general, these ideal limiting equations do not apply to concentrated solutions of nonelectrolytes, and even if modification is introduced to take into account the ionization of strong electrolytes [*e.g.*, multiplication of the right-hand member of (7-5-17) by ζ], interionic attraction results in significant departure from ideal behavior at quite low ionic concentration. If we have measured the extent of deviation from ideal dilute behavior by some other experimental means, and have expressed the results in terms of an activity coefficient for the solute, then in the same manner in which we derived Eqs. (7-5-8) we may derive corresponding equations for the boiling-point elevation

$$\left(\frac{dT}{dx_2}\right)_p = \frac{RT^2}{\lambda_1}\frac{1}{1-x_2}\left[1 + x_2\left(\frac{d\ln\gamma_2^\circ}{dx_2}\right)_{T,p}\right] \qquad (7\text{-}5\text{-}18a)$$

$$\left(\frac{dT}{dm_2}\right)_p = \frac{RT^2}{\lambda_1}\frac{\bar{M}_1}{1000\text{ g/kg}}\left[1 + m_2\left(\frac{d\ln\gamma_2'}{dm_2}\right)_{T,p}\right] \qquad (7\text{-}5\text{-}18b)$$

$$\left(\frac{dT}{dm_2}\right)_p = \frac{RT^2}{\lambda_1}\frac{\bar{M}_1\zeta}{1000\text{ g/kg}}\left[1 + m_2\left(\frac{d\ln\gamma_\pm}{dm_2}\right)_{T,p}\right] \qquad (7\text{-}5\text{-}18c)$$

The last of these equations, in particular, reduces in dilute solutions of strong electrolytes to the approximate form

$$\left(\frac{dT}{dm_2}\right)_p = \zeta k_B'\left[1 + m_2\left(\frac{d\ln\gamma_\pm}{dm_2}\right)_{T,p}\right] \qquad (m_2 \to 0) \qquad (7\text{-}5\text{-}19)$$

The factor multiplying the ideal molal boiling-point elevation: $\zeta k_B'$ in Eq. (7-5-19) is the same as the factor entering Eq. (7-5-8c), except for the difference in the temperatures at which the two equations are applied. If we introduce the Debye-Hückel limiting law [compare Eq. (7-5-8d)], then it becomes evident that for electrolytes of the higher charge types, one may expect significant deviation from ideal dilute behavior even at concentrations of only 0.01m in water. In Fig. 7-22, boiling-point elevations for some extremely dilute aqueous solutions have been plotted, mostly taken from an investigation by E. Plake.[1] One sees that at con-

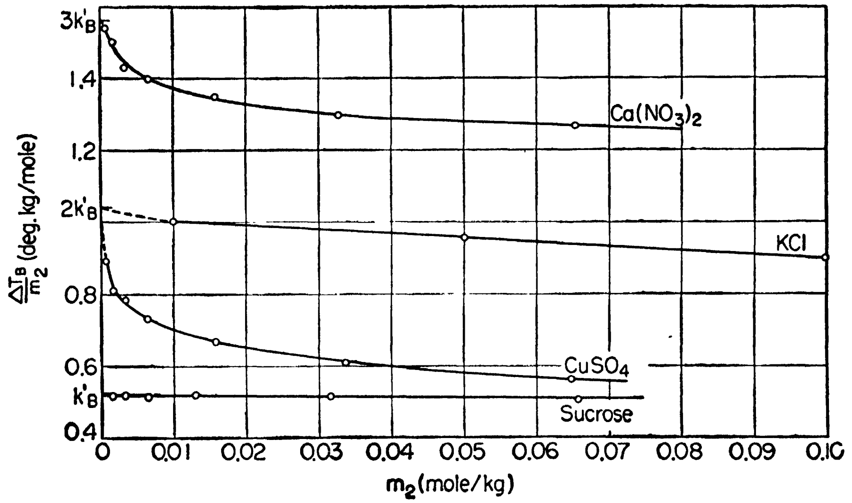

FIG. 7-22. Molal boiling-point elevations for aqueous solutions of various nonvolatile solutes. [*Data of E. Plake, Z. physik. Chem.*, (A)**172**, 113–128 (1935), *and of B. Saxton and R. P. Smith, J. Am. Chem. Soc.*, **54**, 2626–2636 (1932).]

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[1] E. Plake, *Z. physik. Chem.*, (A)**172**, 113–128 (1935).

centrations below 0.01*m*, the curves for the electrolytes show the expected trend. Had one confined one's attention, however, to concentrations exceeding 0.05*m*, one might have been puzzled to find that $CuSO_4$ raises the boiling point of water hardly any more than the nonelectrolyte, sucrose, at the same molal concentration; in fact, at higher concentrations (0.3*m*), the molal boiling-point elevation for $CuSO_4$ becomes actually less than that for sucrose.

One could in principle develop Eqs. (7-5-18) in forms suitable for integration and the calculation of solute activity coefficients from boiling-point elevation data, just as we shall presently do for the analogous freezing-point equations. In practice, however, boiling points are quite troublesome to measure precisely, and have not constituted an important source of information concerning the thermodynamic properties of solutions.

b. Osmotic Pressure. The discovery of osmosis is attributed to Abbé Nollet, who in 1748 observed that if a sugar solution enclosed in a parchment container is lowered into a vessel of pure water, the water tends to diffuse through the parchment, building up a considerable pressure inside. The cue to this remarkable behavior rests in the selective action of the membrane, which permits water to transfuse freely, but not sugar. Since the thermodynamic potential of the pure water, $\bar{F}_{1(l)}$, is higher than the thermodynamic potential of the water originally in the solution, the water tends to flow in the one direction until a sufficient hydrostatic pressure has been built up to raise ϕ_1 [in accordance with Eq. (7-1-24)] enough to satisfy the equilibrium requirement

$$\phi_1 = \bar{F}_{1(l)} \tag{7-5-20}$$

[the second of Eqs. (7-5-1)]. The *osmotic pressure* is defined as the excess pressure that must be applied to the solution in order to maintain equilibrium with the pure solvent, separated from it by a semipermeable diaphragm impervious to the solute.

From this brief description, it is clear that the magnitude of the osmotic pressure is a thermodynamic equilibrium property of the solution and solvent, independent of the nature of the membrane and the mechanism of transfusion of the solvent. This fact was pointed out by J. H. van't Hoff, who gave the first theoretical analysis of the problem,[1] although its general nature had previously been described by J. Willard Gibbs, before any quantitative experimental data existed. The nature of the membrane may well influence the rate of attainment of equilibrium, however, and the mechanism of transfusion presents a number of problems that

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[1] J. H. van't Hoff, *Z. physik. Chem.*, **1**, 481–508 (1887).

have not yet received generally satisfactory answers.[1] Artificial semipermeable membranes based on certain colloidal inorganic precipitates were first introduced by M. Traube in 1867, and the first reliable measurements of osmotic pressure were madé by W. Pfeffer in 1877, using membranes of $Cu_2Fe(CN)_6$ prepared by precipitation within the pores of porous clay cells. · The measurement of osmotic pressure has been brought to a high degree of refinement through the work of H. N. Morse and J. C. W. Frazer and their students in this country, and of Lord Berkeley and E. G. J. Hartley in England.[2]

Let us represent by $(\phi_1)^\circ$ the thermodynamic potential of the solvent in the solution when the solution is at the pressure P° applied during the measurements to the pure solvent (ordinarily the pressure of the atmosphere). If sufficient pressure P is now applied to the solution until ϕ_1 becomes equal to $\bar{F}_{1(l)}$, then according to Eq. (7-1-24),

$$(\phi_1)^\circ + \int_{P^\circ}^{P} v_1\,dP = (\bar{F}_{T,P^\circ})_{1(l)} \qquad (7\text{-}5\text{-}21)$$

The value of $P - P^\circ$ satisfying Eq. (7-5-21) becomes by hypothesis equal to the osmotic pressure, π, under the given conditions (with the pure solvent at T and P°); in this equation, v_1 represents the partial molal volume of the solvent corresponding to the given composition, to be expressed as a function of P. Now, as an excellent approximation for most liquid solutions under moderate pressures, we may treat v_1 as sensibly independent of pressure. Thus, in the case of water itself, the total compressibility between 0 and 1000 atm at room temperature is less than 5 per cent, and in case we should have to deal with pressures exceeding several hundred atmospheres, we could reduce the error resulting from the compressibility of the liquid to negligible proportions by regarding v_1 as representing the average value over the pressure range in question, rather than the ordinary value at 1 atm. Therefore we may reduce Eq. (7-5-21) to the general form

$$\pi v_1 = (\bar{F}_{T,P^\circ})_{1(l)} - (\phi_1)^\circ \qquad (T \text{ const}) \qquad (7\text{-}5\text{-}22)$$

Now, if we may assume that the equilibrium vapor phase of the solution at the temperature T satisfies the ideal-gas law, then we may relate $(\phi_1)^\circ$ to $(\bar{F}_{T,P^\circ})_{1(l)}$ through the partial vapor pressure of the solvent, in the form

$$(\phi_1)^\circ = (\bar{F}_{T,P^\circ})_{1(l)} + RT\ln\left(\frac{p_1}{p_1^\circ}\right) + \int_{P^\circ}^{p_1^\circ} \bar{V}_1\,dp + \int_{p}^{P^\circ} v_1\,dp \qquad (T \text{ const}) \qquad (7\text{-}5\text{-}23)$$

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[1] For discussion, see W. M. Clark, "Topics in Physical Chemistry," Chap. XI, The Williams & Wilkins Company, Baltimore, 1948.

[2] A review of this work has been given by J. C. W. Frazer in H. S. Taylor's "A Treatise on Physical Chemistry," 2d ed., Chap. VII, D. Van Nostrand Company, Inc., New York, 1931.

[compare Eq. (7-3-2), where the pressure P° was taken to be 1 atm]. The last two terms represent, respectively, the change in $\bar{F}_{1(l)}$ for the pure solvent between the pressure P° and its own vapor pressure p_1°, and the change in ϕ_1 between the vapor pressure of the solution p (which need not necessarily be the same as p_1 if the solute happens to be volatile) and the reference pressure P°. When P° is of order 1 atm, these two terms may generally be ignored as insignificantly small. Then, introducing Eq. (7-5-23) in (7-5-22),

$$\pi = \frac{RT}{v_1} \ln \frac{p_1^\circ}{p_1} \qquad (T \text{ const}) \qquad (7\text{-}5\text{-}24)$$

This equation, first derived by A. W. Porter,[1] provides an exact thermodynamic connection, within the reasonably legitimate assumptions we have noted, between the osmotic pressure and the lowering of the solvent's partial vapor pressure. It involves the particular nature of the solute and its concentration only through their influence on the value of v_1; in sufficiently dilute solutions, in fact, we may replace v_1 generally by $\bar{V}_{1(l)}$ [compare Eq. (7-3-24)], and in many cases, such as that of sucrose in water, this approximation may be extended to high solute concentrations with little error. Experimental data testing Eq. (7-5-24) are presented in Table 7-7.

We may express $\ln (p_1^\circ/p_1) = -\ln [1 - (\Delta p_1/p_1^\circ)]$ as a power series in terms of $(\Delta p_1/p_1^\circ)$, and thus put (7-5-24) in the form

$$\pi = \frac{RT}{v_1} \frac{\Delta p_1}{p_1^\circ} \left[1 + \frac{1}{2}\left(\frac{\Delta p_1}{p_1^\circ}\right) + \frac{1}{3}\left(\frac{\Delta p_1}{p_1^\circ}\right)^2 + \cdots \right] \qquad (7\text{-}5\text{-}25)$$

In sufficiently dilute solutions, we need retain only the leading term of the series, and may at the same time replace v_1 by the approximation $\bar{V}_{1(l)}$; thus

$$\pi = \frac{RT}{\bar{V}_{1(l)}} \frac{\Delta p_1}{p_1^\circ} \qquad \left(\frac{\Delta p_1}{p_1^\circ} \to 0\right) \qquad (7\text{-}5\text{-}26)$$

The error in this approximation has nothing to do with the ideality of the solution, but may be estimated from a comparison of the first and second terms of the series in (7-5-25); *e.g.*, the error is within 1 per cent if $\Delta p_1/p_1^\circ$ does not exceed 0.02. Equation (7-5-26) shows that in sufficiently dilute solution the osmotic pressure is directly proportional to the vapor-pressure depression of the solvent. The relatively small magnitude of $\bar{V}_{1(l)}$ results in a huge magnification factor for π as compared with $(\Delta p_1/p_1^\circ)$; thus, the factor $RT/\bar{V}_{1(l)}$ for water at 25°C has the value 1354.0 atm, and a 1m sucrose solution has an osmotic pressure exceeding 25 atm.

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[1] A. W. Porter, *Proc. Roy. Soc.* (*London*), (A)**79**, 519–528 (1907).

TABLE 7-7. OSMOTIC-PRESSURE DATA

$Ca_2Fe(CN)_6$ in H_2O at 0°C*

m_2, moles/kg	$\frac{\Delta p}{m_2 p_1^\circ}$	$\frac{p_1^\circ}{p_1}$	v_1, ml/mole	π (calc.), atm	π (obs.), atm
0.1024	......	......	18.018	......	2.54
1.075	0.0315	1.0351	17.678	43.74	41.22
1.353	0.0399	1.0571	17.530	71.59	70.84
1.469	0.0448	1.0704	17.455	87.39	87.09
1.617	0.0521	1.0922	17.379	113.72	112.84
1.711	0.0569	1.1079	17.339	132.48	130.66

Sucrose in H_2O at 30°C†

m_2, moles/kg	$\frac{\Delta p}{m_2 p_1^\circ}$	$\frac{p_1^\circ}{p_1}$	π (calc.), atm	π (obs.), atm
0.1	0.0180	1.0018	2.47	2.47
1.0	0.0194	1.0198	26.95	27.22
2.0	0.0209	1.0436	58.67	58.37
3.0	0.0225	1.0724	96.10	95.16
4.0	0.0236	1.1042	136.27	138.96
5.0	0.0246	1.1402	180.4	187.3
6.0	0.0252	1.1781	225.4	232.3
6.5 (satd)	0.0255	1.1988	249.3	252.8

* Osmotic pressures and vapor pressures by the Earl of Berkeley, E. G. J. Hartley, and C. V. Burton, *Trans. Roy. Soc.* (*London*), (A)**209**, 177–203, 319–336 (1909). Values of v_1 were computed from density measurements by Berkeley, Hartley, and Burton, given in the "International Critical Tables," Vol. III, p. 74, 1928.

† Osmotic pressures taken from smoothed data of J. C. W. Frazer and R. T. Myrick, *J. Am. Chem. Soc.*, **38**, 1907–1922 (1916), and of P. Lotz and J. C. W. Frazer, *ibid.*, **43**, 2501–2507 (1921). Vapor pressures from work of Berkeley, Hartley, and Burton, given in the "International Critical Tables," Vol. III, p. 293, 1928. The value of v_1 is constant at 18.094 ml/mole, the solution volume being practically additive.

Now, for an ideal dilute solution, satisfying Raoult's law (7-5-5), Eq. (7-5-26) may be put in the form

$$\pi = \frac{RT}{\bar{V}_{1(l)}} x_2 \qquad (x_2 \rightarrow 0) \qquad (7\text{-}5\text{-}27)$$

Equation (7-5-27) relates the osmotic pressure to the solute concentration, for all concentrations at which the solvent satisfies Raoult's law. It is therefore generally valid for sufficiently dilute solutions of nonelectrolytes. As an approximation in dilute solution, we may replace $x_2 = n_2/(n_1 + n_2)$ by n_2/n_1, with the result

$$\pi = \frac{RT}{\bar{V}_{1(l)}} \frac{n_2}{n_1} = \frac{n_2 RT}{V_1} \qquad \left(\frac{n_2}{n_1} \rightarrow 0\right) \qquad (7\text{-}5\text{-}28)$$

where V_1 represents the volume of pure solvent containing n_2 moles of solute.[1] Or finally, since at the lowest solute concentrations the volume of the solvent will not differ significantly from the volume of the solution

$$\pi = \frac{n_2RT}{V} = C_2RT \qquad (C_2 \rightarrow 0) \qquad \text{(7-5-29)}$$

Equation (7-5-29) is known as van't Hoff's osmotic-pressure equation.[2] Because of the similarity in form between Eq. (7-5-29) and the ideal-gas equation of state, van't Hoff was led to draw an analogy between the behavior of the osmotic pressure of a solute in liquid solution and the behavior of the pressure of a gas; in fact, he based his entire theory of solutions on this analogy, and W. Nernst later based his theory of the emfs of galvanic cells on similar reasoning. We see, however, that Eq. (7-5-29) is merely the limiting form of the more general ideal dilute-solution equation (7-5-27), and that the problem of deviations from Eqs. (7-5-29) or (7-5-27) at high solute concentrations is but another aspect of the general problem of deviations from Raoult's law. In other words, osmotic-pressure data give us no new kind of information not readily obtainable from other thermodynamic sources (except possibly the effect of high pressures on v_1); Eq. (7-5-29) is logically implied by Raoult's vapor-pressure law (7-3-14) (with appropriate simplifying assumptions valid in dilute solution), which in the thermodynamic form (7-3-15) constitutes a much more general empirical starting point for the construction of a theory of solutions.

We could of course use osmotic-pressure data directly to measure the thermodynamic properties of the solution, as a substitute for or as a supplement to other methods of investigation. Thus, Eq. (7-5-22) measures directly the thermodynamic potential $(\phi_1)^\circ$ of the solvent in the solution, at T and P°, relatively to the molal free energy $(\bar{F}_{T,P^\circ})_{1(l)}$ of the pure solvent; in terms of the solvent's activity function,

$$-\ln a_1 = \frac{\pi v_1}{RT} \qquad (\text{at } T \text{ and } P^\circ) \qquad \text{(7-5-30)}$$

From measurements of $\ln a_1$ thus obtained for various solute concentrations, we could by integrating the Gibbs-Duhem equation in one of the forms, (7-3-73), (7-3-90), or (7-4-27), determine the activity coefficient of the solute. The method is favored particularly at low solute concentrations by the fact that the osmotic pressure is comparatively large in

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[1] This modification of van't Hoff's equation (7-5-29) was proposed originally by H. N. Morse and J. C. W. Frazer, *J. Am. Chem. Soc.*, **34**, 1–99 (1905).

[2] J. H. van't Hoff, *loc. cit.*

magnitude; thus, π for a 0.005m KCl solution in water at 25°C is about 0.25 atm.[1] Unfortunately, the technique of high-precision osmotic-pressure measurements is rather difficult, and relatively few investigators have used it for this purpose in ordinary thermodynamic investigation. It has served a very useful purpose, however, in the study of high polymers, both because of the ease with which semipermeable membranes may be obtained for this class of solutes and because of the necessity of working at low solute mole fractions.[2]

For solutions of strong electrolytes, we may show by introducing (7-5-30) in the Gibbs-Duhem equation in the form (7-4-26) that in general

$$\left(\frac{d\pi}{dm_2}\right)_{T,P^\circ} = \zeta \frac{RT}{v_1} \frac{\bar{M}_1}{1000 \text{ g/kg}} \left[1 + m_2 \left(\frac{d \ln \gamma_\pm}{dm_2}\right)_{T,P^\circ}\right] \qquad (7\text{-}5\text{-}31)$$

subject to the assumption only that v_1 is practically independent of pressure. In dilute solution, we may express this relationship in the approximate form

$$\pi = \zeta C_2 RT \left[1 + \frac{1}{m_2} \int_0^{m_2} m_2 \left(\frac{d \ln \gamma_\pm}{dm_2}\right)_{T,P^\circ} dm_2\right] \qquad (7\text{-}5\text{-}32)$$

from which, given the theoretical or empirical limiting form of the $\ln \gamma_\pm$ vs. m_2 relationship as $m_2 \to 0$, we may compute the extent of deviation from van't Hoff's ideal equation (7-5-29) in the modified form for strong electrolytes

$$\pi = \zeta C_2 RT \qquad (C_2 \to 0) \qquad (7\text{-}5\text{-}33)$$

From the discussion leading to Eq. (7-5-8d), it is evident that deviation from (7-5-33) will be appreciable for electrolytes of the higher charge types, even at solute concentrations as low as 0.01 mole/liter in water.

c. Freezing-point Depression. When the solution begins to freeze, provided that the solid phase consists of the *pure crystalline solvent*, and not a solid solution or compound with the solute, then at equilibrium, the third of conditions (7-5-1) must be satisfied,

$$\phi_1 = \bar{F}_{1(\text{c})} \qquad (7\text{-}5\text{-}34)$$

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[1] J. C. W. Frazer and W. A. Patrick, *Z. physik. Chem.*, (A)**130**, 691–698 (1927); F. T. Martin and L. H. Schultz, *J. Phys. Chem.*, **35**, 638–648 (1931).

[2] For detailed discussion of the theory of solutions of high polymers, see, for example, H. Mark, "Physical Chemistry of High Polymeric Systems," Interscience Publishers, Inc., New York, 1940; C. E. H. Bawn, "The Chemistry of High Polymers," Interscience Publishers, Inc., New York, 1948; A. R. Miller, "The Theory of Solutions of High Polymers," Oxford University Press, New York, 1948. For an example of osmotic-pressure measurements applied to a high polymeric system, see the paper by P. J. Flory to which reference is made in Prob. 7-31.

The relative volatility of the solute has no effect on this equilibrium condition, and thus the following freezing-point laws are valid for volatile as well as for nonvolatile solutes. The theory of freezing-point equilibrium is entirely similar to the theory of solubility equilibrium for a solid solute, except for the difference in point of view. For a sufficiently concentrated solution, in many cases, a small shift in the composition of the liquid phase may determine whether the crystalline solvent or the crystalline solute separates out first on cooling. In the former situation, we should say that the solution has begun to freeze, whereas in the latter, we should say that the solution has become saturated with respect to the solute, but this is merely a manner of speaking, which does not detract from the essential similarity of the two processes; in either situation, we should have a state of equilibrium between the liquid solution and one of its pure components in the crystalline state. We must not overlook the possibility that solid solutions or compounds of the components may separate out, but in such cases, the theory to be developed in this section does not apply.

Now, at the normal freezing point of the pure solvent, T_F°, ϕ_1 is invariably smaller (in the algebraic sense) than $\bar{F}_{1(c)} = \bar{F}_{1(l)}$, on account of the presence of the dissolved solute. Since ϕ_1 at given composition increases (algebraically) with decreasing T in proportion to the value of η_1 [Eq. (7-1-26*a*)], whereas $\bar{F}_{1(c)}$ increases with decreasing T in proportion to the value of $\bar{H}_{1(c)}$, and since η_1 is necessarily larger than $\bar{H}_{1(c)}$ [their difference, $\eta_1 - \bar{H}_{1(c)}$, representing the partial molal latent heat of fusion, $(\lambda_{cl})_1$, for the crystalline solvent into the solution], it follows that condition (7-5-34) may be maintained if the temperature of the two phases is lowered sufficiently far below the normal freezing point of the pure solvent. In other words, the freezing point of the solution will be that temperature at which ϕ_1 just overtakes $\bar{F}_{1(c)}$, the pressure generally being held constant [*i.e.*, at 1 atm, though neither ϕ_1 nor $\bar{F}_{1(c)}$ depends sensitively on the pressure]. The freezing point is always defined as the temperature at which crystalline solvent would first begin to appear on cooling, for if the solvent continued to freeze out, the composition of the liquid solution remaining would undergo change, and with it, the instantaneous equilibrium temperature would continue to fall.[1]

Let us express the equilibrium condition (7-5-34) in the more convenient form

$$\frac{\phi_1}{T} = \frac{\bar{F}_{1(c)}}{T}$$

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[1] In precise freezing-point determinations, particularly with water as solvent, a sample of the solution is generally withdrawn for analysis after thermal equilibrium has been established with excess of the solid phase.

which is permissible since the temperatures of the two phases are necessarily equal in all equilibrium states of the system, and let us consider the effect of a small change in composition

$$d\left(\frac{\phi_1}{T}\right) = d\left(\frac{\phi_1}{T}\right)_{T,p} + \left[\frac{d(\phi_1/T)}{dT}\right]_{p,n} dT = d\left(\frac{\bar{F}_{1(c)}}{T}\right) \qquad (p \text{ const})$$

Introducing (6-12) and (7-1-26*a*),

$$\begin{aligned} d\left(\frac{\phi_1}{T}\right)_{T,p} &= \frac{\eta_1 - \bar{H}_{1(c)}}{T^2}\, dT \\ &= \frac{(\lambda_{cl})_1}{T^2}\, dT \qquad (p \text{ const}) \qquad (7\text{-}5\text{-}35) \end{aligned}$$

In the case of a binary solution, for example, we may put this exact thermodynamic relationship in the form

$$\left(\frac{dT}{dx_2}\right)_p = -\frac{T^2}{(\lambda_{cl})_1}\left[\frac{d(\phi_1/T)}{dx_1}\right]_{T,p} \qquad (7\text{-}5\text{-}36)$$

Thermodynamics provides no clue to the relationship between ϕ_1 and x_1, but if we may assume that the equilibrium vapor phase of the solution at the freezing point of the pure solvent satisfies the ideal-gas law (an excellent approximation in most cases, because the vapor pressure is generally so low), then we may establish a direct relationship between the freezing-point depression and the lowering of the partial vapor pressure of the solvent at the pure solvent's normal freezing point, T_F°; for, according to Eq. (7-3-3) [see also (7-5-23)],

$$\left[\frac{d(\phi_1/T)}{dx_1}\right]_{T,p} = R\left(\frac{d \ln p_1}{dx_1}\right)_T = -R\left(\frac{d \ln p_1}{dx_2}\right)_T$$

Therefore upon substitution in (7-5-36),

$$\left(\frac{dT}{dx_2}\right)_p = \frac{RT^2}{(\lambda_{cl})_1}\left(\frac{d \ln p_1}{dx_2}\right)_T \qquad (7\text{-}5\text{-}37)$$

or integrating from $x_2 = 0$, where the pure solvent is at its own freezing point, T_F°, and has vapor pressure p_1°,

$$\int_{T_F^\circ}^{T_F^\circ - \Delta T_F} \frac{(\lambda_{cl})_1}{RT^2}\, dT = \ln \frac{p_1}{p_1^\circ} \qquad (7\text{-}5\text{-}38)$$

The term on the left refers to constant pressure (*i.e.*, 1 atm), with $(\lambda_{cl})_1$ equal to the instantaneous partial molal heat of fusion associated with the particular liquid composition having the freezing point T, but the term on the right refers to the constant temperature, T_F°. The only way in which the properties of the particular solute or its concentration influence the relationship (7-5-38) is through the term $(\lambda_{cl})_1$, *i.e.*, through η_1. In sufficiently dilute solutions, the value of $(\lambda_{cl})_1$ clearly approaches $(\bar{L}_{cl})_1$, the molal latent heat of fusion of the pure solvent, but even in fairly concentrated solutions, in many cases, the difference between η_1 and $\bar{H}_{1(l)}$ may remain quite small.

Now, for an ideal solution, in which the solvent empirically satisfies Raoult's law [Eq. (7-3-15)], and by implication, therefore, Eq. (7-3-20) as well, Eq. (7-5-36) reduces to

$$\left(\frac{dT}{dx_2}\right)_p = -\frac{RT^2}{(\bar{L}_{cl})_1}\frac{1}{x_1} = -\frac{RT^2}{(\bar{L}_{cl})_1}\frac{1}{1-x_2} \qquad \text{(ideal soln)} \qquad (7\text{-}5\text{-}39)$$

which assumes the integral form

$$\int_{T_F^\circ}^{T_F^\circ-\Delta T_F} \frac{(\bar{L}_{cl})_1}{RT^2}\,dT = \ln(1-x_2) \qquad \text{(ideal soln)} \qquad (7\text{-}5\text{-}40)$$

The latent heat of fusion varies with temperature according to (3-48),

$$\frac{d(\bar{L}_{cl})_1}{dT} = (\bar{C}_p)_{1(l)} - (\bar{C}_p)_{1(c)} \qquad (7\text{-}5\text{-}41)$$

but to a first order of approximation, in solutions sufficiently dilute so that ΔT_F is not large, we may neglect this variation, and regard $(\bar{L}_{cl})_1$ as approximately constant, equal to its value at the freezing point of the pure solvent; thus, (7-5-40) assumes the limiting form

$$-\frac{(\bar{L}_{cl})_1}{R}\left(\frac{1}{T_F} - \frac{1}{T_F^\circ}\right) = \ln(1-x_2) \qquad \text{(ideal soln)} \qquad (7\text{-}5\text{-}42)$$

[compare Eq. (7-3-36)]. We could readily derive a second-order approximation to $(\bar{L}_{cl})_1$ in Eq. (7-5-40) by assuming a linear dependence on T [introducing constant mean heat-capacity values in (7-5-41)], but in general, Raoult's law does not apply accurately at solute concentrations so high that this factor need be given serious consideration in applications of (7-5-42). In fact, in sufficiently dilute ideal solutions, we may neglect x_2 altogether in the denominator of the right-hand member of Eq. (7-5-39), in comparison with 1, and thus obtain the integral equation in the approximate limiting form

$$\Delta T_F = \frac{R(T_F^\circ)^2}{(\bar{L}_{cl})_1}x_2 \qquad (x_2 \rightarrow 0) \qquad (7\text{-}5\text{-}43)$$

This well-known freezing-point law is therefore a thermodynamic implication of the solvent's conforming to Raoult's empirical dilute-solution law, in the general form (7-3-15). The factor

$$k_F = \frac{R(T_F^\circ)^2}{(\bar{L}_{cl})_1} \tag{7-5-44}$$

is a property of the pure solvent, known as its *mole-fraction freezing-point constant;* thus, its value for water is 103.24 deg. The ideal limiting law (7-5-43) is also commonly expressed in terms of the molality of the solute, in the form

$$\Delta T_F = k_F' m_2 \qquad (m_2 \to 0) \tag{7-5-45}$$

$$k_F' = k_F \frac{\bar{M}_1}{1000 \text{ g/kg}} \tag{7-5-46}$$

where the factor k_F' [see Eq. (7-3-78)] is known as the *molal freezing-point constant;* its value for water is 1.860 deg kg/mole.

Equation (7-5-45) has of course been used extensively for the measurement of molecular weights of substances dissolved in appropriate solvents. Since, however, the freezing-point depression can be measured with extremely high precision,[1] much higher than is ordinarily necessary for molecular weight determinations, the freezing-point method has constituted an important source of experimental information concerning the precise thermodynamic properties of solutions. The theory, and practical graphical methods of computation, have been extensively developed by Lewis and Randall, along the following lines.[2] The fundamental freezing-point equilibrium relation (7-5-35) may be expressed in terms of the solvent's activity function a_1 in the form

$$(d \ln a_1)_{T,p} = \frac{(\lambda_{cl})_1}{RT^2}\, dT \tag{7-5-47}$$

By integrating down from the freezing point of the pure solvent, T_F°, where $a_1 = 1$ ($x_1 = 1$), we could correlate the freezing point $T_F = T_F^\circ - \Delta T_F$ corresponding to each composition with an activity value a_1 at the constant temperature T_F° [we could obtain the same result by substituting $a_1 = p_1/p_1^\circ$ in Eq. (7-5-38)]. By introducing these solvent activity values in the Gibbs-Duhem equation and integrating, we could then compute activity or activity-coefficient values for the solute. A more sensitive method, however, is to compute the activity coefficient of the solute directly by application of the Gibbs-Duhem relation to (7-5-47); for this purpose, it is convenient at temperatures near the freezing point of the pure solvent to replace the variable part of T by the variable $\theta = T_F^\circ - T$,

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[1] For a description of the experimental technique, see G. Scatchard, P. T. Jones, and S. S. Prentiss, *J. Am. Chem. Soc.*, **54**, 2676–2690 (1932).

[2] Lewis and Randall, *op. cit.*, Chaps. XXIII and XXVII.

where θ represents the freezing-point depression. Thus, introducing the molal activity coefficient γ_2' for a nonelectrolytic solute by means of Eq. (7-3-89),

$$-\frac{\bar{M}_1}{1000\text{ g/kg}}\,(dm_2 + m_2\,d\ln\gamma_2') = -\frac{(\lambda_{cl})_1}{RT^2}\,d\theta$$

Hence

$$d\ln\gamma_2' = \frac{1000\text{ g/kg}}{\bar{M}_1}\,\frac{(\lambda_{cl})_1}{RT^2}\,\frac{d\theta}{m_2} - \frac{dm_2}{m_2} \tag{7-5-48}$$

Let us first apply this equation to small values of m_2 and θ (though not necessarily so small that the solvent satisfies Raoult's law), assuming that $(\lambda_{cl})_1$ may be replaced by $(\bar{L}_{cl})_1$, and regarding the entire coefficient of $(d\theta/m_2)$ in the first term on the right of Eq. (7-5-48) as sensibly constant for small changes of temperature; the value of this coefficient is then equal to k_F', defined by Eq. (7-5-46),

$$d\ln\gamma_2' = -\frac{1}{m_2}\left(dm_2 - \frac{1}{k_F'}\,d\theta\right) \qquad (\theta \to 0) \tag{7-5-49}$$

Integrating by parts,

$$\ln\gamma_2' = -\left(1 - \frac{\theta}{m_2k_F'}\right) - \int_0^{m_2} \frac{\left(1 - \dfrac{\theta}{m_2k_F'}\right)}{m_2}\,dm_2 \tag{7-5-50}$$

Equation (7-5-50) is quite analogous in form to Eq. (7-3-90); the integral, whose integrand would vanish if the solution satisfied the ideal limiting law (7-5-45), may be easily evaluated by graphical means from sufficiently precise freezing-point data.

Table 7-8 presents freezing-point data for dilute solutions of *n*-propanol in water, taken from work of T. J. Webb and C. H. Lindsley.[1] One sees that even at a concentration as low as $0.01m$, there is in this case a small but detectable deviation from ideal behavior as represented by Eq. (7-5-45). In Fig. 7-23, the quantity $\left(1 - \dfrac{\theta}{m_2k_F'}\right)$ has been plotted against m_2, and from the smoothed values represented by the curve, values of $\left(1 - \dfrac{\theta}{m_2k_F'}\right)\Big/ m_2$ have been plotted against m_2 in Fig. 7-24. Both curves have been plotted on a large scale, and from Fig. 7-24, one may readily estimate the value of the integral appearing in Eq. (7-5-50) by graphical integration. The lower part of Table 7-8 shows the compu-

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[1] T. J. Webb and C. H. Lindsley, *J. Am. Chem. Soc.*, **56**, 874–878 (1934).

tation of γ_2' for n-propanol in water at 0°C at various molalities, according to Eq. (7-5-50).

We may easily demonstrate that the companion equation to (7-5-50) in the case of an electrolytic solute has the form

$$\ln \gamma_\pm = -\left(1 - \frac{\theta}{\zeta m_2 k_F'}\right) - \int_0^{m_2} \frac{\left(1 - \frac{\theta}{\zeta m_2 k_F'}\right)}{m_2}\, dm_2 \tag{7-5-51}$$

[compare Eq. (7-4-27)].

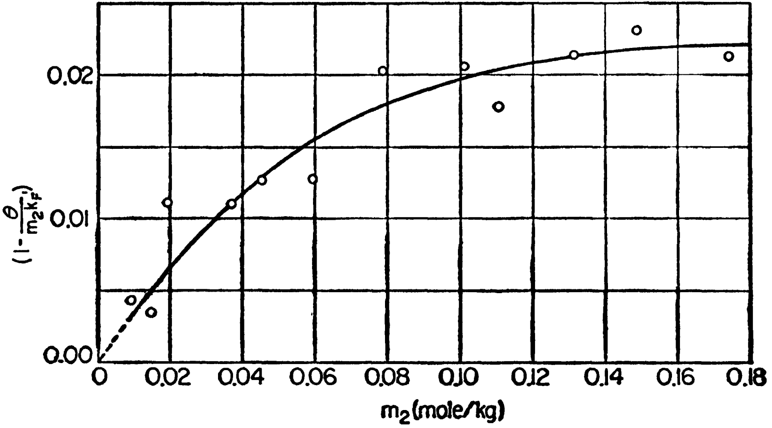

Fig. 7-23. Freezing-point-depression data for solutions of n-propanol in water: plot of $\left(1 - \frac{\theta}{m_2 k_F'}\right)$ vs. m_2. [*Data of T. J. Webb and C. H. Lindsley, J. Am. Chem. Soc.*, **56**, 874–878 (1934).]

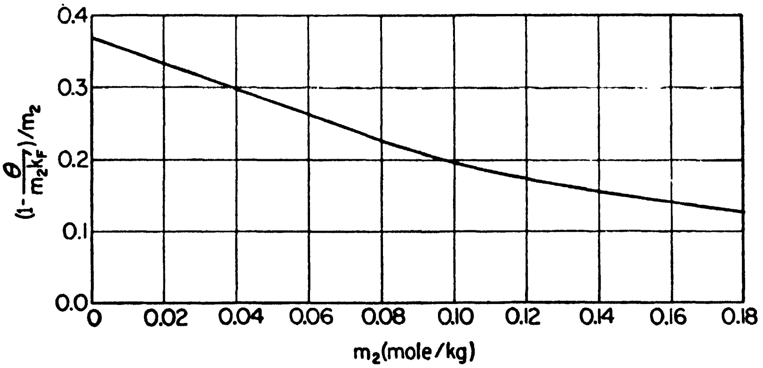

Fig. 7-24. Freezing-point-depression function: $\left(1 - \frac{\theta}{m_2 k_F'}\right) \Big/ m_2$ plotted against m_2 for solutions of n-propanol in water. (*From smoothed data of Fig.* 7-23.)

We may take approximate account of the variation with temperature of the coefficient of $(d\theta/m_2)$ in Eq. (7-5-48) for comparatively large values of θ by ignoring at the outset the heat of dilution, and assuming that

$(\lambda_{cl})_1$ may be replaced by $(\bar{L}_{cl})_1$; this is generally a fair approximation; in the case of $1m$ H_2SO_4, for example, where according to Table 4-11 (at 25°C), $\eta_1 - \bar{H}_{H_2O(l)} \sim -5$ cal/mole, the error in replacing $(\lambda_{cl})_1$ by $(\bar{L}_{cl})_1 = 1436.3$ cal/mole (at 0°C) would be only of order 0.35 per cent, but in many other cases, the error would be smaller, even at higher solute concentrations. Now, $(\bar{L}_{cl})_1$ for the pure solvent varies with temperature according to the Kirchhoff formula, (7-5-41). Let us suppose that we may neglect the comparatively small variation of $(\Delta\bar{C}_p)_1 = (\bar{C}_p)_{1(l)} - (\bar{C}_p)_{1(c)}$ itself with temperature, over the freezing-point range in which we are interested; then, as a good approximation,

$$(\bar{L}_{cl})_1 = (\bar{L}^\circ_{cl})_1 - (\Delta\bar{C}_p)_1\theta \tag{7-5-52}$$

where $(\bar{L}^\circ_{cl})_1$ represents the molal latent heat of fusion at the normal freezing point of the pure solvent. Upon substitution in Eq. (7-5-48),

$$d \ln \gamma_2' = \frac{(\bar{L}^\circ_{cl})_1 - (\Delta\bar{C}_p)_1\theta}{R(T^\circ_F - \theta)^2}\left(\frac{1000\text{ g/kg}}{\bar{M}_1}\right)\frac{d\theta}{m_2} - \frac{dm_2}{m_2} \tag{7-5-53}$$

We may expand the coefficient of $(d\theta/m_2)$ in the form

$$\begin{aligned}\frac{(\bar{L}^\circ_{cl})_1 - (\Delta\bar{C}_p)_1\theta}{R(T^\circ_F - \theta)^2}\,\frac{1000\text{ g/kg}}{\bar{M}_1} &= \frac{(\bar{L}^\circ_{cl})_1}{R(T^\circ_F)^2}\,\frac{1000\text{ g/kg}}{\bar{M}_1}\,\frac{\left[1 - \dfrac{(\Delta\bar{C}_p)_1\theta}{(\bar{L}^\circ_{cl})_1}\right]}{\left[1 - \dfrac{\theta}{T^\circ_F}\right]^2}\\ &= \frac{1}{k'_F}\left[1 - \frac{(\Delta\bar{C}_p)_1\theta}{(\bar{L}^\circ_{cl})_1}\right]\left[1 + \frac{2\theta}{T^\circ_F} + \frac{3\theta^2}{(T^\circ_F)^2} + \cdots\right]\\ &= \frac{1}{k'_F}\left[1 + \left(\frac{2}{T^\circ_F} - \frac{(\Delta\bar{C}_p)_1}{(\bar{L}^\circ_{cl})_1}\right)\theta\right]\end{aligned}$$

neglecting terms in the series of order higher than that of θ/T°_F. Thus

$$\begin{aligned}d \ln \gamma_2' &= \frac{1}{k'_F}\left[1 + \left(\frac{2}{T^\circ_F} - \frac{(\Delta\bar{C}_p)_1}{(\bar{L}^\circ_{cl})_1}\right)\theta\right]\frac{d\theta}{m_2} - \frac{dm_2}{m_2}\\ &= -\frac{1}{m_2}\left(dm_2 - \frac{1}{k'_F}\,d\theta\right) + \frac{1}{k'_F}\left(\frac{2}{T^\circ_F} - \frac{(\Delta\bar{C}_p)_1}{(\bar{L}^\circ_{cl})_1}\right)\frac{\theta\,d\theta}{m_2}\end{aligned} \tag{7-5-54}$$

If we compare Eq. (7-5-54) with Eq. (7-5-49), we see that the last term on the right of (7-5-54) amounts to a correction added to the right of (7-5-49), in which no account was taken of the variation of $(\bar{L}_{cl})_1/T^2$ with temperature. Thus, integrating the first term on the right of (7-5-54) just as before, we obtain

TABLE 7-8. FREEZING-POINT-DEPRESSION DATA FOR n-PROPANOL IN H_2O*

m_2, moles/kg	θ, deg	θ/m_2, deg kg/mole	$1 - \frac{\theta}{m_2k_F'}$
0.00919	0.01702	1.8520	0.0043
0.01468	0.02721	1.8535	0.0035
0.01967	0.03618	1.8393	0.0111
0.03742	0.06884	1.8396	0.0110
0.04542	0.08342	1.8366	0.0126
0.05978	0.10977	1.8362	0.0128
0.07832	0.14274	1.8225	0.0202
0.10090	0.18383	1.8219	0.0205
0.11020	0.20131	1.8268	0.0178
0.13146	0.23929	1.8202	0.0214
0.14850	0.26983	1.8170	0.0231
0.17407	0.31684	1.8202	0.0214

m_2, moles/kg	$1 - \frac{\theta}{m_2k_F'}$	$\int_0^{m_2}\frac{\left(1 - \frac{\theta}{m_2k_F'}\right)dm_2}{m_2}$	$\ln\gamma_2'$	γ_2', 0°C
0.01	0.0035	0.0036	−0.0071	0.9929
0.02	0.0066	0.0070	−0.0136	0.9867
0.05	0.0138	0.0162	−0.0300	0.9705
0.10	0.0197	0.0280	−0.0477	0.9534
0.15	0.0219	0.0364	−0.0583	0.9434

* Freezing-point data of T. J. Webb and C. H. Lindsley, *J. Am. Chem. Soc.*, **56**, 874–878 (1934).

$$\ln\gamma_2' = -\left(1 - \frac{\theta}{m_2k_F'}\right) - \int_0^{m_2}\frac{\left(1 - \frac{\theta}{m_2k_F'}\right)}{m_2}\,dm_2 + \left(\frac{2}{T_F^\circ} - \frac{(\Delta\bar{C}_p)_1}{(\bar{L}_{cl}^\circ)_1}\right)\int_0^\theta \frac{\theta}{m_2k_F'}\,d\theta \qquad (7\text{-}5\text{-}55)$$

The corresponding equation for a strong electrolyte is:

$$\ln\gamma_\pm = -\left(1 - \frac{\theta}{\zeta m_2k_F'}\right) - \int_0^{m_2}\frac{\left(1 - \frac{\theta}{\zeta m_2k_F'}\right)}{m_2}\,dm_2 + \left(\frac{2}{T_F^\circ} - \frac{(\Delta\bar{C}_p)_1}{(\bar{L}_{cl}^\circ)_1}\right)\int_0^\theta \frac{\theta}{\zeta m_2k_F'}\,d\theta \qquad (7\text{-}5\text{-}56)$$

The coefficient of the integral appearing in the last terms of Eqs. (7-5-55) and (7-5-56) is a property of the pure solvent; for water, it has the value

+0.00112/deg. The entire correction term is small except at relatively high solute concentrations, and the integral itself may be evaluated easily by means of graphical integration. Lewis and Randall have developed further empirical methods for corrections when it becomes necessary to take account of the deviation of $(\lambda_{cl})_1$ from $(\bar{L}_{cl})_1$ at high solute concentrations.

In the case of an electrolytic solute, the extrapolation to zero concentration called for by the integral appearing in Eq. (7-5-51) [the second term on the right of Eq. (7-5-56)] may be carried out precisely by introduction of the Debye-Hückel limiting law as approximation function. In order to simplify the notation, let

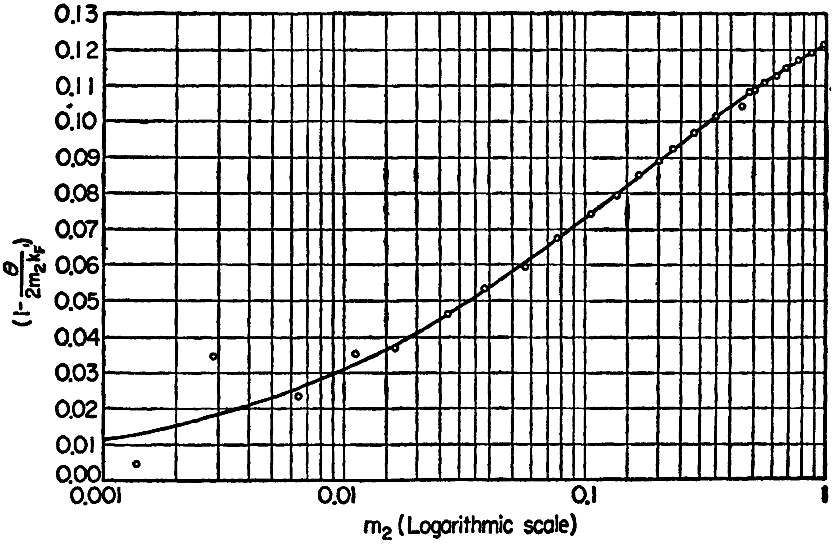

FIG. 7-25. Freezing-point-depression data for solutions of KCl in water: plot of $j = \left(1 - \frac{\theta}{2m_2k_F'}\right)$ vs. log m_2. [*Data of G. Scatchard and S. S. Prentiss, J. Am. Chem. Soc.*, **55**, 4355–4362 (1933).]

$$j \equiv 1 - \frac{\theta}{\zeta m_2 k_F'} \tag{7-5-57}$$

Then Eq. (7-5-56) assumes the form

$$\ln \gamma_\pm = -j - \int_0^{m_2} \frac{j}{m_2}\,dm_2 + \left(\frac{2}{T_F^\circ} - \frac{(\Delta\bar{C}_p)_1}{(\bar{L}_{cl}^\circ)_1}\right) \int_0^\theta (1 - j)\,d\theta \tag{7-5-58}$$

In Fig. 7-25, j has been plotted against log m_2 for aqueous KCl solutions, from work of G. Scatchard and S. S. Prentiss.[1] It is evident that even at concentrations below $0.01m$, there is significant deviation from ideal strong electrolyte behavior, which would call for $j = 0$. One will note that the area under the curve in Fig. 7-25 between any two values of m_2

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[1] G. Scatchard and S. S. Prentiss, *J. Am. Chem. Soc.*, **55**, 4355–4362 (1933).

represents 0.4343 $\int_{m_2'}^{m_2''} (j/m_2)dm_2$, so that one may use this figure for graphically computing the contribution to the second term on the right of Eq. (7-5-58) from some low concentration, such as $m_2 = 0.1$ mole/kg, up to the higher concentrations; the figure is not suitable, however, for extrapolation to $m_2 = 0$, since j remains significantly different from 0 even at the lowest solute concentrations for which experimental measurements are feasible. Now, if we substitute the general thermodynamic relation (7-5-47) in the Gibbs-Duhem equation (7-4-26) for electrolytes, we may readily show that

$$-\left(\frac{dT}{dm_2}\right)_p = \left(\frac{d\theta}{dm_2}\right)_p = \frac{RT^2}{(\lambda_{cl})_1}\,\frac{\bar{M}_1\zeta}{1000\text{ g/kg}}\left[1 + m_2\left(\frac{d\ln\gamma_\pm}{dm_2}\right)_{T,p}\right] \qquad (7\text{-}5\text{-}59)$$

[compare Eqs. (7-5-8*c*) and (7-5-19)]. This equation reduces in dilute solution, where we may assume that $(\lambda_{cl})_1 = (\bar{L}_{cl})_1$, and may neglect the variation of $(\bar{L}_{cl})_1$ with temperature, to

$$\left(\frac{d\theta}{dm_2}\right)_p = \zeta k_F'\left[1 + m_2\left(\frac{d\ln\gamma_\pm}{dm_2}\right)_{T,p}\right] \quad (m_2 \to 0) \qquad (7\text{-}5\text{-}60)$$

If we introduce the Debye-Hückel limiting law (7-4-28) in the form

$$-\ln\gamma_\pm = 2.303A'm_2^{1/2}$$

where A' equals z_+z_-A, multiplied by the numerical factor appropriate to the particular type of electrolyte for converting $\sqrt{\mu}$ to $\sqrt{m_2}$ [see (7-4-31*a*); the factors given there should be multiplied by 0.9615 for correction to H_2O at 0°C], then

$$\lim_{m_2\to 0}\left(\frac{d\theta}{dm_2}\right)_p = \zeta k_F'\left(1 - \frac{2.303}{2}A'm_2^{1/2}\right)$$

Integrating,

$$\lim_{m_2\to 0}\frac{\theta}{m_2} = \zeta k_F'\left(1 - \frac{2.303}{3}A'm_2^{1/2}\right)$$

or, expressed in terms of j [Eq. (7-5-57)],

$$\lim_{m_2\to 0} j = \frac{2.303}{3}A'm_2^{1/2} \qquad (7\text{-}5\text{-}61)$$

Let us introduce the variable

$$\delta_j \equiv j - \frac{2.303}{3}A'm_2^{1/2} \qquad (7\text{-}5\text{-}62)$$

Then Eq. (7-5-58) may be put in the form

$$-\log \gamma_\pm = \frac{j}{2.303} + \frac{2}{3} A' m_2^{1/2} + \int_0^{m_2} \frac{\delta_j}{2.303 m_2}\, dm_2 - \frac{C}{2.3} \int_0^\theta (1 - j)\, d\theta \tag{7-5-63}$$

where C represents the constant multiplying the integral in the last member of (7-5-58); for example, for a 1:1 electrolyte in aqueous solution,

$$-\log \gamma_\pm = \frac{j}{2.303} + 0.3263 m_2^{1/2} + \int_0^{m_2} \frac{\delta_j}{2.303 m_2}\, dm_2 - 0.00049 \int_0^\theta (1 - j)\, d\theta \tag{7-5-63a}$$

where

$$\delta_j = j - 0.3757 m_2^{1/2}$$

We are not assuming that the electrolyte actually satisfies the Debye-Hückel approximation at any of the finite concentrations for which experimental data can be obtained; Eq. (7-5-63) remains in fact an exact formula, within the assumptions involved in Eqs. (7-5-56) or (7-5-58) themselves; but we have replaced the integral appearing in the second member of Eq. (7-5-58) by an integral involving the deviation measure δ_j, which if the electrolyte ultimately conforms to the Debye-Hückel limiting law, should converge more rapidly as $m_2 \to 0$ than the original integral involving j itself. In Table 7-9, smoothed values of j, taken from the data of Scatchard and Prentiss shown in Fig. 7-25, are presented for dilute aqueous KCl solutions, together with δ_j values calculated according to Eq. (7-5-62);[1] in Fig. 7-26, $\delta_j/2.303m_2$ has been plotted against m_2, and since the scale of the plot is comparatively large, one has little difficulty in estimating by graphical integration the value of $\int_0^{m_2} (\delta_j/2.303m_2)dm_2$, recorded in the sixth column of Table 7-9. At concentrations below 0.05m, the value of the last term in Eq. (7-5-63) or Eq. (7-5-63a) is altogether negligible. The lower part of Table 7-9 contains j values and $-\log \gamma_\pm$ values for KCl at concentrations from 0.1 to 1.0m, as given by Scatchard and Prentiss. The results may be compared with those of the vapor-pressure measurements (at 25°C) recorded in Table 7-5.

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[1] Scatchard and Prentiss, *ibid.* Their j values are reported in terms of older values of the natural constants, for example, $k_F' = 1.858$ deg kg/mole. We have retained their older value of $A' = 0.4870$ in the computations entering Table 7-9. Scatchard and Prentiss used a more elaborate extrapolation function than (7-5-62), based on the more general form of the Debye-Hückel limiting law, (7-4-32), with an added empirical term linear in μ. Equations (7-5-62) and (7-5-63) serve adequately, however, to illustrate the method.

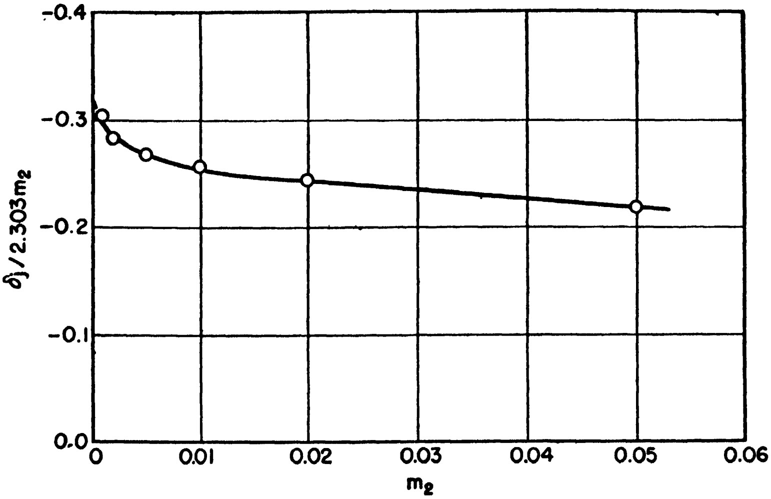

FIG. 7-26. Freezing-point-depression function $\delta_j/2.303m_2$ plotted against m_2 for dilute aqueous solutions of KCl. (*Data of Table* 7-9.)

TABLE 7-9. FREEZING-POINT DATA FOR AQUEOUS KCl SOLUTIONS*

Dilute Solutions

m_2, moles/kg	j	δ_j	$\frac{j}{2.303}$	$\frac{2}{3}A'm_2^{1/2}$	$\int_0^{m_2}\frac{\delta_j}{2.303m_2}\,dm_2$	$-\log\gamma_\pm$
0.001	0.0111	−0.0007	0.0048	0.0103	−0.0003	0.0148
0.002	0.0154	−0.0013	0.0067	0.0145	−0.0006	0.0206
0.005	0.0233	−0.0031	0.0101	0.0230	−0.0014	0.0317
0.01	0.0315	−0.0059	0.0137	0.0325	−0.0028	0.0434
0.02	0.0417	−0.0112	0.0181	0.0459	−0.0053	0.0587
0.05	0.0586	−0.0250	0.0254	0.0726	−0.0123	0.0857

Concentrated Solutions

m_2, moles/kg	j	$-\log\gamma_\pm$
0.1	0.0734	0.1121
0.2	0.0890	0.1430
0.3	0.0978	0.1632
0.4	0.1038	0.1782
0.5	0.1082	0.1903
0.6	0.1119	0.2006
0.7	0.1149	0.2093
0.8	0.1175	0.2171
1.0	0.1218	0.2302

* Data of G. Scatchard and S. S. Prentiss, *J. Am. Chem. Soc.*, **55**, 4355–4362 (1933).

In order to correlate thermodynamic data obtained in this way at the freezing point of the solvent with corresponding data obtained by other methods at higher temperatures, one must have information concerning the heat of solution. The equation for the change of ln $\gamma_\pm$ with temperature for given composition has been discussed previously [Eq. (7-4-41)].

7-6. Heterogeneous Equilibrium in General. We have seen that the *variance* of a homogeneous phase or solution containing C components is by nature $C + 1$. Thus, the variance of a homogeneous substance of fixed composition is 2, and for each dimension in which the composition can be independently and continuously varied, the variance increases by 1. This means, for example, that the intensive properties of a CO_2-N_2 gas mixture are completely fixed and reproducible at a given temperature, pressure, and composition (as specified for example by either mole fraction, y_{CO_2} *or* y_{N_2}); any *three* of the independently variable intensive properties of the system serve in this case to define its state; if there were given, for example, the temperature, pressure, and density of the gas, and one knew that it consisted of the two components, CO_2 and N_2, then the composition and all the other intensive properties would be implied, so that in this case, one could actually use the density at the given temperature and pressure to measure the composition. The extensive properties, such as the total volume, the total heat capacity, etc., depend also on the total mass, but as we have previously noted, when one has specified the values of as many of the independently variable intensive properties as correspond to the variance, $C + 1$, then each extensive property is fixed in relation to the others, in the sense that all are then in direct proportion to the total mass. If one has a homogeneous mixture containing *three* substances of fixed composition, with respect to each of which the composition may be continuously varied (perhaps within certain solubility limits), then it is a fact of experience that it takes *four* of the independently variable properties of the system to determine its state. For example, an aqueous solution containing 5 per cent by weight of NaCl and 12 per cent by weight of KCl would have a perfectly definite density, viscosity, specific heat, etc., at a specified temperature and pressure, but the properties at fixed temperature and pressure for a specified percentage of NaCl could still vary with the KCl concentration, and for fixed composition, they would depend on temperature and pressure (just as for a pure chemical substance, whose composition is inherently fixed). We use the term *number of components* in the sense of Secs. 7-1 and 3-1. In a mixture of NO_2 and N_2O_4 at ordinary temperatures and pressures, for example, since one cannot vary independently the amounts of NO_2 and of N_2O_4 present, the system has but one component, in agreement with its observed variance of 2; in doubtful cases, in fact, one might *define* the correct number of components of a given homogeneous phase by $v - 1$, where v represents its *observed* variance. We are furthermore excluding from consideration effects such as that of a strong magnetic or electric field, or of large variations in altitude, or of surfaces bounding the phase, etc., which may also influence the variance in special circumstances.

Now, if the C components are distributed among P different homogeneous phases, then in general the total variance of all P independent phases is represented by $P(C + 1)$. If the system of P phases is in a state of equilibrium, however, then the equilibrium conditions impose certain restrictions on the variance. One of these sets of restrictions is represented by the condition for *thermal stability*

$$T' = T'' = T''' = \cdot \cdot \cdot = T^{(P)} \tag{7-6-1}$$

If the temperatures of the phases were not equal, they could not be at equilibrium with each other; this condition is equivalent to our original concept of what is meant by temperature equality. A second independent set of restrictions is represented by the condition for *mechanical stability*

$$p' = p'' = p''' = \cdot \cdot \cdot = p^{(P)} \tag{7-6-2}$$

In the absence of mechanical barriers that would prevent free access to all parts of the system by any of the phases, the pressure has to be uniform throughout; otherwise the pressure differences would tend to set up relative motions among the phases.[1]

Finally, there are C conditions (7-1-20) governing the distribution of the different independent components among the phases

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[1] Variations due to hydrostatic pressure, such as one may encounter in a fluid phase at different heights, do not disturb the argument, because while the equilibrium pressure on some phase that may be at the bottom of the fluid column would be greater than the equilibrium pressure on some phase that may be near the top, there would still be an *explicit relation* between the two pressures, determined solely by the density of the fluid and the difference in height; the existence of such a *relation*, independent of conditions (7-6-1) and (7-6-3) is all that is required for the argument that follows. The thermodynamic potentials in the fluid phase would also vary with height, but in such a way that at equilibrium $\phi_i + gh\bar{M}_i$ would be constant for each component throughout the column. Therefore, while Eqs. (7-6-3) would not be quite true in this case, nevertheless at equilibrium, the thermodynamic potential of a given component in some phase at height h would differ from the thermodynamic potential of the same component in some other phase at height h_0 only by the amount $g(h - h_0)\bar{M}_i$, independently of temperature and pressure; the existence of such a relation is all that is required of Eqs. (7-6-3) in the argument that follows. See J. Willard Gibbs, "Collected Works," Vol. I, pp. 144*ff.*, Longmans, Green & Co., Inc., New York, 1928.

$$\left.\begin{array}{l}\phi_1' = \phi_1'' = \phi_1''' = \cdots = \phi_1^{(P)} \\ \phi_2' = \phi_2'' = \phi_2''' = \cdots = \phi_2^{(P)} \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \phi_C' = \phi_C'' = \phi_C''' = \cdots = \phi_C^{(P)}\end{array}\right\} \qquad (7\text{-}6\text{-}3)$$

because each component otherwise would tend to move from any phase in which its thermodynamic potential were higher to another phase in which its thermodynamic potential were lower at the same temperature and pressure.

The restrictions (7-6-1), (7-6-2), and (7-6-3) amount to $(P - 1)(C + 2)$ independent relations at equilibrium among the $P(C + 1)$ otherwise independent variables that determine the states of all P phases; thus, instead of C different temperatures, there is but one common temperature throughout the system when the different phases are in equilibrium with each other; likewise, there is but one common pressure, and but one common value of the thermodynamic potential of component 1, one common value of the thermodynamic potential of component 2, . . . , and one common value of the thermodynamic potential of component C. Therefore the net variance in the equilibrium conditions for a particular number of components, C, and a particular number of phases, P, is

$$v = C - P + 2 \qquad (7\text{-}6\text{-}4)$$

Relation (7-6-4) is the famous *phase rule* of J. Willard Gibbs. It implies restrictions of a quite general nature on the number of different phases that can coexist under externally imposed conditions of various sorts; otherwise expressed, it implies general restrictions on the number of independently variable properties of a system consisting of several different phases at equilibrium.

The applications of the phase rule are so extensive that many excellent treatises have been written, solely devoted to work in this field.[1] Its

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[1] The significance of the phase rule was first appreciated, following Gibbs's original deduction, by J. H. van't Hoff, who used it as a classifying principle in his great work on the analysis of the Stassfurt salt deposits, "Zur Bildung der ozeanischen Salzablagerungen," Friedrich Vieweg & Sohn, Brunswick, 1905–1909. At van't Hoff's suggestion, it was used by B. Roozeboom in experimental studies summarized in his monumental treatise, "Die Heterogenen Gleichgewichte," Friedrich Vieweg & Sohn, Brunswick, 1901–1904. Among recent works, we may mention W. C. Blasdale, "Equilibria in Saturated Salt Solutions," Reinhold Publishing Corporation, New York, 1927; S. T. Bowden, "Phase Rule and Phase Reactions," The Macmillan Company, New York, 1938; A. Findlay, "The Phase Rule and Its Applications," 8th ed., Longmans, Green & Co., Inc., New York, 1939; F. F. Purdon and V. W. Slater, "Aqueous Solution and the Phase Diagram," Edward Arnold & Co., London, 1946. The use of the phase rule is implicit, however, in many other works dealing with phase transitions at high pressures, distillation, metallography, solubility, etc.

main value has been as a classifying principle. For example, it makes clear the essential similarity between the behavior on boiling and the behavior on freezing of such a simple system as a solution of NaCl in water. When this solution is boiled at constant pressure, the two-component system, whose variance in general is equal to $(4 - P)$, has a variance of 1 ($P = 2$, with imposition of the additional condition of constant pressure); to each composition, there corresponds a particular boiling point, the boiling point rising as the water boils off. But when the solution has become so concentrated that a third phase, solid NaCl, begins to appear, then the system becomes invariant; the saturated NaCl solution has a constant boiling point, just like pure water, at the given pressure, and it continues to boil without further change in its composition (*i.e.*, the water boils off and the NaCl crystallizes out at such relative rates as to leave the liquid composition unchanged until the liquid has all boiled away). On the other hand, when the solution begins to freeze, we again have two phases at constant pressure,[1] and to each composition, there corresponds a particular freezing point, which falls as the water freezes out. Again, when the solution has become so concentrated that a third phase, solid NaCl, appears, the system becomes invariant, and the saturated NaCl solution has a constant freezing point, just like pure water. In this case, the ice and the NaCl then continue to crystallize out together in the characteristic form known as the *eutectic mixture,* in the same proportions as in the equilibrium liquid solution, until the liquid has all disappeared; the eutectic composition is of course generally unrelated to the composition of the saturated solution at the boiling point. As another example, if one evaporates at constant temperature a solution of $NaNO_3$ and KCl in water, then this three-component two-phase system (consisting of liquid and vapor phases) under the restriction of constant temperature has a variance of 2; one may have within certain limits any concentration of $NaNO_3$ and any concentration of KCl, the vapor pressure then being determined by the values of these two independent variables. When through evaporation of the water, the solution has become so concentrated that some one of the four possible salts, $NaNO_3$, KCl, KNO_3, or NaCl, begins to crystallize out (the particular one depending on the original concentrations and relative solubilities), the concentration of the liquid may still continue to undergo change with continued evaporation of the water. But when the solution has become so further concentrated that a second solid phase begins to appear (again, regardless of which particular one it happens to be, as determined by the original composi-

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[1] If one counts the atmosphere as a third phase in this case, then one must also count air as a third component, leaving the variance unchanged except in so far as air dissolved in the water affects its state slightly.

tion), then the system becomes invariant, behaving like the saturated NaCl solution in equilibrium with the one solid phase at the boiling point; it will have a unique vapor pressure, and further loss of water by evaporation from the liquid phase can take place only along with deposition of the two crystalline phases in such relative proportions as to leave the liquid composition unchanged until one of the phases (the liquid solution itself in this case) has disappeared. The value of such a classifying principle in the study of the variety of reactions that may take place during the crystallization of complex salt solutions is manifest.

The phase rule is used directly also in the analysis of experimental phase equilibrium data. Thus, a common method of determining the nature of alloys, minerals, and other solid mixtures of various kinds consists of so-called *thermal analysis;* molten samples of various compositions are allowed to cool more or less uniformly at constant (atmospheric) pressure, and the temperature followed as a function of time; the appearance of each new phase is indicated by a temporary decrease in the slope of the cooling curve, and when in particular a sufficient number of phases has appeared to cancel the variance, the temperature then halts until some one of the phases disappears. By correlating the temperatures at which each new phase first puts in its appearance, for various values of the original composition, one may put together the phase diagram for the system, and in the simpler cases, even infer the nature and composition of the various solid phases, without further chemical analysis. A similar technique is used in high-pressure analysis, where the sample is subjected to compression at various constant temperatures, and the volume noted for successive values of the pressure; at each invariant state, there is a halt in the p vs. V curve, the volume change at such values of the pressure corresponding evidently to phase transitions. In this way, for example, the various phases of solid water at high pressures were discovered, and also the effects of high pressures on the melting points and transitions points of many other solid substances.[1]

For our present purpose, let us discuss briefly one special case of heterogeneous equilibrium, that of the distribution of a third component between two slightly miscible liquids, *e.g.*, I_2 between CS_2 and H_2O. For such a three-component two-phase system, the variance in general is 3, but if the temperature and pressure are held constant, then the variance becomes 1. This means that at constant temperature and pressure, the

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[1] See, for example, G. Tammann, "States of Aggregation," English translation by R. F. Mehl, D. Van Nostrand Company, Inc., New York, 1925; E. Cohen, "Physico-chemical Metamorphosis and Problems in Piezochemistry," McGraw-Hill Book Company, Inc., New York, 1926; P. W. Bridgman, "The Physics of High Pressure," The Macmillan Company, New York, 1931.

concentration of the third component (the "solute") is independently variable in but one of the two liquid phases, the equilibrium concentration in the other phase being determined by the concentration in the first phase. The quantity $m_{2(A)}/m_{2(B)}$, or $C_{2(A)}/C_{2(B)}$ (these quantities having different though related numerical values), is known as the *distribution coefficient* of the solute, component 2, between the solvents A and B. From what has just been stated, the distribution coefficient at given pressure will be a function of the temperature, and of either $m_{2(A)}$ or $m_{2(B)}$, whichever one chooses to regard as independently variable. Measurement of the distribution ratio is of great practical importance in the operation of extraction, whether for the purpose of removing an undesired solute by washing the solution with a second solvent immiscible with the first, or for the purpose of concentrating a desired solute in a different solvent, from which it may be more conveniently recovered in the pure state.

The basic equilibrium condition that applies in this case, assuming that temperature and pressure have been equalized between the two phases, is

$$\phi_{2(A)} = \phi_{2(B)} \tag{7-6-5}$$

Assuming that the solute is a nonelectrolyte in both phases, we may express (7-6-5) in terms of activity coefficient notation by means of Eqs. (7-3-107); thus

$$\phi'_{2(A)} + RT \ln m_{2(A)} + RT \ln \gamma'_{2(A)} = \phi'_{2(B)} + RT \ln m_{2(B)} + RT \ln \gamma'_{2(B)}$$

from which we may derive as the thermodynamic expression for the molal distribution coefficient, K',

$$K' \equiv \frac{m_{2(A)}}{m_{2(B)}} = \frac{\gamma'_{2(B)}}{\gamma'_{2(A)}} \exp \frac{\phi'_{2(B)} - \phi'_{2(A)}}{RT} \tag{7-6-6}$$

In this equation, $\phi'_{2(B)}$ and $\phi'_{2(A)}$ technically represent "constants" for component 2 in the two liquid media consisting, respectively, of component B saturated with component A and of component A saturated with component B, but they will actually be independent of the values of $m_{2(B)}$ and $m_{2(A)}$, respectively, only if the presence of the solute, component 2, does not significantly alter the mutual solubilities of the two liquid solvents. This condition is by no means universally satisfied; for example, by adding sufficient acetic acid to water and chloroform, one may increase the mutual solubilities of the two liquid phases to such an extent that they ultimately become completely miscible with each other. Let us, however, confine our attention to situations in which the solute does not significantly alter the mutual solubilities of the two liquid solvents. In that case, we may express (7-6-6) in the form

$$K' \equiv \frac{m_{2(A)}}{m_{2(B)}} = \frac{\gamma'_{2(B)}}{\gamma'_{2(A)}} K'_0 \tag{7-6-7}$$

where K'_0 denotes a constant for the system, whose value is theoretically given by

$$RT \ln K'_0 = \phi'_{2(B)} - \phi'_{2(A)} \tag{7-6-8}$$

The values of $\gamma'_{2(B)}$ and $\gamma'_{2(A)}$ in Eq. (7-6-7) still refer to liquid B saturated with A, and liquid A saturated with B, respectively, rather than to the pure liquids, B and A, but if they are but slightly miscible, this distinction will generally not be significant. Now, as the solute concentrations in both phases are decreased, we may suppose that ultimately either or both approach ideal behavior, in the sense that

$$\lim_{m_{2(A)}\to 0} \gamma'_{2(A)} = 1; \qquad \lim_{m_{2(B)}\to 0} \gamma'_{2(B)} = 1 \tag{7-6-9}$$

This will *not* necessarily be so if the solute undergoes some special transformation, such as dissociation, polymerization, or reaction with the solvent, in either phase; distribution data in such cases constitute actually a quantitative means of studying the reaction. Assuming, however, that both solutions conform to Raoult's law in the ordinary sense as the solute concentration in either is made sufficiently small, then we may determine precisely the value of the so-called "thermodynamic distribution coefficient" K'_0 by extrapolating actual values of K' measured at finite concentrations, to zero solute concentration:

$$K'_0 = \lim_{m_{2(A)}\to 0} \frac{m_{2(A)}}{m_{2(B)}} \qquad (T,\ p \text{ const}) \tag{7-6-10}$$

In this way, we may obtain the difference between the ϕ'_2 values of the solute in the two solvents through Eq. (7-6-8), this difference representing the difference between the thermodynamic potentials of component 2 in hypothetical ideal dilute solutions at $m_2 = 1$ mole/kg in either solvent, or the so-called "standard" free-energy change for the transfer of 1 mole of the solute from ideal $1m$ solution in A to ideal $1m$ solution in B. Equation (7-6-10) serves itself as an approximation at sufficiently low solute concentrations, but does not necessarily continue to apply for concentrated solutions. A comparison of K' with K'_0, however, gives us the ratio of the activity coefficients in the two solvents [Eq. (7-6-7)]; if the activity coefficient values have been determined in the one solvent, or better still, if one of the two liquid solutions remains ideal over the composition ranges under investigation, then one may use precisely determined values of K', together with (7-6-10), to establish activity coefficient values in the other.

We could equally well write Eqs. (7-6-7) and (7-6-8) in terms of the molar concentrations, $C_{2(A)}$ and $C_{2(B)}$ [compare Eqs. (7-3-96) to (7-3-105)],

$$K'' \equiv \frac{C_{2(A)}}{C_{2(B)}} = \frac{\gamma''_{2(B)}}{\gamma''_{2(A)}} K''_0 \tag{7-6-11}$$

where K''_0 satisfies the relation

$$RT \ln K''_0 = \phi''_{2(B)} - \phi''_{2(A)} \tag{7-6-12}$$

and, provided that both solutions conform to Raoult's law at sufficiently low solute concentrations,

$$K''_0 = \lim_{C_{2(A)} \to 0} \frac{C_{2(A)}}{C_{2(B)}} \qquad (T, p \text{ const}) \tag{7-6-13}$$

The relationship between K'' and K' is evidently a purely formal one, depending on the relation (7-3-97) between m_2 and C_2 in the two solvents.

Examples of distribution coefficient data are given in Tables 7-10 and 7-11. Table 7-10 presents data for I_2 distributed between CS_2 and H_2O, from work of G. Herrero;[1] Fig. 7-27 shows K'' plotted against $(C_{I_2})_{H_2O}$, from which one obtains $K''_0 = 568$. Substituting in (7-6-11),

TABLE 7-10. DISTRIBUTION OF I_2 BETWEEN CS_2 AND H_2O AT 25°C*

$(C_{I_2})_{CS_2}$, moles/liter	$(C_{I_2})_{H_2O}$, moles/liter	$K'' = \frac{(C_{I_2})_{CS_2}}{(C_{I_2})_{H_2O}}$
0.16297	0.0002749	592
0.23696	0.0003939	602
0.30995	0.0005119	605
0.33753	0.0005519	611
0.38794	0.0006249	620
0.49692	0.0007918	627
0.54191	0.0008468	639
0.60191	0.0009248	650

* From data of G. Herrero, reported in Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIIa, p. 659, 1935.

$$\begin{aligned} I_2(a''_2 = 1 \text{ in } CS_2) &= I_2(a''_2 = 1 \text{ in } H_2O); \\ \Delta F_{298.16} &= \phi''_{I_2(H_2O)} - \phi''_{I_2(CS_2)} \\ &= RT \ln 568 = 3758 \text{ cal/mole} \end{aligned}$$

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[1] Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIIa, p. 659, 1935.

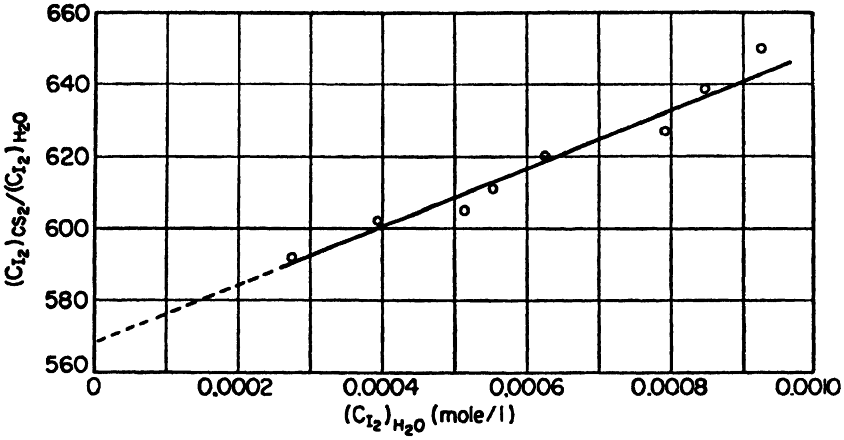

Fig. 7-27. Distribution of I_2 between carbon disulfide and water at 25°C. (*Data of G. Herrero.*)

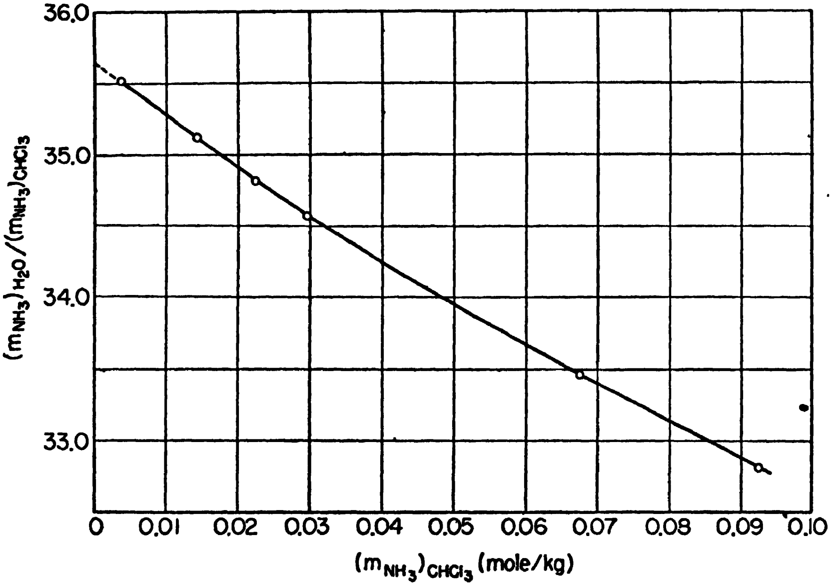

Fig. 7-28. Distribution of NH_3 between water and chloroform at 25°C. (*Data of H. E. Matthews and C. W. Davies.*)

Table 7-11 presents data for NH_3 distributed between water and chloroform, from work of H. E. Matthews and C. W. Davies.[1] In this case, a correction has to be made for ionization of NH_3 in the aqueous solution; condition (7-6-5) presumably applies only to the free NH_3, since the ions, NH_4^+ and OH^-, apparently do not enter the $CHCl_3$ phase. The figures given in the fifth column represent K' for the free NH_3 in both phases, and in Fig. 7-28, K' has been plotted against $(m_{NH_3})_{CHCl_3}$, yielding as $m_{NH_3} \rightarrow 0$, $K'_0 = 35.637$. Thus

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[1] H. E. Matthews and C. W. Davies, *J. Chem. Soc.*, 1435–1439 (1933).

$$NH_3(a_2' = 1 \text{ in } H_2O) = NH_3(a_2' = 1 \text{ in } CHCl_3);$$

$$\begin{aligned}\Delta F_{298.16} &= \phi'_{NH_3(CHCl_3)} - \phi'_{NH_3(aq)}\\ &= RT \ln 35.637 = 2117.2 \text{ cal/mole}\end{aligned}$$

TABLE 7-11. DISTRIBUTION OF NH_3 BETWEEN H_2O AND $CHCl_3$ AT 25°C*

$(m_{NH_3})_{H_2O}$	$(m_{NH_3})_{CHCl_3}$	$\dfrac{(m_{NH_3})_{H_2O}}{(m_{NH_3})_{CHCl_3}}$	α in H_2O	K' (corr. for ionization)
(0)	(0)	......	....	(35.637)
0.12890	0.003587	35.934	0.01186	35.509
0.49757	0.01408	35.333	0.005936	35.123
0.77957	0.02229	34.981	0.00470	34.819
1.0264	0.02957	34.707	0.00399	34.567
2.2678	0.06762	33.538	0.00235	33.460
3.0349	0.09233	32.868	0.00191	32.806

* Data of H. E. Matthews and C. W. Davies, *J. Chem. Soc.*, 1435–1439 (1933).

7-7. Donnan Equilibrium. In Sec. 7-6*b*, we considered the equilibrium of a solution separated from pure solvent by means of a semipermeable membrane that freely transmits the solvent but not the solute. This situation gives rise to the familiar phenomenon of osmosis, and we found that pressure had to be applied to the solution in order to maintain equilibrium; the effect of the applied pressure is to restore the thermodynamic potential of the solvent in the solution back to its value for the pure solvent at the given temperature and ordinary pressure.

There is another type of membrane, useful in colloid chemistry, known as a dialyzing membrane. This type of membrane, which may consist, for example, of a thin film of collodion or of cellophane, transmits not only the solvent, which is generally water, but also the smaller types of solute particles, including ions of the simpler inorganic salts. They are impermeable, however, to the macromolecules encountered in colloid chemistry, such as gelatin, albumen, rubber latex, colloidal iron hydroxide, etc. They are commonly used in the freeing by elution of a colloidal dispersion from solute impurities of lower molecular weight.

Now, most colloids bear charges in solution, and behave generally as electrolytes; the mobility of the colloidal ion is of course much lower than that of ordinary ions, because of its much greater size, and this accounts in part for the distinctive properties of colloidal dispersions. Gelatin and many other proteins are actually amphoteric; in aqueous solutions more acid than pH = 4.7, gelatin behaves as a cation, while in solutions more basic than pH = 4.7, it behaves as an anion. The simpler proteins are high copolymers of certain amino acids, and apparently the presence of free carboxyl and free amino groups in the structure accounts for the acid and basic properties, as shown by the pioneer work of Jacques Loeb.[1]

It occurred to F. G. Donnan,[2] in 1911, that if one had a membrane transmitting certain kinds of ions, but not others, then an unequal distribution of the ions that can pass through the membrane must be set up on either side at equilibrium, as a result of the requirement of electrical neutrality on both sides. To be specific, let us consider the distribution of the ions of NaCl across a dialyzing membrane on one side of which there is present the compound NaR, the ion R^- being unable to pass through the membrane; thus, in Donnan's original experimental work, he chose the relatively simple compound, congo red, the sodium salt of tetraazodiphenylnaphthionic acid, whose molecular weight is about 620, and in a later investigation, he used KCl in the presence of $K_4Fe(CN)_6$, the $Fe(CN)_6^{----}$ ion being unable to pass through a suitably prepared $Cu_2Fe(CN_6)$ membrane (precipitated in parchment), permeable to KCl in aqueous solution.[3] Since NaCl and the solvent H_2O can both transfuse through the membrane, the general requirement for equilibrium is that

$$\left.\begin{aligned}(\phi_{H_2O})_i &= (\phi_{H_2O})_o\\ (\phi_{NaCl})_i &= (\phi_{NaCl})_o\end{aligned}\right\} \tag{7-7-1}$$

subscript i representing conditions inside the membrane, where NaR is also present, and subscript o representing conditions outside, where only NaCl is present. For mathematical simplicity, let us suppose that we are dealing with 1 kg of solvent on either side. Since the thermodynamic potential of the strong electrolyte, NaCl, is given in general by Eq. (7-4-20), in the form

$$\phi_{NaCl} = \phi'_{NaCl(aq)} + RT \ln m_{Na^+}m_{Cl^-}\gamma_\pm^2$$

the second of the equilibrium conditions (7-7-1) reduces to

$$(m_{Na^+})_i(m_{Cl^-})_i(\gamma_\pm)_i^2 = (m_{Na^+})_o(m_{Cl^-})_o(\gamma_\pm)_o^2 \tag{7-7-2}$$

assuming that the presence of the other solute, NaR, on the inside does not significantly affect the value of $\phi'_{NaCl(aq)}$. No such condition as (7-7-2) applies to NaR, because this substance cannot get through the membrane. There remains, however, the requirement of electrical neutrality on both sides of the membrane:

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[1] J. Loeb, "Proteins and the Theory of Colloidal Behavior," McGraw-Hill Book Company, Inc., New York, 1922.

[2] F. G. Donnan, *Z. Elektrochem.*, **17**, 572–581 (1911); also, *Chem. Revs.*, **1**, 73–90 (1924).

[3] F. G. Donnan and A. B. Harris, *J. Chem. Soc.*, **99**, 1554–1577 (1911); F. G. Donnan and A. J. Allmand, *ibid.*, **105**, 1941–1963 (1914).

$$\left.\begin{aligned}(m_{\mathrm{Na}^+})_i &= (m_{\mathrm{Cl}})_i + (m_{R^-})_i \\ (m_{\mathrm{Na}^+})_o &= (m_{\mathrm{Cl}^-})_o\end{aligned}\right\} \tag{7-7-3}$$

Let us obtain an approximate solution of the system of equations (7-7-2) and (7-7-3) by supposing that at reasonably low concentrations of NaR, the mean ionic activity coefficient of NaCl will be the same on either side of the membrane; then, combining (7-7-3) with (7-7-2),

$$[(m_{\mathrm{Cl}^-})_i + (m_R)_i](m_{\mathrm{Cl}^-})_i = (m_{\mathrm{Cl}^-})_o^2 \tag{7-7-4}$$

Let R_0 represent the total number of moles of NaR, and C_0 the total number of moles of NaCl introduced originally in the system; then

$$\left.\begin{aligned}(m_{R^-})_i &= R_0 \\ (m_{\mathrm{Cl}^-})_i + (m_{\mathrm{Cl}^-})_o &= C_0\end{aligned}\right\} \tag{7-7-5}$$

in view of our assumption that there is 1 kg of the solvent on either side (this assumption is not necessary, but eliminates circumlocution in the argument). Substituting in (7-7-4) and solving for $(m_{\mathrm{Cl}^-})_o$,

$$\begin{aligned}[R_0 + C_0 - (m_{\mathrm{Cl}^-})_o][C_0 - (m_{\mathrm{Cl}^-})_o] &= (m_{\mathrm{Cl}^-})_o^2 \\ (m_{\mathrm{Cl}^-})_o &= \frac{C_0(R_0 + C_0)}{2C_0 + R_0}\end{aligned} \tag{7-7-6}$$

Substituting back in the second of Eqs. (7-7-5), and solving for $(m_{\mathrm{Cl}^-})_i$

$$(m_{\mathrm{Cl}^-})_i = \frac{C_0^2}{2C_0 + R_0} \tag{7-7-7}$$

Combining (7-7-6) with (7-7-7), we finally obtain

$$\frac{(m_{\mathrm{Cl}^-})_o}{(m_{\mathrm{Cl}^-})_i} = 1 + \frac{R_0}{C_0} \tag{7-7-8}$$

The distribution of Cl^- on the two sides of the membrane is thus determined by the ratio of NaR to NaCl present in the entire system, assuming that we are dealing with equal quantities of solvent on both sides. For example, if R_0/C_0 is but $1/10$, there will tend to be a 10 per cent higher concentration of Cl^- outside than inside the membrane, and there will consequently be a considerable difference in the behavior of the system from what we might expect if the diffusion of Cl^- were totally uninhibited.

The data in Table 7-12, obtained by Donnan and Allmand for $K_4Fe(CN)_6$-KCl solutions separated from KCl solutions by means of $Cu_2Fe(CN)_6$ membranes, illustrate the working of the theory. The Donnan distribution equation (7-7-8) has been abundantly confirmed in many other cases, and in particular in the case of the proteins. Thus, Jacques Loeb demonstrated that in the analogous case of cationic gelatin in dilute HCl solution, separated by a collodion dialyzing membrane from a dilute HCl solution containing no gelatin, the H^+ concentration at equilibrium was lower on the gelatin side than on the gelatin-free side of the membrane, the ratio being governed by a relationship similar to that of (7-7-8); in fact, he used the Donnan equilibrium as one of the central pieces of evidence in his brilliant exposition of the essential similarity between the physical chemical properties of the proteins and those of ordinary chemical substances, allowing merely for the difference in molecular size and complexity.[1] Donnan and Guggenheim have extended the theoretical analysis of Donnan equilibria to include the effect of deviations from ideal behavior, as represented by the activity coefficients which in the approximate treatment we canceled out of Eq. (7-7-2), and to include also more complex types of equilibria, involving more than three different kinds of ions.[2] The essential characteristics are illustrated, however, by the simple case we have described.

TABLE 7-12. DONNAN EQUILIBRIUM FOR $K_4Fe(CN)_6$-KCl*

Equilibrium concentrations, g-eq/liter			$1 + \frac{R_0}{C_0}$	$\frac{(Cl^-)_o}{(Cl^-)_i}$	$\frac{(K^+)_i}{(K^+)_o}$
$K_4Fe(CN)_6$ in	KCl in	KCl out			
0.0100	0.0187	0.0225	1.242	1.20	1.28
0.0102	0.0460	0.0497	1.107	1.08	1.13
0.0094	0.2277	0.2278	1.021	1.00	1.04
0.0946	0.0082	0.0264	3.73	3.22	3.89
0.0983	0.0888	0.1162	1.48	1.31	1.61
0.0973	0.2210	0.2513	1.21	1.14	1.27

* Data of F. G. Donnan and A. J. Allmand, *J. Chem. Soc.*, **105**, 1941–1963 (1914).

Because of the Donnan distribution, the osmotic pressure of NaR within the membrane may be significantly lowered when a diffusing electrolyte such as NaCl is also present. In order to show this, let us calculate the excess of total ionic concentration inside over total ionic concentration outside after equilibrium has been established:

$$m_i - m_o = (m_{R^-})_i + (m_{Na^+})_i + (m_{Cl^-})_i - (m_{Na^+})_o - (m_{Cl^-})_o$$

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[1] Loeb, *op. cit.*, Chap. VIII.

[2] F. G. Donnan and E. A. Guggenheim, *Z. physik. Chem.*, (A)**162**, 346–360 (1932); F. G. Donnan, *ibid.*, (A)**168**, 369–380 (1934).

Introducing Eqs. (7-7-3), (7-7-6), and (7-7-7),

$$\begin{aligned} m_i - m_o &= 2R_0 + 2(m_{\text{Cl}^-})_i - 2(m_{\text{Cl}^-})_o \\ &= 2R_0 \left[\frac{C_0 + R_0}{2C_0 + R_0}\right] = 2R_0 \left[1 - \frac{1}{\left(2 + \frac{R_0}{C_0}\right)}\right] \end{aligned} \qquad (7\text{-}7\text{-}9)$$

If the NaCl were not present, the osmotic pressure in dilute solution would ideally be proportional to $2R_0$ [Eq. (7-5-33)]; as C_0 is increased in relation to R_0, however, the factor multiplying $2R_0$ in Eq. (7-7-9) decreases from 1 ultimately to 0.5, as shown in Table 7-13. The presence of the diffusing electrolyte has in other words the same net effect as though it had repressed the ionization of the nondiffusing electrolyte. This effect on the osmotic pressure has been confirmed experimentally.

TABLE 7-13. IDEAL DONNAN EQUILIBRIUM DISTRIBUTION

$\frac{R_0}{C_0}$	$\frac{(m_{\text{Cl}^-})_o}{(m_{\text{Cl}^-})_i}$	$\frac{(m_i - m_o)}{2R_0}$
0	1.0	(0.500)
0.01	1.01	0.502
0.1	1.1	0.524
1	2	0.667
10	11	0.917
100	101	0.990
∞	∞	1.000

Since the molecular weights of typical colloids such as the proteins and starches are much larger than those of ordinary inorganic salts, it takes a comparatively small quantity of a diffusing electrolyte such as NaCl, considered on a weight basis, to produce a low value of R_0/C_0. Equation (7-7-9) thereby implies that a small proportion by weight of a diffusing electrolyte may have a marked effect in lowering the osmotic pressure of a nondiffusing electrolyte with respect to a dialyzing membrane. This effect undoubtedly has physiological implications in relation to the transfusion of water through living tissues, which are not, however, our present concern. The magnitude of the effect, like the magnitude of osmotic pressure itself, depends in no way on the mechanism of transfusion through the membrane (an interesting problem in itself), but is governed solely by thermodynamic equilibrium principles.

General References for Chapter 7

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Problems

7-1. From Fig. 7-5, estimate by the tangent-intercept method $\zeta_{C_2H_4}$ in a mixture containing $y_A = 0.25$ at each of the four pressures represented, and using Eq. (7-2-14), determine by graphical integration the value of $\nu_{C_2H_4}$ for the given mixture at each pressure. (Check your results against Fig. 7-9.)

7-2. (*a*) Using Figs. 6-2 to 6-4, estimate fugacity coefficients of N_2 and H_2 in a $1N_2{:}3H_2$ gas mixture at 0°C under total pressures of 200, 600, and 1000 atm, assuming Amagat's law, and compare with the actual values represented in Fig. 7-7.

(*b*) Do the same for a 1:1 mixture of argon and ethylene at 24.95°C under total pressures of 50 and 125 atm, comparing with the actual values given in Fig. 7-9.

7-3. Test the Duhem-Margules relationship (7-3-8) on the data for CS_2-acetone solutions presented in Fig. 7-10*e* at $x_{CS_2} = 0.25$, 0.50, and 0.75.

7-4. Given the following information for $x_{CH_3OH} = 0.50$ methanol-water solution at 59.4°C: $p = 433$ mm Hg, $(dp/dx_{CH_3OH})_T = 360$ mm Hg, $y_{CH_3OH} = 0.81$, estimate by means of Eq. (7-3-9*a*) the effect on the equilibrium vapor composition of a change from $x_{CH_3OH} = 0.50$ to $x_{CH_3OH} = 0.60$ in the liquid composition (compare Fig. 7-10*d*).

7-5. From Fig. 7-11*b*, estimate the Henry's law constant for $CH_3OH(l)$ in $H_2O(l)$ at 25°C, and calculate the value of $\phi^\circ_{CH_3OH(aq)} - \bar{F}^\circ_{CH_3OH(l)}$. Calculate also the thermodynamic potentials of CH_3OH and H_2O at $x_{CH_3OH} = 0.10$ relative to their values at infinitely dilute solution in $H_2O(l)$.

7-6. From the data presented in Fig. 7-10*e*, calculate thermodynamic potentials relative to the pure liquids for CS_2 and acetone at 29.2°C in solutions containing $x_{CS_2} = 0.20$, 0.40, 0.60, and 0.80, and compute the "excess" free energy of solution per mole of solution formed, over the ideal value given by Eq. (7-3-31), at each composition.

7-7. Using the ideal-solution equation (7-3-39), estimate the effect on the boiling point of adding 10 mole per cent of chlorobenzene to benzene, whose normal boiling point is 80.10°C and latent heat of vaporization is 7353 cal/mole. The vapor pressure of pure chlorobenzene at 80.10°C is 149.5 mm Hg.

7-8. Using smoothed data from the curves in Fig. 7-10*d*, calculate activity coefficients relative to the pure liquids for CH_3OH and H_2O in their solutions at 59.4°C for $x_{CH_3OH} = 0.2$, 0.4, 0.6, and 0.8, and compute van Laar constants from the data at each composition. Using the mean values of the constants, estimate γ_{CH_3OH} and γ_{H_2O}, and also p_{CH_3OH} and p_{H_2O}, at $x_{CH_3OH} = 0.5$, and compare with the actual data given by Fig. 7-10*d*.

7-9. Calculate van Laar constants for solutions of *n*-propanol and water at 87.7°C (the azeotropic boiling point at 1 atm) from the azeotropic composition: 56.83 mole per cent H_2O (the "International Critical Tables," Vol. 3, p. 318, 1928); the vapor pressures of the pure components at the given temperature are respectively 0.688 and 0.634 atm.

Using Eqs. (7-3-56) and (7-3-57), estimate the vapor pressure at 87.7°C of a solution containing 5.0 mole per cent propanol.

The best values of the van Laar constants at 25°C are given in Fig. 7-13c. With the aid of Eq. (7-3-60), estimate from your values at 87.7°C the total molal heat of solution of *n*-propanol (l) in H_2O(l), and of H_2O(l) in *n*-propanol (l).

7-10. From the following data for the ethyl alcohol–ethyl acetate azeotrope at various pressures, calculate van Laar constants at each temperature, neglecting the specific effect of the pressure differences on the activity coefficients in the liquid state:

p, mm Hg	t, °C	$x_{C_2H_5OH}$
200	38.4	0.334
400	54.9	0.396
600	65.4	0.436
760	71.8	0.464
900	76.5	0.485

("International Critical Tables," Vol. III, p. 323, 1928; look up the necessary vapo pressures of the pure components).

From plots of A_1 and A_2, vs. $1/T$, estimate the mean total heats of solution of ethyl alcohol (l) in ethyl acetate (l) and of ethyl acetate (l) in ethyl alcohol (l), and estimate also the partial vapor pressures and total vapor pressure of the 50 mole per cent solution at 60°C.

7-11. The following solubility data have been reported for NH_3(g) in H_2O(l) at 25°C (F. E. C. Scheffer and H. J. de Wijs, in Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement I, p. 303, 1927):

C_{NH_3}, moles/liter	p_{NH_3}, mm Hg
0.0618	0.791
0.1883	2.41
0.339	4.41
0.601	7.96
1.005	13.46
1.242	16.94
1.618	22.38

Correcting C_{NH_3} for ionization at the lower concentrations, calculate p_{NH_3}/C_{NH_3} at each concentration, and calculate the Henry's law constant for NH_3(g) in H_2O(l). From this value, calculate the standard free energy of solution: $\phi''_{NH_3(aq)} - \bar{F}^\circ_{NH_3(g)}$.

The partial pressure of NH_3(g) in equilibrium with a solution containing 10.35 moles/liter at 25°C is 173.9 mm Hg (Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement I, p. 304, 1927). Calculate γ''_{NH_3} in this solution. Calculate also γ'_{NH_3}, the solution containing 10.34 moles/kg H_2O.

7-12. The following data have been obtained by R. H. Wright and O. Maass (Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIIc, p. 2527, 1936) for the solubility of H_2S(g) in water at 10, 25, and 40°C:

10°C		25°C		40°C	
p_{H_2S}, mm Hg	C_{H_2S}, moles/liter	p_{H_2S}, mm Hg	C_{H_2S}, moles/liter	p_{H_2S}, mm Hg	C_{H_2S}, moles/liter
294.7	0.0597	369.1	0.0497	431.6	0.0426
606	0.1220	754	0.1010	879	0.0858
905	0.1801	1120	0.1499	1315	0.1260
1270	0.2511	1557	0.2050	1798	0.1722
1558	0.3060	1911	0.2544	2223	0.2149
2103	0.4099				

(*a*) Calculate $\lim_{C_2 \to 0} (p_2/C_2)$ at each temperature, and determine therefrom the standard free energy of solution, $\phi''_{H_2S(aq)} - \bar{F}^\circ_{H_2S(g)}$, at 25°C, and the mean standard enthalpy of solution, $\eta^\circ_{H_2S(aq)} - \bar{H}^\circ_{H_2S(g)}$. Compare the latter result with

$$\Delta H_s = -4.52 \text{ kcal}$$

at 20°C obtained by H. Zeumer and W. A. Roth (Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIIc, p. 2747, 1936) from direct calorimetric measurements. (In this case, most of the heat of solution represents heat evolved on condensation of H_2S from the gaseous to the liquid state; the latent heat of vaporization of H_2S(l) at its normal boiling point, 212.85°K, is 4.463 kcal/mole.)

(*b*) Calculate ν_{H_2S} at the highest pressure given in the table at 25°C, using Berthelot's equation of state (Prob. 6-10), and calculate accordingly the value of γ''_{H_2S} in the corresponding aqueous solution.

7-13. The partial pressures of Br_2 from its solutions in CCl_4(l) were measured at 25°C by G. N. Lewis and H. Storch [*J. Am. Chem. Soc.*, **39**, 2544–2554 (1917)], with the following results:

x_{Br_2}	p_{Br_2}, mm Hg
0.00394	1.52
0.00420	1.60
0.00599	2.39
0.0102	4.27
0.0130	5.43
0.0236	9.57
0.0238	9.83
0.0250	10.27

By plotting p_{Br_2}/x_{Br_2} vs. x_{Br_2}, show that Br_2 in CCl_4(l) satisfies Henry's law over the dilute composition range, and evaluate the Henry's law constant, k_2.

They found also that when Br_2 was distributed between CCl_4(l) and H_2O(l) containing 0.001*m* HCl or H_2SO_4 to repress hydrolysis, the distribution ratio in dilute solution had the constant value $m_{Br_2(H_2O)}/x_{Br_2(CCl_4)} = 0.371$. Furthermore the vapor pressure of pure Br_2(l) at 25°C is 213 mm Hg. Calculate $\phi'_{Br_2(aq)}$, *i.e.*, the standard free-energy change for the process

$$Br_2(l) = Br_2(aq)$$

Calculate also the activity coefficient γ' of Br_2 in the saturated aqueous solution, in which $m_{Br_2} = 0.207$ mole/kg, assuming that the thermodynamic potential of Br_2 in the saturating liquid phase [Br_2(l) saturated with H_2O] is practically the same as in pure Br_2(l).

7-14. Using the data in Fig. 7-11*b* and the result of Prob. 7-5, calculate mole-fraction activity coefficients γ° for CH_3OH relatively to the infinitely dilute solution in water at $x_{CH_3OH} = 0.20$, 0.40, 0.60, 0.80, and 1.00. Calculate also the value of $\phi'_{CH_3OH(aq)} - \bar{F}^\circ_{CH_3OH(l)}$, the standard free energy of solution to form the hypothetical ideal dilute solution at 1*m* concentration.

7-15. The solubility of $Ba(OH)_2{\cdot}8H_2O$(c) in water at 25°C is 0.2296 mole/kg H_2O, and the activity coefficient in the saturated solution, from emf data by H. S. Harned and C. M. Mason [*J. Am. Chem. Soc.*, **54**, 1439–1442 (1932)] is $\gamma_\pm = 0.358$. Calculate the standard free energy of solution.

One may assume in this case that ϕ_{H_2O} in the saturated solution is practically equal to $\bar{F}^\circ_{H_2O(l)}$ of pure water.

7-16. The solubility of $Al(NO_3)_3{\cdot}9H_2O$(c) in water at 25°C is 3.161 moles/kg; the mean ionic activity coefficient in the saturated solution, whose vapor pressure is 14.370 mm Hg, is $\gamma_\pm = 1.16$ (as a 3:1 electrolyte), from vapor-pressure measurements by J. N. Pearce and L. E. Blackman [*J. Am. Chem. Soc.*, **57**, 24–27 (1935)]. Calculate the standard free energy of solution: $\phi'_{Al(NO_3)_3(aq)} - \bar{F}^\circ_{Al(NO_3)_3{\cdot}9H_2O(c)}$.

7-17. Given from a variety of experimental sources that the mean ionic activity coefficient of KCl in 1*m* aqueous solution at 25°C has the value $\gamma_\pm = 0.606$ (W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," pp. 318–327, Prentice-Hall, Inc., New York, 1938), calculate from the data in Table 7-5 the mean ionic activity coefficient in the saturated solution, and calculate the standard free energy of solution: $\phi'_{KCl(aq)} - \bar{F}^\circ_{KCl(c)}$. Estimate by interpolation the value of m_2 at which the thermodynamic potential of KCl in aqueous solution is actually equal to $\phi'_{KCl(aq)}$ (that is, $m_2\gamma_\pm = 1$).

7-18. The following vapor-pressure data have been obtained for aqueous solutions of $HClO_4$ at 25°C by J. N. Pearce and A. F. Nelson [*J. Am. Chem. Soc.*, **55**, 3075–3081 (1933)]:

m, moles/kg	*p*, mm Hg	*m*, moles/kg	*p*, mm Hg
0	23.752	3.1512	20.192
0.10016	23.672	4.2734	18.387
0.20064	23.593	5.4347	16.308
0.40257	23.429	6.6372	13.935
0.60655	23.254	7.8719	11.490
0.81037	23.067	9.1723	9.016
1.01589	22.870	10.513	6.838
2.0661	21.693	11.905	4.982

Using (7-4-27), evaluate $\gamma_\pm$ at integral values of *m* from 1 to 12 moles/kg H_2O. The integral may be evaluated from $m = 0$ to $m = 0.5$ mole/kg by taking note of the fact that $\gamma_\pm$ for $HClO_4$ is practically identical with that of HCl up to that concentration; therefore set $\gamma_\pm$ at $m = 0.5$ mole/kg in Eq. (7-4-27) equal to that of HCl, as read from Fig. 7-18. Evaluate the integral from $m = 0.5$ mole/kg up by graphical means.

7-19. R. A. Robinson and D. A. Sinclair [*J. Am. Chem. Soc.*, **56**, 1830–1835 (1934)] have worked out a clever isopiestic vapor-pressure method for measuring activity coefficients of nonvolatile solutes by equilibrating their solutions through the vapor phase with solutions of a standard nonvolatile solute (*e.g.*, KCl or H_2SO_4) whose activity coefficient has been established precisely as a function of solute concentration. In this way, the concentration m_2 at which the "unknown" solute gives rise to the same solvent partial vapor pressure, or thermodynamic potential ϕ_1, as the concentration m_0 of the standard solute is determined by analysis of the two solutions after equilibrium has been established between them. Prove that for two 1:1 electrolytes, where m_2 and m_0 represent respective molalities satisfying the isopiestic condition,

$$\ln \frac{(\gamma\pm)_2}{(\gamma\pm)_0} = \ln \frac{m_0}{m_2} + 2 \int_0^{a_0} \frac{\left(\frac{m_0}{m_2} - 1\right)}{a_0^{1/2}}\, d(a_0^{1/2})$$

where $a_0 \equiv m_0(\gamma_\pm)_0$. (The relationship is put in this form, in terms of $a_0^{1/2}$, because the integral then converges particularly rapidly as $a_0 \rightarrow 0$.)

7-20. The following (selected) pairs of solute concentrations giving rise to the same water vapor pressure were determined at 25°C for KCl and LiI by R. A. Robinson and D. A. Sinclair [*J. Am. Chem. Soc.*, **56**, 1830–1835 (1934)]:

m_{KCl}	m_{LiCl}	m_{KCl}	m_{LiCl}
0.1235	0.1197	1.334	1.098
0.1714	0.1630	1.757	1.392
0.2034	0.1910	2.079	1.613
0.2646	0.2485	2.625	1.956
0.5751	0.5176	2.909	2.127
0.7964	0.6852	3.596	2.529
1.160	0.9705	4.183	2.832
		4.81	3.152

Plot $\left(\frac{m_{KCl}}{m_{LiI}} - 1\right) \Big/ a_{KCl}^{1/2}$ vs. $a_{KCl}^{1/2}$, using for $(\gamma_\pm)_{KCl}$ the results summarized in the following table (draw a large-scale graph for interpolation),

m_{KCl}	$(\gamma_\pm)_{KCl}$	m_{KCl}	$(\gamma_\pm)_{KCl}$
0.1	0.766	1.5	0.581
0.2	0.715	2.0	0.572
0.3	0.684	2.5	0.569
0.5	0.648	3.0	0.570
0.7	0.624	4.0	0.578
1.0	0.602	4.8	0.590

and evaluating the integral called for by the equation derived in the preceding problem by graphical means, compute $(\gamma_\pm)_{LiI}$ at m_2 = 0.5, 1.0, 2.0, and 3.0 moles/kg H_2O.

What further information is required for the establishment of $\phi'_{\text{LiI(aq)}}$ relatively to $\bar{F}^\circ_{\text{LiI(c)}}$?

7-21. The partial pressure of HCl(g) from the more concentrated aqueous solutions has been measured at 25°C by S. J. Bates and H. D. Kirschman [*J. Am. Chem. Soc.*, **41,** 1991–2001 (1919)], with the following (selected) results:

m_{HCl}, moles/kg	p_{HCl}, mm Hg
3.240	0.00780
5.041	0.0557
6.018	0.1487
7.148	0.385
8.950	1.819
9.990	4.260

Calculate the thermodynamic potential of HCl at each concentration, relative to $\bar{F}^\circ_{\text{HCl(g)}}$. Given that $\gamma_\pm = 1.759$ at $m = 4$ mole/kg, from emf data by H. S. Harned and R. W. Ehlers [*J. Am. Chem. Soc.*, **55,** 2179–2193 (1933)] (see Chap. 9), calculate $\gamma_\pm$ at each of the above concentrations (plot log p_{HCl} vs. m_{HCl} for interpolating to find the value of p_{HCl} at $m_{\text{HCl}} = 4$ moles/kg.) From the fact that $\gamma_\pm = 0.796$ at $m = 0.1$ mole/kg (emf data), calculate also the partial pressure of HCl at that concentration.

7-22. From the following freezing-point-depression data obtained by T. J. Webb and C. H. Lindsley [*J. Am. Chem. Soc.*, **56,** 874–878 (1934)], for solutions of ethanol in water, calculate γ' of C_2H_5OH at $m_2 = 0.1$, 0.2, and 0.5 mole/kg H_2O:

m_2, moles/kg H_2O	θ, deg
0.009815	0.01833
0.01879	0.03493
0.03503	0.06522
0.07423	0.13706
0.13477	0.24821
0.18263	0.33535
0.3092	0.5666
0.4150	0.7579
0.5160	0.9396

From the following additional data by A. Lalande (Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIIc, p. 2679, 1936), calculate γ' at $m_2 = 5$ moles/kg H_2O:

m_2, moles/kg H_2O	θ, deg
1.038	1.92
2.137	4.00
4.174	8.06
6.888	14.66

7-23. From the following freezing-point-depression data obtained by G. Scatchard, S. S. Prentiss, and P. T. Jones [*J. Am. Chem. Soc.*, **56,** 805–807 (1934)], for solutions of $KClO_3$ in $H_2O(l)$, determine the mean ionic activity coefficient $\gamma_\pm$ of $KClO_3$ in the saturated solution at the eutectic point, and calculate therefrom the value of

$$\phi'_{\text{KClO}_3\text{(aq)}} - \bar{F}^\circ_{\text{KClO}_3\text{(c)}}$$

at the eutectic temperature:

m_2, moles/kg H_2O	j, Eq. (7-5-57)
0.001	0.0105
0.002	0.0144
0.005	0.0221
0.01	0.0308
0.02	0.0435
0.05	0.0686
0.10	0.0960
0.20	0.1325
0.2515	0.1481 (eutectic; $t = -0.7955°C$)

7-24. The following freezing-point data were obtained by G. Scatchard, S. S. Prentiss, and P. T. Jones [*J. Am. Chem. Soc.*, **56,** 805–807 (1934)], for solutions of $KClO_4$ in $H_2O(l)$:

m_2, moles/kg H_2O	θ, deg
0.003612	0.01316
0.006690	0.02421
0.009872	0.03509
0.016215	0.05712
0.030369	0.10541
0.048335	0.16359 (eutectic)

Determine the mean ionic activity coefficient $\gamma_\pm$ of $KClO_4$ in the saturated solution, and calculate therefrom the value of $\phi'_{KClO_4(aq)} - \bar{F}^\circ_{KClO_4(c)}$. The enthalpy of solution at 18°C is 11,740 cal/mole (1 in 400 H_2O); neglecting the variation of this quantity with temperature, estimate the correction of $\phi'_{KClO_4(aq)} - \bar{F}^\circ_{KClO_4(c)}$ from 0 to 25°C.

7-25. Plot the data for HCl and for CsCl shown in Figs. 7-18 and 7-19 in the form of $\log \gamma_\pm + A\sqrt{\mu}$ vs. μ, and from the limiting slope in dilute solution, determine B' for each electrolyte in Eq. (7-4-34). Calculate therefrom the respective values of d_i, and test how well Eq. (7-4-32) reproduces the data at the higher concentrations.

Repeat, using the data for $CaCl_2$.

7-26. Introducing the Debye-Hückel limiting law (7-4-31) in the limiting boiling-point-elevation law (7-5-19), derive a formula for the molal boiling-point elevation $\Delta T_b/m_2$ for a strong 2:1 electrolyte in sufficiently dilute solution. Test the formula by plotting $\Delta T_b/m_2$ against $m_2^{1/2}$ from the following data for K_2SO_4 solutions [E. Plake, *Z. physik. Chem.*, (A)**172,** 113–128 (1935)], noting the $m_2 = 0$ intercept and the value of the limiting slope:

m_2, moles/kg	ΔT_b, deg
0.000809	0.00123
0.00162	0.00242
0.00324	0.00467
0.00647	0.00915
0.0158	0.0214
0.0348	0.0446
0.0654	0.0808
0.164	0.191
0.327	0.363

7-27. Introducing the Debye-Hückel limiting law (7-4-31) in the osmotic-pressure equation (7-5-32), derive a limiting expression in dilute solution for the osmotic pressure of a strong 1:1 electrolyte. Test the formula by plotting $\pi/\zeta C_2RT$ vs. $m_2^{1/2}$ for the following data obtained by J. C. W. Frazer and W. A. Patrick [*Z. physik. Chem.*, (A) **130,** 691–698 (1927)] in the case of dilute aqueous KCl solutions at 24.85°C:

m_2, moles/kg	π, mm Hg
0.00836	278.7
0.00539	186.0
0.00175	62.8
0.00047	17.4

By what per cent does the observed osmotic pressure deviate from the ideal van't Hoff expression for a strong 1:1 electrolyte at the highest concentration represented in the table?

7-28. R. H. Stokes and R. A. Robinson [*J. Am. Chem. Soc.*, **70,** 1870–1878 (1948)] have modified the Debye-Hückel limiting law to take into account the presumed hydration of the ions. They have obtained as a result the formula (at 25°C):

$$\log \gamma_\pm = -\frac{0.5092 z_1 z_2 \sqrt{\mu}}{1 + 0.3286 d \sqrt{\mu}} - \frac{n}{\zeta} \log a_1 - \log \left[1 - 0.018(n - \zeta) m_2\right]$$

where d is an empirical parameter representing the mean ionic diameter (in angstrom units) of the hydrated ions (generally larger than the value in the corresponding Debye-Hückel formula), and n is another parameter representing the number of water molecules "bound" by the ζ ions produced by each "molecule" of electrolyte. For KCl, they have proposed $n = 1.9$ and $d = 3.63$ between $m_2 = 0.1$ and 4.0 mole/kg. Test this formula at $m = 1$, 2, 3, and 4 mole/kg, against the following experimental data (compare Table 7-5), noting that μ is equal to the molar *volume* concentration for the 1:1 electrolyte:

m_2, moles/kg H_2O	Density, g/ml	p_{H_2O}, mm Hg	$\gamma_\pm$, obs
0	0.9971	23.752	1.000
1	1.0415	23.017	0.604
2	1.0816	22.243	0.573
3	1.1191	21.497	0.569
4	1.1526	20.696	0.577

For $BaCl_2$, they have proposed $n = 7.7$ and $d = 4.45$, between $m = 0.1$ and 1.8 moles/kg. Test their formula at $m = 1.0$ mole/kg, where $\gamma_\pm(\text{obs}) = 0.395$; the vapor pressure of the solution (for computing $\log a_1$) is 22.77 mm Hg, and the density may be found (by interpolation) in the "International Critical Tables."

7-29. Using the thermal data for HCl-H_2O solutions given in Table 4-10, plot Q_s vs. $m_2^{1/2}$ for selected values of the concentration up to $1HCl:100H_2O$, and test the validity of the theoretical limiting slope given by Eq. (7-4-43c) (note that the change of Q_s with concentration is equal in magnitude but opposite in sign to the change of Φ_h). Confirm the value of Q_s° given in Table 4-10 by extrapolation of your graph to $m_2 = 0$.

7-30. F. H. MacDougall [*J. Am. Chem. Soc.*, **52,** 1390–1393 (1930)], obtained the following (selected) data for the solubility of silver acetate in water and in aqueous KNO_3 solutions at 25°C:

m_{KNO_3}, moles/kg H_2O	ρ, g/ml	m_{AgAc}, moles/kg H_2O	C_{AgAc}, moles/liter	
0	1.0047	0.06685	0.06642	0.06642
0.2001	1.0180	0.07659	0.07547	0.2727
0.4010	1.0298	0.08171	0.07982	0.4715
0.8021	1.0537	0.08786	0.08449	0.8558
1.5437	1.0944	0.09453	0.08828	1.5180
3.0139	1.1653	0.10163	0.08960	2.8807

Assuming the Debye-Hückel limiting law in the form (7-4-32), where for the saturated solution

$$C_{AgAc}(\gamma''_{\pm})_{AgAc} = (K_c^\circ)^{1/2}$$

use the first two sets of data to obtain the two constants: K_c° (the thermodynamic molar concentration solubility product) and Bd_i. From the value of K_c° so derived, calculate from the data experimental values of $(\gamma''_{\pm})_{AgAc}$ at each set of conditions given, and determine the range of validity of Eq. (7-4-32). (Compare also F. H. MacDougall and J. Rehner, *J. Am. Chem. Soc.*, **56,** 369–372 (1934).]

7-31. The osmotic pressure of a polyisobutylene sample in cyclohexane and in benzene has been measured by P. J. Flory [*J. Am. Chem. Soc.*, **65,** 372–382 (1943)], using a collodion type of membrane. The results at 25°C are given in the following table:

Concentration, c_2, g/liter	Osmotic pressure, π, g/cm²	
	C_6H_{12}	C_6H_6
20.0	12.10	2.145
15.0	6.80	1.575
10.0	3.12	1.025
7.5	1.79	
5.0	0.93_5	0.505
2.5	0.36	

Plot π/c_2 for both solvents against c_2, and by extrapolating to $c_2 \rightarrow 0$, calculate the molecular weight of the high polymer in both solvents. Estimate the per cent of deviation of the observed osmotic pressure from the ideal van't Hoff value at the highest solute concentration given in the table for both solvents.

CHAPTER 8

CHEMICAL EQUILIBRIUM

In this chapter, we shall explore the thermodynamic conditions for equilibrium of a chemical transformation. Since chemical equilibria are usually studied under conditions of constant specified temperature and pressure, the equilibrium conditions are most conveniently represented in terms of the Gibbs free-energy function. Extensive free-energy tables have been compiled, bearing to equilibrium data a relationship analogous to the relationship between enthalpy tables and thermochemical data. Such free-energy tables have been of inestimable value in the correlation of equilibrium data for diverse reactions and in the prediction of the courses of chemical transformations under hitherto untested conditions.

8-1. Free Energy and Equilibrium of a Chemical Transformation. Let us consider a general chemical transformation, whose chemical equation is represented by

$$aA + bB + \cdots = lL + mM + \cdots \tag{8-1-1}$$

The associated free-energy change has the form

$$\Delta F = l\phi_L + m\phi_M + \cdots - a\phi_A - b\phi_B - \cdots \tag{8-1-2}$$

where for substances participating as pure phases, the thermodynamic potential ϕ may be replaced by the corresponding molal free energy, determined solely by temperature and pressure, but for constituents of solutions, ϕ may depend on the composition as well. At any rate, the value of ΔF is determined solely by the initial states of the reactants and the final states of the products. According to the general thermodynamic condition (5-61) for equilibrium,

$$\left.\begin{aligned} (\Delta F)_{T,p} &= 0 & &(W' = 0) \\ l\phi_L + m\phi_M + \cdots &= a\phi_A + b\phi_B + \cdots & &(T, p \text{ const}) \end{aligned}\right\} \tag{8-1-3}$$

Whenever the reactants and products are in equilibrium, they will be in states satisfying this relationship.

Equation (8-1-3) represents in most general form the *law of mass action*, as we shall observe in the development of the following applications.[1]

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[1] This law was first stated as an empirical principle by C. M. Guldberg and P. Waage, "Études sur les affinités chimiques," Brögger and Christie, Christiania, 1867.

a. Reactions Involving Pure Liquids and Pure Crystalline Phases Only

Example:

$$Ag(c) + \tfrac{1}{2}Hg_2Cl_2(c) = AgCl(c) + Hg(l)$$

At given temperature and pressure:

$$\Delta F = \bar{F}_{AgCl(c)} + \bar{F}_{Hg(l)} - \bar{F}_{Ag(c)} - \tfrac{1}{2}\bar{F}_{Hg_2Cl_2(c)}$$

Since the molal free energies of the individual pure chemical substances are completely determined by T and p, it follows that the value of ΔF is fixed at given temperature and pressure, independently of any effect of the masses of the participating substances present. At given temperature and pressure, the reaction can go only in the one direction or in the other (whichever corresponds to the negative value of ΔF), so long as one does not expend energy in nonthermal form on the system [compare Eq. (5-58) in general]. At 25°C and 1 atm, $\Delta F^\circ_{298.16} = -1065$ cal.[1]

The effect of pressure on ΔF may be estimated from Eq. (6-10), applied term by term,

$$\left(\frac{d\Delta F}{dp}\right)_T = \Delta V \tag{8-1-4}$$

Since at 25°C and 1 atm, $\Delta V = -2.7$ ml, ΔF changes with pressure at the rate of -0.065 cal/atm for this reaction. The effect of temperature follows from the application of Eq. (6-12) term by term to ΔF:

$$\frac{d(\Delta F^\circ/T)}{dT} = -\frac{\Delta H^\circ}{T^2} \tag{8-1-5}$$

Equation (8-1-5) represents a special case of *van't Hoff's law*, of which further applications will be given presently. According to this equation, there could conceivably be some temperature at the given pressure (1 atm) at which ΔF° might undergo a change of sign; only at such a unique transition temperature, where $\Delta F^\circ = 0$, could a system of the type under consideration be in a state of equilibrium at 1 atm pressure. In the present example, it happens that $\Delta H^\circ_{298.16} = 1276$ cal;[2] therefore according to (8-1-5), ΔF° changes with temperature at a rate of about -0.8 cal/deg. As a matter of fact, ΔF° remains negative for the reaction down at least as far as the freezing point of the mercury.

However, in the closely related system,

$$Na_2SO_4{\cdot}10H_2O(c) = Na_2SO_4(c) + 10H_2O(l, \text{satd } Na_2SO_4)$$

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[1] From data compiled by W. M. Latimer, "Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, 1938. The value of ΔF for this reaction has been measured directly by electrochemical means, to be discussed in Chap. 9 [see Eq. (9-2-5)].

[2] F. D. Rossini, *J. Research Natl. Bur. Standards*, **9**, 679–702 (1932).

which differs from the preceding system in that the liquid phase here contains both components at relatively high concentrations, there actually is such a transition point, at 32.38°C (the transition temperature varies slightly with pressure); at higher temperatures, $Na_2SO_4{\cdot}10H_2O(c)$ tends to go out of existence, while at lower temperatures, $Na_2SO_4(c)$ in contact with the saturated solution tends to take up water to form the crystalline hydrate. We may represent the free-energy change at 1 atm in general by the equation

$$\begin{aligned}\Delta F &= \bar{F}^\circ_{Na_2SO_4(c)} + 10\phi_{H_2O} - \bar{F}^\circ_{Na_2SO_4\cdot 10H_2O(c)}\\ &= \bar{F}^\circ_{Na_2SO_4(c)} + 10\bar{F}^\circ_{H_2O(l)} + 10RT\ln a_1^* - \bar{F}^\circ_{Na_2SO_4\cdot 10H_2O(c)}\end{aligned}$$

where a_1^* represents the activity of H_2O in the saturated solution. The vapor pressure of the saturated solution at the transition temperature has been measured, and has the value 0.0405 atm;[1] the vapor pressure of pure water at the same temperature is 0.0480 atm; therefore according to (7-3-45) [compare also (7-5-4)], $a_1^* = 0.0405/0.0480 = 0.844$. With ΔF known to be zero at the transition point, we thus obtain the following experimental relationship among the standard molal free energies of the pure compounds

$$\begin{aligned}\Delta F^\circ = \bar{F}^\circ_{Na_2SO_4(c)} + 10\bar{F}^\circ_{H_2O(l)} - \bar{F}^\circ_{Na_2SO_4\cdot 10H_2O(c)} &= -10RT\ln 0.844\\ &= 1030\text{ cal}\quad (T = 305.54°\text{K})\end{aligned}$$

from which the value of any one $\bar{F}^\circ_{305.54}$ could be calculated from established values of the other two.

b. Reactions between Pure Liquid or Crystalline Phases and a Pure Gas Phase

Example:

$$CaCO_3(c) = CaO(c) + CO_2(g)$$

At given temperature:

$$\begin{aligned}\Delta F &= \bar{F}^\circ_{CaO(c)} + (\bar{F}^\circ_{CO_2(g)} + RT\ln p_{CO_2}) - \bar{F}^\circ_{CaCO_3(c)}\\ &= \Delta F^\circ_T + RT\ln p_{CO_2}\end{aligned}$$

assuming that CO_2 satisfies the ideal-gas law at the pressures under consideration. Therefore, from the equilibrium condition (8-1-3),

$$RT\ln p_{CO_2} = -\Delta F^\circ_T \tag{8-1-6}$$

At high CO_2 pressures, we could write

$$RT\ln p_{CO_2}\nu_{CO_2} = -\Delta F^\circ_T \tag{8-1-6a}$$

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[1] "International Critical Tables," Vol. VII, p. 305, McGraw-Hill Book Company, Inc., New York, 1930.

where ν_{CO_2} represents the fugacity coefficient of CO_2 at the temperature T and pressure p_{CO_2}, neglecting the relatively small effect of pressure on the free energies of the solid phases. Thus, we conclude that at each temperature, there is a particular value of p_{CO_2} [the so-called *dissociation pressure* of $CaCO_3(c)$] at which equilibrium may be maintained; at lower CO_2 pressures, $CaCO_3(c)$ tends to decompose, whereas at higher pressures, $CaO(c)$ tends to take up CO_2. The dissociation pressures for this system at temperatures up to the eutectic point of CaO-$CaCO_3$ are presented in Table 8-1, from work of F. H. Smyth and L. H. Adams.[1] At these temperatures and pressures, the deviation of CO_2 from ideal-gas behavior is inappreciable. The constant ΔF_T° for the reaction at each temperature is called the *standard free energy of reaction;* it represents what the change in free energy would be if each substance were in its standard state, *i.e.*, in this case as a pure phase at 1 atm. Its value at each temperature is listed in the third column of Table 8-1. Evidently, if we had independent information concerning the $\bar{F}_T^\circ$ values for any two of the three chemical substances, we could use the present data to calculate $\bar{F}_T^\circ$ for the third. In examples of this type, a large negative value of ΔF_T° evidently represents a high dissociation pressure, greater than 1 atm, whereas a large positive value represents a low dissociation pressure, lower than 1 atm.

TABLE 8-1. DISSOCIATION PRESSURE OF $CaCO_3(c)$*

$CaCO_3(c) = CaO(c) + CO_2(g)$

T, °K	p_{CO_2}, atm	ΔF_T°, cal
1115.4	0.4513	1763.5
1126.0	0.5245	1443.9
1127.6	0.5317	1415.4
1142.0	0.6722	901.4
1177.4	1.157	− 341.0
1179.6	1.151	− 329.7
1210.1	1.770	− 1373.0
1322.4	6.439	− 4894.1
1355.6	8.892	− 5886.5
1430.8	18.687	− 8324.7
1499.4	34.333	−10536.2
1514.0	39.094	−11029.5

* F. H. Smyth and L. H. Adams, *J. Am. Chem. Soc.*, **45**, 1167–1184 (1923).

The effect of temperature on the dissociation pressure may be deduced by application of Eq. (8-1-5):

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[1] F. H. Smyth and L. H. Adams, *J. Am. Chem. Soc.*, **45**, 1167–1184 (1923); see also the "International Critical Tables," Vol. VII, p. 297, McGraw-Hill Book Company, Inc., New York, 1930.

$$\frac{d(\Delta F_T^\circ/T)}{dT} = -R\frac{d \ln p_{CO_2}}{dT} = -\frac{\Delta H_T^\circ}{T^2} \tag{8-1-7}$$

Thus

$$\frac{d \ln p_{CO_2}}{dT} = \frac{\Delta H_T^\circ}{RT^2} \tag{8-1-8}$$

This equation also is a special case of the more general van't Hoff relation, and bears a close resemblance to the Clausius-Clapeyron equation for the vapor pressure of a pure liquid or solid, in the form (6-69). In Eq. (8-1-8), ΔH_T° represents the standard enthalpy of reaction, and varies with T according to Kirchhoff's law (4-14). We may therefore use the observed values of p_{CO_2} taken over a range of temperatures to establish the value of ΔH_T°. For this purpose, let us put Eq. (8-1-8) in the convenient equivalent form

$$\frac{d \log p_{CO_2}}{d(1/T)} = -\frac{\Delta H_T^\circ}{2.3026R} \tag{8-1-9}$$

which shows that if we plot log p_{CO_2} vs. $1/T$, then the slope at any value of T will represent $-\Delta H_T^\circ/2.3026R$; over temperature ranges sufficiently small so that the variation of ΔH_T° with temperature is inappreciable, the curve will be practically a straight line. The data of Table 8-1 have been plotted in this way in Fig. 8-1. Smyth and Adams have given an

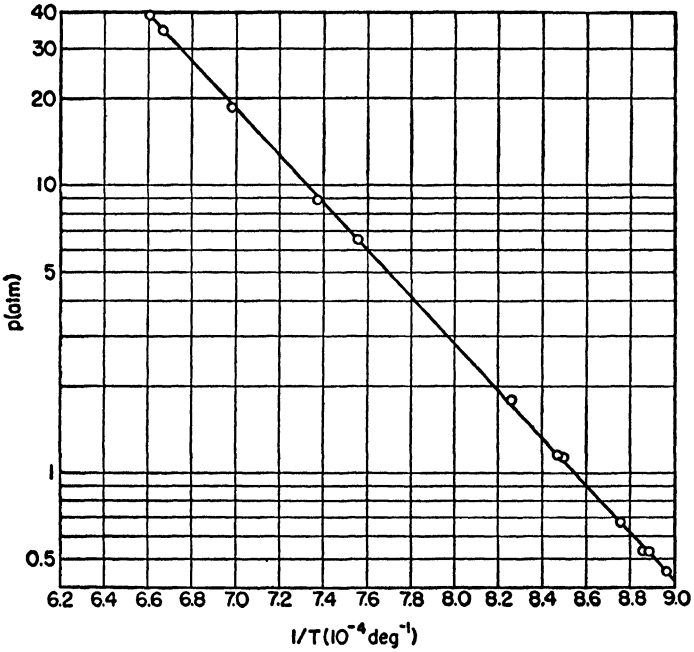

FIG. 8-1. Log p_{CO_2} vs. $1/T$ for equilibrium of the reaction $CaCO_3(c) = CaO(c) + CO_2(g)$. (*Data of F. H. Smyth and L. H. Adams.*)

empirical equation that fits their data closely; with p in atm,

$$\log p_{CO_2} = -\frac{11{,}355}{T} - 5.388 \log T + 26.238 \qquad (8\text{-}1\text{-}10)$$

We may therefore calculate the value of ΔH°_T analytically by applying (8-1-9) to (8-1-10),

$$\frac{d \log p_{CO_2}}{d(1/T)} = -11{,}355 + \frac{5.388}{2.3026} T$$

$$\Delta H^\circ_T = 51{,}957 - 10.707T \quad (1100\text{–}1500°\text{K}) \qquad (8\text{-}1\text{-}11)$$

Now, the heat of this reaction has been measured thermochemically at room temperature by H. L. J. Bäckström, from the difference between the heats of solution of CaO(c) and of $CaCO_3$(c, calcite) in dilute HCl;[1] thus

$$\Delta H^\circ_{298.16} = 42{,}600 \pm 200 \text{ cal}$$

Let us use K. K. Kelley's heat-capacity equations to calculate thermochemical values of ΔH°_T at the high temperatures:[2]

$$CaCO_3(c)\colon \bar{C}^\circ_p = 19.68 + 11.89 \times 10^{-3}T - \frac{3.076 \times 10^5}{T^2} \quad (273\text{–}1033°\text{K})$$

$$CaO(c)\colon \bar{C}^\circ_p = 10.00 + 4.84 \times 10^{-3}T - \frac{1.080 \times 10^5}{T^2} \quad (273\text{–}1173°\text{K})$$

$$CO_2(g)\colon \bar{C}^\circ_p = 10.34 + 2.74 \times 10^{-3}T - \frac{1.955 \times 10^5}{T^2} \quad (273\text{–}1200°\text{K})$$

Thus, the value of ΔC°_p for the reaction is represented by

$$\Delta C^\circ_p = 0.66 - 4.31 \times 10^{-3}T + 0.041 \times \frac{10^5}{T^2} \quad (273\text{–}1033°\text{K})$$

We shall ignore the contribution of the last term, which is relatively small in this case, and thus we may derive a purely thermochemical equation for ΔH°_T in the form

$$\begin{aligned}\Delta H^\circ_T &= 42{,}600 + \int_{298.16}^{T} (0.66 - 4.31 \times 10^{-3}T)\,dT \\ &= 42{,}595 + 0.66T - 2.16 \times 10^{-3}T^2 \quad (273\text{–}1033°\text{K}) \qquad (8\text{-}1\text{-}12)\end{aligned}$$

The ranges of Eqs. (8-1-11) and (8-1-12) do not quite overlap, but let us compare them at 900, 1000, 1100, and 1170°K (the latter temperature corresponding to $p_{CO_2} = 1$ atm):

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[1] H. L. J. Bäckström, *J. Am. Chem. Soc.*, **47**, 2437–2442, 2443–2449 (1925).

[2] K. K. Kelley, *U.S. Bur. Mines Bull.* 371 (1934).

T, °K	ΔH°_T (thermal), Eq. (8-1-12), cal	ΔH°_T (equilibrium), Eq. (8-1-11), cal
900	41,430	42,320
1000	41,100	41,250
1100	40,650	40,180
1170	40,410	39,430

The agreement at 900 and 1000°K is excellent; the discrepancy at higher temperatures results at least in part from failure of the simple empirical heat-capacity equations over the extended temperature range.

Let us now use Eq. (8-1-12) in order to integrate Eq. (8-1-7) down to 298.16°K, using the empirical equation (8-1-10) in order to extrapolate the equilibrium data slightly until they come within the proper range of (8-1-12); thus, at $T = 1000$°K, $\log p_{CO_2} = -1.281$, $(\Delta F^\circ_T/T) = 5.860$. Hence

$$\begin{aligned}\frac{\Delta F^\circ_{298}}{298} - 5.860\,\frac{\text{cal}}{\text{deg}} &= -\int_{1000}^{298}\left(\frac{42595}{T^2} + \frac{0.66}{T} - 2.16\times10^{-3}\right)dT\\ &= -42595\,(1/1000 - 1/298) - 0.66\ln 298/1000\\ &\qquad + 2.16\times10^{-3}\,(298 - 1000)\\ &= 99.40\ \text{cal/deg}\\ \Delta F^\circ_{298.16} &= 31{,}380\ \text{cal}\end{aligned}$$

This figure is slightly uncertain, because the heat-capacity equations and the equilibrium data do not quite overlap. Bäckström, using the heat-capacity equation,

$$\Delta C^\circ_p = -3.34 + 1.378\times10^{-2}T - 4.13\times10^{-6}T^2$$

derived the result

$$\Delta F^\circ_{298.16} = 31{,}258\ \text{cal}$$

If we apply Eq. (8-1-6), we may now calculate formally the value of p_{CO_2} at 25°C; it turns out to be 0.973×10^{-23} atm. This minute number has of course no practical significance. Theoretically it is important because of its implication that even though the reaction

$$CaCO_3(c) = CaO(c) + CO_2(g)$$

apparently goes completely to the left at room temperature, nevertheless it is in principle reversible, and we can even calculate a CO_2 pressure below which the reaction would tend to go to the right; this hypothetical p_{CO_2} is, of course, merely another unit for measuring ΔF°_T, until we attain temperatures high enough for the pressure to come within the range of direct physical observation.

An exactly comparable situation exists in the equilibrium of many crystalline hydrates with their anhydrous forms, or lower hydrates.

Example:

$$Na_2SO_4{\cdot}10H_2O(c) = Na_2SO_4(c) + 10H_2O(g)$$

At given temperature:

$$\begin{aligned}\Delta F &= \bar{F}^\circ_{Na_2SO_4(c)} + 10\bar{F}^\circ_{H_2O(g)} + 10RT\ln p_{H_2O} - \bar{F}^\circ_{Na_2SO_4\cdot 10H_2O(c)} \\ &= \Delta F^\circ_T + RT\ln (p_{H_2O})^{10}\end{aligned}$$

where, however, the standard free energy of reaction ΔF°_T, as represented here, contains a term for water in the gaseous not the normal liquid state at ordinary temperatures. Thus, for equilibrium,

$$RT\ln (p_{H_2O})^{10} = -\Delta F^\circ_T \tag{8-1-13}$$

and therefore the equilibrium value of p_{H_2O} is fixed at each temperature. Table 8-2 presents the dissociation pressure for this system at various temperatures. At higher partial water-vapor pressures than the equilibrium values given in the table, the anhydrous salt tends to take on water to form the hydrate, while at lower partial water-vapor pressures, the hydrate tends to dissociate to form the anhydrous salt. These tendencies are completely independent of the quantities of the two solid phases present, so long as both are there; a mixture of the two solids, in sufficient bulk so that neither runs the risk of being completely consumed, may be used as a means of maintaining an atmosphere of constant humidity, within an enclosure.

In this case, Eq. (8-1-7) takes the form

$$\frac{d(\Delta F^\circ/T)}{dT} = -10R\frac{d\ln p_{H_2O}}{dT} = -\frac{\Delta H^\circ}{T^2}$$

or

$$\frac{d\log p_{H_2O}}{d(1/T)} = -\frac{\Delta H^\circ}{10 \times 2.303R} \tag{8-1-14}$$

Applying Eq. (8-1-13) in particular at 25°C, we may calculate the value of the standard free energy of the reaction at that temperature:

$$\begin{aligned}\Delta F^\circ_{298.16} &= \bar{F}^\circ_{Na_2SO_4(c)} + 10\bar{F}^\circ_{H_2O(g)} - \bar{F}^\circ_{Na_2SO_4\cdot 10H_2O} \\ &= -10RT\ln 0.0252 = 21{,}800 \text{ cal}\end{aligned}$$

From this result, the value of any one of the three standard molal free energies can be determined from the values of the other two, obtained from other sources. The value of $\Delta \bar{F}^\circ_{298.16}$ so measured represents the free-energy change that would take place if 1 mole of $Na_2SO_4 \cdot 10H_2O(c)$ were to decompose completely into $Na_2SO_4(c)$ and $H_2O(g)$ at a hypothetical pressure of 1 atm at 25°C.

TABLE 8-2. DISSOCIATION PRESSURE OF $Na_2SO_4 \cdot 10H_2O(c)$*

t, °C	p_{H_2O}, atm
0	0.0050
5	0.0068
10	0.0092
15	0.0128
20	0.0183
25	0.0252
27	0.0276
29	0.0316
31	0.0367
32.4	0.0405

* Selected from the "International Critical Tables," Vol. VII, p. 304, McGraw-Hill Book Company, Inc., New York, 1930.

In cases of this kind, the water-vapor dissociation pressure has to be smaller than the vapor pressure of water from the saturated aqueous solution of the compound, or more precisely, the thermodynamic potential of water in the equilibrium gas phase in the presence of the two crystalline phases has to be smaller than its thermodynamic potential in the saturated aqueous solution at the same temperature; otherwise the hydrate will tend to "melt," or dissolve in its own water of hydration. This actually happens to $Na_2SO_4 \cdot 10H_2O(c)$ at temperatures above 32.4°C; above this temperature, the hydrate decomposes into a mixture of anhydrous salt and saturated aqueous solution, while the dry anhydrous salt, on the other hand, instead of taking up water vapor to form the hydrate, deliquesces when the partial pressure of water vapor in the surrounding atmosphere becomes greater than the vapor pressure of the saturated solution. At the transition temperature itself, the dissociation pressure is just equal to the partial vapor pressure of water from the saturated aqueous solution, as we saw in a preceding example.

It would be conceivable on purely thermodynamic grounds that there might exist a reaction of this general type, in which a solid compound decomposed to give rise to some gaseous constituent, for which ΔH°_T might be negative and for which the dissociation pressure would therefore decrease with rising temperature. No such case is known, however. The decomposition is invariably endothermic, no doubt for the same reason that the sublimation of a pure chemical substance is endothermic; it is always necessary to supply energy in order to overcome the intermolecular attraction holding the potential gas molecules in the crystalline lattice, whether this attraction is of the van der Waals type that exists even among similar molecules or whether it shows the saturation characteristics that we associate with chemical compound formation.

c. Gas Reactions

Example:

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) = NH_3(g)$$

This reaction was first systematically studied by F. Haber, who thereby founded a new chemical industry of incalculable value.[1] Applying Eqs. (8-1-2) and (7-2-5), we obtain at sufficiently low pressures (ideal-gas range)

$$\begin{aligned}\Delta F &= \bar{F}^\circ_{NH_3(g)} + RT\ln p_{NH_3} - \tfrac{1}{2}\bar{F}^\circ_{N_2(g)} - \tfrac{1}{2}RT\ln p_{N_2} - \tfrac{3}{2}\bar{F}^\circ_{H_2(g)} \\ &\qquad - \tfrac{3}{2}RT\ln p_{H_2} \quad (T \text{ const}) \\ &= \Delta F^\circ_T + RT\ln\frac{p_{NH_3}}{p_{N_2}{}^{1/2}p_{H_2}{}^{3/2}}\end{aligned}$$

Therefore at equilibrium, according to (8-1-3),

$$RT\ln\frac{p_{NH_3}}{p_{N_2}{}^{1/2}p_{H_2}{}^{3/2}} = -\Delta F^\circ_T \tag{8-1-15}$$

Since the value of ΔF°_T is determined solely by the properties of the pure gases and is a constant at given temperature, therefore so long as the gas mixture behaves as an ideal gas, the expression

$$K_p \equiv \frac{p_{NH_3}}{p_{N_2}{}^{1/2}p_{H_2}{}^{3/2}} \tag{8-1-16}$$

remains constant, and constitutes the familiar law-of-mass-action or *equilibrium constant* for the reaction, expressed in terms of partial pressures. At pressures outside the ideal-gas region, we may use Eq. (7-2-9) for the thermodynamic potentials of the gases, in place of the ideal expression (7-2-5), and the general equilibrium condition (8-1-3) then leads to the equation

$$RT\ln\frac{(p_{NH_3}\nu_{NH_3})}{(p_{N_2}\nu_{N_2})^{1/2}(p_{H_2}\nu_{H_2})^{3/2}} = -\Delta F^\circ_T$$

or introducing K_p defined as before [Eq. (8-1-16)],

$$RT\ln K_p + RT\ln\frac{\nu_{NH_3}}{\nu_{N_2}{}^{1/2}\nu_{H_2}{}^{3/2}} = -\Delta F^\circ_T \tag{8-1-17}$$

Thus, the equilibrium "constant" K_p actually varies with pressure, in a manner that could be predicted if we had sufficient information concerning the deviation of the mixture from ideal-gas behavior, translated in

[1] F. Haber, *Z. Elektrochem.*, **20**, 597–604 (1914).

terms of the fugacity coefficients ν_{NH_3}, ν_{N_2}, and ν_{H_2} (Sec. 7-2). Table 8-3 presents selected values of K_p at various temperatures and pressures, from experimental work of A. T. Larson and R. L. Dodge.[1] The partial pressures in the expression for K_p are of course conventional partial pressures, defined in accordance with Eq. (7-2-8); in other words, the value of K_p for this particular reaction is calculated from the equilibrium composition of the gas mixture by means of the expression

TABLE 8-3. EQUILIBRIUM DATA FOR THE AMMONIA SYNTHESIS*

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) = NH_3(g)$$

$$K_p = \frac{y_{NH_3}}{y_{N_2}^{1/2}\, y_{H_2}^{3/2}} \frac{1}{p}$$

p, atm	350°C	400°C	450°C	500°C
10	0.0266	0.0129	0.00659	0.00381
30	0.0273	0.0129	0.00676	0.00386
50	0.0278	0.0130	0.00690	0.00388
100	......	0.0137	0.00725	0.00402
300	......	......	0.00884	0.00498
600	......	......	0.01294	0.00651
1000	......	......	0.02328	

* A. T. Larson and R. L. Dodge, *J. Am. Chem. Soc.*, **45**, 2918–2930 (1923); Larson, *ibid.*, **46**, 367–372 (1924).

$$K_p = \frac{y_{NH_3}}{y_{N_2}^{1/2} y_{H_2}^{3/2}} \frac{1}{p} \tag{8-1-18}$$

Figure 8-2 shows the equilibrium value of y_{NH_3} from a mixture containing N_2 and H_2 originally in 1:3 molal proportion, plotted against p for several values of T; increase of pressure has a marked effect on the equilibrium yield of NH_3, particularly at the lower temperatures where K_p is larger.

One may determine the value of the fugacity coefficient factor

$$K_\nu \equiv \frac{\nu_{NH_3}}{\nu_{N_2}^{1/2} \nu_{H_2}^{3/2}} \tag{8-1-19}$$

from the experimental K_p values at given temperature by taking

$$K_p K_\nu = \lim_{p \to 0} K_p = K_p^\circ \qquad (T \text{ const}) \tag{8-1-19a}$$

We should like, however, to be able to estimate the value of this factor from other data unrelated to the reaction itself for the purpose of making

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[1] A. T. Larson and R. L. Dodge, *J. Am. Chem. Soc.*, **45**, 2918–2930 (1923); Larson, *ibid.*, **46**, 367–372 (1924).

thermodynamic predictions of the equilibrium conditions at high pressures from observed values of the equilibrium conditions at low pressures. Now, the actual measurement of individual fugacity coefficients in mixtures containing more than two chemical substances is an extremely difficult assignment; in this particular reaction the deviation from ideal-gas behavior at the lower pressures is no doubt mainly the result of the presence of the ammonia, rather than of the other two components, but as we saw in Sec. 7-2, even nitrogen and hydrogen deviate significantly from ideal behavior in mixtures at pressures of order 100 atm or more.

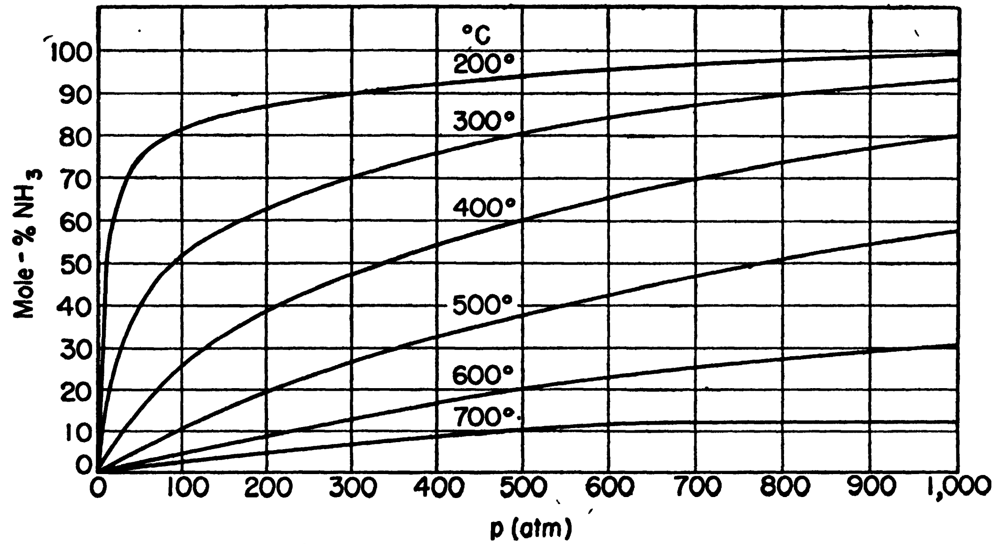

FIG. 8-2. Equilibrium mole per cent NH_3 in a $1N_2{:}3H_2$ gas mixture at various temperatures and pressures. [*A. T. Larson, J. Am. Chem. Soc.*, **46**, 371 (1924), *with permission.*]

This general problem has been attacked by R. H. Newton and B. F. Dodge in the following way.[1] As we have seen in Sec. 6-1, the fugacity coefficients of many gases may be represented quite accurately as generalized functions of their reduced temperatures and pressures (theory of corresponding states); Figs. 6-2 to 6-4 were so constructed by Newton from experimental equation-of-state data for a number of different gases. Newton and Dodge have proposed that the fugacity coefficients of the constituents in a gas mixture may be estimated from such charts by assuming reduced temperatures and reduced pressures based on the temperature and pressure of the mixture; as we have noted in Sec. 7-2, this idea is based essentially on the supposition that the gas mixture satisfies Amagat's law. The following table was prepared by them to represent

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[1] R. H. Newton and B. F. Dodge, *Ind. Eng. Chem.*, **27**, 577–581 (1935); R. H. Newton, *ibid.*, 302–306 (1935).

conditions in a N_2-H_2-NH_3 equilibrium mixture at 450°C and 300 atm:[1]

Gas	T_c	p_c	$T = 723°K$; $p = 300$ atm		
			T_r	p_r	ν (Fig. 6-3)
H_2	33.2	12.8	17.53	14.4	1.09
N_2	126.0	33.6	5.73	8.94	1.14
NH_3	406.	111.6	1.78	2.69	0.91

Thus, for the ammonia synthesis,

$$K_\nu = \frac{0.91}{(1.14)^{1/2}(1.09)^{3/2}} = 0.750 \quad (723°\text{K, } 300 \text{ atm})$$

Now, K_p° has an estimated experimental value of 0.00664 at 450°C; therefore the observed value of K_ν from the equilibrium data is

$$K_\nu = \frac{0.00664}{0.00884} = 0.751$$

in excellent agreement with the value estimated by the theory of corresponding states and Amagat's law. One will observe that for this particular reaction, at 450°C, the estimated thermodynamic potential of NH_3 up to quite high pressures is less than the value given by the ideal-gas law (or Dalton's law), this temperature being below the Boyle point for ammonia; but for N_2 and H_2, the thermodynamic potential is greater at all pressures than the value given by the ideal-gas law. Each of these ideal-gas-law deviations thus happens to operate in the same direction, tending to make ammonia relatively more stable at high pressures than one would expect according to the ideal-gas law from its stability at low pressures; thus, there is a nearly fourfold increase in the value of K_p itself from 1 atm to 1000 atm at 450°C, which combined with the ordinary mass-action effect of pressure as represented in Eq. (8-1-18) results in a substantial improvement in the equilibrium yield of ammonia at superhigh pressures (1000 atm) as compared with ordinary industrial high pressures (*e.g.*, of order 200 atm).

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[1] For the gases having the lowest critical temperatures, H_2, He, and Ne, Newton found that the charts fit the data better if one empirically assigns them reduced temperatures defined by $T_r = T/(T_c + 8)$ and reduced pressures defined by

$$p_r = \frac{p}{(p_c + 8)}$$

The quantity K_p° satisfying the relationships

$$\left.\begin{aligned} K_p^\circ &= K_pK_\nu = \lim_{p\to 0} K_p \\ RT\ln K_p^\circ &= -\Delta F_T^\circ \end{aligned}\right\} \tag{8-1-20}$$

is called the *thermodynamic equilibrium constant* for the gas reaction. It is a true constant at given temperature, and at sufficiently low pressures is equal to the ordinary law-of-mass-action equilibrium constant expressed in terms of partial pressures. But our discussion has shown that the ordinary "constant" K_p is really constant only in so far as the mixture behaves as an ideal gas. When we are able to measure or estimate the extent of deviation from ideal-gas behavior by means of other information, independent of the equilibrium data themselves, then we may predict the effect of such deviation at high pressures on the equilibrium conditions, in terms of the factor K_ν.

The effect of temperature on K_p° is determined by the application of Eq. (8-1-5) to (8-1-20):

$$\frac{d\ln K_p^\circ}{dT} = -\frac{1}{R}\frac{d(\Delta F_T^\circ/T)}{dT} = \frac{\Delta H_T^\circ}{RT^2} \tag{8-1-21}$$

Equation (8-1-21) constitutes a general relationship between the equilibrium constant, K_p°, and the enthalpy of the reaction, ΔH_T°, known as *van't Hoff's law*. It may be put also in the equivalent form

$$\frac{d\log K_p^\circ}{d(1/T)} = -\frac{\Delta H_T^\circ}{2.3026R} \tag{8-1-22}$$

from which it is evident that if one plots $\log K_p^\circ$ vs. $1/T$, the slope will represent $-\Delta H_T^\circ/2.3026R$. Since ΔH_T° changes comparatively slowly with T, the curve will not deviate greatly from a straight line. In Fig. 8-3, $\log K_p^\circ$ has been plotted against $1/T$ for the ammonia synthesis.

Equation (8-1-22) constitutes an important indirect method for the determination of enthalpies of reaction, particularly for reactions at high temperatures, or for relatively slow reactions, where direct thermal measurement may be out of the question. If we have precise heat-capacity data for the participating substances, then both ΔH_T° and ΔF_T° may be extrapolated beyond the range of direct equilibrium measurements. Thus, from the equilibrium data plotted in Fig. 8-3, we may deduce for the ammonia synthesis a value of $\Delta H_{723}^\circ = -12{,}740$ cal (at 450°C). Let us use Kelley's approximate heat-capacity equations in order to represent ΔH_T° as a function of T:[1]

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[1] K. K. Kelley, *U.S. Bur. Mines Bull.* **371** (1934).

$$\begin{aligned} NH_3(g)&: \bar{C}_p^\circ = 6.70 + 6.30 \times 10^{-3}T \quad (300 - 800°K)\\ N_2(g)&: \bar{C}_p^\circ = 6.50 + 1.00 \times 10^{-3}T \quad (300 - 3000°K)\\ H_2(g)&: \bar{C}_p^\circ = 6.62 + 0.81 \times 10^{-3}T \quad (273 - 2500°K)\end{aligned}$$

Thus

$$\Delta C_p^\circ = -6.48 + 4.58 \times 10^{-3}T$$

Substituting in the Kirchhoff equation (4-14), and integrating from $T = 723°K$,

$$\begin{aligned}\Delta H_T^\circ &= -12{,}740 - 6.48(T - 723) + 2.29 \times 10^{-3}(T^2 - 723^2)\\ &= -9{,}252 - 6.48T + 2.29 \times 10^{-3}T^2\end{aligned}$$

This equation leads to a value of ΔH_T° at 20°C (293°K) of −10,950 cal; Haber's more precise heat-capacity equation for $NH_3(g)$ leads to −11,080 cal. Direct thermochemical measurements by G. Becker and W. A. Roth, based on the heats of combustion of ammonium oxalate and oxalic acid, combined with their heats of solution and the heat of neutralization of oxalic acid with ammonia in aqueous solution, have led to $\Delta H_{293}^\circ = -11{,}010$ cal,[1] in excellent agreement with the high-temperature equilibrium data.

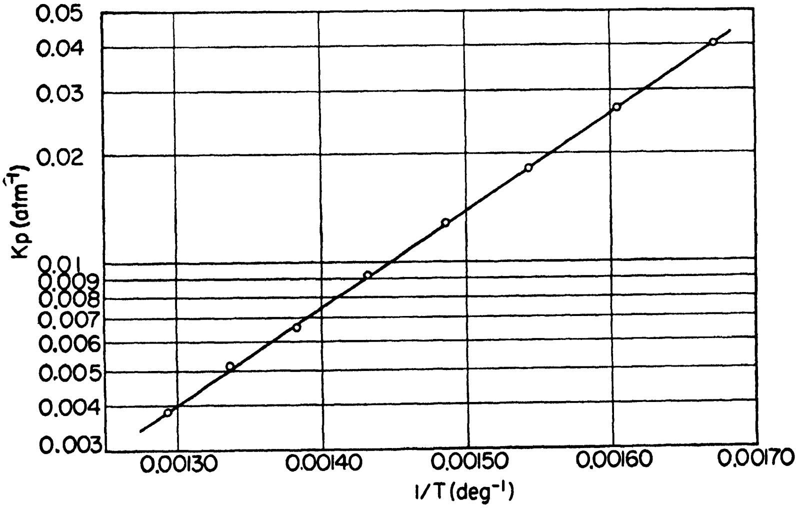

FIG. 8-3. Log K_p vs. $1/T$ at constant pressure of 10 atm for the ammonia synthesis $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) = NH_3(g)$. (*Data of A. T. Larson and R. L. Dodge.*)

We may now substitute the empirical equation for ΔH_T° in the general equation for ΔF_T°, obtained by integrating (8-1-21),

$$\frac{\Delta F_T^\circ}{T} - \frac{\Delta F_{T_s}^\circ}{T_s} = -\int_{T_s}^{T} \frac{\Delta H_T^\circ}{T^2}\,dT \qquad (8\text{-}1\text{-}23)$$

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[1] Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIIc, p. 2747, 1936.

to derive the value of $\Delta F^\circ_{298.16}$, selecting the high-temperature equilibrium result $K^\circ_p = 0.00664$ atm^{-1} at $T = 723.16$°K,

$$\frac{\Delta F^\circ_T}{T} = -R \ln K^\circ_p = 9.962 \qquad (T = 723.16°\text{K})$$

Thus

$$\begin{aligned} 9.962 - \frac{\Delta F^\circ_{298.16}}{298.16 \text{ deg}} &= - \int_{298.16}^{723.16} \left(-\frac{9252}{T^2} - \frac{6.48}{T} + 2.29 \times 10^{-3} \right) dT \\ &= -9252 \left(\frac{1}{723.16} - \frac{1}{298.16} \right) + 6.48 \ln \frac{723.16}{298.16} \\ &\qquad - 2.29 \times 10^{-3}(723.16 - 298.16) \\ &= 22.946 \\ \Delta F^\circ_{298.16} &= -3870 \text{ cal} \end{aligned} \tag{8-1-24}$$

Using the more precise data of molecular spectroscopy, according to the methods outlined in Chap. 10, F. D. Rossini has adopted for this important natural constant the value[1]

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) = NH_3(g); \qquad \Delta F^\circ_{298.16} = -3976 \text{ cal} \tag{8-1-24a}$$

It represents the *standard free energy of formation* of $NH_3(g)$ from its elements. The corresponding value of K°_p at 25°C, calculated from $\Delta F^\circ_{298.16}$ by means of Eq. (8-1-20), is 821 atm^{-1}. The thermodynamic equilibrium conditions are therefore much more favorable at 25°C than at 450°C, but the reaction proceeds immeasurably slowly at room temperature. On the other hand, one may readily show by means of Eq. (8-1-23) that at temperatures of order 1000°K or higher, ammonia is almost completely dissociated into its elements, even at pressures of several hundred atmospheres.

The principles outlined in this and the preceding subsection are easily generalized for any kind of reaction involving pure solids and liquids with a gas phase that may contain several constituents; thus, in general,

$$\lim_{p \to 0} RT \ln K_p = RT \ln K^\circ_p = -\Delta F^\circ_T \qquad (T \text{ const}) \tag{8-1-25}$$

$$\frac{d(\Delta F^\circ_T/T)}{d(1/T)} = \Delta H^\circ_T \tag{8-1-26}$$

The term K_p contains in the numerator the equilibrium partial pressure of each gaseous product and in the denominator the equilibrium partial pressure of each gaseous reactant, raised to powers equal to the coefficients appearing in the chemical equation for the reaction. The con-

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[1] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D.C., Dec. 31, 1947.

stant, ΔF_T°, consists of the difference between the standard molal free energies of all the products and the standard molal free energies of all the reactants, each multiplied by the appropriate coefficient as it appears in the chemical equation for the reaction; this standard free energy of reaction thus represents what the free-energy change would be for the amount of reaction represented by the chemical equation, if each reactant and product were at 1 atm, but of course it is generally actually measured through the measurement of K_p (with all partial pressures expressed in atm) and the application of Eq. (8-1-25). Thus, pure solid and liquid substances influence the values of ΔF_T° and of K_p°, but their effect on the equilibrium conditions is practically constant with pressure unless one goes to pressures so high that $\int_{1\text{ atm}}^{p} \bar{V}_{T,p}\,dp$ becomes significant in comparison with $\bar{F}_T^\circ$. How we choose to represent the chemical equation for the reaction is to some extent arbitrary; the relative proportions of the reactants and products are fixed by nature, but the entire equation could be multiplied through by a constant factor; the value of ΔF_T° would then be multiplied by the same factor, and the value of K_p° would be raised by a power equal to that factor; we could also write the reaction in the opposite sense, so that the former reactants would appear as products and the former products as reactants; this would merely change the sign of ΔF_T°, and would invert K_p°. Let us consider one further example.

Example:

$$\mathrm{HgO(c,red)} = \mathrm{Hg(g)} + \tfrac{1}{2}\mathrm{O_2(g)}$$

$$\Delta F = \bar{F}^\circ_{\mathrm{Hg(g)}} + RT\ln p_{\mathrm{Hg}} + \tfrac{1}{2}\bar{F}^\circ_{\mathrm{O_2(g)}} + \tfrac{1}{2}RT\ln p_{\mathrm{O_2}} - \bar{F}^\circ_{\mathrm{HgO(c,red)}} \qquad (T\ \text{const})$$

assuming that the vapor phase may be treated as a mixture of ideal gases. Thus, at equilibrium,

$$RT\ln p_{\mathrm{Hg}}p_{\mathrm{O_2}}^{1/2} = -\Delta F_T^\circ = -[\bar{F}^\circ_{\mathrm{Hg(g)}} + \tfrac{1}{2}\bar{F}^\circ_{\mathrm{O_2(g)}} - \bar{F}^\circ_{\mathrm{HgO(c,red)}}]$$

In this case,

$$p_{\mathrm{Hg}}p_{\mathrm{O_2}}^{1/2} = K_p; \qquad \lim_{p\to 0} RT\ln K_p = RT\ln K_p^\circ = -\Delta F_T^\circ$$

If we are dealing with an equilibrium vapor phase that is made up entirely of evaporated solid, so that its composition is the same as that of the solid (that is, $y_{\mathrm{Hg}} = \frac{2}{3}$; $y_{\mathrm{O_2}} = \frac{1}{3}$), then p itself is fixed at each temperature, just as in the case of $\mathrm{CaCO_3}$; for approximately (within the ideal-gas-law assumption, which will be entirely satisfactory in this case for pressures not greatly in excess of 1 atm)

$$p_{\mathrm{Hg}} = \tfrac{2}{3}p; \qquad p_{\mathrm{O_2}} = \tfrac{1}{3}p$$

therefore

$$\frac{2}{3^{3/2}} p^{3/2} = K_p$$

This relation of course does not apply in general if one should introduce an excess of either Hg(g) or O_2(g) into the mixture. Table 8-4 presents the "dissociation pressure" of HgO(c,red) at various temperatures, together with the calculated value of $-R \ln K_p$, from data of Taylor and Hulett, as presented by Randall and Langford in the "International Critical Tables."[1] In Fig. 8-4, $-R \ln K_p$ is plotted against $1/T$; according to Eqs. (8-1-25) and (8-1-26), the slope represents the value of ΔH°_T. By

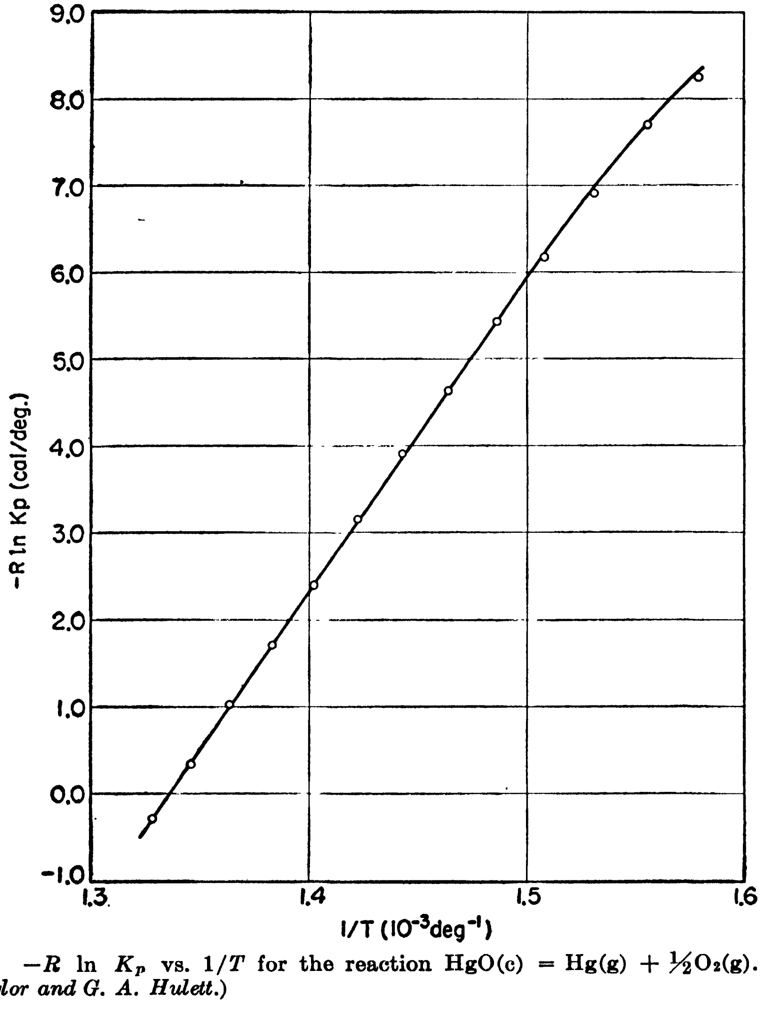

FIG. 8-4. $-R \ln K_p$ vs. $1/T$ for the reaction HgO(c) = Hg(g) + $\frac{1}{2}O_2$(g). (*Data of G. B. Taylor and G. A. Hulett.*)

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[1] "International Critical Tables," Vol. VII, p. 259, McGraw-Hill Book Company, Inc., New York, 1930; G. B. Taylor and G. A. Hulett, *J. Phys. Chem.*, **17**, 565–592 (1913).

introducing the corresponding heat-capacity data to represent how ΔH_T° varies with T, the data may be extrapolated down to 25°C; thus, M. Randall in the "International Critical Tables" gives the values

$$\mathrm{HgO(c,red)} = \mathrm{Hg(g)} + \tfrac{1}{2}\mathrm{O_2(g)}$$

$$\left.\begin{aligned}\Delta H^\circ_{298.1} &= 36{,}290 \text{ cal}\\ \Delta F^\circ_{298.1} &= 21{,}582 \text{ cal}\end{aligned}\right\} \qquad (8\text{-}1\text{-}27)$$

These values represent the hypothetical enthalpy and free energy of reaction if each gas were produced as an ideal gas at a partial pressure of 1 atm at 25°C. If we wish to apply these results to Hg(l), we may introduce the value given by K. K. Kelley for the free energy of vaporization:[1]

TABLE 8-4. EQUILIBRIUM PRESSURE OF HgO*
$\mathrm{HgO(c, red)} = \mathrm{Hg(g)} + \tfrac{1}{2}\mathrm{O_2(g)}$

t, °C	p, atm	$-R \ln K_p$, cal/deg
360	0.1185	8.262
370	0.1422	7.719
380	0.1858	6.923
390	0.2370	6.195
400	0.3040	5.451
410	0.3990	4.642
420	0.5095	3.911
430	0.6550	3.159
440	0.8450	2.402
450	1.067	1.709
460	1.339	1.030
470	1.679	0.3554
480	2.081	−0.2862

* "International Critical Tables," Vol. VII, p. 259, McGraw-Hill Book Company, Inc., New York, 1930.

$$\mathrm{Hg(l)} = \mathrm{Hg(g)}; \qquad \Delta F^\circ_{298.1} = 7590 \text{ cal}$$

Thus, we obtain for the standard free energy of formation of HgO(c)

$$\mathrm{Hg(l)} + \tfrac{1}{2}\mathrm{O_2(g)} = \mathrm{HgO(c,red)}; \qquad \Delta F^\circ_{298.1} = -13{,}990 \text{ cal} \qquad (8\text{-}1\text{-}27a)$$

Equation (8-1-6), which represented equilibrium conditions for the dissociation of $\mathrm{CaCO_3(c)}$, and Eq. (8-1-13), which represented similarly

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[1] K. K. Kelley, *U.S. Bur. Mines Bull.* 383 (1935), from spectroscopic data for the gas and vapor-pressure data. Mercury vapor contains a small proportion of $\mathrm{Hg_2}$ molecules, about 7 per cent at the normal boiling point, 630°K and 1 atm. This effect has not been taken into consideration in the data of Table 8-4, but should introduce little error at the relatively low pressures concerned, except possibly at the higher temperatures.

equilibrium conditions for the dissociation of $Na_2SO_4 \cdot 10H_2O(c)$, are evidently special cases of the general equilibrium law (8-1-25). The Clausius-Clapeyron equation in the ideal-gas form (6-69) may also be regarded as a special case of the general equilibrium law (8-1-25)-(8-1-26). All follow from application of the same basic principle, represented by Eq. (8-1-3), or ultimately, by Eq. (5-61).

d. Reactions in Liquid Solution

Example:

$$CH_3COOH + C_2H_5OH = CH_3CO{-}OC_2H_5 + H_2O$$

The esterification of acetic acid with ethyl alcohol is one of the first reactions to be studied quantitatively from the point of view of establishing the equilibrium conditions. This reaction in the liquid state was first studied by Berthelot and St. Gilles, who showed that the reaction was reversible and that the equilibrium concentrations were related according to a law essentially similar to the one formulated several years later by Guldberg and Waage.[1] Now, on the basis of Eq. (7-3-28) we may propose that if the four liquids form a solution that is not far from ideal over the entire range of compositions, then at given temperature, practically independently of pressure at moderate pressures,

$$\Delta F = \bar{F}^\circ_{EtOAc} + RT \ln x_{EtOAc} + \bar{F}^\circ_{H_2O} + RT \ln x_{H_2O} - \bar{F}^\circ_{HAc} - RT \ln x_{HAc} - \bar{F}^\circ_{EtOH} - RT \ln x_{EtOH}$$

Therefore as an approximation at equilibrium, applying condition (8-1-3),

$$RT \ln \frac{x_{EtOAc}x_{H_2O}}{x_{HAc}x_{EtOH}} = -(\bar{F}^\circ_{EtOAc} + \bar{F}^\circ_{H_2O} - \bar{F}^\circ_{HAc} - \bar{F}^\circ_{EtOH}) = -\Delta F^\circ_T$$

Since the terms on the right are constant at the given temperature, being properties of the four pure liquids, therefore the expression on the left must also be constant, within the assumption that each constituent satisfies Raoult's law,

$$K_x \equiv \frac{x_{EtOAc}x_{H_2O}}{x_{HAc}x_{EtOH}}; \qquad RT \ln K_x = -\Delta F^\circ_T \qquad \text{(ideal concentrated soln)} \tag{8-1-28}$$

We cannot expect Eq. (8-1-28) to be valid in general, but as a matter of

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[1] M. Berthelot and L. Péan de St. Gilles, *Ann. chim. et phys.*, (3) **65**, 385–422 (1862); (3) **66**, 5–110 (1862); (3) **68**, 225–359 (1863); Berthelot, *ibid.*, (5) **14**, 437–441 (1878). See also the discussion of this reaction by G. Edgar in H. S. Taylor's "A Treatise on Physical Chemistry," 2d ed., Chap. VIII, D. Van Nostrand Company, Inc., New York, 1931, and by G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," pp. 173–176, Reinhold Publishing Corporation, New York, 1932.

fact, Berthelot and St. Gilles found that the quantity we have represented by K_x in Eq. (8-1-28) was indeed constant for this particular reaction over a wide range of initial conditions, its value being about 4. Furthermore, they found that the value of this so-called *mole-fraction equilibrium constant* was practically independent of temperature over the range of investigation. Since by the application of the general thermodynamic relation (8-1-5) to (8-1-28)

$$\frac{d \ln K_x}{dT} = -\frac{1}{R}\frac{d(\Delta F^\circ_T/T)}{dT} = \frac{\Delta H^\circ_T}{RT^2} \tag{8-1-29}$$

[another form of van't Hoff's law; compare Eq. (8-1-21)], we may therefore conclude that the heat of this particular reaction is practically zero; this conclusion is in general agreement with thermal calculation based on the known heats of combustion of acetic acid, ethyl alcohol, and ethyl acetate. Substituting the experimental value of K_x in Eq. (8-1-28), we may compute for the standard free-energy change,

$$\begin{aligned}\mathrm{CH_3COOH(l) + C_2H_5OH(l)} &= \mathrm{CH_3COOC_2H_5(l) + H_2O(l)};\\ \Delta F^\circ_{298} &= -RT \ln 4 = -820 \text{ cal}\end{aligned}$$

Because of the form of ΔF°_{298} in this particular case, its value represents what the net free-energy change would be per mole of acetic acid or ethanol reacting, if each reactant started as a pure liquid at 25°C and 1 atm and if each product ended as a pure liquid at 25°C and 1 atm.

Example:

$$\mathrm{CH_3COOH(aq) = CH_3COO^-(aq) + H^+(aq)} \tag{8-1-30}$$

This classic reaction is perhaps not a chemical transformation in the ordinary sense, and yet its equilibrium conditions may be treated formally by the same general methods. In fact, the success of this procedure for the ionization of weak electrolytes was one of the strong points that convinced W. Ostwald originally of the essential correctness of Arrhenius's ionization theory.[1] There is excellent reason for us to express the equation for the ionization of acetic acid in water in the Brønsted-Lowry form

$$\mathrm{HAc(aq) + H_2O = H_3O^+(aq) + Ac^-(aq)} \tag{8-1-31}$$

So long, however, as we regard the standard states of the participating substances as one of infinite dilution in water, we cannot distinguish between the two equations (8-1-30) and (8-1-31) by any physical measurements based ultimately only on Raoult's law and its thermodynamic implications.

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[1] S. Arrhenius, *J. Am. Chem. Soc.*, **34**, 353–364 (1912).

We may represent the free energy of the reaction (8-1-30) formally by means of the equation

$$
\begin{aligned}
\Delta F &= \phi_{\mathrm{Ac}^-} + \phi_{\mathrm{H}^+} - \phi_{\mathrm{HAc}} \\
&= \phi''_{\mathrm{Ac}^-(\mathrm{aq})} + RT \ln C_{\mathrm{Ac}^-}\gamma''_{\mathrm{Ac}^-} + \phi''_{\mathrm{H}^+(\mathrm{aq})} + RT \ln C_{\mathrm{H}^+}\gamma''_{\mathrm{H}^+} - \phi''_{\mathrm{HAc(aq)}} \\
&\qquad - RT \ln C_{\mathrm{HAc}}\gamma''_{\mathrm{HAc}} \quad (T,\ p \text{ const}) \qquad (8\text{-}1\text{-}32)
\end{aligned}
$$

where we have expressed all concentrations in moles per liter [compare Eq. (7-3-107*c*)]. The quantitites entering this equation are related to their molal counterparts through Eqs. (7-3-97) to (7-3-105). Let us write

$$(\Delta F_T^\circ)_C = \phi''_{\mathrm{H}^+(\mathrm{aq})} + \phi''_{\mathrm{Ac}^-(\mathrm{aq})} - \phi''_{\mathrm{HAc(aq)}} \qquad (8\text{-}1\text{-}33)$$

Therefore introducing the general equilibrium condition (8-1-3) in (8-1-32),

$$RT \ln \frac{C_{\mathrm{H}^+}C_{\mathrm{Ac}^-}}{C_{\mathrm{HAc}}} \frac{\gamma''_{\mathrm{H}^+}\gamma''_{\mathrm{Ac}^-}}{\gamma''_{\mathrm{HAc}}} = -(\Delta F_T^\circ)_C \qquad (8\text{-}1\text{-}34)$$

Since the expression $(\Delta F_T^\circ)_C$ is a constant for the reaction at the particular temperature, the expression on the left of Eq. (8-1-34) is constant for all equilibrium states of the reaction at the given temperature. Let

$$K_C \equiv \frac{C_{\mathrm{H}^+}C_{\mathrm{Ac}^-}}{C_{\mathrm{HAc}}} \qquad (8\text{-}1\text{-}35)$$

$$K_C^\circ = K_C \frac{\gamma''_{\mathrm{H}^+}\gamma''_{\mathrm{Ac}^-}}{\gamma''_{\mathrm{HAc}}} = K_C \frac{(\gamma''_\pm)^2}{\gamma''_{\mathrm{HAc}}} \qquad (8\text{-}1\text{-}36)$$

where

$$RT \ln K_C^\circ \equiv -(\Delta F_T^\circ)_C \qquad (8\text{-}1\text{-}37)$$

The quantity K_C represents the familiar law-of-mass-action expression or *ionization constant* for the reaction, which turns out therefore to be not actually constant with concentration; the quantity K_C° is called the *thermodynamic ionization constant* of HAc, and is by definition constant at the given temperature. If each of the "substances" H^+, Ac^-, and HAc behaves as an independent ideal solute in sufficiently dilute solution, then

$$K_C^\circ = \lim_{C_2 \to 0} K_C \qquad (8\text{-}1\text{-}38)$$

where C_2 represents the stoichiometric concentration of the acetic acid, without regard to its state in solution.

Now, K_C may be measured by a variety of methods, of which one of the most precise is the conductimetric method.[1] These methods measure

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[1] See D. A. MacInnes, "The Principles of Electrochemistry," pp. 342*ff*., Reinhold Publishing Corporation, New York, 1939, for methods of interpreting the electrical conductivity of weak electrolytes to determine the degree of ionization.

essentially the degree of ionization of the solute at various values of the concentration; thus, letting α represent this quantity in the present example,

$$K_C = \frac{\alpha^2}{1 - \alpha} \frac{1}{C} \tag{8-1-39}$$

Equation (8-1-39) represents Ostwald's ideal dilution law, neglecting deviations from ideal dilute-solution behavior. In Table 8-5 are presented the values of α, as determined by D. A. MacInnes and T. Shedlovsky from conductivity measurements at various acetic acid concentrations (taken in comparison with the conductivities of NaAc, NaCl, and HCl at the same ionic concentration), and the values of K_C computed therefrom according to Eq. (8-1-39).[1] One sees that while the variation of K_C with concentration over the given range is small, it is nevertheless regular and significant.

TABLE 8-5. IONIZATION OF ACETIC ACID IN WATER AT 25°C*

C_2, moles/liter	α	$K_C \times 10^5$	$(K_C \times 10^{-1.018\sqrt{\alpha C_2}}) \times 10^5$
0.000028014	0.53926	1.768_2	1.752_2
0.00011135	0.32771	1.778_7	1.753_8
0.00015321	0.28751	1.777_5	1.750_2
0.00021844	0.24767	1.781_0	1.750_7
0.00102831	0.12377	1.797_4	1.750_8
0.00136340	0.10857	1.803_4	1.752_6
0.00241400	0.082900	1.809_0	1.750_3
0.00344065	0.070022	1.814_0	1.749_6
0.00591153	0.054011	1.823_0	1.748_7
0.0098421	0.042224	1.832_0	1.746_9
0.012829	0.037096	1.834	1.743
0.020000	0.029875	1.840	1.738
0.050000	0.019048	1.849	1.721
0.052303	0.018649	1.854	1.723
0.100000	0.013496	1.846	1.695
0.119447	0.012359	1.847	1.689
0.200000	0.0094960	1.821	1.645
0.230785	0.0088268	1.814	1.633

* D. A. MacInnes and T. Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1429–1438 (1932).

Now, according to Eq. (8-1-36), the ratio of K_C° to K_C depends on the quantity $(\gamma_\pm'')^2/\gamma_{HAc}''$. At the very low concentrations represented in Table 8-5, one may surely assume that the undissociated acetic acid behaves like an ideal solute; therefore the change of K_C with concentra-

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[1] D. A. MacInnes and T. Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1429–1438 (1932); this work is reviewed by MacInnes in "The Principles of Electrochemistry."

tion in this dilute range must be practically entirely attributable to the term $\gamma''_\pm$, representing the mean ionic activity coefficient of the two singly charged ions, H^+ and Ac^-. At the low ionic concentrations involved (much lower than in the case of a strong electrolyte at the same stoichiometric concentration), one may look to the Debye-Hückel limiting law, Eq. (7-4-31), for calculating the value of $\gamma''_\pm$, assuming that departure of the ions of acetic acid from ideal behavior as independent solutes may be attributed entirely to interionic attraction, at least at the lower concentrations in Table 8-5. Thus

$$\log (\gamma''_\pm)^2 = -1.018\sqrt{\alpha C_2} \qquad (8\text{-}1\text{-}40)$$

(noting that only the concentration of the ionized part of the acetic acid, represented by $C_2\alpha$, contributes to the ionic strength). In the last column of Table 8-5 are given the values of K_C multiplied by the value of $(\gamma''_\pm)^2$ given by Eq. (8-1-40). One sees that over the lowest concentrations, this quantity is quite constant, within experimental error, providing a sensitive test and confirmation of the Debye-Hückel approximation. In this way, MacInnes and Shedlovsky obtained

$$K_C^\circ = 1.753 \times 10^{-5} \text{ mole/liter}$$

as the thermodynamic ionization constant of acetic acid at 25°C. At the higher acetic acid concentrations the Debye-Hückel approximation is no doubt faulty, largely because the presence of the undissociated acetic acid begins to change the nature of the liquid medium, in particular, to lower its dielectric constant.

The molal thermodynamic ionization constant K_m° is related to K_C° by [compare Eq. (7-3-100)]

$$K_m^\circ = \frac{K_C^\circ}{\rho_1} = \frac{1.753 \times 10^{-5} \text{ mole/liter}}{0.99707 \text{ kg/liter}} = 1.758 \times 10^{-5} \text{ mole/kg} \qquad (8\text{-}1\text{-}41)^1$$

Using this value of K_m° let us translate in terms of $(\Delta F_T^\circ)_m$,

$$(\Delta F_T^\circ)_m = \phi'_{H^+(aq)} + \phi'_{Ac^-(aq)} - \phi'_{HAc(aq)} = -RT \ln K_m^\circ = 6485 \text{ cal} \qquad (8\text{-}1\text{-}42)$$

The value of $(\Delta F_T^\circ)_m$ represents what the free-energy change would be if 1 mole of HAc in a hypothetical ideal solution at $1m$ concentration were to ionize completely into H^+ and Ac^-, as hypothetically ideal solutes, both at $1m$ concentration. Since we have agreed to let $\phi'_{H^+(aq)} = 0$ by convention, the result, Eq. (8-1-42), therefore measures the difference between

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[1] This value for K_m° is in excellent agreement with $K_m^\circ = 1.754 \times 10^{-5}$ mole/kg obtained by H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **54**, 1350–1357 (1932), from emf measurements, using the theory to be described in Chap. 9.

$\phi'_{Ac^-(aq)}$ and $\phi'_{HAc(aq)}$. The value of $\phi'_{HAc(aq)}$ may be measured independently from partial vapor-pressure measurements of HAc from aqueous solutions at higher concentrations, where ionization is slight and easily corrected for [one must, however, take into consideration equilibrium between HAc and $(HAc)_2$ in the vapor phase]. Similar data may be used to determine ϕ' values for the anions of other weak acids in aqueous solution, relative ultimately to the standard free energies of the chemical elements.

By applying Eq. (7-3-91) term by term to Eq. (8-1-42), we may derive the expression for the variation of K°_m with temperature

$$\frac{d \ln K^\circ_m}{d(1/T)} = -\frac{1}{R}\frac{d[(\Delta F^\circ_T)_m/T]}{d(1/T)} = -\frac{\Delta\eta^\circ}{R} \tag{8-1-43}$$

where $\Delta\eta^\circ$ represents the enthalpy of reaction (*i.e.*, of ionization) in infinitely dilute solution. Table 8-6 represents the value of K°_m for the ionization of acetic acid at various temperatures, as determined by H. S. Harned and R. W. Ehlers from emf measurements.[1] From these data, one sees that at 25°C the enthalpy of ionization of acetic acid must be close to zero, in agreement with the fact that the heat of neutralization of acetic acid, by direct thermochemical measurement, is practically the same as that of a strong acid.[2]

TABLE 8-6. THERMODYNAMIC IONIZATION CONSTANT K°_m OF ACETIC ACID IN AQUEOUS SOLUTION

t, °C	K°_m, 10^{-5} mole/kg
0	1.657
10	1.729
20	1.753
25	1.754
30	1.750
40	1.703
50	1.633
60	1.542

* H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **55**, 652–656 (1933).

The foregoing treatment is readily generalized to include more complex types of equilibria, involving solids, other liquid phases, or gases in equilibrium with a liquid solution. Let us consider one further example.

Example:

$$AgBr(c) + 2NH_3(aq) = Ag(NH_3)_2^+(aq) + Br^-(aq)$$

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[1] H. S. Harned and R. W. Ehlers, *ibid.*, **55**, 652–656 (1933).

[2] T. W. Richards and B. J. Mair, *ibid.*, **51**, 737–740 (1929), obtained 13,544 cal/mole as the heat of neutralization of HAc(400 H_2O) with NaOH(400 H_2O) at 20°C, while T. W. Richards and L. P. Hall, *ibid.*, 731–736, obtained 13,786 cal/mole as the heat of neutralization of HCl (400 H_2O) with NaOH(400 H_2O) at 20°C.

For this reaction in general, at given temperature and pressure,

$$\Delta F = \phi'_{\mathrm{Ag(NH_3)_2^+(aq)}} + RT \ln m_{\mathrm{Ag(NH_3)_2^+}}\gamma'_{\mathrm{Ag(NH_3)_2^+}} + \phi'_{\mathrm{Br^-(aq)}} + RT \ln m_{\mathrm{Br^-}}\gamma'_{\mathrm{Br^-}} \\ - \bar{F}^{\circ}_{\mathrm{AgBr(c)}} - 2\phi'_{\mathrm{NH_3(aq)}} - 2RT \ln m_{\mathrm{NH_3}}\gamma'_{\mathrm{NH_3}}$$

Thus, introducing the general condition for equilibrium (8-1-3),

$$RT \ln K_m K_{\gamma'} = -(\Delta F^{\circ}_T)_m \qquad (8\text{-}1\text{-}44)$$

where, by definition,

$$K_m \equiv \frac{m_{\mathrm{Ag(NH_3)_2^+}}\, m_{\mathrm{Br^-}}}{m^2_{\mathrm{NH_3}}}$$

$$K_{\gamma'} \equiv \frac{\gamma'_{\mathrm{Ag(NH_3)_2^+}}\,\gamma'_{\mathrm{Br^-}}}{(\gamma'_{\mathrm{NH_3}})^2} = \left(\frac{\gamma_{\pm}}{\gamma'_{\mathrm{NH_3}}}\right)^2$$

$$(\Delta F^{\circ}_T)_m \equiv \phi'_{\mathrm{Ag(NH_3)_2^+(aq)}} + \phi'_{\mathrm{Br^-(aq)}} - \bar{F}^{\circ}_{\mathrm{AgBr(c)}} - 2\phi'_{\mathrm{NH_3(aq)}}$$

Thus, if the solution were ideal, K_m would be constant for the reaction. In fact, however, K_m departs from the ideal limiting value, K°_m, to the extent that the quantity we have represented by $K_{\gamma'}$ deviates from 1. It is known that NH_3 in aqueous solution satisfies Henry's law quite well at least up to 1m concentration; therefore the change of $K_{\gamma'}$ with solute concentration in dilute solution is due almost entirely to the deviation of $\gamma_{\pm}$, the mean ionic activity coefficient of $Ag(NH_3)_2Br$, from 1. We may therefore express (8-1-44) in the form

$$K_m K_{\gamma'} = K^{\circ}_m$$
$$-\log K_m^{1/2} - \log \gamma_{\pm} = -\tfrac{1}{2} \log K^{\circ}_m$$

assuming that $\gamma'_{\mathrm{NH_3}} = 1$ in the more dilute solutions. We may estimate the value of $-\log \gamma_{\pm}$ at low ionic strength by means of the Debye-Hückel limiting law (7-4-31) for strong 1:1 electrolytes; it is of course necessary to take into account the ionization of NH_4OH in computing the ionic strength.

Table 8-7 presents experimental data for the reaction, as compiled by M. Randall and J. O. Halford for the "International Critical Tables."[1] The sixth column presents $-\log K_m^{1/2} + 0.509\mu^{1/2}$, which according to the Debye-Hückel approximation in the limiting form (7-4-31), with $\gamma'_{\mathrm{NH_3}}$ assumed equal to 1, should represent $-\tfrac{1}{2} \log K^{\circ}_m$. By means of an actual graphical extrapolation of $-\log K_m^{1/2}$ vs. $\mu^{1/2}$ to $\mu = 0$, Randall and Halford obtained for this quantity the value

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[1] "International Critical Tables," Vol. VII, p. 270, McGraw-Hill Book Company, Inc., New York, 1930; see also M. Randall and J. O. Halford, *J. Am. Chem. Soc.*, **52**, 192–194 (1930), for calculations involving equilibria of other complex ions of silver.

$$-\tfrac{1}{2}\log K_m^\circ = 2.537$$
$$K_m^\circ = 8.4 \times 10^{-6}$$
$$(\Delta F_T^\circ)_m = -RT \ln K_m^\circ = 6922 \text{ cal} \quad (T = 298.16°\text{K})$$

Since the values of $\phi'_{\text{Br}^-(\text{aq})}$, $\phi'_{\text{NH}_3(\text{aq})}$, and $\bar{F}^\circ_{\text{AgBr(c)}}$ are obtainable from other sources, this piece of information provides us with a value of $\phi'_{\text{Ag(NH}_3)_2{}^+(\text{aq})}$.

TABLE 8-7. EQUILIBRIUM OF AgBr(c) WITH AQUEOUS AMMONIA*
$\text{AgBr(c)} + \text{NH}_3\text{(aq)} = \text{Ag(NH}_3)_2{}^+\text{ (aq)} + \text{Br}^-\text{ (aq)}$

Total m_{NH_3}	Total m_{AgBr}	$m_{\text{NH}_4\text{OH}}$, free	$-\log K_m^{1/2}$	$\mu^{1/2}$	$-\log K_m^{1/2} + 0.509\mu^{1/2}$
0.1932	0.00060	0.1901	2.501	0.0504	2.527
0.3849	0.00120	0.3797	2.500	0.0630	2.532
0.5741	0.00179	0.5682	2.502	0.0724	2.539
0.7573	0.00223	0.7488	2.526	0.0789	2.566
1.965	0.00692	1.944	2.449	0.1166	2.508
3.024	0.01163	2.992	2.410	0.1257	2.474
5.244	0.02443	5.181	2.326	0.1894	2.422

* "International Critical Tables," Vol. VII, p. 270, McGraw-Hill Book Company, Inc., New York, 1930.

8-2. Free Energies of Formation. Equilibrium data, then, provide us with information concerning the relative values of the standard molal free energies of chemical substances in conventionally chosen reference states. Thus, by means of the general formula,

$$\Delta F_T^\circ = -RT \ln K^\circ \tag{8-2-1}$$

equilibrium constants expressed in the conventional forms outlined in Sec. 8-1 may be translated into differences between the free energies of the products and reactants of the chemical reaction, in corresponding reference states. The significance of Eq. (8-2-1) is that since the free energy of a given substance is one of its properties, determined solely by its state, the contribution of the given substance to ΔF_T°, and hence to the value of K°, of any reaction in which it may take part is determined solely by its state, independently of the other substances that may be involved in the reaction. It is therefore possible for us to assign to each chemical substance a relative value of $\bar{F}_T^\circ$, at a given temperature, that will correlate in the form of a single number all information concerning the equilibrium behavior of the substance with respect to other substances, in much the same manner that its standard enthalpy of formation correlates its thermochemical behavior.

Now, just as in the case of standard enthalpies, the standard molal free energy of each chemical element in any one allotropic form at a given standard temperature and pressure remains quite arbitrary for ordinary chemical purposes, since we have no way of intercomparing the free energies of the elements, short of transmutation experiments. Therefore we conventionally assign to each *chemical element* in its most stable allotropic form at standard conditions of 25°C and 1 atm a *zero* molal free energy: $\bar{F}^\circ_{298.16} = 0$. To each pure *chemical compound* (and to other metastable allotropes of the elements) we then assign a value of $\bar{F}^\circ_{298.16}$ equal to its *standard molal free energy of formation* from the elements, in their most stable allotropic forms, at 25°C and 1 atm.

Thus, the equilibrium data for the Haber reaction, summarized in Eq. (8-1-24),

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) = NH_3(g); \qquad \Delta F^\circ_{298.16} = -3976 \text{ cal}$$

give us immediately the free energy of formation of $NH_3(g)$:

$$\bar{F}^\circ_{298.16} = -3976 \text{ cal}$$

In a similar manner, the free energies of formation of certain other compounds may be determined, if they can be brought directly to equilibrium with their elements; data obtained at temperatures other than the standard temperature, 25°C, may be corrected to that temperature through application of the van't Hoff equation

$$\frac{d(\Delta F^\circ_T/T)}{d(1/T)} = \Delta H^\circ_T \tag{8-2-2}$$

In this equation, ΔH°_T may be measured either by direct thermochemical means, or by the application of Eq. (8-2-2) itself to equilibrium data obtained over a series of temperatures; it may be represented as a function of T through heat-capacity data for the reactants and products, by means of the Kirchhoff equation

$$\Delta H^\circ_T = \Delta H^\circ_{T_0} + \int_{T_0}^{T} \Delta C^\circ_p \, dT \tag{8-2-3}$$

where $\Delta H^\circ_{T_0}$ represents the known value of ΔH° at any one temperature, T_0.

Proceeding stepwise from those compounds for which direct equilibrium data are available with respect to their elements, new equilibrium data for reactions involving such compounds or the chemical elements with a single new compound provide us with the free energy of formation of the new compound. Each independent reaction for which equilibrium data can be measured among substances whose standard free energies of formation have already been determined serves as a cross check on the accuracy of the previous data. In this way (along with additional infor-

mation to be discussed in Sec. 8-3), tables containing standard free energies of formation of many compounds have been compiled, which essentially summarize equilibrium data for all conceivable chemical reactions among the substances included. The extension of such tables to include additional compounds, and refinement in the self-consistency and precision of the information they contain, is one of the primary objectives of chemical thermodynamics.

The first systematic study of the thermodynamic data needed in the investigation of equilibrium conditions for a group of important reactions was by F. Haber, "Thermodynamik der technischen Gas Reaktionen," R. Oldenbourg, Munich, 1905. The outstanding compilation prior to 1930 was by G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York, 1923; this book summarized many of the authors' original contributions in this field. In 1930, existing free-energy data were critically reviewed by M. Randall, as special editor, in the "International Critical Tables," Vol. VII, pp. 224–353, 1930, published by the McGraw-Hill Book Company for the National Research Council. Extensive free-energy data, not critically evaluated, are compiled in Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIb, pp. 1591–1602, 1931 and Supplement IIIc, pp. 2836–2852, 1936, published originally by Springer-Verlag, Berlin; one should note in using these tables that the data in Supplement IIb have signs opposite to the usual American and present international custom. The free energies of organic compounds were critically reviewed by G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," Reinhold Publishing Corporation, New York, 1932. The free energies of inorganic compounds and of ions in aqueous solution were critically reviewed by W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, 1938. In 1947, the National Bureau of Standards published an extensive summary of properties of the hydrocarbons, including their free energies and enthalpies of formation, Selected Values of Properties of Hydrocarbons, *Natl. Bur. Standards Circ.* C461 (1947). The National Bureau of Standards is at present compiling an extensive table of "Selected Values of Chemical Thermodynamic Properties," F. D. Rossini, project director, which is being issued quarterly in loose-leaf form; this is a very ambitious project, and should ultimately supersede previous compilations. During the last 20 years, many new data on the thermodynamic properties of gases have been obtained from molecular-spectroscopic sources (Chap. 10); these data are being assimilated with the data obtained from equilibrium and thermal studies; critical compilations of molecular-spectroscopic data are included in G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., New York, 1945; "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., New York, 1950; A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," John Wiley & Sons, Inc., New York, 1947.

For substances in liquid solution in a particular solvent, the application of Eq. (8-2-1) involves in the term on the left, not the standard molal free energy of the substance in the pure state, but a special standard molal free energy of formation *in solution* in the given solvent, ϕ'; this will be so if the term K° on the right has been set up formally in the conventional law-of-mass-action manner in terms of *molalities* and *molal activity coefficients, i.e.*, with each mole of reactant in the solution represented by a factor in the denominator of K° equal to its molality (multiplied by an appropriate activity coefficient) and with each mole of product in the solution represented by a similar factor in the numerator of K°. While it would be technically possible to eliminate the quantities ϕ' and express the conditions for equilibrium in a reaction in liquid solution directly in terms of $\bar{F}^\circ$'s for the pure reactants and products, we could do this in general only by abandoning the law of mass action, which has a mathematically convenient form, and is in fact approximately valid in sufficiently dilute solution. Therefore it is convenient to include in our tables, wherever the necessary data are available, not only the value of $\bar{F}^\circ_{298.16}$ for the pure compound but also the value of $\phi'_{298.16}$ in various liquid solvents, particularly in water. The value of ϕ' may be related to the value of $\bar{F}^\circ$ directly from equilibrium data between the pure compound and the solution, through the methods described in Chap. 7; thus, for equilibrium between $NH_3(g)$ and $NH_3(aq)$,

$$NH_3(g) = NH_3(aq)$$

$$(\bar{F}^\circ_T)_{NH_3(g)} + RT \ln p_{NH_3} = \phi'_{NH_3(aq)} + RT \ln m_{NH_3}\gamma'_{NH_3}$$

$$\Delta F^\circ_T = \phi'_{NH_3(aq)} - \bar{F}^\circ_{NH_3(g)} = -RT \ln \frac{m_{NH_3}\gamma'_{NH_3}}{p_{NH_3}} = -RT \ln \left(\lim_{m \to 0} \frac{m_{NH_3}}{p_{NH_3}} \right)$$

From measured values of the partial pressure of NH_3 in equilibrium with solutions of various molalities at 25°C, which actually satisfy Henry's law rather well, $\lim\limits_{m \to 0} m_{NH_3}/p_{NH_3} = 56.7$ (mole/kg H_2O)/atm (according to Lewis and Randall). Thus

$$\phi'_{NH_3(aq)} - \bar{F}^\circ_{NH_3(g)} = -2390 \text{ cal}$$

Combining this result with the value of $\bar{F}^\circ_{NH_3(g)}$ as established directly from equilibrium measurements with N_2 and H_2 at high temperatures (-3976 cal/mole), $\phi'_{NH_3(aq)} = -6366$ cal/mole; *i.e.*,

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) = NH_3(aq); \qquad \Delta F^\circ_{298.16} = -6366 \text{ cal}$$

If one sets up the law-of-mass-action expression K° with molar concentrations C instead of molalities m, then the term ΔF°_T on the left of Eq. (8-2-1) will involve slightly different terms, ϕ'', for the reactants and products in solution, where each ϕ'' is related to the corresponding ϕ' by means of Eq. (7-117a),

$$\phi'' = \phi' - RT \ln \rho_1$$

where ρ_1 represents the density of the pure solvent; for aqueous solutions at 25°C, $\phi'' = \phi' + 1.7$ cal.

The general modifications for electrolytes have been noted in Sec. 7-4, and also in some of the examples considered in Sec. 8-1d. We may treat each ionic reactant and product formally as an independent solute, so long as every thermodynamic operation is consistent with the over-all electrical neutrality of each phase in which the ions may be present. In order to assign values of ϕ' to individual ions in a particular medium, it has become the custom to assign $\phi'_{H^+} = 0$, at least in aqueous solutions, and a similar convention would be needed in other solvents if the experimental data were sufficiently extensive to warrant systematic analysis.

Appendix 2 includes standard free energies of formation for a selected group of chemical substances. From such a table, one may reconstruct the value of $\Delta F^\circ_{298.16}$ for any reaction among the substances included. Even more significantly, one may predict the value of $\Delta F^\circ_{298.16}$ for hitherto untested reactions among them. Such a compilation evidently introduces the utmost economy in the correlation of equilibrium data. By working back through Eqs. (8-2-3), (8-2-2), and (8-2-1), one may translate this information into theoretical equilibrium yields under various conditions of temperature, pressure, and composition.

The standard free energy of formation is thus a quantitative measure of the relative tendency of a chemical substance to enter into chemical transformations with other substances. The higher its value, in the algebraic sense, the greater is the extent to which it tends to undergo transformation from its standard state, though of course the over-all tendency of a particular transformation is determined by the net free-energy difference between all the reactants and all the products. A substance whose standard free energy of formation happens to be positive at a given temperature is thermodynamically metastable toward decomposition into its own elements; when the decomposition would be accompanied by a large volume increase (*e.g.*, gas evolution), together with evolution of heat to raise the temperature locally and speed up the reaction, the situation may be fraught with disastrous possibilities, as Lewis and Randall noted in the case of NH_4NO_3(c), ordinarily regarded as a reasonably stable compound.[1]

It should be emphasized throughout that the second law of thermody-

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[1] G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," p. 606, McGraw-Hill Book Company, Inc., New York, 1923.

namics is essentially *negative* in character; it denies the possibility of certain transformations [*e.g.*, of any transformation for which $(\Delta F)_{T,p} > -W'$], but it does not guarantee that any change shown to be thermodynamically feasible will in fact take place. Otherwise diamonds would not exist, and ammonia could be synthesized at room temperature. The second law gives us no information concerning the rate at which equilibrium will be attained, though thermodynamic data may be extremely helpful in the elucidation of reaction mechanisms. Situations may arise also in which competing processes take place, which one did not take into account.

8-3. The Entropy of Reaction and the Third Law of Thermodynamics. We have seen in Sec. 6-2 that the entropy of a chemical substance in any state at temperature T and pressure p may be related to its value $\bar{S}^\circ_{T_s}$ in some standard reference state at temperature T_s and pressure p_0 through the general equation

$$\bar{S}_{T,p} = \bar{S}^\circ_{T_s} + \int_{T_s}^{T} \bar{C}^\circ_p \, d\ln T - \int_{p_0}^{p} \left(\frac{d\bar{V}}{dT}\right)_p dp \tag{8-3-1}$$

The second term on the right of Eq. (8-3-1) represents the change of $\bar{S}$ with temperature at the constant pressure p_0, while the third term represents the change of $\bar{S}$ with pressure at the constant temperature T. For pure liquids and solids, p_0 is taken to be 1 atm, and for moderate pressures, the third term on the right of (8-3-1) may usually be neglected; for an ideal gas, this term would reduce to $-R \ln (p/p_0)$, but for a real gas at finite pressures, it may be evaluated from actual equation-of-state data [compare Eq. (6-44)]; for gases, the standard reference state is taken to be that of a hypothetical ideal gas at $p_0 = 1$ atm, as explained in Sec. 6-2. Furthermore, for a constituent of a solution at given temperature, as shown in Chap. 7, we may write in general

$$\sigma_i = \frac{\eta_i - \phi_i}{T} \tag{8-3-2}$$

or, introducing Eq. (7-3-82) for a solute in liquid solution in a given medium,

$$\sigma_i = \frac{\eta_i}{T} - \frac{\phi'_i}{T} - R \ln m_i\gamma'_i \tag{8-3-3}$$

This relation may be put also in the form [compare Eqs. (7-1-26*a*), (7-3-82), and (4-37)]

$$\sigma_i = \sigma'_i - R \ln m_i\gamma'_i - RT\left(\frac{d \ln \gamma'_i}{dT}\right)_{p,n} \tag{8-3-4}$$

where

$$\sigma'_i = \frac{\Phi^\circ_h - \phi'_i}{T} \tag{8-3-5}$$

The equation corresponding to (8-3-4) for a strong electrolyte, $A_{\zeta_+}B_{\zeta_-}$, would be

$$\sigma_i = \sigma_i' - R \ln m_A^{\zeta_+} m_B^{\zeta_-} + \zeta RT \ln \gamma_\pm - \zeta RT \left(\frac{d \ln \gamma_\pm}{dT}\right)_{p,n} \tag{8-3-6}$$

where we could regard σ_i' as a sum of ionic entropies, if in the given medium, such as water, we adopt the preliminary convention,

$$\sigma'_{\mathrm{H^+(aq)}} = 0 \tag{8-3-7}$$

[compare Eq. (7-4-14)].

Now, the entropy of a chemical transformation

$$aA + bB + \cdots = lL + mM + \cdots \tag{8-3-8}$$

$$\Delta S = l\bar{S}_L + m\bar{S}_M + \cdots - a\bar{S}_A - b\bar{S}_B - \cdots \tag{8-3-9}$$

(where it is understood that for any constituent of a solution, we substitute the partial molal entropy σ_i in place of the molal entropy $\bar{S}_i$ of the pure component), may be calculated from reversible equilibrium data establishing the value of ΔF and calorimetric data establishing the value of ΔH, adjusted to the same temperature and pressure, through the general relationship

$$\Delta S = \frac{\Delta H - \Delta F}{T} \qquad (T \text{ const}) \tag{8-3-10}$$

Equation (8-3-10) is actually nothing more than a definition of the relationship among the three quantities, ΔS, ΔH, and ΔF. Or, we could calculate ΔS directly from reversible equilibrium data at several temperatures in the form

$$\Delta S = -\left(\frac{d\,\Delta F}{dT}\right)_p \tag{8-3-11}$$

The explicit calculation of ΔS by means of Eqs. (8-3-10) or (8-3-11) would in fact produce no new information not already implied by knowledge of ΔH and ΔF, if it were not for the further empirical observations to be discussed in this section. In fact, we have so far been eliminating all explicit reference to ΔS by combining Eqs. (8-3-10) and (8-3-11) in the form of van't Hoff's relation

$$\left[\frac{d(\Delta F_T/T)}{d(1/T)}\right]_p = \Delta H_T \tag{8-3-12}$$

ΔF and ΔH being more immediately related to familiar experimental properties of the reaction (the equilibrium constant and the heat of reaction, respectively) than ΔS. In this section, we shall now discuss an independent method of measuring ΔS directly from purely thermal data, which lends to ΔS important physical significance in its own right; this method of establishing ΔS, combined with standard thermochemical measurement of ΔH, serves through Eq. (8-3-10) to determine the value of ΔF and by implication the thermodynamic equilibrium constant for the reaction, without the need for setting up a single reversible or equilibrium state of the reaction itself. The value of such a principle is manifest, and its importance in modern chemical technology can hardly be overestimated.

Let us consider a reaction among pure crystalline solids at standard pressure of 1 atm; then, according to Eq. (8-3-1),

$$\Delta S_T^\circ = \Delta S_{T_1}^\circ + \int_{T_1}^{T} \Delta C_p^\circ \frac{dT}{T} \tag{8-3-13}$$

Suppose we examine what happens as $T \to 0$. We have seen in Sec. 3-4 that the molal heat capacities of crystalline solids in general approach zero as $T \to 0$; they do so, when sufficiently low temperatures have been reached, according to the empirical law $\bar{C}_p^\circ = aT^3$ [Eq. (3-55)], where for the simpler types of crystals the value of a can be evaluated theoretically from heat-capacity data at higher temperatures or from the elastic constants of the crystal, according to the theory of Debye or the extended treatment given by Born and von Kármán and by Blackman. For our present purpose, however, we need merely note that ΔS_T° for reactions among pure crystalline solids evidently approaches in each case a finite limit as $T \to 0$, whose value we may represent by the symbol ΔS_0°. If $\Delta S_0^\circ = \lim_{T\to 0} \Delta S_T^\circ$ remains finite, then, according to Eq. (8-3-10), the values of ΔH_T° and ΔF_T° for such reactions must approach each other as $T \to 0$. This was indeed noted as an empirical fact by T. W. Richards in 1903, from the trend of free-energy data obtained over a range of temperatures by means of galvanic cells (by methods discussed in Chap. 9).[1] The question arose: Do they approach each other asymptotically, so that in the limit as $T \to 0$

$$\lim_{T\to 0} \left(\frac{d\Delta F_T^\circ}{dT}\right) = \lim_{T\to 0} \left(\frac{d\Delta H_T^\circ}{dT}\right) \tag{8-3-14}$$

or does a finite difference persist between the limiting slopes of the ΔF_T° vs. T and the ΔH_T° vs. T relationships? The answer to this question, while not implied by the first and second laws of thermodynamics, is of considerable theoretical and practical importance, because if Eq. (8-3-14) is empirically true, then in view of empirical and theoretical heat-capacity information, which indicates that

[1] T. W. Richards, *Z. physik. Chem.*, **42**, 129–154 (1902).

$$\lim_{T\to 0}\left(\frac{d\Delta H_T^\circ}{dT}\right) = \lim_{T\to 0}\,(\Delta C_p^\circ) = 0 \tag{8-3-15}$$

Eq. (8-3-10) implies that

$$\lim_{T\to 0}\Delta S_T^\circ = \Delta S_0^\circ = 0 \tag{8-3-16}$$

On the basis of the experimental evidence available at the time, Walther Nernst,[1] in an important paper published in 1906, came to the conclusion that condition (8-3-16) was indeed satisfied by many reactions involving pure crystalline phases. A wealth of additional evidence has since been accumulated, and also a few exceptions discovered, whose general nature we shall discuss in Chap. 10.

It follows that we may assign to all substances satisfying *Nernst's heat theorem* (8-3-16), or the so-called *third law of thermodynamics*, for all reactions in which they participate, a common value of the standard molal entropy $\bar{S}_0^\circ$ in the pure crystalline state at 0°K. It is convenient and sensible for us to let this common zero-point entropy have the conventional value, *zero*, as suggested originally by Max Planck:[2]

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[1] W. Nernst, *Nachr. kgl. Ges. Wiss. Göttingen, Math.-physik. Klasse*, (1906), pp. 1–40. Nernst later summarized his work in "Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes," W. Knapp, Halle, 1918, translated by G. Barr as "The New Heat Theorem," E. P. Dutton & Co., Inc., New York, 1926.

[2] M. Planck, *Ber. deut. chem. Ges.*, **45**, 5–23 (1912). In view of the formal thermodynamic relationship $F = H - TS$, which essentially defines F [Eq. (5-59)], one might at first suppose that convention (8-3-17), which applies alike to elements and compounds, might clash with our previous conventions to let $\bar{H}_{T_s}^\circ$ and $\bar{F}_{T_s}^\circ$ represent standard enthalpies and free energies of formation from the elements at $T_s = 298.16$°K. Reflection shows, however, that the formal relationship $\bar{F}_T^\circ = \bar{H}_T^\circ - T\bar{S}_T^\circ$ has no physical significance except in connection with *changes* of state; the first and second laws of thermodynamics, as well as the third law, Eq. (8-3-16), are statements concerning *changes* taking place in thermodynamic systems. For changes involving only the pure chemical substance itself, the "absolute" values assigned to $\bar{F}$ and $\bar{H}$ in any one reference state are entirely immaterial, and, likewise, only differences in the value of $\bar{S}$ between two different states have any meaning; the convention (8-3-17) has in fact no bearing at all on such changes. For chemical changes, likewise, only ΔF, ΔH, and ΔS values have direct physical significance, and therefore it is not inconsistent for us to assign to a chemical element a zero $\bar{H}_{T_s}^\circ$, a zero $\bar{F}_{T_s}^\circ$, but a finite $\bar{S}_{T_s}^\circ$ [on the basis of convention (8-3-17)], with the understanding that such values have significance only when recombined with corresponding values for other chemical substances in the form of $\Delta H_{T_s}^\circ$, $\Delta F_{T_s}^\circ$, and $\Delta S_{T_s}^\circ$ for some chemical transformation, including in particular transformations representing the formations of chemical compounds from their elements in standard reference states. In other words, the new physical principle represented by Eq. (8-3-16) implies that $\bar{S}_{T_s}^\circ$ values determined by experiment on the pure chemical substance in relation to the convention (8-3-17) (or any other convention that would assign a *uniform* value, not necessarily 0, to $\bar{S}_0^\circ$ for pure crystalline solids), will satisfy the relationship $\Delta F_{T_s}^\circ = \Delta H_{T_s}^\circ - T_s\Delta S_{T_s}^\circ$

$$\lim_{T\to 0} \bar{S}^\circ_T = \bar{S}^\circ_0 = 0 \quad \text{(most pure crystalline solids)} \tag{8-3-17}$$

Let us examine how the convention (8-3-17) is actually applied and how the principle (8-3-16) is tested. For a chemical substance in the crystalline state that undergoes no phase transition and shows no other irregularity in thermal behavior between 0°K and T, Eq. (8-3-1) upon introduction of (8-3-17) may be put in the form

$$\bar{S}^\circ_T = \int_0^T \bar{C}^\circ_p \, d \ln T \tag{8-3-18}$$

In particular, with $T = T_s$ (*e.g.*, 298.16°K), the evaluation of this integral gives us a standard value $\bar{S}^\circ_{T_s}$ of the molal entropy at the standard reference temperature T_s. The integral is generally evaluated in two parts; its value up from the lowest temperature at which $\bar{C}^\circ_p$ has actually been measured may be determined by graphical integration from a plot of $\bar{C}^\circ_p$ vs. log T; the balance, from 0°K to the temperature at which the measurements begin, is determined by means of an extrapolation. The more reliable series of measurements for the purpose extend down at least to liquid hydrogen temperatures (about 14°K); some investigations have extended down to liquid helium temperatures. The extrapolation may consist either of the simple approximation $\frac{1}{3}\bar{C}^{\circ\prime}_p$, where $\bar{C}^{\circ\prime}_p$ represents the observed heat capacity at a sufficiently low temperature, within the range of the T^3 law,[1] or more precisely of the fitting of a modified Debye function to the observed data, with an appropriate empirically determined value of the parameter θ.[2] A detailed discussion of the extrapolation has been given by K. K. Kelley.[3] Figure 8-5*a* shows, for example, $\bar{C}^\circ_p$ plotted against T for AgCl(c) from measurements by K. Clusius and P. Harteck (10 to 126°K) and by E. D. Eastman and R. T. Milner (15 to 293°K); in Fig. 8-5*b*, the same data have been plotted in the form of $\bar{C}^\circ_p$ vs. log T.[4] Graphical integration between 10°K and 298.16°K has

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for any chemical transformation involving other chemical substances whose $\bar{S}^\circ_{T_s}$ values have been determined on the basis of the same convention. This relationship applies in particular to the formation of a chemical compound from its elements.

[1] If $\bar{C}^\circ_p = aT^3$ at sufficiently low values of T, then $\int_0^{T'} (\bar{C}^\circ_p/T)dT = aT'^3/3 = \bar{C}^{\circ\prime}_p/3$. In principle, the T^3 law applies to $\bar{C}_v$, but at liquid hydrogen temperatures the difference between $\bar{C}^\circ_p$ and $\bar{C}_v$ [Eq. (3-41); see also Eq. (3-57)] has usually become negligible.

[2] The entropy integral (8-3-18) where $\bar{C}^\circ_p$ is represented by the Debye function $D(\theta/T)$, Eq. (3-54), has been tabulated as a function of θ/T; see Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement I, p. 707, 1927.

[3] K. K. Kelley, *U.S. Bur. Mines Bull.* 434 (1941).

[4] K. Clusius and P. Harteck, *Z. physik. Chem.*, **134,** 243–263 (1928); E. D. Eastman and R. T. Milner, *J. Chem. Phys.*, **1,** 444–456 (1933).

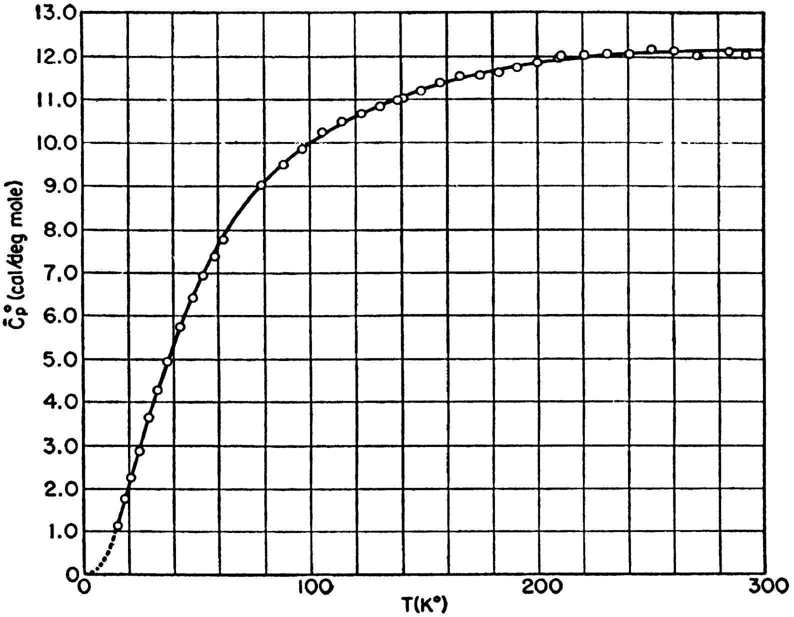

FIG. 8-5*a*. $\bar{C}_p^\circ$ vs. T for AgCl(c). (*Data of E. D. Eastman and R. T. Milner.*)

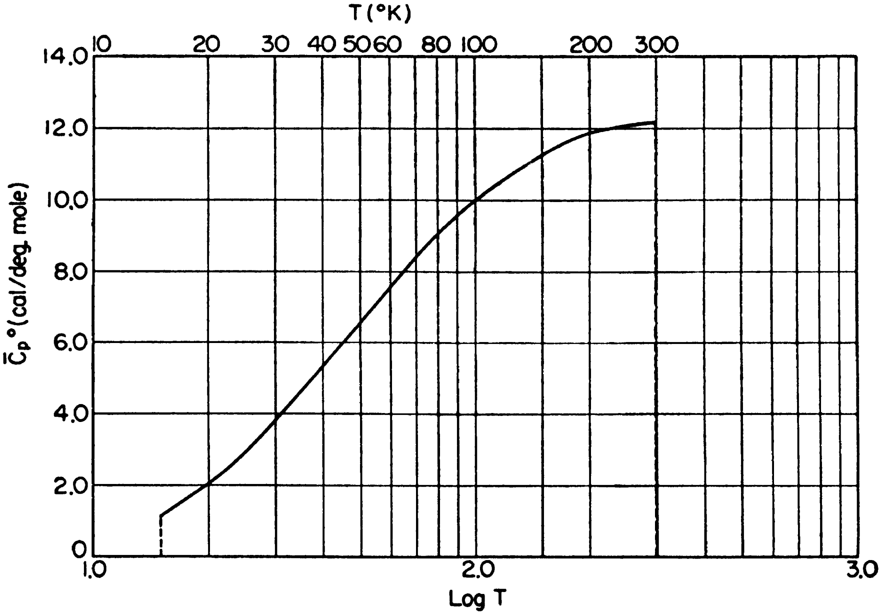

FIG. 8-5*b*. $\bar{C}_p^\circ$ plotted against log T for AgCl(c). (*Smoothed data of Fig.* 8-5*a*.)

yielded $\bar{S}^\circ_{298.16} - \bar{S}^\circ_{10} = 22.83$ eu/mole, while the extrapolation from 10°K to 0°K has yielded $\bar{S}^\circ_{10} - \bar{S}^\circ_0 = 0.14$ eu/mole. Thus, in view of (8-3-17),

$$(\bar{S}^\circ_{298.16})_{\mathrm{AgCl(c)}} = 22.97 \pm 0.10 \text{ eu/mole} \tag{8-3-19}$$

From similar data for Ag(c), which in this case extend down to 1.35°K (below which the entropy extrapolation to 0°K is negligible), K. K. Kelley has compiled a best value:[1]

$$(\bar{S}^\circ_{298.16})_{\mathrm{Ag(c)}} = 10.20 \pm 0.05 \text{ eu/mole} \tag{8-3-20}$$

For the slightly more involved case of a substance that melts at temperature T°_F with latent heat of fusion $\bar{L}^\circ_{cl}$ and boils at normal boiling point T°_B with latent heat of vaporization $\bar{L}^\circ_{lg}$, within the temperature range, 0 to T, the standard molal entropy of the gas at T, based on the supposition that the 0°K crystalline phase satisfies the third law, is given by the generalization of (8-3-18)

$$\bar{S}^\circ_T = \int_0^{T_F^\circ} (\bar{C}^\circ_p)_c \, d \ln T + \frac{\bar{L}^\circ_{cl}}{T^\circ_F} + \int_0^{T_B^\circ} (\bar{C}^\circ_p)_l \, d \ln T + \frac{\bar{L}^\circ_{lg}}{T^\circ_B} + \int_{T_B^\circ}^{T} (\bar{C}^\circ_p)_g \, d \ln T \tag{8-3-21}$$

To this expression, one must add a correction to reduce to the ideal-gas entropy at T°_B and 1 atm [*e.g.*, through Eq. (6-45); see also Prob. 6-10]. The first integral on the right of (8-3-21) is evaluated in the same manner as before: graphical integration between T°_F and the lowest temperature to which the actual measurements of $(\bar{C}^\circ_p)_c$ reach, combined with an extrapolation below. The generalization of (8-3-21) to include possible reversible phase transitions between different crystalline phases below the melting point is sufficiently obvious.

In Fig. 8-6*a*, $\bar{C}^\circ_p$ has been plotted against T for Cl_2, from measurements by W. F. Giauque and T. M. Powell,[2] and in Fig. 8-6*b*, the same data, taken from their smoothed results, have been plotted in the form of $\bar{C}^\circ_p$ vs. log T. Table 8-8 presents the summary of their calculations; their correction for deviation of $Cl_2(g)$ from ideal-gas behavior at its normal boiling point at 1 atm was made by means of Berthelot's equation (see Prob. 6-10). Their evaluation of the last term in Eq. (8-3-21) for $Cl_2(g)$ between its normal boiling point and 298.16°K was based not on actual calorimetric data but on the considerably more precise molecular spectroscopic method, which we shall consider in Chap. 10.

Combining the result summarized in Table 8-8 with the previous results, (8-3-19) and (8-3-20), we may infer on the basis of the third law

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[1] K. K. Kelley, *U.S. Bur. Mines Bull.* 434 (1941.)

[2] W. F. Giauque and T. M. Powell, *J. Am. Chem. Soc.*, **61**, 1970–1974 (1939).

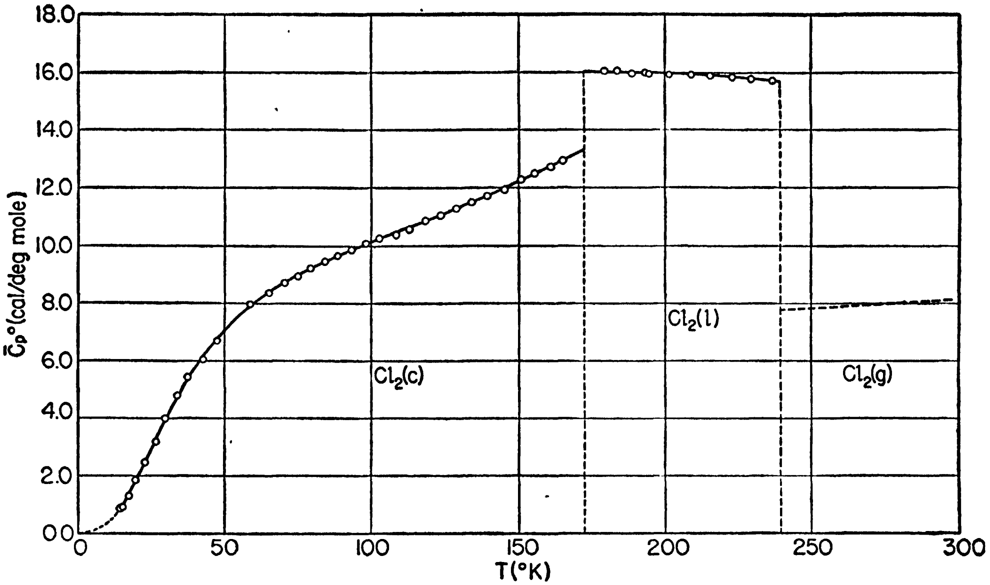

FIG. 8-6a. $\bar{C}_p$° vs. T for Cl_2. (*Data of W. F. Giauque and T. M. Powell; values for* $Cl_2(g)$ *derived by calculation from spectroscopic data as described in Chap.* 10.)

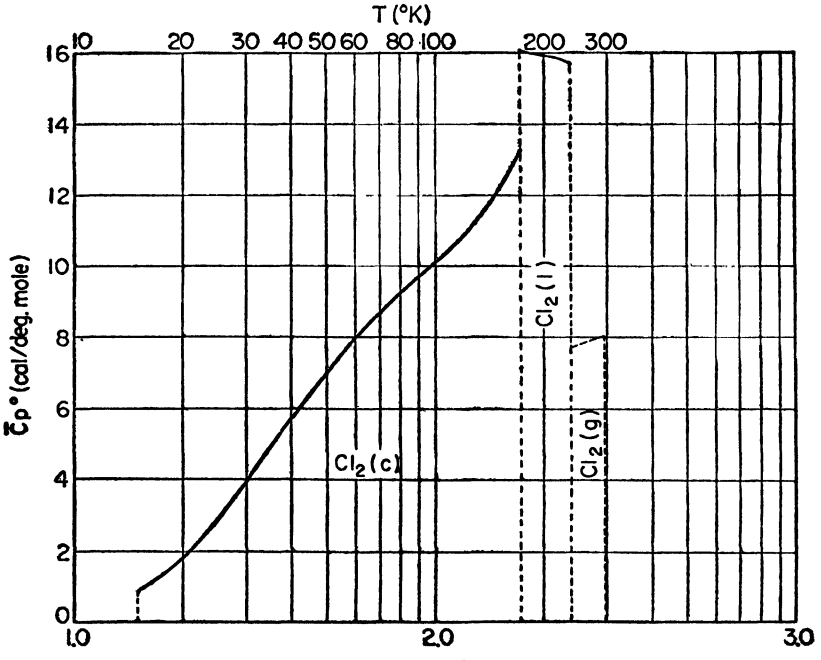

FIG. 8-6b. $\bar{C}_p$° plotted against log T for Cl_2. (*Smoothed data of Fig.* 8-6a.)

(8-3-17) for the formation of AgCl(c) from its elements

$$Ag(c) + \tfrac{1}{2}Cl_2(g) = AgCl(c); \qquad \Delta S^\circ_{298.16} = 22.97 - 10.20 - \tfrac{1}{2}(53.32)$$
$$= -13.89 \pm 0.15 \text{ eu} \qquad (8\text{-}3\text{-}22)$$

TABLE 8-8. CALCULATION OF THE ENTROPY OF $Cl_2(g)$[*]

	Eu/mole
Crystals, 0–15°K, Debye function, with $\theta = 115$ deg	0.331
Crystals, 15–172.12°K, graphical	16.573
Fusion, $T_F^\circ = 172.12$°K, $\bar{L}_{cl} = 1531$ cal/mole	8.895
Liquid, 172.12–239.05°K, graphical	5.231
Vaporization, $T_B^\circ = 239.05$°K, $\bar{L}_{lg} = 4878$ cal/mole	20.406
Correction to ideal gas at 239.05°K and 1 atm	0.12
Ideal gas, 239.05–298.16°K, spectroscopic	1.76
$(\bar{S}^\circ_{298.16})_{Cl_2(g)} =$	53.32 ± 0.10

[*] W. F. Giauque and T. M. Powell, *J. Am. Chem. Soc.*, **61**, 1970–1974 (1939).

This result may be compared with the experimental value of

$$\Delta S^\circ_{298.16} = -13.76 \pm 0.10 \text{ eu}$$

obtained for this reaction by R. H. Gerke, from direct measurement of the temperature coefficient of ΔF [Eq. (8-3-11)] given by emf data, as described in Chap. 9; the agreement is excellent.[1] One may test the third law independently for this reaction by taking into consideration W. A. Roth's and A. Bertram's direct calorimetric determination of

$$\Delta H^\circ_{298.16} = -30{,}800 \text{ cal}^\dagger$$

Introducing this result with the third-law value of $\Delta S^\circ_{298.16}$ in Eq. (8-3-10), we obtain for $\Delta F^\circ_{298.16}$

$$\Delta F^\circ_{298.16} = -30{,}800 \text{ cal} - 298.16 \text{ deg } (-13.89 \text{ eu})$$
$$= -25{,}980 \text{ cal}$$

as compared with Gerke's direct experimental value for $\Delta F^\circ_{298.16}$ itself of $-26{,}210$ cal.

The number of such examples of the power of the third law could be multiplied indefinitely. By implication, the third law enables us to calculate equilibrium conditions for reactions at ordinary and high temperatures from purely thermal data in the form

$$\Delta F^\circ_T = -RT \ln K^\circ = \Delta H^\circ_T - T\,\Delta S^\circ_T \qquad (8\text{-}3\text{-}23)$$

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[1] R. H. Gerke, *J. Am. Chem. Soc.*, **44**, 1684–1704 (1922); his result of

$$\Delta S_{298.16} = -13.73 \text{ eu}$$

with $Cl_2(g)$ at a pressure of 1 atm, has been corrected for deviation of $Cl_2(g)$ from ideal-gas behavior at 298.16°K and 1 atm according to Berthelot's equation of state.

[†] Reported by W. A. Roth in Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIIc, p. 2760, 1936, and corrected from 18°C to 25°C.

without the necessity for setting up a single preliminary equilibrium experiment. Thus, the entropies of the chemical substances $CaCO_3$ (calcite), CaO(c), and CO_2(g) have all been determined from low-temperature heat-capacity measurements; K. K. Kelley's excellent critical compilation gives the results:[1]

$$\begin{aligned} CaCO_3(\text{calcite}): \bar{S}^\circ_{298} &= 22.2 \pm 0.2 \text{ eu/mole} \\ CaO(c): \bar{S}^\circ_{298} &= 9.5 \pm 0.2 \text{ eu/mole} \\ CO_2(g): \bar{S}^\circ_{298} &= 51.1 \pm 0.1 \text{ eu/mole} \end{aligned}$$

Therefore for the reaction,

$$CaCO_3(\text{calcite}) = CaO(c) + CO_2(g); \qquad \Delta S^\circ_{298} = +38.4 \text{ eu}$$

Combining this third-law entropy of reaction, deduced entirely from measurements conducted on the separate pure chemical substances, with the enthalpy of reaction recorded in Sec. 8-1*b*, $\Delta H^\circ_{298} = 42{,}600$ cal, as derived from thermochemical measurements of the heats of solution of $CaCO_3$(calcite) and CaO(c) in dilute hydrochloric acid, we obtain

$$\begin{aligned} \Delta F^\circ_{298} &= 42{,}600 \text{ cal} - (298 \text{ deg})(38.4 \text{ eu}) \\ &= 31{,}150 \pm 200 \text{ cal} \end{aligned}$$

We could easily extend the calculations to higher temperatures, from further knowledge only of the heat capacities of the separate substances, and thus predict the dissociation pressure at any temperature from purely thermal data. We may compare the value of ΔF°_{298} just calculated on the basis of the third law with the value of 31,260 derived by Bäckström from the extrapolation down to 298°K of actual equilibrium data obtained at high temperatures; the agreement is indeed excellent.

As one further illustration, let us consider the third-law entropies of N_2(g), H_2(g), and NH_3(g), for which Kelley has compiled the following values:

$$\begin{aligned} N_2(g): \bar{S}^\circ_{298} &= 45.9 \pm 0.1 \text{ eu/mole} \\ H_2(g): \bar{S}^\circ_{298} &= 31.3 \pm 0.1 \text{ eu/mole} \\ NH_3(g): \bar{S}^\circ_{298} &= 45.9 \pm 0.1 \text{ eu/mole} \end{aligned}$$

These values have all been supplanted by the more precise values obtainable from a statistical molecular analysis of the spectra of the three gases, as we shall observe in Chap. 10; but they serve to illustrate the usefulness and essential validity of the third law. Thus, for the ammonia synthesis (hypothetical) at 298°K,

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) = NH_3(g); \qquad \Delta S^\circ_{298} = -24.0 \text{ eu}$$

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[1] K. K. Kelley, Contribution to the Data on Theoretical Metallurgy. IX. The Entropies of Inorganic Substances. Revision (1940) of Data and Methods of Calculation. *U.S. Bur. Mines Bull.* 434 (1941).

Let us combine this value of ΔS°_{298} with the thermochemical value of $\Delta H^\circ_{298} = -11{,}040$, from the work of Becker and Roth, quoted in Sec. 8-1c,

$$\begin{aligned}\Delta F^\circ_{298} &= -11{,}040 \text{ cal} - (298 \text{ deg})(-24.0 \text{ eu}) \\ &= 3880 \pm 60 \text{ cal}\end{aligned}$$

This result agrees within experimental error with the value of ΔF°_{298} derived by extrapolation (based on heat-capacity data) from high-temperature equilibrium measurements [compare Eq. (8-1-24)].

The third law of thermodynamics has been used extensively by W. M. Latimer and his associates in the establishment of standard ionic entropies in aqueous solution.[1] For many electrolytes, the enthalpies of formation in solution (Φ°_h, or $\lim\limits_{m_2 \to 0} \eta_2$) are known, but the free energies of formation in solution (ϕ'_2) cannot be measured directly by equilibrium or emf methods, because of the slowness or irreversibility of the available reactions. In such cases, the establishment of σ'_2 independently from thermal data has permitted the calculation of ϕ'_2 through the general relation (8-3-5). A specific example will illustrate the method, and the types of experimental information required.

For KIO_3(c), from heat-capacity measurements between 17.30 and 298.16°K, together with a Debye function extrapolation between 0 and 17.30°K, J. E. Ahlberg and W. M. Latimer found that

$$(\bar{S}^\circ_{298.16})_{KIO_3(c)} = 36.20 \text{ eu/mole}\dagger$$

The solubility of this salt in water at 25°C is 0.43 mole/kg; while the value of $\gamma^*_\pm$ for the saturated solution has not been directly measured, Ahlberg and Latimer assigned the value $\gamma^*_\pm = 0.52$, by analogy with $AgNO_3$ at the same concentration (compare also Fig. 7-19). Therefore

$$\phi_{KIO_3(0.43m)} = \phi'_{KIO_3(aq)} + 2RT \ln m^*_2\gamma^*_\pm = \bar{F}^\circ_{KIO_3(c)}$$

from which we obtain for the standard free energy of solution

$$KIO_3(c) = KIO_3(aq); \qquad \Delta F^\circ = \phi'_{KIO_3(aq)} - \bar{F}^\circ_{KIO_3(c)} = 1770 \text{ cal}$$

This quantity represents the free-energy change that would take place if 1 mole of KIO_3(c) were to be dissolved in a hypothetical ideal dilute solution of KIO_3 (completely ionized) at 1*m* concentration. In this case, $\bar{F}^\circ_{KIO_3(c)}$ is not independently known. Now, the total heat of solution at infinite dilution has been measured by F. D. Rossini, leading to the

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[1] W. M. Latimer, P. W. Schutz, and J. F. G. Hicks, *J. Chem. Phys.*, **2**, 82–84 (1934); W. M. Latimer, *Chem. Rev.*, **18**, 349–358 (1936); many subsequent papers published in the *Journal of the American Chemical Society.*

† J. E. Ahlberg and W. M. Latimer, *J. Am. Chem. Soc.*, **56**, 856–858 (1934).

conclusion

$$KIO_3(c) = KIO_3(aq); \qquad \Delta H^\circ = (\Phi_h^\circ)_{KIO_3(aq)} - \bar{H}^\circ_{KIO_3(c)} = 6340 \text{ cal}$$

Therefore, according to the general thermodynamic relationship (8-3-10),

$$KIO_3(c) = KIO_3(aq); \qquad \Delta S^\circ = \sigma'_{KIO_3(aq)} - \bar{S}^\circ_{KIO_3(c)} = \frac{6340 - 1770}{298.16} \text{ eu}$$
$$= 15.3 \text{ eu}$$

This quantity represents the entropy change that would take place if 1 mole of $KIO_3(c)$ were to be dissolved in a hypothetical ideal dilute solution of KIO_3 at 1*m* concentration. Combining with the third-law entropy value for $KIO_3(c)$,

$$\sigma'_{KIO_3(aq)} = 36.2 + 15.3 = 51.5 \text{ eu/mole}$$

The value of σ_{KIO_3} at finite concentrations in real solutions is of course represented by Eq. (8-3-6). From $\sigma'_{K^+(aq)} = 24.6$ eu/mole calculated by Latimer, Schutz, and Hicks from similar data for other potassium salts, with ultimate reference to the convention (8-3-7), Ahlberg and Latimer thereupon drew the conclusion that for $IO_3^-(aq)$ at 298.16°K,

$$\sigma'_{IO_3^-(aq)} = 26.9 \text{ eu/mole}$$

This standard ionic entropy of $IO_3^-(aq)$ could now be combined with the value derived for some other cation, together with the heat of solution, solubility, and activity coefficient in the saturated solution of the corresponding salt, to determine $\bar{S}^\circ_{298.16}$ for the pure crystalline iodate, without the need for low-temperature heat-capacity data; or, if one had the standard enthalpy of formation of the pure compound, as well as the enthalpy of solution, so that the value of Φ_h° itself could be computed, then the ionic entropies *relative to the elements in their standard states* (at 25°C and 1 atm), introduced in Eq. (8-3-6), would provide the value of ϕ', the standard free energy of formation of the strong electrolyte in aqueous solution. One should note that Latimer's ionic entropies, like the entropies of ordinary chemical substances, refer to the third-law convention (8-3-17), as well as to (8-3-7), so that one would write formally for the standard entropy *of formation* of $IO_3^-(aq)$ at 298.16°K:

$$\tfrac{1}{2}I_2(c) + \tfrac{3}{2}O_2(g) + e = IO_3^-(aq)$$
$$\Delta S^\circ_{298.16} = 26.9 - \tfrac{1}{2}(27.9) - \tfrac{3}{2}(49.03) \text{ eu}$$
$$= -60.6 \text{ eu}$$

(The symbol for the electron included in this equation has purely formal significance, since one can carry out a reaction leading to the formation of an ion in solution only to the accompaniment of some other reaction leading to the formation of other ions of equivalent opposite charge.)

The apparent exceptions to the third law, as well as its general theoretical import, can be understood only in terms of the statistical molecular interpretation of thermodynamics, to which we shall turn in Chap. 10 [see in particular the discussion following Eq. (10-36)]. Its practical value, when due allowance is made for exceptional cases, stands unquestioned.

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Problems

8-1. The pressure of water vapor required to maintain equilibrium between $CaSO_4 \cdot 2H_2O(c)$ and $CaSO_4 \cdot \frac{1}{2}H_2O(c)$ at various temperatures is as follows ("International Critical Tables," Vol. VII, p. 296, 1930):

t, °C	p_{H_2O}, atm
17	0.00661
25	0.0120
48	0.0617
60	0.1180
72	0.2366

Plot log p_{H_2O} vs. $1/T$, and calculate $\Delta F°$ and $\Delta H°$ for the reaction

$$CaSO_4 \cdot 2H_2O(c) = CaSO_4 \cdot \tfrac{1}{2}H_2O(c) + \tfrac{3}{2}H_2O(g)$$

at 25°C. Compare your ΔH° value with that determined in Prob. 4-10 from heats of solution of the two hydrates in water.

NOTE: $\bar{H}^\circ_{H_2O(g)} - \bar{H}^\circ_{H_2O(l)} = 10.514$ kcal/mole at 25°C.

8-2. The dissociation pressure of $CaSO_4 \cdot 2H_2O(c)$ in equilibrium with $CaSO_4$(c, soluble anhydrite) has also been measured and found to be $p_{H_2O} = 0.0188$ atm at 25°C. Calculate ΔF° for the dissociation reaction at that temperature, and calculate also the dissociation pressure of $CaSO_4 \cdot \frac{1}{2}H_2O(c)$, using the data from the preceding problem.

8-3. The equilibrium pressure of water vapor for the reaction

$$Ca(OH_2)(c) = CaO(c) + H_2O(g)$$

has been measured by S. Tamaru and K. Siomi (Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIIc, p. 2578, 1936), who approached equilibrium from both directions. The following are typical results:

t, °C	p_{H_2O}, mm Hg
420.9	94.0
461.8	245.6
482.9	402.8
503.4	618.1

Determine the mean value of $(d \log p)/dT$ over the given temperature range, and calculate the value of ΔH° at 700°K.

The heat capacity of $Ca(OH)_2(c)$ at high temperatures is not known precisely, but $\Delta H^\circ = 15.43 \pm 0.09$ kcal for the reaction

$$Ca(OH)_2(c) = CaO(c) + H_2O(l)$$

at 25°C from straightforward calorimetry. Using the latent heat of vaporization of H_2O at 298.16°K, 10.514 kcal/mole, assume that ΔH° for the dissociation of $Ca(OH)_2(c)$ may be represented as a linear function of T between 298.16 and 700°K, and calculate ΔF° for the reaction at 25°C.

8-4. Using the free-energy data given in Appendix 2, calculate the ranges of $H_2O(g)$ partial pressures over which each of the $CuSO_4$ hydrates, $CuSO_4 \cdot 5H_2O(c)$, $CuSO_4 \cdot 3H_2O(c)$, and $CuSO_4 \cdot H_2O(c)$, and $CuSO_4(c)$ itself, is thermodynamically stable at 25°C.

8-5. The equilibrium between $NH_3(g)$ and $H_2Se(g)$ over $NH_4HSe(c)$ has been studied over the temperature range 15 to 30°C by F. F. Mikus and F. J. Poss [*J. Am. Chem. Soc.*, **71,** 429–431 (1949)]. Following are the mean dissociation pressures of the solid:

t, °C	p, mm Hg	t, °C	p, mm Hg
15.0	6.8	24.8	14.0
17.0	7.7	27.7	18.0
19.0	9.1	29.3	20.9
21.0	10.2	30.1	23.1
23.0	12.0		

Plot log K_p vs. t, and calculate $\Delta F°$, $\Delta H°$, and $\Delta S°$ at 25°C for the reaction

$$NH_4HSe(c) = NH_3(g) + H_2Se(g)$$

The spectroscopically determined entropies of $NH_3(g)$ and $H_2Se(g)$ are, respectively, 46.03 and 52.9 eu/mole [K. K. Kelley, *U.S. Bur. Mines Bull.* 434 (1941)]. Calculate $\bar{S}°_{298.16}$ of $NH_4HSe(c)$.

8-6. The dissociation pressure of $NaHCO_3(c)$ for the reaction

$$2NaHCO_3(c) = Na_2CO_3(c) + H_2O(g) + CO_2(g)$$

has the following values, according to the "International Critical Tables," Vol. VII, p. 305, 1930:

t, °C	p, atm
30	0.0082
50	0.0395
70	0.1584
90	0.5451
110	1.6481

Plot log p vs. $1/T$, and from the slope and the intercept on the 298.16°K abscissa (by a slight extrapolation), calculate $\Delta F°$, $\Delta H°$, and $\Delta S°$ at 298.16°K.

What would be the equilibrium p_{H_2O} if $NaHCO_3(c)$ were heated in an atmosphere of $CO_2(g)$ to 90°C at a total pressure of 1 atm?

8-7. J. McMorris and D. M. Yost [*J. Am. Chem. Soc.*, **53**, 2625–2631 (1931)] studied the equilibrium in the reaction

$$\tfrac{1}{2}I_2(g) + \tfrac{1}{2}Br_2(g) = IBr(g)$$

by heating weighed quantities of I_2 in sealed flasks with $CuBr_2(c)$. The partial pressure of $Br_2(g)$ is known for the dissociation reaction

$$CuBr_2(c) = \tfrac{1}{2}Br_2(g) + CuBr(c)$$

and satisfies the equation

$$\log p_{Br_2}\ (\text{atm}) = -\frac{4921.2}{T} + 8.7874$$

over the temperature range in question. The extent of reaction was determined by freezing the vapor phase rapidly with liquid air and measuring the total halogen content ($n_{Br_2} + n_{I_2} + n_{IBr}$) by iodimetric titration. The following typical results were obtained at 115°C:

	I	II
Volume of flask (ml)	430	115.5
Initial I_2 (moles)	12.74×10^{-4}	3.85×10^{-4}
Equilibrium total halogen (moles)	15.37×10^{-4}	4.60×10^{-4}

Noting that for this reaction, $K_p° = K_c°$, independently of the particular unit of pressure or concentration, calculate $K_p°$ for both sets of conditions, assuming that the equilibrium vapor may be regarded as an ideal-gas mixture.

At 151.2°C, they obtained $K_p° = 10.83$, and at 176.0°C, $K_p° = 9.99$. The value of

ΔC_p° for the reaction is practically zero. Calculate ΔH° from the results at the three temperatures, and calculate the value of ΔF° at 298.16°K; calculate also the value of ΔS°. What further data would be needed for the determination of the standard free energy of formation of IBr(c)?

8-8. (*a*) The vapor density of acetic acid has been studied by T. M. Fenton and W. E. Garner (*J. Chem. Soc.*, 1930, pp. 694–700) who found in typical runs at 132°C the following ratios of apparent molecular weights to formula weight ($\bar{M}_{\mathrm{CH_3COOH}}$):

p, atm	$\bar{M}_{\mathrm{apparent}}/\bar{M}_{\mathrm{CH_3COOH}}$
0.4862	1.301
0.6056	1.341

Calculate from each result a value of K_p for the assumed reaction:

$$2\mathrm{HAc(g)} = \mathrm{(HAc)_2(g)}.$$

(*b*) They obtained the following average results at several different temperatures:

t, °C	K_p, atm^{-1}
110	3.72
132	1.329
156	0.479
184	0.168

From a graphic plot of log K_p vs. $1/T$, obtain by extrapolation the value of K_p at 25°C, and calculate also the mean value of the enthalpy of dissociation of the dimer.

(*c*) The vapor pressure of liquid acetic acid at 25°C is 0.0200 atm. From the result of part (*b*), calculate the fraction of monomeric molecules in the equilibrium vapor phase, and calculate ΔF° for the process $\mathrm{HAc(l)} = \mathrm{HAc(g)}$.

(*d*) W. A. Kaye and G. S. Parks [*J. Chem. Phys.*, **2**, 141–142 (1934)] found for the partial vapor pressure of acetic acid (mixture of monomer and dimer) over a 1.316*m* aqueous solution, 0.000290 atm, and over a 2.890*m* solution, 0.000635 atm, both at 25°C. Calculate the equilibrium partial pressure of monomeric molecules for each concentration, and estimate $\lim\limits_{m\to 0} p_{\mathrm{HAc}}/m_{\mathrm{HAc}}$, correcting for the slight degree of ionization at both concentrations. Calculate accordingly the standard free energy of solution $\phi_{\mathrm{HAc(aq)}} - \bar{F}^\circ_{\mathrm{HAc(l)}}$. [See also K. Fredenhagen and H. Liebster, *Z. physik. Chem.*, (A)**162**, 449–453 (1932).]

8-9. (*a*) From the following selected data of M. Bodenstein and W. Pohl [*Z. Elektrochem.*, **11**, 373–384 (1905)] for the reaction

$$\mathrm{SO_3(g)} = \mathrm{SO_2(g)} + \tfrac{1}{2}\mathrm{O_2(g)}$$

T, °K	$-R \ln K_p$, cal/mole deg
801	6.84
852	5.21
900	3.73
953	2.33
1000	1.23

calculate ΔF° and ΔH° at 900°K.

(*b*) The heat capacities of the three gases, calculated from molecular spectroscopic constants by the method described in Chap. 10, are as follows:

Gas	$\bar{C}_p^\circ$, cal/mole deg		
	400°K	700°K	1000°K
$SO_2(g)$	10.35	12.11	12.90
$O_2(g)$	7.194	7.885	8.335
$SO_3(g)$	14.05	17.85	19.75

Express ΔC_p° as a function of T in the form $\Delta \bar{C}_p^\circ = a + bT + cT^2$, and calculate ΔH°, ΔF°, and ΔS° for the reaction at 298.16°K. [Compare W. H. Stockmayer, G. M. Kavanagh, and H. S. Mickley, *J. Chem. Phys.*, **12**, 408–412 (1944).]

(*c*) Using the data in the preceding problem, calculate the equilibrium ratio p_{SO_3}/p_{SO_2} in a gas mixture containing originally $2SO_2:1O_2$ when heated to 900°K at 1 atm. If instead the SO_2 is prepared by burning sulfur in an excess of air such that the equilibrium p_{O_2} is maintained at 0.15 atm, calculate p_{SO_3}/p_{SO_2} at 900°K under such conditions.

(*d*) The dissociation pressure of $Fe_2(SO_4)_3(c)$ into $Fe_2O_3(c)$ and the equilibrium mixture of $SO_3(g)$, $SO_2(g)$, and $O_2(g)$ at 953°K is 0.333 atm ("International Critical Tables," Vol. 7, p. 279, 1930). Using the data in part (*a*), calculate p_{SO_3} in the equilibrium gas phase, and calculate ΔF_{953}° for the reaction

$$Fe_2(SO_4)_3(c) = Fe_2O_3(c) + 3SO_3(g)$$

What further information would one have to obtain in order to use this result for calculating the standard free energy of formation of $Fe_2(SO_4)_3(c)$ at 298.16°K relative to that of $Fe_2O_3(c)$?

8-10. (*a*) H. Flood and O. J. Kleppa [*J. Am. Chem. Soc.*, **69**, 998–1002 (1947)] have measured the equilibrium in the reaction

$$V_2O_5(c) + SO_2(g) = V_2O_4(c) + SO_3(g)$$

with the following (selected) results:

T, °K	$-\log (p_{SO_3}/p_{SO_2})$
831	1.813
857	1.770
878	1.740
906	1.695
918	1.668

The value of ΔC_p° is practically negligible [heat-capacity data for the oxides of vanadium have been measured by O. A. Cook, *J. Am. Chem. Soc.*, **69**, 331–333 (1947)]. Calculate the value of ΔH°, and the value of $\Delta F_{298.16}^\circ$.

(*b*) The form of $V_2O_4(c)$ in the above experiments is the β modification, stable above 345°K, the normal form at 298.16°K being the α modification. The latent heat of transformation at the normal transition point being 2050 cal/mole, and the difference between the heat capacities of the two forms being negligible [O. A. Cook, *J. Am. Chem. Soc.*, **69**, 331–333 (1947)], calculate $\Delta F_{298.16}^\circ$ for the transformation

$$V_2O_4(c, \alpha) = V_2O_4(c, \beta)$$

and calculate $\Delta H°$ and $\Delta F°$ at 298.16°K for the reaction

$$V_2O_5(c) + SO_2(g) = V_2O_4(c, \alpha) + SO_3\ (g)$$

8-11. (*a*) Combining the data given in Probs. 8-9 and 8-10, calculate the dissociation pressure

$$V_2O_5(c) = V_2O_4(c, \beta) + \tfrac{1}{2}O_2(g)$$

for the dissociation of $V_2O_5(c)$ at 900°K. Using the results of Probs. 8-9 and 8-10, calculate also $\Delta F°$ and $\Delta H°$ at 298.16°K for the reaction

$$V_2O_5(c) = V_2O_4(c, \alpha) + \tfrac{1}{2}O_2(g)$$

(*b*) The third-law entropies of $V_2O_5(c)$ and $V_2O_4(c, \alpha)$, from low-temperature calorimetry, are, respectively, 31.3 ± 0.5 and 24.5 ± 0.3 eu/mole, at 298.16°K. Using the entropy value of $O_2(g)$ given in Appendix 2, compare the consistency of these results with the result of part (*a*).

8-12. The equilibrium for the dehydrogenation of benzyl alcohol to benzaldehyde over a Cu-MgO catalyst has been studied by A. H. Cubberley and M. B. Mueller [*J. Am. Chem. Soc.*, **68**, 1149–1151 (1946)]. For the reaction

$$C_6H_5CH_2OH(g) = C_6H_5CHO(g) + H_2(g)$$

they obtained for K_p at 1 atm the following (selected) results:

t, °C	K_p, atm
200	0.177
225	0.264
250	0.558
275	1.09
300	2.14

By plotting log K_p vs. $1/T$, determine the value of $\Delta H°$ at 250°C. Using the estimated heat-capacity equations,

$$\begin{aligned} C_6H_5CH_2OH(g)&: \bar{C}_p^\circ = 4.59 + 0.0801T \\ C_6H_5CHO(g)&: \bar{C}_p^\circ = 4.65 + 0.0715T \\ H_2(g)&: \bar{C}_p^\circ = 6.50 + 0.0009T \end{aligned}$$

express $\Delta H°$ and $\Delta F°$ as functions of T, and calculate $\Delta H°$, $\Delta F°$, and $\Delta S°$ at 298.16°K.

8-13. E. D. Eastman and P. Robinson [*J. Am. Chem. Soc.*, **50**, 1106–1114 (1928)] studied the equilibrium between tin and water vapor at elevated temperatures

$$Sn(l) + 2H_2O(g) = SnO(c) + 2H_2(g)$$

One method they used was to saturate $H_2(g)$ with water by passing it through liquid water in a thermostat and then passing the gas mixture over tin heated in a bulb of silica glass. The tin was heated to a temperature at which it came to equilibrium with the gas mixture of such predetermined composition, the appearance of the tin showing whether it was in an oxidizing or a reducing atmosphere. In one such experiment, with the total (barometric) pressure at 751.6 mm Hg, hydrogen saturated with water vapor at 89.92°C was in equilibrium with Sn(l) and SnO(c) at a temperature of 655°C. Calculate the value of K_p for that temperature.

From extended measurements, they obtained the following "best" equilibrium data at various temperatures:

t, °C	$p_{H_2}/p_{H_2O} = (K_p)^{1/2}$
650	0.456
700	0.340
750	0.266
800	0.213
850	0.174
900	0.144

From a plot of log K_p vs. $1/T$, determine $\Delta F°$, $\Delta H°$, and $\Delta S°$ at 1000°K.

8-14. The thermodynamic properties of $H_2O(g)$ and of $H_2(g)$ at high temperatures are well known. Thus, from data summarized in "Selected Values of Chemical Thermodynamic Properties," Series III, National Bureau of Standards, Washington, D. C., 1948-1949 (see also E. W. Geyer and E. A. Bruges, "Tables of Properties of Gases," Longmans, Green & Co., Inc., New York, 1948):

Gas	$\bar{H}^\circ_{1000} - \bar{H}^\circ_{298}$, cal/mole	$\bar{S}^\circ_{1000} - \bar{S}^\circ_{298}$, eu/mole
$H_2O(g)$	6240.3	10.512
$H_2(g)$	4942.0	8.493

The existence of such tables makes it unnecessary for us to be repeatedly integrating heat-capacity equations, where these substances are involved. Using the following empirical heat-capacity equations [K. K. Kelley, *U.S. Bur. Mines Bull.* 371 (1934)]:

$$\text{SnO(c)}: \bar{C}^\circ_p = 9.40 + 3.62 \times 10^{-3}T \qquad (273\text{–}1273°\text{K})$$
$$\text{Sn(l)}: \bar{C}^\circ_p = 6.6 \qquad (504.9\text{–}1273°\text{K})$$
$$\text{Sn(c)}: \bar{C}^\circ_p = 5.05 + 4.80 \times 10^{-3}T \qquad (273\text{–}504.9°\text{K})$$

the latent heat of fusion of tin being 1720 cal/mole at the normal melting point, 504.9°K, calculate $\bar{H}^\circ_{1000} - \bar{H}^\circ_{298}$ and $\bar{S}^\circ_{1000} - \bar{S}^\circ_{298}$ for SnO(c) and for Sn(c, l), and calculate the changes in $\Delta H°$ and $\Delta S°$ of the reaction in Prob. 8-13 between 1000 and 298.16°K. Calculate finally $\Delta H°$, $\Delta S°$, and $\Delta F°$ at 298.16°K for the reaction

$$\text{Sn(c)} + 2H_2O(g) = \text{SnO(c)} + 2H_2(g)$$

What further information is necessary in order to be able to compute the standard enthalpy and free energy of formation of SnO(c) from these results?

8-15. The equilibrium in the reduction of NiO(c) by CO(g)

$$\text{NiO(c)} + \text{CO(g)} = \text{Ni(c)} + CO_2(g)$$

has been studied by M. Watanabe, with the following (selected) results (Landolt, Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIIc, p. 2558-1936):

t°C	p_{CO_2}/p_{CO}
663	453.5
716	332.3
754	255.4
793	207.3
852	157.7

From a plot of log K_p vs. $1/T$, determine $\Delta F°$, $\Delta H°$, and ΔS at 1000°K.

Using the following information for $CO_2(g)$ and $CO(g)$, taken from "Selected Values of Chemical Thermodynamic Properties," Series III,

Gas	$\bar{H}^\circ_{1000} - \bar{H}^\circ_{298}$, cal/mole	$\bar{S}^\circ_{1000} - \bar{S}^\circ_{298}$, eu/mole
$CO_2(g)$	7983.9	13.270
$CO(g)$	5184.4	8.816

together with the following thermal data for Ni(c) and NiO(c) [K. K. Kelley, *U.S. Bur. Mines Bull.* 371 (1934)]:

$$\text{Ni}(c, \alpha)\text{: } \bar{C}^\circ_p = 4.26 + 0.00640T \qquad (273\text{–}626°\text{K})$$
$$\text{Ni}(c, \alpha) = \text{Ni}(c, \beta); \qquad \Delta H^\circ_{626} = 92 \text{ cal/mole}$$
$$\text{Ni}(c, \beta)\text{: } \bar{C}^\circ_p = 6.99 + 0.000905T \qquad (626\text{–}1725°\text{K})$$
$$\text{NiO}(c)\text{: } \bar{C}^\circ_p = 11.3 + 0.00215T \qquad (273\text{–}1273°\text{K})$$

calculate the corrections to $\Delta H°$ and $\Delta S°$ from 1000 to 298.16°K, and calculate $\Delta H°$, $\Delta S°$, and $\Delta F°$ for the reaction

$$\text{NiO}(c) + \text{CO}(g) = \text{Ni}(c, \alpha) + \text{CO}_2(g)$$

at 298.16°K.

8-16. From the equilibrium constants at 1000°K of the reactions

$$\text{C}(c, \text{graphite}) + \text{CO}_2(g) = 2\text{CO}(g); \qquad (K^\circ_p)_{1000} = 1.900 \text{ atm}$$
$$\text{CO}(g) + \text{H}_2\text{O}(g) = \text{CO}_2(g) + \text{H}_2(g); \qquad (K^\circ_p)_{1000} = 1.374$$

as calculated by D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer, and F. D. Rossini [*J. Research Natl. Bur. Standards*, **34,** 143–161 (1945)], calculate from the data in Prob. 8-15 the equilibrium p_{CO} and the equilibrium p_{H_2O}/p_{H_2} at 1000°K for the respective reactions

$$\text{NiO}(c) + \text{C}(c, \text{graphite}) = \text{Ni}(c) + \text{CO}(g)$$
$$\text{NiO}(c) + \text{H}_2(g) = \text{Ni}(c) + \text{H}_2\text{O}(g)$$

From the calculated equilibrium constant,

$$\text{CO}(g) + \tfrac{1}{2}\text{O}_2(g) = \text{CO}_2(g); \qquad (K^\circ_p)_{1000} = 1.582 \times 10^{10} \text{ atm}^{-1/2}$$

(Wagman *et al.*, *loc. cit.*), calculate also the dissociation pressure of NiO(c):

$$\text{NiO}(c) = \text{Ni}(c) + \tfrac{1}{2}\text{O}_2(g)$$

at 1000°K.

8-17. The equilibrium of austenite (and of other iron-carbon alloys) with gas mixtures of CO and CO_2 has been investigated by R. P. Smith [*J. Am. Chem. Soc.*, **68,** 1163–1175 (1946)]. For the reaction

$$\text{CO}_2(g) + \text{C}(\text{dissolved in } \gamma \text{ iron}) = 2\text{CO}(g)$$

he obtained at 1000°C and 1 atm total pressure the following (selected) results for the per cent by weight of C taken up by electrolytic iron at various values of the p^2_{CO}/p_{CO_2} ratio:

p^2_{CO}/p_{CO_2}, atm	per cent C, by weight
1.98	0.0360
2.49	0.0487
3.12	0.0563
4.21	0.0740
7.29	0.133
13.8	0.242
43.4	0.655
84.1	1.081
130.2	1.462

From direct measurement of the equilibrium between graphite and gas mixtures of CO and CO_2 at the same temperature, he obtained for the reaction

$$CO_2(g) + C(c, \text{graphite}) = 2CO(g); \qquad K_p = 138.6 \text{ atm}$$

Estimate by graphical extrapolation of the austenite equilibrium data the solubility of graphite in γ iron at 1000°C, and calculate the activity of C in austenite relative to pure graphite at each of the above compositions. Prepare a graph of a_C vs. x_C, and determine whether as $x_C \rightarrow 0$, carbon dissolved in γ iron satisfies Henry's law ($a_C/x_C = k$). (Consult the original paper for further details of this extremely interesting investigation.)

8-18. (*a*) Equilibrium in the methanol synthesis from CO(g) and H_2(g) was studied by R. H. Newton and B. F. Dodge [*J. Am. Chem. Soc.*, **56,** 1287–1291 (1934)], who approached equilibrium from both directions by passing the gas mixture over a copper-zinc catalyst at 3 atm; methanol was determined by condensing it out of the equilibrium mixture by rapid cooling with liquid air. Following are the average results obtained at three temperatures:

$$CO(g) + 2H_2(g) = CH_3OH(g)$$

t, °C	K_p, atm^{-2}
225	0.00608
250	0.00232
276	0.00088

The enthalpy of the reaction at 25°C may be computed from the precisely established heats of combustion [to CO_2(g) and H_2O(l)] determined by F. D. Rossini:

Gas	ΔH (combustion)
CH_3OH(g)	−182,550 cal/mole
H_2(g)	− 68,313 cal/mole
CO(g)	− 67,623 cal/mole

Using the heat-capacity equations,

$$\begin{aligned} CH_3OH(g)&: \bar{C}_p^\circ = 2.0 + 0.03T \\ H_2(g)&: \bar{C}_p^\circ = 6.62 + 0.00081T \\ CO(g)&: \bar{C}_p^\circ = 6.60 + 0.00120T \end{aligned}$$

express ΔH° as a function of T, and calculate its value at 250°C (523°K); compare with the value deduced from the equilibrium data of Newton and Dodge.

(*b*) Integrate your thermochemical expression for $\Delta H^\circ/T^2$ with respect to T, and calculate a value of $(\Delta F^\circ/T)$ at 298.16°K from each of the above equilibrium results. From the average, compute ΔF° and also $\Delta S^\circ = (\Delta H^\circ - \Delta F^\circ)/T$ at 298.16°K.

(*c*) From low-temperature heat-capacity measurements by K. K. Kelley [*J. Am. Chem. Soc.*, **51,** 180–187 (1929)], the third-law entropy of $CH_3OH(g)$ at 298.16°K is 56.8 eu/mole (compare Prob. 6-13 for correlation of the ideal-gas entropy with the liquid entropy at that temperature). Using the entropies for CO(g) and $H_2(g)$ given in Appendix 2, compare the third-law value of $\Delta S^\circ_{298.16}$ with the value derived from the actual equilibrium data.

8-19. Using Newton's method to estimate the fugacity coefficients of the gases in the equilibrium mixture, estimate the value of K_p for the methanol synthesis of the preceding problem at 250°C and 100 atm (look up the necessary critical constants). Estimate the per cent conversion of a $1CO{:}2H_2$ gas mixture under these conditions.

From the data given in the preceding problem, calculate K_p° at 350°C, where the rate of attainment of equilibrium is much greater. What is the per cent conversion of a $1CO{:}2H_2$ mixture at that temperature at 1 atm total pressure? Estimate the effect on K_p of increasing the pressure to 100 atm (using Newton's method), and estimate the per cent conversion of a $1CO{:}2H_2$ gas mixture under these conditions.

8-20. The following equilibrium conditions have been established at 25°C for the reaction

$$CaCO_3(c, \text{calcite}) + H_2CO_3(aq) = Ca^{++}(aq) + 2HCO_3^-(aq)$$

(M. Randall, in the "International Critical Tables," Vol. 7, pp. 296–297, 1930):

$C_{H_2CO_3}$, moles/liter	$C_{Ca^{++}}$ $(=\frac{1}{2}C_{HCO_3^-})$, moles/liter	$\mu^{1/2}$
0.00269	0.00370	0.105
0.00363	0.00414	0.111
0.0100	0.00604	0.135
0.0373	0.00973	0.171
0.333	0.0224	0.259
0.550	0.0260	0.279

[for the last measurement, the solid phase is $Ca(HCO_3)_2(c)$]. The ionic strength in the third column has been computed from the equilibrium ionic concentrations. Calculate log K_c at each condition, and from a plot of log K_c vs. $\mu^{1/2}$, determine the value of log K_c°. Note that $\log K_c - \log K_c^\circ = -3 \log \gamma_\pm + \log \gamma''_{H_2CO_3}$. Assuming that the last term is negligible at the lower solute concentrations, does the limiting slope of the log K_c vs. $\mu^{1/2}$ relationship satisfy the Debye-Hückel limiting law for the 1:2 electrolyte, $Ca(HCO_3)_2$?

Using for the established standard free energies of formation of $CaCO_3(c)$ and $H_2CO_3(aq)$ the values $\bar{F}^\circ_{CaCO_3(c)} = -207{,}430$ cal and $\phi'_{H_2CO_3(aq)} = -149{,}170$ cal (W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, 1938), calculate the value of $(\phi'_{Ca^{++}(aq)} + 2\phi'_{HCO_3^-(aq)})$.

Calculate the value of $\gamma_\pm^3$ for the last condition given in the table, assuming that $\gamma''_{H_2CO_3}$ still remains equal to 1 (this assumption is not necessarily correct); if the equilibrium solid phase is actually $Ca(HCO_3)_2(c)$ for that condition, calculate its thermodynamic solubility product accordingly.

8-21. The first and second thermodynamic dissociation constants of carbonic acid have the following values at 25°C: $(K_c^\circ)_1 = 4.52 \times 10^{-7}$ and $(K_c^\circ)_2 = 5.59 \times 10^{-11}$ (D. A. MacInnes, "The Principles of Electrochemistry," p. 211, Reinhold Publishing Corporation, New York, 1939). Combining with the results of the preceding problem, calculate the thermodynamic solubility product of $CaCO_3$(c).

8-22. From the data for carbonic acid given in the two preceding problems, calculate the values of $\phi'_{HCO_3^-(aq)}$ and $\phi'_{CO_3^=(aq)}$ at 25°C. Combining with the result of Prob. 8-20, calculate the value of $\phi'_{Ca^{++}(aq)}$. Describe fundamental measurements that would serve to determine the independent values of the standard free energies of formation of $CaCO_3$(c) and of H_2CO_3(aq) given in Prob. 8-20.

8-23. (*a*) The thermodynamic secondary ionization constant of sulfuric acid has been determined by W. J. Hamer [*J. Am. Chem. Soc.*, **56,** 860–864 (1934)], essentially by an emf method based on buffer mixtures of $NaHSO_4$ and Na_2SO_4. Following are selected results:

$$HSO_4^-(aq) = H^+(aq) + SO_4^=(aq)$$

t, °C	K_m°
0	0.0145
10	0.0140
20	0.0129
25	0.0122
30	0.0114
40	0.00961
50	0.00781

Calculate $\phi'_{SO_4^=(aq)} - \phi'_{HSO_4^-(aq)}$, $\eta^\circ_{SO_4^=(aq)} - \eta^\circ_{HSO_4^-(aq)}$, and $\sigma'_{SO_4^=(aq)} - \sigma'_{HSO_4^-(aq)}$ at 25°C.

(*b*) Assuming that $K_{\gamma'}$ for this reaction may be estimated in dilute solution as the ratio of $\gamma_\pm$ for a typical 2:1 electrolyte such as Na_2SO_4 to that for a typical 1:1 electrolyte such as NaCl (see Fig. 7-19), estimate the degree of secondary ionization of H_2SO_4 in $0.1m$ and in $0.001m$ aqueous solution (determine the total ionic strength by successive approximations). [Compare M. S. Sherrill and A. A. Noyes, *J. Am. Chem. Soc.*, **48,** 1861–1873 (1926).] Estimate the quantity of heat evolved from the progress of this ionization alone as 1 mole of H_2SO_4 is diluted from $0.1m$ to $0.001m$ concentration.

8-24. (*a*) The standard enthalpy of formation of H_2S(g), from calorimetric measurement of its heat of combustion, is −4800 cal/mole, and its enthalpy of solution in water is −4520 cal/mole, according to measurements at 20°C by H. Zeumer and W. A. Roth [*Z. Elektrochem.*, **40,** 777–783 (1934)] (compare also Prob. 7-12). The correction to 25°C may be neglected in comparison with the experimental error, which is about ±200 cal/mole for each determination. The entropy of H_2S(g) at 298.16°K, from low-temperature thermal measurements by W. F. Giauque and R. W. Blue [*J. Am. Chem. Soc.*, **58,** 831–837 (1936)], is 49.10 ± 0.10 eu/mole. From solubility measurements by R. H. Wright and O. Maass [*Can. J. Research*, **6,** 94–101 (1932)], the limiting value of C_{H_2S}/p_{H_2S} at 25°C is 0.103 mole/liter atm. Using for H_2(g) the entropy value: 31.21 eu/mole, and for S(c, rhombic) the value 7.62 eu/mole at 25°C, calculate the standard enthalpy and free energy of formation of H_2S(aq), and also $\sigma'_{H_2S(aq)}$, at that temperature.

(*b*) The heat of neutralization of H_2S(aq) by the addition of 1 mole NaOH(aq)/mole H_2S(aq) is 8180 cal/mole, as determined by Zeumer and Roth, while the heat of neutralization of a strong acid by a strong base has the value 13,360 cal/mole H_2O (at 25°C). The primary ionization constant of H_2S(aq) has the value 1.15×10^{-7} (D. M. Yost and H. Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, 1944). Using the results of part (*a*), calculate the enthalpy and free energy of formation of $HS^-(aq)$, and also its entropy at 25°C.

8-25. (*a*) The secondary ionization constant of $H_2S(aq)$ is about 1.0×10^{-15} at 25°C. Using the results of the preceding problem, calculate $\phi'_{S^{=}(aq)}$. What further information is required in order to determine the entropy of $S^{=}(aq)$?

(*b*) The enthalpy of formation of ZnS(c) has been measured at 20°C by H. Zeumer and W. A. Roth by combustion with Na_2O_2 of ZnS(c) and of an equivalent mixture of Zn(c) with S(c, rhombic). They obtained $\Delta H° = -41{,}500 \pm 900$ cal/mole, the correction to 25°C being negligible (Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIIc, p. 2764, 1936). Using the third-law entropies: 13.8 ± 0.2 eu/mole for ZnS(c), and 9.95 ± 0.05 for Zn(c), together with the value for S(c, rhombic) given in Prob. 8-24 [K. K. Kelley, *U.S. Bur. Mines Bull.* 434 (1941)], calculate the standard free energy of formation of ZnS(c), and using for $Zn^{++}(aq)$: $\phi'_{Zn^{++}(aq)} = -35{,}176$ cal/mole (from emf data, as described in Chap. 9), calculate the thermodynamic solubility product of ZnS(c).

Note: The actual solubility of this and other sulfides in water is influenced by the extensive hydrolysis of $S^{=}(aq)$ to $HS^-(aq)$, as well as by slow attainment of equilibrium in some cases [see I. M. Kolthoff, *J. Phys. Chem.*, **35**, 2711–2721 (1931)].

8-26. Using the thermal data for NH_3 given in Prob. 3-24, plot $\bar{C}_p^\circ/T$ vs. T, and by graphical integration, using below 15°K, the Debye extrapolation, $\bar{S}_{15}^\circ = \frac{1}{3}(\bar{C}_p^\circ)_{15}$, determine $\bar{S}$ for $NH_3(g)$ at its normal boiling point, 239.7°K and 1 atm. Using Berthelot's equation of state, find $\bar{S}°$ at that temperature (Prob. 6-10). The difference, $\bar{S}_{298.16}^\circ - \bar{S}_{239.7}^\circ$, for $NH_3(g)$ being 1.81 eu/mole, calculate $\bar{S}_{298.16}^\circ$. [Compare R. Overstreet and W. F. Giauque, *J. Am. Chem. Soc.*, **59**, 254–259 (1937).]

8-27. (*a*) The heat capacity of benzene has been measured by G. D. Oliver, M. Eaton, and H. M. Huffman [*J. Am. Chem. Soc.*, **70**, 1502–1505 (1948)], with the following (smoothed and selected) results:

T, °K	$\bar{C}_p^\circ$, cal/mole deg	T, °K	$\bar{C}_p^\circ$, cal/mole deg
13	0.685	100	12.050
14	0.830	120	13.310
15	0.995	140	14.700
20	2.000	160	16.230
25	3.145	180	18.020
30	4.300	200	20.010
35	5.385	220	22.320
40	6.340	240	24.880
50	7.885	260	27.760
60	9.065	278.69(c)	30.760
70	9.975	278.69(l)	31.52
80	10.750	298.16	32.52
90	11.430		

From a plot of $(\bar{C}_p^\circ/T)$ vs. T, or of $\bar{C}_p^\circ$ vs. $\log T$, determine by graphical integration $\bar{S}_{298.16}^\circ$ of $C_6H_6(l)$; the latent heat of fusion at the melting point, 278.69°K, is 2358.1 cal/mole; it is sufficiently precise to assume that below 13°K, the solid satisfies the T^3 law, and that $\bar{S}_{13}^\circ = \frac{1}{3}(\bar{C}_p^\circ)_{13}$.

(*b*) The vapor pressure of $C_6H_6(l)$ at 298.16°K is 95.13 mm Hg, and the latent heat of vaporization at that temperature, 8090 cal/mole. Calculate $\bar{S}^\circ_{298.16}$ for C_6H_6(g), assuming that the saturated vapor satisfies the ideal-gas law. What further information is required in order to use these results to calculate the standard free energies of formation of C_6H_6(l) and C_6H_6(g)?

8-28. The entropy of crystalline urea has been measured according to the third law from low-temperature heat-capacity data by R. A. Ruehrwein and H. M. Huffman [*J. Am. Chem. Soc.*, **68,** 1759–1761 (1946)], who obtained: $\bar{S}^\circ_{298.16} = 25.00 \pm 0.05$ eu/mole. The heat of combustion has been measured by H. M. Huffman [*J. Am. Chem. Soc.*, **62,** 1009–1011 (1940)], who obtained $\Delta H^\circ_{298.16} = -151{,}053$ cal/mole [the products being CO_2(g), N_2(g), and H_2O(l)]. Using data found in Appendix 2, calculate the standard enthalpy, entropy, and free energy of formation of $CO(NH_2)_2$(c) at 298.16°K. Calculate also the equilibrium constant of the reaction

$$CO_2(g) + 2NH_3(g) = H_2O(g) + CO(NH_2)_2(c)$$

and compare with the experimental value: $K_p = 0.615$ atm^{-2} obtained by G. N. Lewis and G. H. Burrows [*J. Am. Chem. Soc.*, **34,** 1515–1529 (1912)].

8-29. The entropy of *n*-butane(l) at 298.16°K has been determined from low-temperature thermal measurements by J. G. Aston and G. H. Messerly [*J. Am. Chem. Soc.*, **62,** 1917–1923 (1940)], and is 55.2 eu/mole (by a relatively small extrapolation above the normal boiling point, −0.50°C); the entropy of *iso*-butane(l) at 298.16°K has also been determined, by J. G. Aston, R. M. Kennedy, and S. C. Schumann [*J. Am. Chem. Soc.*, **62,** 2059–2063 (1940)], the value for the liquid under its own vapor pressure being 52.09 eu/mole. The heats of combustion for the liquid state at 25°C are, respectively, 682,840 and 681,620 cal/mole, as determined by F. D. Rossini, *J. Research Natl. Bur. Standards*, **12,** 735–750 (1934); **15,** 357–361 (1935). Calculate $\Delta F^\circ_{298.16}$ for the isomerization

$$n\text{-}C_4H_{10}(l) = iso\text{-}C_4H_{10}(l)$$

and assuming an ideal concentrated solution, calculate the theoretical equilibrium mole fractions of the two isomers in the liquid phase. [Compare C. W. Montgomery, J. H. McAteer, and N. W. Franke, *J. Am. Chem. Soc.*, **59,** 1768–1769 (1937), who found 78 to 82 per cent isobutane in the liquid phase, after 2 months over an $AlBr_3$ catalyst at 27°C; see also F. D. Rossini, E. J. R Prosen, and K. S. Pitzer, *J. Research Natl. Bur. Standards*, **27,** 529–541 (1941), for calculations of the isomerization equilibrium in the gas phase at higher temperatures.]

8-30. R. R. Wenner ("Thermochemical Calculations," Chap. VIII, McGraw-Hill Book Company, Inc., New York, 1941) has shown that the entropies of many inorganic compounds of a given structure and charge type may be estimated with a fair degree of accuracy from a plot of log $\bar{M}$ vs. $\bar{S}^\circ_{298}$, which turns out to be approximately linear. Construct such a plot for salts of the type M^+X^-, using the following $\bar{S}^\circ_{298}$ values taken from the compilation by K. K. Kelley [*U.S. Bur. Mines Bull.* 434 (1941)]:

LiF(c): 9.7 ± 0.5 eu/mole
KBr(c): 22.6 ± 0.5
KCl(c): 19.8 ± 0.1
KI(c): 24.1 ± 0.5
RbCl(c): 21.2 ± 1.0
AgBr(c): 25.6 ± 0.1
AgCl(c): 23.0 ± 0.1
AgI(c): 27.6 ± 0.4 eu/mole
NaCl(c): 17.3 ± 0.5
NaF(c): 13.1 ± 0.5
TlBr(c): 26.8 ± 1.0
TlCl(c): 25.6 ± 1.5
TlI(c): 29.9 ± 1.0

Use the plot to predict the entropy of LiH(c) (experimental value from low-temperature thermal data: 5.9 ± 0.5 eu/mole). Estimate also the entropy of NaI(c). (Consult the reference cited for other useful semiempirical correlations.)

8-31. The following experimental third-law entropies have been obtained for straight-chain alkane hydrocarbons at 298.16°K by various investigators [see H. M. Huffman, G. S. Parks, and M. Barmore, *J. Am. Chem. Soc.*, **53**, 3876–3888 (1931); K. S. Pitzer, *Chem. Rev.*, **27**, 39–57 (1940); *Ind. Eng. Chem.*, **36**, 829–831 (1944)]:

Hydrocarbon	$\bar{S}^\circ_{298.16}$, eu/mole	
	Gas	Liquid
Methane, CH_4	44.5	
Ethane, C_2H_6	54.8	
Propane, C_3H_8	60.5	
n-Butane, C_4H_{10}	74.0	55.2
n-Pentane, C_5H_{12}	83.5	
n-Hexane, C_6H_{14}	92.3	70.8
n-Heptane, C_7H_{16}	101.3	78.9
n-Octane, C_8H_{18}	110.0	86.0
n-Nonane, C_9H_{20}	.....	93.9
n-Decane, $C_{10}H_{22}$	.....	102.5
n-Undecane, $C_{11}H_{24}$	.....	110.9
n-Dodecane, $C_{12}H_{26}$	.....	118.1
n-Eicosane, $C_{20}H_{42}$	.....	180.5
n-Pentacosane, $C_{25}H_{52}$	.....	217.0
n-Tritriacosane, $C_{33}H_{68}$	.....	280.1

Plot $\bar{S}^\circ_{298.16}$ for the liquid and the ideal-gas states against the number of carbon atoms in the chain. Estimate the values of $\bar{S}^\circ_{298.16}$ for *n*-$C_{10}H_{22}$(g), and for *n*-$C_{22}H_{46}$(l). [Compare H. M. Huffman, G. S. Parks, and M. Barmore, *J. Am. Chem. Soc.*, **53**, 3876–3888 (1931)]. Chain branching invariably tends to lower the entropy, to an extent depending more or less on the extent of branching; see H. M. Huffman, G. S. Parks, and S. B. Thomas, *J. Am. Chem. Soc.*, **52**, 3241–3251 (1930) for data on the isomeric heptanes; D. R. Douslin and H. M. Huffman, *J. Am. Chem. Soc.*, **68**, 1704–1708 (1946), for data on the isomeric hexanes; etc.]

CHAPTER 9

THERMODYNAMICS OF GALVANIC CELLS

We have confined our attention so far mainly to processes for which no nonthermal energy is exchanged by the thermodynamic system with its environment except in the form of mechanical work of expansion or compression, associated with changes in its volume. The galvanic cell constitutes a mechanism whereby all or part of the free-energy change taking place in the system may be diverted into electrical form. Since the electrical measurements may be conducted with high precision, and what is even more important, since a relatively small potential difference corresponds to a large free-energy change, so that we may conveniently study chemical systems in states far from their ordinary chemical equilibrium states simply by applying moderate potential differences to the corresponding galvanic cells, emf data for carefully selected types of galvanic cells have constituted an important source of thermodynamic information. In this chapter, we shall review the principles underlying their use for this purpose.

9-1. General Theory of Reversible Galvanic Cells. Let us review briefly the terminology used in describing galvanic cells, most of which was originated by Michael Faraday. Every galvanic cell consists of two metallic conductors, or *electrodes*, separated by one or more electrolytically conducting liquids in series called *electrolytes*. We know that the flow of electricity through the electrodes is electronic, whereas electricity is transported through the electrolyte by means of charged material particles, or *ions*. Therefore it follows that at one of the electrodes, some material particle (not necessarily the conducting ion itself) gives up electrons to the electrode, a type of chemical change known generally as an *oxidation*, whereas at the other, some material particle accepts electrons from the electrode, a chemical change known generally as a *reduction*. Every galvanic cell, and every electrolytic cell as well, operates by means of an oxidation taking place at the one electrode, called by definition the *anode*, and a reduction simultaneously taking place at the other, called by definition the *cathode*. These electrode reactions proceed at such rates as to satisfy *Faraday's law:*

$$1 \text{ gram-equiualent} \equiv 1 \text{ faraday } (\mathfrak{F}) = 96{,}485.3 \pm 10.0 \text{ coulombs} \qquad \text{(9-1-1)}$$

The term *anion* is applied to any ion that tends to migrate within the cell toward the anode, while the term *cation* is applied to any ion that tends to migrate within the cell toward the cathode; anions are negatively charged ions, and cations are positively charged ions. Following the customary sign convention, we label that electrode negative (−) which serves as a source of negative electricity (electrons) to the external circuit, and that electrode positive (+) which serves as a source of positive electricity (*i.e.*, accepts electrons from the external circuit). Thus, the anode of a galvanic cell is its (−) terminal, and the cathode is its (+) terminal.

Let E' denote the instantaneous *potential difference* across the electrodes as the *quantity of electricity* dj flows through the cell and the external circuit. Then according to straightforward electrical principles (essentially, the definition of E'), the *quantity of electrical energy* spent by the cell on the external circuit is measured by $E'\,dj$. If the cell is regarded as a thermodynamic system, then this quantity represents work W' done by the system on its environment in a nonthermal form other than mechanical work of expansion [compare Eqs. (3-17) and (3-18)], *i.e.*,

$$d'W' = E'\,dj \tag{9-1-2}$$

In this equation, if E' is measured in **volts** and j in **coulombs**, then W' is to be represented in **joules**. In view of Faraday's law (9-1-1), however, it is convenient in working with galvanic cells for us to measure j in **faradays**; with E' in volts, W' is then represented according to Eq. (9-1-2) in **volt gram-equivalents** (volt-eq). In order to transform volt gram-equivalents to *defined calories* [Eq. (2-24)], we may make use of the conversion factor[1]

$$1 \text{ volt-eq} = 96{,}485.3 \pm 10.0 \text{ joules} = 23{,}060.5 \pm 2.4 \text{ cal} \tag{9-1-3}$$

Ordinarily, we shall not enter this conversion factor explicitly in our equations, for one could just as well represent W' and other energy measures directly in volt gram-equivalents, or in joules; but in numerical calculations involving Eq. (9-1-2) and other similar relations, it is to be understood that the numerical relationship implied calls for a self-consistent set of units.

Now, the value of E', as we have noted in Sec. 5-1, depends not only on our cell but also on the nature of the external circuit. Thus, if the external circuit consists simply of a metallic conductor of resistance R_e, so that all of the electrical energy received from the cell is thermally dissipated there, then

$$E' = E\,\frac{R_e}{R_e + R_i} \tag{9-1-4}$$

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[1] Emf values reported prior to Jan. 1, 1948, in *international volts* should, however, be multiplied by the old conversion factor: 23,068.1 ± 2.4 cal/int volt-eq. This factor has been used generally on the older emf data reported throughout this chapter.

where R_i represents the internal resistance of the cell and E the *electromotive force of the circuit,* which represents by definition the net quantity of energy expended per unit quantity of electricity sent completely around the circuit; in this case, the quantity of energy expended per quantity of electricity dj is $E'\,dj$ in the external circuit, and $(E - E')dj$ within the cell itself. For this simple circuit, the value of E is evidently a true property of the cell, for it represents the potential difference between the electrodes when the cell is on open circuit: $E = \lim\limits_{R_e \to \infty} E'$. It is commonly called the *emf of the cell.*[1] The cell emf, E, may be measured approximately by means of a voltmeter; this is essentially a current-measuring instrument having a high resistance, R_v; according to Ohms' law, the current flowing through the complete circuit of voltmeter and cell in series is equal to $E/(R_v + R_i)$, so that if R_v is considerably larger than R_i for any cell to which the meter may be applied, then the current is approximately proportional to E, and the instrument may be calibrated to read E directly in volts. It may be measured far more precisely, however, by means of a potentiometer. In the potentiometer circuit, a sensitively and precisely controlled potential difference, derived ultimately with reference to a specially designed standard cell (the Weston normal cell) having an extremely stable and reproducible emf, is impressed on the electrodes of the "unknown" cell through a galvanometer in series with the cell. The setting of the potentiometer is adjusted until the applied potential difference is just sufficient to balance that of the cell, the sensitivity of the adjustment being determined by the galvanometer sensitivity and the internal resistance of the cell. With the current actually flowing through the cell thereby reduced practically to zero, the applied potential difference, which may be read directly from the setting of the potentiometer, is practically equal to the potential difference across the cell's electrodes on open circuit, and therefore measures the emf of the cell. Since the potentiometer measures the cell emf without discharging it to any appreciable extent, the measurement therefore does not change significantly the state of the cell reaction; it measures in other words the differential or instantaneous value of E. The upper limit to the energy the cell could theoretically deliver to the environment (in the form of the external circuit) in electrical form while it is in a given state with emf E is determined by the relation

$$W' = jE \qquad (9\text{-}1\text{-}5)$$

where j represents the quantity of electricity flowing through the cell.

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[1] Some authors prefer to call this quantity the *potential difference* of the cell, since the electromotive force (which is not really a force at all) is technically defined as a property of a *circuit* only.

The electrical energy produced by a galvanic cell always appears at the expense of the energy of some spontaneous change taking place in the cell, representing the net effect of the two electrode reactions, together with any change that may result from the ionic migration by which electricity is transported through the cell. This change necessarily satisfies the general limitation (5-58) imposed by the second law of thermodynamics:

$$W' \leqq -(\Delta F)_{T,p} \qquad (9\text{-}1\text{-}6)$$

Since galvanic cells are usually studied at constant temperature and pressure throughout the cell, Eq. (9-1-6) represents the most convenient form in which to apply the second law.[1] In view of (9-1-5), we may express this limitation in the form

$$E \leqq -\frac{\Delta F}{j} \qquad (T, p \text{ const}) \qquad (9\text{-}1\text{-}7)$$

Since j merely depends on the amount of change, in accordance with Faraday's law, the relation (9-1-7) shows in general how E is determined by the initial and final states of the thermodynamic system, before and after the quantity of change corresponding to the free-energy change ΔF has taken place.

The distinction between the so-called *free-energy decrease* and the *total energy* released by the process taking place in the cell has been noted in Chap. 5. Thus, for a change taking place at constant temperature and pressure, in the absence of changes in ordinary mechanical energy, such as might for example be associated with the influence of gravity, we may write

$$-\Delta F = -\Delta U - p\,\Delta V + T\,\Delta S \qquad (T, p \text{ const}) \qquad (9\text{-}1\text{-}8)$$

Here, $-\Delta U$ represents the total energy released by the thermodynamic system constituting the cell, and $-\Delta U - p\,\Delta V$ the net energy excluding the effect of volume changes admitted under the condition of constant pressure; thus, the term $T\,\Delta S$ represents in formal mathematical language the limitation on utilization of energy embodied in the second law of thermodynamics, and through (9-1-7), the implied limitation on the emf of a galvanic cell that may be based on the process under consideration. Equation (9-1-8) may be expressed also in the form

$$-\Delta F = -\Delta H + T\,\Delta S \qquad (T, p \text{ const}) \qquad (9\text{-}1\text{-}9)$$

where $-\Delta H$ represents the quantity of energy released in thermal form when $W' = 0$.

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[1] For an experimental study of cells with the electrodes at two different temperatures, see J. C. Goodrich, F. M. Goyan, E. E. Morse, R. G. Preston, and M. B. Young, *J. Am. Chem. Soc.*, **72**, 4411–4418 (1950), based on earlier theoretical studies by E. D. Eastman.

Certain types of cells have been discovered for which the ideal limit

$$E = -\frac{\Delta F}{j} \qquad (T,\ p \text{ const}) \qquad (9\text{-}1\text{-}10)$$

is actually closely attained. These are cells in which the process taking place in the cell and giving rise to the electrical energy is reversed in exact detail when one applies to the electrodes a potential difference E' slightly greater than the cell's own emf, E. For if ΔF merely changes its sign when electricity flows through the cell either in the one direction or in the other, then taking E in (9-1-7) as positive in the one sense (when electricity is flowing in the "spontaneous" direction, corresponding to negative ΔF) and negative in the other, E can satisfy (9-1-7) generally only by satisfying Eq. (9-1-10). An example of such a cell is the following:

$$\text{Ag(c), AgCl(c)}|\text{KCl(aq, }1m)|\text{Hg}_2\text{Cl}_2\text{(c), Hg(l)} \qquad (9\text{-}1\text{-}11)$$

for which the emf at 25°C and 1 atm has the value 0.0455 volt. Following the custom of American theoretical electrochemists, we associate a positive value of E with the symbolic representation of the cell in the form (9-1-11) in which the left-hand electrode tends to be the negative terminal, *i.e.*, in which negative electricity tends to flow spontaneously within the cell from right to left; then the corresponding change taking place in the cell has a free-energy change whose sign, as well as magnitude, is given by Eq. (9-1-10), in the sense that if E is assigned a positive value, then the spontaneous direction of the cell process is the one associated with flow of negative electricity within the cell from right to left.[1] When the cell (9-1-11) is being discharged, the following reversible reactions take place at the two electrodes:

Anode reaction: $\text{Ag(c)} + \text{Cl}^-(1m\ \text{KCl}) = \text{AgCl(c)} + e$
Cathode reaction: $\frac{1}{2}\text{Hg}_2\text{Cl}_2\text{(c)} + e = \text{Hg(l)} + \text{Cl}^-(1m\ \text{KCl})$

One will note that if the cell were steadily discharged for a long period of time, a concentration polarization effect would take place, *i.e.*, a local depletion of KCl around the anode, and a local increase in the concentration of KCl around the cathode, which thermal diffusion would tend to counteract; such polarization would tend in fact to lower the emf. Otherwise, however, the net cell reaction corresponding to $j = 1\mathfrak{F}$ is

$$\text{Ag(c)} + \tfrac{1}{2}\text{Hg}_2\text{Cl}_2\text{(c)} = \text{AgCl(c)} + \text{Hg(l)} \qquad (9\text{-}1\text{-}12)$$

and it is the free energy of this chemical transformation that is being

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[1] The reader should be cautioned against the opposite European custom, *e.g.*, in Landolt-Börnstein, "Physikalisch-chemische Tabellen," in which the emf associated with the cell (9-1-11) would be written as −0.0455 volt.

measured by E, in accordance with Eq. (9-1-10), as we shall show in detail in the following section. The reversible or irreversible character of the cell's behavior is in part determined by the nature of the two electrode reactions, and by the chemical and physical form of the electrodes themselves. It is generally necessary, however, to eliminate liquid-liquid junctions in order to ensure thermodynamic reversibility, for as we have indicated in Sec. 5-1, and as we shall consider at greater length in Sec. 9-3, the electrical migration of ions across a boundary separating two different electrolytes is more or less irreversible, to an extent depending on circumstances. The cell (9-1-11) has only the one electrolyte, whose concentration in this particular instance undergoes no net change as a result of the cell reaction.[1]

Because of Eq. (9-1-10), the study of reversible galvanic cells affords a singularly valuable source of chemical thermodynamic data. The large magnitude of the conversion factor (9-1-3) implies that we may study in this way chemical reactions having large negative free-energy changes, in states far from those of ordinary chemical equilibrium. One will perceive from the value of this conversion factor that for $j = 1$ g-eq, a precision of ± 0.1 mv in the determination of E, which is comparatively easy to attain, corresponds to a precision of ± 2.3 cal in ΔF.

The general thermodynamic relations (6-9) and (6-10), applied term by term to the components of ΔF in Eq. (9-1-7), permit us to derive relationships for the temperature and the pressure coefficients of E for a thermodynamically reversible galvanic cell

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[1] The cell (9-1-11) contains actually three electrolytes, AgCl, KCl, and Hg_2Cl_2, and we should properly represent it symbolically by

$$\mathrm{Ag(c),\ AgCl(c)}\left|\begin{array}{c}\text{KCl (aq) satd}\\ \text{with AgCl}\end{array}\right\|\mathrm{KCl(aq)}\left\|\begin{array}{c}\text{KCl(aq) satd}\\ \text{with Hg}_2\text{Cl}_2\end{array}\right|\mathrm{Hg_2Cl_2(c),\ Hg(l)} \qquad (9\text{-}1\text{-}11a)$$

Its behavior is irreversible to the extent that during discharge, Ag^+ ions migrate from the anode region into the middle region of the cell, whereas when a potential difference is applied exceeding that of the cell, so that reaction (9-1-12) is reversed, then Hg_2^{++} ions migrate from the region surrounding the mercury electrode into the middle region. These two processes are clearly irreversible in the thermodynamic sense. Because of the low solubilities of AgCl(c) and Hg_2Cl_2(c), however, the overwhelming fraction of the current through the cell is transported by the ions of KCl, so that the junction effects can be neglected; the net transfer of approximately t_+ mole of KCl per faraday from the anode compartment to the cathode compartment as the cell is discharged (where t_+ represents the transference number of the cation) evidently involves no differential change of free energy, if the solubilities of AgCl(c) and Hg_2Cl_2(c) are so low that their presence does not significantly affect ϕ_{KCl}. We shall study liquid-junction processes at greater length in Sec. 9-3, but we shall suppose that for the cells under consideration in this and the following section, liquid-junction effects are negligible, if not actually zero in principle.

$$j\left(\frac{dE}{dT}\right)_p = \Delta S \tag{9-1-13}$$

$$j\left(\frac{dE}{dp}\right)_T = -\Delta V \tag{9-1-14}$$

Equation (9-1-13) is particularly important, because it permits us to measure entropy changes of chemical reactions directly from emf data; this has been a valuable method of verifying third-law entropy values. If we substitute (9-1-13) in (9-1-9), we may derive an expression for the enthalpy of the cell reaction in terms of the temperature coefficient of the emf, in the form

$$\Delta H = -jE + Tj\left(\frac{dE}{dT}\right)_p \tag{9-1-15}$$

Equation (9-1-15), known as the *Gibbs-Helmholtz relation,* may be put also in the equivalent form, convenient for graphical computation of ΔH,

$$\Delta H = -j\left[\frac{d(E/T)}{d(1/T)}\right]_p \tag{9-1-16}$$

9-2. Cells without Liquid Junctions. We shall review in this section several types of reversible galvanic cells that have yielded important thermodynamic information. As we have already seen, no truly reversible cell can be set up having a liquid-liquid junction between two different electrolytes. Therefore all the cells considered in this section are without liquid-liquid junctions. It is convenient for us to discuss such cells in two general categories, depending on whether the emf is insensitive or sensitive to the concentration of the electrolyte.

a. Electrode Cells. These are cells whose emfs are determined entirely by the states of substances present at the electrodes, in phases distinct from the electrolyte itself.

Example:

$$\text{Ag(c), AgCl(c)}|\text{M}^+\text{Cl}^-(\text{aq}, m)|\text{Hg}_2\text{Cl}_2\text{(c), Hg(l)} \tag{9-2-1}$$

where M^+ represents K^+, Na^+, H^+, etc. The electrode reactions of this cell have been discussed in Sec. 9-1. Reproducible Hg(l), Hg_2Cl_2(c) electrodes are relatively easy to prepare, purification of the materials being the principal concern. Reproducible Ag(c), AgCl(c) electrodes call for metallic silver free of mechanical strains; the silver is usually prepared by electrolytic or chemical deposition of fresh silver on a platinum base, followed by electrolytic deposition of AgCl from aqueous HCl with the silver electrode as anode.[1] According to the net cell reaction (9-1-12) at 1 atm,

$$\mathrm{Ag(c)} + \tfrac{1}{2}\mathrm{Hg_2Cl_2(c)} = \mathrm{AgCl(c)} + \mathrm{Hg(l)} \quad (T, 1\ \mathrm{atm}) \qquad (9\text{-}2\text{-}2)$$

the free-energy change involves only pure chemical substances (liquid and solid) in standard states

$$\Delta F = \bar{F}^\circ_{\mathrm{AgCl(c)}} + \bar{F}^\circ_{\mathrm{Hg(l)}} - \bar{F}^\circ_{\mathrm{Ag(c)}} - \tfrac{1}{2}\bar{F}^\circ_{\mathrm{Hg_2Cl_2(c)}} \qquad (9\text{-}2\text{-}3)$$

(compare Sec. 8-1*a*). Therefore, according to (9-1-10);

$$E = E^\circ = -\frac{1}{1\ \text{g-eq}}\,\Delta F^\circ \qquad (9\text{-}2\text{-}4)$$

The emf at given temperature is therefore fixed, independently of the composition of the electrolyte and even of the particular cation, provided only that the cation be one showing no particular chemical or electrochemical interaction with the electrode materials.[2] The cell has been studied by R. H. Gerke, using 1*m* KCl and also 1*m* HCl as the electrolyte.[3] He obtained at 25°C a mean value of $E = 0.0455$ int volt. Thus, using the conversion factor (9-1-3);

$$\begin{aligned}\Delta F^\circ_{298} &= -1\ \text{g-eq} \times 0.0455\ \text{volt}\\ &= -1050\ \text{cal}\end{aligned} \qquad (9\text{-}2\text{-}5)$$

We saw in Sec. 8-1*a* that the chemical reaction (9-2-3) cannot be brought to a state of chemical equilibrium at any known temperature or pressure; nevertheless its free energy may be measured with convenience and precision by means of the galvanic cell (9-2-1). The value of ΔF° in this case measures essentially the difference between the standard free energies of formation of AgCl(c) and $\tfrac{1}{2}\mathrm{Hg_2Cl_2(c)}$; an independent measurement of either $\bar{F}^\circ_{\mathrm{AgCl(c)}}$ or $\bar{F}^\circ_{\mathrm{Hg_2Cl_2(c)}}$, taken in connection with the experimental result (9-2-5), serves to determine the other.

Gerke determined also the temperature coefficient of E; this was in fact his primary purpose in the investigation. From the mean result at 25°C, $(dE^\circ/dT)_p = 0.000338$ volt/deg, we may obtain, from Eq. (9-1-13),

$$\Delta S^\circ_{298} = 1\ \text{g-eq} \times 0.000338\ \text{volt/deg} = 7.80\ \text{eu} \quad (\text{emf}) \qquad (9\text{-}2\text{-}6)$$

This result may be compared directly with that deduced from the third

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[1] Directions for preparing Ag(c), AgCl(c) electrodes have been given by A. S. Brown, *J. Am. Chem. Soc.*, **56**, 646–649 (1934). We should distinguish between reversible and reproducible behavior. An impure or a strained silver electrode may behave reversibly in a cell such as (9-2-1), but of course it may give different results from those of a pure silver electrode, free of strain. The presence of a less "noble" impurity, such as Pb, may introduce irreversible behavior as well.

[2] See, however, footnote on page 535.

[3] R. H. Gerke, *J. Am. Chem. Soc.*, **44**, 1684–1704 (1922).

law of thermodynamics; using the third-law entropies compiled by K. K. Kelley:[1]

$$\begin{aligned}\Delta S^\circ_{298} &= \bar{S}^\circ_{\mathrm{AgCl(c)}} + \bar{S}^\circ_{\mathrm{Hg(l)}} - \bar{S}^\circ_{\mathrm{Ag(c)}} - \tfrac{1}{2}\bar{S}^\circ_{\mathrm{Hg_2Cl_2(c)}} \\ &= 23.0 + 18.5 - 10.2 - 23.0 \\ &= 8.3 \pm 0.8 \text{ eu} \qquad \text{(third law)} \qquad (9\text{-}2\text{-}7)\end{aligned}$$

the most uncertain individual third-law entropy being that of $Hg_2Cl_2(c)$. The agreement is within experimental error, the value obtained from Gerke's measurements in this case being probably the more precise.

Combining (9-2-5) with (9-2-6) according to (9-1-9), we may compute the standard enthalpy of the cell reaction (9-2-2)

$$\Delta H^\circ_{298} = -1050 \text{ cal} + (298.16 \text{ deg})(7.80 \text{ eu}) = +1276 \text{ cal} \qquad (9\text{-}2\text{-}8)$$

The effect of pressure on the emf of the cell (9-2-1) has been measured by G. Timofeev, who obtained $(dE/dp)_T = (2.66 \pm 0.20) \times 10^{-6}$ volt/atm, using $0.1M$ KCl as the electrolyte and pressures up to 1500 atm.[2] We may compare this experimental result with that calculated by the application of Eq. (9-1-14); with $\Delta V = -2.7$ ml,

$$\begin{aligned}\left(\frac{dE}{dp}\right)_T &= \frac{2.7 \text{ ml}}{1 \text{ g-eq}} \times \frac{0.1013 \text{ joule}}{\text{ml atm}} \times \frac{1 \text{ volt g-eq}}{96{,}485 \text{ joules}} \\ &= 2.8 \times 10^{-6} \text{ volt/atm}\end{aligned}$$

The agreement between the observed and the theoretical values is excellent.

The cell (9-2-1) has been set up also with $0.1m$ NaCl in methanol as the electrolyte; P. S. Buckley and H. Hartley thereby obtained $E = 0.0496$ volt at 25°C.[3]

Example:

$$Hg(l), Hg_2Cl_2(c)|HCl(aq, m)|Cl_2(g), (Pt\text{-}Ir) \qquad (9\text{-}2\text{-}9)$$

The electrode reactions are

Anode reaction: $Hg(l) + Cl^-(HCl, aq) = \tfrac{1}{2}Hg_2Cl_2(c) + e$
Cathode reaction: $\tfrac{1}{2}Cl_2(g) + e = Cl^-(HCl, aq)$

giving rise to the net reaction, for $j = 1\mathfrak{F}$,

$$Hg(l) + \tfrac{1}{2}Cl_2(g) = \tfrac{1}{2}Hg_2Cl_2(c) \qquad (9\text{-}2\text{-}10)$$

The reversible chlorine electrode was first used by E. Müller, who found that an inert metal, such as platinum-iridium alloy, could serve as a

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[1] K. K. Kelley, *U.S. Bur. Mines Bull.* 434 (1941).

[2] G. Timofeev, *Z. physik. Chem.*, **86**, 113–128 (1913).

[3] P. S. Buckley and H. Hartley, *Phil. Mag.*, (7) **8**, 320–324 (1929).

carrier for $Cl_2(g)$ in a solution containing Cl^-.[1] The free energy of the cell reaction (9-2-10) has the form

$$\Delta F = \tfrac{1}{2}\bar{F}^{\circ}_{Hg_2Cl_2(c)} - \bar{F}^{\circ}_{Hg(l)} - \tfrac{1}{2}\phi_{Cl_2} \tag{9-2-11}$$

where ϕ_{Cl_2} represents the thermodynamic potential of Cl_2 in the gas phase (a mixture of Cl_2 with N_2) over the cathode. If we assume that the gas satisfies the ideal-gas law,

$$\phi_{Cl_2} = \bar{F}^{\circ}_{Cl_2(g)} + RT \ln p_{Cl_2}$$

where p_{Cl_2} represents the partial pressure of the chlorine, then Eq. (9-2-11) assumes the form

$$\Delta F = \Delta F^{\circ} - \tfrac{1}{2}RT \ln p_{Cl_2}$$

This equation may be corrected for deviation from ideality by multiplication of p_{Cl_2} by an experimentally determined fugacity coefficient, whose value will differ but little from unity at pressures below 1 atm. Thus, according to the fundamental relationship (9-1-10),

$$E = E^{\circ} + \frac{RT}{1 \text{ g-eq}} \ln (p_{Cl_2})^{1/2} \tag{9-2-12}$$

In other words, the emf should vary with p_{Cl_2} in such a way that the expression

$$E - \frac{RT}{1 \text{ g-eq}} \ln (p_{Cl_2})^{1/2} = E^{\circ} \tag{9-2-13}$$

stays constant at given temperature. The value of the constant E° measures the standard free-energy change of the cell reaction, in accordance with the definition

$$E^{\circ} = -\frac{1}{\mathfrak{J}}\Delta F^{\circ} \tag{9-2-14}$$

It represents what the emf of the cell would be if each substance were present in its standard state, which in this case would be the pure states at 1 atm for Hg(l) and $Hg_2Cl_2(c)$, and a hypothetical ideal-gas state at 1 atm for $Cl_2(g)$.

In Müller's original work, condition (9-2-13) was not at all satisfied, a result which he attributed to the possible hydrolysis of chlorine in aqueous solution. G. N. Lewis and F. F. Rupert were able to obtain consistent results by using chlorine at low partial pressures mixed with air.[2] Later, N. Kameyama, H. Yamamoto, and S. Oka succeeded in obtaining consistent results even at chlorine partial pressures approaching 1 atm, by

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[1] E. Müller, *Z. physik. Chem.*, **40**, 158–168 (1902).

[2] G N. Lewis and F. F. Rupert, *J. Am. Chem. Soc.*, **33**, 299–307 (1911).

using chlorine diluted with nitrogen, and saturated KCl as the electrolyte.[1] Both sets of data are given in Table 9-1. The values of $E°$ from the work of Lewis and Rupert run slightly lower than those from the work of Kameyama, Yamamoto, and Oka, but the general average for the two sets, $E° = 1.0903$ volts, is in close agreement with independent measurements by R. H. Gerke, who also measured the temperature coefficient,

TABLE 9-1. EMF OF THE REACTION: $Hg(l) + \frac{1}{2}Cl_2(g) = \frac{1}{2}Hg_2Cl_2(c)$

$Hg(l), Hg_2Cl_2(c)|HCl\ (aq,\ 0.1m)|Cl_2(p_{Cl_2}\ \text{in air}),\ (Pt\text{-}Ir)$*

p_{Cl_2}, atm	E_{298}, volts	$E_{298} - 0.059161 \log (p_{Cl_2})^{1/2}$, volts
0.00293	1.0150	1.0899
0.00298	1.0154	1.0901
0.00629	1.0242	1.0893
0.00631	1.0243	1.0894
0.0124	1.0330	1.0894
0.0125	1.0330	1.0893
0.0243	1.0419	1.0896
0.0247	1.0421	1.0896
0.0249	1.0424	1.0898
0.0490	1.0508	1.0896
0.0492	1.0509	1.0896
0.0495	1.0510	1.0896
Mean......	....	1.0896 ± 0.0002 volt

$Hg(l), Hg_2Cl_2(c)|KCl\ (aq,\ satd)|Cl_2(p_{Cl_2}\ \text{in}\ N_2),\ (Pt\text{-}Ir)$†

p_{Cl_2}, atm	E_{298}, volts	$E_{298} - 0.059161 \log (p_{Cl_2})^{1/2}$, volts
0.0675	1.0578	1.0924
0.0712	1.0583	1.0922
0.1137	1.0626	1.0905
0.1495	1.0662	1.0906
0.228	1.0726	1.0916
0.283	1.0746	1.0903
0.616	1.0838	1.0900
0.833	1.0885	1.0908
0.956	1.0899	1.0905
Mean......	....	1.0910 ± 0.0007 volt

* Data of G. N. Lewis and F. F. Rupert, *J. Am. Chem. Soc.*, **33**, 299–307 (1911).

† Data of N. Kameyama, H. Yamamoto, and S. Oka, *J. Soc. Chem. Ind., Japan*, **29**, 679–686 (1926); *Proc. Imp. Acad. (Tokyo)*, **3**, 41–43 (1927).

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[1] N. Kameyama, H. Yamamoto, and S. Oka, *J. Soc. Chem. Ind., Japan*, **29**, 679–686 (1926); *Proc. Imp. Acad. (Tokyo)*, **3**, 41–43 (1927).

$(dE^\circ/dT) = -0.000945$ volt/deg.[1] The effect of the chlorine pressure (9-2-12) on the emf of this cell is of course a special case of the general law (9-1-14) for the effect of pressure on the emf, the value of ΔV for the reaction (9-2-10) being practically equal to $-\frac{1}{2}\bar{V}_{\mathrm{Cl_2(g)}}$. The expression $(RT/j)\ln(\ \ )$, which recurs throughout the thermodynamic theory of galvanic cells, gives rise to a numerical factor having the equivalent values at 25°C

$$\left.\begin{aligned} \frac{RT}{j}\ln(\ \ ) &= \frac{1364.28 \pm 0.09\ \text{cal}}{j}\log(\ \ ) \\ &= \frac{0.059161 \pm 0.000004\ \text{volt-eq}}{j}\log(\ \ ) \end{aligned}\right\} \tag{9-2-15}$$

The particular cell under consideration measures the standard molal free energy of formation of $Hg_2Cl_2(c)$; for rewriting the cell equation (9-2-10) with $j = 2\mathfrak{F}$,

$$2Hg(l) + Cl_2(g) = Hg_2Cl_2(c)$$

and introducing the experimental value of E° in (9-2-14), we obtain

$$\Delta F^\circ_{298} = -2\ \text{g-eq} \times 1.0903\ \text{volts} = -50{,}302\ \text{cal} \tag{9-2-16}$$

Likewise, from Gerke's measurements of the temperature coefficient of E°, we may obtain as the standard entropy of formation of $Hg_2Cl_2(c)$

$$\Delta S^\circ_{298} = -2\ \text{g-eq} \times 0.000945\ \text{volt/deg} = -43.6\ \text{eu} \tag{9-2-17}$$

From Kelley's critical compilation, the third-law entropies of Hg(l) and $Cl_2(g)$ at 298°K are, respectively, 18.5 ± 0.2 and 53.3 ± 0.1 eu/mole; combining these values with the result (9-2-17), we may derive for $Hg_2Cl_2(c)$: $\bar{S}^\circ_{298} = 46.7$ eu/mole. The directly established third-law entropy of $Hg_2Cl_2(c)$ is $\bar{S}^\circ_{298} = 46.0 \pm 1.4$ eu/mole.[2] We may compute the standard enthalpy of formation of $Hg_2Cl_2(c)$ by combining (9-2-16) and (9-2-17) in Eq. (9-1-9),

$$\Delta H^\circ_{298} = -50{,}302\ \text{cal} - (298.16\ \text{deg})(43.6\ \text{eu}) = -63{,}300\ \text{cal}$$

These experimental results for the cell (9-2-9), taken in connection with the results obtained for the previously considered cell, (9-2-1), serve to determine the thermodynamic properties of AgCl(c); for taking (9-2-16) and (9-2-5) in the forms

$$\begin{aligned} Hg(l) + \tfrac{1}{2}Cl_2(g) &= \tfrac{1}{2}Hg_2Cl_2(c); & \Delta F^\circ_{298} &= -25{,}151\ \text{cal} \\ Ag(c) + \tfrac{1}{2}Hg_2Cl_2(c) &= Hg(l) + AgCl(c); & \Delta F^\circ_{298} &= -1{,}050\ \text{cal} \end{aligned}$$

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[1] Gerke, *loc. cit.*

[2] K. K. Kelley, *U.S. Bur. Mines Bull.* 434 (1941).

we may compute for the reaction

$$Ag(c) + \tfrac{1}{2}Cl_2(g) = AgCl(c); \qquad \Delta F^\circ_{298} = -26{,}201 \text{ cal} \qquad (9\text{-}2\text{-}18)$$

Now, the emf of the cell

$$Ag(c),\ AgCl(c)|HCl(aq,\ 1m)|Cl_2(g),\ (Pt\text{-}Ir) \qquad (9\text{-}2\text{-}19)$$

whose cell reaction is represented by Eq. (9-2-18), has been measured directly by Gerke, who obtained $E^\circ_{298} = 1.1362$ volts;[1] substituting in (9-2-14),

$$\Delta F^\circ_{298} = -1 \text{ g-eq} \times 1.1362 \text{ volts} = -26{,}210 \text{ cal} \qquad (9\text{-}2\text{-}20)$$

The excellent agreement between (9-2-18) and (9-2-20) constitutes direct experimental confirmation of the principles embodied in the second law of thermodynamics. Gerke measured also the temperature coefficient of E° for this cell, obtaining $(dE^\circ/dT) = -0.000595$ volt/deg; from this result, one may compute directly the standard entropy of the reaction (9-2-18)

$$\Delta S^\circ_{298} = -1 \text{ g-eq} \times 0.000595 \text{ volt/deg} = -13.73 \text{ eu} \qquad (9\text{-}2\text{-}21)$$

We have compared this experimental result with the third-law calculation in Sec. 8-3.

Example:

$$(Pt),\ H_2(g)|NaOH(aq,\ m)|HgO(c),\ Hg(l) \qquad (9\text{-}2\text{-}22)$$

This cell is not strictly an electrode cell, since H_2O is one of the products of the cell reaction. Since, however, ϕ_{H_2O} does not depend sensitively on the electrolyte concentration, the behavior of the cell at low electrolyte concentrations resembles in many respects that of the cell (9-2-9). The two electrode reactions are

$$\text{Anode reaction: } H_2(g) + 2OH^-(NaOH,\ aq,\ m) = 2H_2O(NaOH,\ aq,\ m) + 2e$$

$$\text{Cathode reaction: } HgO(c) + H_2O(NaOH,\ aq,\ m) + 2e = Hg(l) + 2OH^-(NaOH,\ aq,\ m)$$

The net cell reaction corresponding to $j = 2\mathfrak{F}$ is

$$H_2(g) + HgO(c) = Hg(l) + H_2O(NaOH,\ aq,\ m) \qquad (9\text{-}2\text{-}23)$$

The Hg(l),HgO(c) electrode was shown to be reversible with respect to $OH^-(aq)$ by J. N. Brønsted, who first studied the cell (9-2-22).[2] This electrode is one of the closest approaches we have to a reversible oxygen electrode; no one has succeeded in preparing a reversible electrode in which $O_2(g)$ itself is one of the reacting substances. The reversible

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[1] Gerke, *loc. cit.*

[2] J. N. Brønsted, *Z. physik. Chem.*, **65**, 84–92, 744 (1909).

hydrogen electrodes in modern use are variants of the hydrogen electrode described originally by J. H. Hildebrand.[1] A stream of pure hydrogen is bubbled slowly through the electrolyte surrounding a platinum-foil electrode, on which has been deposited by electrolysis a film of finely divided platinum black, capable of adsorbing many times its volume of hydrogen. Directions for platinizing electrodes, and for protecting them from "poisoning," have been described by several investigators.[2] In ordinary use, the hydrogen gas becomes saturated with solvent vapor (usually water), and its partial pressure is equal to the barometric pressure less the partial vapor pressure of the solvent in the electrolyte.

The free-energy change corresponding to the reaction (9-2-23) has the form

$$\begin{aligned}\Delta F &= \bar{F}^\circ_{\mathrm{Hg(l)}} + \phi_{\mathrm{H_2O}} - \phi_{\mathrm{H_2}} - \bar{F}^\circ_{\mathrm{HgO(c)}} \\ &= \Delta F^\circ + RT \ln a_{\mathrm{H_2O}} - RT \ln p_{\mathrm{H_2}} \qquad (9\text{-}2\text{-}24)\end{aligned}$$

where

$$\Delta F^\circ = \bar{F}^\circ_{\mathrm{Hg(l)}} + \bar{F}^\circ_{\mathrm{H_2O(l)}} - \bar{F}^\circ_{\mathrm{H_2(g)}} - \bar{F}^\circ_{\mathrm{HgO(c)}} \qquad (9\text{-}2\text{-}25)$$

We may therefore represent the cell's emf according to Eq. (9-1-10) in the form

$$E = E^\circ - \frac{RT}{2\text{ g-eq}} \ln \frac{a_{\mathrm{H_2O}}}{p_{\mathrm{H_2}}} \qquad (9\text{-}2\text{-}26)$$

where, as before,

$$E^\circ = -\frac{1}{j}\Delta F^\circ \qquad (9\text{-}2\text{-}27)$$

Equation (9-2-26) may be expressed in the equivalent form

$$E - \frac{RT}{1\text{ g-eq}} \ln (p_{\mathrm{H_2}})^{1/2} = E^\circ - \frac{RT}{2\text{ g-eq}} \ln a_{\mathrm{H_2O}} \qquad (9\text{-}2\text{-}28)$$

[compare Eq. (9-2-13)], from which one sees that by extrapolating the value of the expression on the left (E "corrected" to $p_{\mathrm{H_2}} = 1$ atm) to zero electrolyte concentration, where $a_{\mathrm{H_2O}} \rightarrow 1$, one obtains the value of E°. Y. Kobayashi and H. Wang showed that at 25°C this value of E corrected to $p_{\mathrm{H_2}} = 1$ atm could be represented by the empirical equation

$$E_{(p_{\mathrm{H_2}}=1\text{ atm})} = 0.92550 + 0.00005792m + 0.00036421m^3 \quad \text{(volts)}$$

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[1] J. H. Hildebrand, *J. Am. Chem. Soc.*, **35**, 847–871 (1913); in this paper, Hildebrand demonstrated the application of the hydrogen electrode to the potentiometric titration of acids and bases.

[2] See, for example, W. M. Clark, "The Determination of Hydrogen Ions," 3d ed., The Williams & Wilkins Company, Baltimore, 1928; S. Popoff, A. H. Kunz, and R. D. Snow, *J. Phys. Chem.*, **32**, 1056–1060 (1928).

from which is derived the value of $E^\circ_{298} = 0.9255$ volt.[1] Substituting this value in Eq. (9-2-27), we obtain for the standard free energy of the reaction (9-2-23)

$$\begin{aligned}\Delta F^\circ_{298} &= -2 \text{ g-eq} \times 0.9255 \text{ volt} \\ &= -42{,}700 \text{ cal}\end{aligned} \tag{9-2-29}$$

According to (9-2-25), this quantity measures the difference between the standard free energies of formation of $H_2O(l)$ and $HgO(c)$.

Now, by introducing the value of $\bar{F}^\circ_{HgO(c)}$ derived from high-temperature thermal-equilibrium data, −13,990 cal, as shown in Eq. (8-1-27*a*), Sec. 8-1*c*, we may derive from the experimental result (9-2-29) a value for the important natural constant $\bar{F}^\circ_{H_2O(l)}$, the standard molal free energy of formation of $H_2O(l)$ at 298.16°K; thus $\bar{F}^\circ_{H_2O(l)} = -56{,}690$ cal/mole. This result is in perfect agreement with the value of −56,689.9 cal/mole accepted by F. D. Rossini for "Selected Values of Chemical Thermodynamic Properties" from a critical survey of other methods, including spectroscopic data for $H_2O(g)$, according to the method outlined in Chap. 10.[2]

Kobayashi and Wang also determined the temperature coefficient of E° for the cell (9-2-22), obtaining $(dE^\circ/dT) = -0.000285$ volt/deg, from which the standard entropy of reaction has the value

$$\Delta S^\circ_{298} = \bar{S}^\circ_{Hg(l)} + \bar{S}^\circ_{H_2O(l)} - \bar{S}^\circ_{H_2(g)} - \bar{S}^\circ_{HgO(c)} = -13.15 \text{ eu} \tag{9-2-30}$$

Example:

$$\text{Ag(l)}|\text{AgCl (in KCl)}|\text{Ag}_x\text{Au}_{1-x}\text{(l)} \tag{9-2-31}$$

This interesting cell has been studied at high temperatures by C. Wagner and G. Engelhardt, the electrolyte consisting of AgCl dissolved in molten KCl; electrical contact with the molten-metal electrodes was made through graphite leads.[3] One electrode consists of pure silver, and the other, of silver at mole fraction x alloyed with gold. The electrode reactions corresponding to $j = 1\mathfrak{F}$ are

Anode reaction: $\text{Ag(l)} = \text{Ag}^+\text{(AgCl in KCl)} + e$
Cathode reaction: $\text{Ag}^+\text{(AgCl in KCl)} + e = \text{Ag(l}, x_{Ag} \text{ in Au)}$

The electrical energy is therefore derived from the free energy of the net change:

$$\text{Ag(l)} = \text{Ag(l}, x_{Ag} \text{ in Au)} \tag{9-2-32}$$

This is normally a spontaneous process, as shown by the fact that Ag(l)

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[1] Y. Kobayashi and H. Wang, *J. Sci. Hiroshima Univ.*, (A) **5**, 71–82 (1934).

[2] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D.C., June 30, 1947.

[3] C. Wagner and G. Engelhardt, *Z. physik. Chem.*, (A) **159**, 241–267 (1931).

will readily dissolve in the molten alloy. The cell (9-2-31) constitutes a thermodynamically reversible method of setting up this ordinarily irreversible transformation.

The free-energy change corresponding to (9-2-32) has the form

$$\Delta F = \phi_{\mathrm{Ag}} - \bar{F}^{\circ}_{\mathrm{Ag(l)}}$$

Introducing the mole-fraction activity coefficient γ_{Ag} based on pure Ag(l) as the reference state, in accordance with Eq. (7-3-48),

$$\phi_{\mathrm{Ag}} = \bar{F}^{\circ}_{\mathrm{Ag(l)}} + RT \ln x_{\mathrm{Ag}}\gamma_{\mathrm{Ag}}$$

where γ_{Ag}, the activity coefficient of Ag in the liquid alloy, would equal 1 if the liquid were ideal, in the sense that both components satisfied Raoult's law. Thus, according to (9-1-10), the cell emf should satisfy the equation

$$E = -\frac{1}{\jmath}\Delta F = -\frac{RT}{1\ \text{g-eq}} \ln x_{\mathrm{Ag}}\gamma_{\mathrm{Ag}} \qquad (9\text{-}2\text{-}33)$$

The value of γ_{Ag} may be computed from the observed value of E according to the equivalent relationship,

$$\log \gamma_{\mathrm{Ag}} = -\frac{1\ \text{g-eq}}{2.303RT} E - \log x_{\mathrm{Ag}} \qquad (9\text{-}2\text{-}34)$$

and according to the ideal dilute-solution generalization, should at least approach 1 as $x_{\mathrm{Ag}} \to 1$.

Actual data for the cell at 1087°C (1360°K) are presented in Table 9-2. The values of log γ_{Ag} and of γ_{Ag} computed according to Eq. (9-2-34) are given in the fifth and sixth columns. One sees that the solution deviates to some extent from ideality as the concentration of Au in the alloy is increased, but the deviation is much less than for the solid alloy at lower temperatures (compare Fig. 7-14; the data plotted there, at 200°C, were obtained by a similar method).

A noteworthy feature in the behavior of a cell such as (9-2-31) is that a finite emf, given by Eq. (9-2-33), would exist even if the liquid (or solid) alloy were an ideal concentrated solution ($\gamma_{\mathrm{Ag}} = 1$), so that no *net* energy change was involved in the solution process. The entire electrical energy delivered by the cell at constant temperature would then be derived from the surroundings in thermal form. This result illustrates graphically the impact of the second law of thermodynamics, for from the first law only, we should have no reason to look for electrical energy from a process that ordinarily takes place without releasing any energy. The tendency for pure silver to diffuse into the alloy is governed ideally, however, by an extraenergetic effect: the overwhelmingly greater *random chance* that silver molecules will diffuse throughout the alloy rather than segregate, when no specific orienting influence is present (as in the case of two immiscible liquids). The cell (9-2-31) takes advantage of this more or less purely random tendency on the part of the silver molecules [measured by the ideal entropy of mixing, $\Delta S^\circ = -R \ln x_{\mathrm{Ag}}$, for the process (9-2-32)], and the cell reaction (9-2-32) proceeds, even though it follows that most of the electrical energy developed by the cell at constant temperature has to be taken in thermally from the surroundings. An analogy may be drawn with the production of work by an ideal gas expanding at constant temperature.

TABLE 9-2. EMF DATA FOR THE CELL: $\mathrm{Ag(l)|AgCl(in\ KCl)|Ag_xAu_{1-x}(l)}$*
$T = 1360°\mathrm{K}$

x_{Ag}	E, volts	$\frac{1\ \text{g-eq}}{2.303\ RT} E$	$\log x_{\mathrm{Ag}}$	$\log \gamma_{\mathrm{Ag}}$	γ_{Ag}
0.846	0.021	0.078	−0.072	−0.006	0.986
0.716	0.045	0.167	−0.145	−0.022	0.950
0.602	0.074	0.274	−0.220	−0.054	0.884
0.471	0.114	0.422	−0.327	−0.095	0.804
0.263	0.198	0.734	−0.580	−0.154	0.701

* C. Wagner and G. Engelhardt, *Z. physik. Chem.*, (A)**159**, 241–267 (1931).

Cells similar in structure to (9-2-31), but based on liquid mercury amalgam electrodes, have been studied extensively. For example, the cell

$$\mathrm{Tl}(x' \text{ in Hg})|\mathrm{Tl_2SO_4(aq)}|\mathrm{Tl}(x'' \text{ in Hg})$$

was studied by T. W. Richards and F. Daniels at 20°C.[1] Its emf is independent of the electrolyte concentration, and depends only on the thallium concentrations in the two electrodes. The electrical energy results from the tendency for the thallium to distribute itself at equal concentrations (equal ϕ_{Tl}) between the two solutions. The results establish directly the relative values of ϕ_{Tl} between the two amalgam concentrations.

b. Concentration Cells; Standard Electrode Potentials. These are cells for which the emf depends on the concentration of the electrolyte.

Example:

$$\mathrm{(Pt),\ H_2(g)|HCl(aq,}\ m\mathrm{)|AgCl(c),\ Ag(c)} \qquad (9\text{-}2\text{-}35)$$

This cell has been thoroughly studied by many investigators. The reversible electrode reactions are

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[1] T. W. Richards and F. Daniels, *J. Am. Chem. Soc.*, **41**, 1732–1768 (1919); see also G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," pp. 265–270, McGraw-Hill Book Company, Inc., New York, 1923.

Anode reaction: $\frac{1}{2}H_2(g) = H^+(HCl,\ aq,\ m) + e$

Cathode reaction: $AgCl(c) + e = Ag(c) + Cl^-(HCl,\ aq,\ m)$

and the net cell reaction for $j = 1\mathfrak{F}$ is

$$\tfrac{1}{2}H_2(g) + AgCl(c) = Ag(c) + HCl(aq,\ m) \qquad (9\text{-}2\text{-}36)$$

We may represent the free energy of the reaction (9-2-36) in the form

$$\Delta F = \bar{F}^\circ_{Ag(c)} + \phi_{HCl} - \tfrac{1}{2}\phi_{H_2} - \bar{F}^\circ_{AgCl(c)}$$

Now for the strong electrolyte HCl(aq), we may represent ϕ_{HCl} according to the principles of Eq. (7-4-23), Sec. 7-4, in the form

$$\phi_{HCl} = \phi'_{HCl(aq)} + 2RT \ln m\gamma_\pm$$

where $\phi'_{HCl(aq)}$ is a constant for HCl in the particular solvent, water, at given temperature. Furthermore, we may assume that $H_2(g)$ over the anode satisfies the ideal-gas law

$$\phi_{H_2} = \bar{F}^\circ_{H_2(g)} + RT \ln p_{H_2}$$

Therefore

$$\Delta F = \Delta F^\circ + 2RT \ln m\gamma_\pm - RT \ln (p_{H_2})^{1/2}$$

$$E = E^\circ - \frac{2RT}{1\text{ g-eq}} \ln m\gamma_\pm + \frac{RT}{1\text{ g-eq}} \ln (p_{H_2})^{1/2} \qquad (9\text{-}2\text{-}37)$$

where

$$\Delta F^\circ = -jE^\circ = \bar{F}^\circ_{Ag(c)} + \phi'_{HCl(aq)} - \tfrac{1}{2}\bar{F}^\circ_{H_2(g)} - \bar{F}^\circ_{AgCl(c)} \qquad (9\text{-}2\text{-}38)$$

Let us express Eq. (9-2-37) in the form

$$E' = E - \frac{RT}{1\text{ g-eq}} \ln (p_{H_2})^{1/2} = E^\circ - \frac{2RT}{1\text{ g-eq}} \ln m\gamma_\pm \qquad (9\text{-}2\text{-}39)$$

Thus, E' represents the cell emf corrected to $p_{H_2} = 1$ atm; unless one is deliberately investigating the effect of the hydrogen partial pressure on the results, one usually reports E', rather than E itself, thus eliminating the variable p_{H_2} from further consideration.[1] Equation (9-2-39) may be expressed rather more generally in the form

$$E' = E^\circ - \frac{RT}{1\text{ g-eq}} \ln m_{H^+}m_{Cl^-} - \frac{RT}{1\text{ g-eq}} \ln \gamma_\pm^2 \qquad (9\text{-}2\text{-}40)$$

which presumably would apply if KCl or HNO_3 were also present, so that m_{H^+} would differ from m_{Cl^-}.

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[1] The similar cell, (Pt), $H_2(g,\ p_{H_2})|HCl\ (aq,\ 0.1M)|Hg_2Cl_2(c),\ Hg(l)$, has actually been studied at hydrogen pressures up to more than 1000 atm; see W. R. Hainsworth, H. J. Rowley, and D. A. MacInnes, *J. Am. Chem. Soc.*, **46**, 1437–1443 (1924). Beyond 100 atm, one must correct Eq. (9-2-37) for deviation of $H_2(g)$ from ideal-gas behavior (see Prob. 9-1).

If it were not for interionic attraction, Eq. (9-2-39) with $\gamma_\pm = 1$ would quite simply represent the dependence of E' on the HCl concentration in dilute solution; thus, approximately, E' would decrease by about 0.118 volt for every factor of 10 by which m is increased. We may use the observed value of E', however, to measure $\gamma_\pm$ precisely and, at the same time, to measure the value of the important constant $E°$. Let us rewrite Eq. (9-2-39) in the form

$$E' + \frac{2RT}{1\text{ g-eq}} \ln m = E° - \frac{2RT}{1\text{ g-eq}} \ln \gamma_\pm \qquad (9\text{-}2\text{-}41)$$

from which it is evident that the value of $E°$ may be determined in principle by the extrapolation

$$\lim_{m\to 0} \left(E' + \frac{2RT}{1\text{ g-eq}} \ln m \right) = E° \qquad (9\text{-}2\text{-}42)$$

Having found $E°$ in this way, one may then substitute back in Eq. (9-2-41) to find $\gamma_\pm$ at each concentration.

Table 9-3 contains experimental data for the cell (9-2-35), selected from work of H. S. Harned and R. W. Ehlers at low HCl concentrations and from work of G. Scatchard at higher HCl concentrations. The third column contains the values of the expression on the left of Eq. (9-2-41). One sees that in this case, the deviation from ideal dilute-solution behavior (which would be represented by a constant value of $E' + 0.11832 \log m$) is significant even at concentrations below $0.01m$. The precision with which the data may be extrapolated to find $E°$ may be considerably improved with the help of the Debye-Hückel limiting law (7-4-28),

$$\lim_{m\to 0} \log \gamma_\pm = -0.5082 m^{1/2} \quad (1\!:\!1 \text{ electrolyte in } H_2O \text{ at } 25°) \qquad (9\text{-}2\text{-}43)^1$$

For if instead of extrapolating $(E' + 0.11832 \log m)$ itself, we extrapolate the value of the expression

$$E' + 0.11832 \log m - 0.11832 \times 0.5082 m^{1/2} \qquad \text{(volts)}$$

which would exactly equal $E°$ if the electrolyte conformed to the Debye-Hückel limiting law, then we may expect a more rapid convergence as $m \to 0$ [compare the treatment of freezing-point data for electrolytes, according to Eq. (7-5-63)]. The value of this expression has been computed for the lower electrolyte concentrations in the fourth column of

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[1] The value of the universal constant appearing in Eq. (7-4-31) has been multiplied by $\sqrt{\rho_1}$, where ρ_1, the density of pure water, has the value 0.99707 g/ml at 25°C. This conversion factor is required for transferring from molar concentration to molality [Eq. (7-3-98)].

Table 9-3. If one uses the extended Debye-Hückel formula (7-4-32), then one may construct a still closer approximation function to E°, as shown by A. S. Brown and D. A. MacInnes.[1] On the other hand, if one is using the cell solely for the determination of E° (and by implication, ΔF° for the cell reaction), and has determined $\gamma_\pm$ by other independent means, such as by vapor-pressure or freezing-point measurements (Sec. 7-5), or by the transference method to be described in Sec. 9-3*a*, then one may substitute directly the value of $\gamma_\pm$ in (9-2-41) at given m to calculate E° from the observed value of E at relatively high solute concentrations. From a critical review of all the evidence, MacInnes has accepted the value $E^\circ_{298} = 0.2225$ volt.[2] From this value, substituted in Eq. (9-2-41),

TABLE 9-3. EMF DATA FOR THE CELL: (Pt),H_2(g, 1 atm)|HCl(aq, m)|AgCl(c), Ag(c)*
$T = 298.16°K$

m, moles/kg	E', volts	$E' + 0.11832 \log m$, volts	$E' + 0.11832 \log m$ $-0.11832 \times 0.5082m^{1/2}$, volts	$-\log \gamma_\pm$	$\gamma_\pm$
0	....	(0.2225)	(0.2225)	(0.0000)	(1.000)
0.003215	0.52053	0.22557	0.22216	0.0262	0.942
0.004488	0.50384	0.22603	0.22200	0.0296	0.934
0.005619	0.49257	0.22631	0.22180	0.0321	0.929
0.007311	0.47948	0.22674	0.22160	0.0355	0.922
0.009138	0.46860	0.22732	0.22157	0.0406	0.911
0.011195	0.45861	0.22777	0.22141	0.0448	0.902
0.013407	0.44974	0.22816	0.22120	0.0482	0.895
0.01710	0.43783	0.22876	0.22090	0.0532	0.885
0.02563	0.41824	0.22996	0.22033	0.0634	0.864
0.05391	0.38222	0.23215	0.21819	0.0815	0.829
0.1238	0.34199	0.23464	0.21348	0.1023	0.790
0.2030	0.31774	0.23580	....	0.1124	0.772
0.3981	0.28407	0.23674	....	0.1200	0.759
0.5009	0.27197	0.23644	....	0.1175	0.763
0.5013	0.27195	0.23647	....	0.1183	0.762
0.6367	0.25902	0.23582	....	0.1124	0.772
0.9377	0.23696	0.23365	....	0.0947	0.804
1.0008	0.23290	0.23294	....	0.0879	0.817
1.5346	0.20534	0.22735	....	0.0414	0.909

* Values for 0.003215 to 0.1238*m* from H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **54**, 1350–1357 (1932). Values for 0.2030 to 1.5346*m* from G. Scatchard, *ibid.*, **47**, 641–648 (1925).

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[1] A. S. Brown and D. A. MacInnes, *J. Am. Chem. Soc.*, **57**, 1356–1362 (1935); see also D. A. MacInnes, "The Principles of Electrochemistry," pp. 184–187, Reinhold Publishing Corporation, New York, 1939.

[2] MacInnes, *loc. cit.*

the values of log $\gamma_\pm$ and of $\gamma_\pm$ given in the fifth and sixth columns of Table 9-3 have been computed from the observed emf data.

The value of E° is known as the *standard* emf of the cell. It represents what the value of E would be if each chemical reactant and product were present in its standard state at the given temperature. For HCl(aq), this standard state is that of a hypothetical ideal dilute solution at $m = 1$ mole/kg H_2O, *i.e.*, a state for which $m\gamma_\pm = 1$.[1] Now, according to Eq. (9-2-38), E° for the cell under consideration measures directly the value of the important natural constant $\phi'_{HCl(aq)}$ in relation to the value of $\bar{F}^\circ_{AgCl(c)}$; thus, introducing the accepted value of E° derived from the emf measurements,

$$\begin{aligned}\Delta F^\circ_{298} &= -1 \text{ g-eq} \times 0.2225 \text{ volt} \\ &= -5133 \text{ cal} \qquad (9\text{-}2\text{-}44)\end{aligned}$$

We have already reviewed three independent measurements of $\bar{F}^\circ_{AgCl(c)}$: $-25{,}980$ cal/mole from third law and thermochemical data (Sec. 8-3), $-26{,}201$ cal/mole from the combined emfs of the cells (9-2-1) and (9-2-9) [Eq. (9-2-18)], and $-26{,}210$ cal/mole from direct emf measurements on the cell (9-2-19) [Eq. (9-2-20)]. If we accept $\bar{F}^\circ_{AgCl(c)} = -26{,}200 \pm 10$ cal/mole as the probable value of the standard molal free energy of formation of AgCl(c) at 298.16°K, then the experimental result (9-2-44) leads to $\phi'_{HCl(aq)} = -31{,}330$ cal/mole. From a critical review of all the information, including spectroscopic data for HCl(g), F. D. Rossini has accepted for "Selected Values of Chemical Thermodynamic Properties"[2] the value $-31{,}350$ cal/mole; *i.e.*:

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) = H^+(aq) + Cl^-(aq); \qquad \begin{aligned}\Delta F^\circ_{298} &= \phi'_{HCl(aq)} \\ &= -31{,}350 \text{ cal} \qquad (9\text{-}2\text{-}45)\end{aligned}$$

In accordance with the general convention (7-4-14),

$$\tfrac{1}{2}H_2(g) = H^+(aq) + e; \qquad \Delta F^\circ = \phi'_{H^+(aq)} \equiv 0 \qquad (9\text{-}2\text{-}46)$$

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[1] This rather clumsy terminology is necessary because the value of ϕ_{HCl} decreases without limit, and with it, the value of E increases without limit, as $m \to 0$. But the value of $(\phi_{HCl} - 2RT \ln m)$ approaches a finite limit (represented by $\phi'_{HCl(aq)}$) as $m \to 0$, which represents what the value of ϕ_{HCl} would be at $m = 1$ if the solution continued to satisfy the ideal limiting law $\phi_{HCl} = 2RT \ln m$ at finite solute concentrations. Therefore we accept this $\phi'_{HCl(aq)}$ constant as a standard-state measure of the thermodynamic potential of HCl in aqueous solution. Such a measure obviously depends on the concentration measure employed. No such procedure is required in the case of η_{HCl}, the enthalpy in solution, since η_{HCl} itself approaches a finite limit in the given solvent, as $m \to 0$; therefore η°_{HCl} ($= \Phi^\circ_h$) in ideal dilute solution need imply no reference to the concentration measure.

[2] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D.C., June 30, 1948.

the result (9-2-45) is equivalent to

$$\tfrac{1}{2}Cl_2(g) + e = Cl^-(aq); \qquad \Delta F^\circ_{298} = \phi'_{Cl^-(aq)} = -31{,}350 \text{ cal} \qquad (9\text{-}2\text{-}47)$$

In a cell of the type (9-2-35), it is assumed that the so-called "depolarizer," AgCl(c) in this case, is sufficiently insoluble so that its presence in the electrolyte does not significantly influence the thermodynamic properties.[1]

Harned and Ehlers also measured the emf of the cell (9-2-35) at a series of different temperatures, obtaining

$$\left(\frac{dE^\circ}{dT}\right) = -0.00064 \text{ volt/deg}$$

From this result, we may compute the standard entropy of the cell reaction (9-2-36)

$$\begin{aligned}\Delta S^\circ_{298} &= \bar{S}^\circ_{Ag(c)} + \sigma'_{HCl(aq)} - \tfrac{1}{2}\bar{S}^\circ_{H_2(g)} - \bar{S}^\circ_{AgCl(c)} \\ &= -1 \text{ g-eq} \times 0.00064 \text{ volt/deg} = -14.8 \text{ eu}\end{aligned}$$

Introducing third-law entropies for Ag(c) and AgCl(c), and the spectroscopically determined entropy of $H_2(g)$ from Kelley's critical compilation,[2] we thus obtain

$$\sigma'_{HCl(aq)} = 13.6 \text{ eu/mole} \qquad (T = 298.16^\circ K)$$

This value may be independently cross-checked by the spectroscopically determined value of $\bar{S}^\circ_{HCl(g)}$ (see Table 10-4, Chap. 10), combined with the entropy of solution, which may be calculated from the heat of solution and partial-vapor-pressure data for HCl from concentrated solutions.[3] The value accepted for "Selected Values of Chemical Thermodynamic Properties" is

$$\sigma'_{HCl(aq)} = 13.17 \text{ eu/mole} \quad (T = 298.16^\circ K) \quad (9\text{-}2\text{-}48)$$

In view of the convention (8-3-7), this quantity measures the value of $\sigma'_{Cl^-(aq)}$. One can readily understand how chemical thermodynamic data derived from ordinary equilibrium and thermochemical sources, including third-law entropy data, could be applied to calculate the electrochemical properties of reversible galvanic cells. Taken together, both types of information obtained experimentally serve as cross checks on the reliability and self-consistency of our chemical thermodynamic data.

Following up the implications of the convention (9-2-46), it has become customary to summarize standard emf data in the form of *standard electrode potentials*, corresponding to the two independent electrode reactions

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[1] Recall footnote on page 535.

[2] $\bar{S}^\circ_{Ag(c)} = 10.20 \pm 0.05$ eu/mole; $\bar{S}^\circ_{AgCl(c)} = 23.0 \pm 0.1$ eu/mole; $\bar{S}^\circ_{H_2(g)} = 31.23 \pm 0.01$ eu/mole; K. K. Kelley, *U.S. Bur. Mines Bull.* 434 (1941).

[3] M. Randall and L. E. Young, *J. Am. Chem. Soc.*, **50**, 989–1004 (1928).

taking place in each half of the cell. American theoretical electrochemists write the electrode reactions as *oxidations*, the sign of $E°$ then being represented correctly for a given cell reaction by algebraic addition of the electrode reactions and their corresponding standard electrode potentials, in the sense that a reaction that tends to proceed spontaneously when each reactant and product is in its standard state then has a positive value of $E°$. Starting with the arbitrary convention,

$$\tfrac{1}{2}H_2(g) = H^+(aq) + e; \qquad E° \equiv 0.0000 \text{ volt} \qquad (9\text{-}2\text{-}49)$$

the result $E°_{298} = 0.2225$ volt for the cell (9-2-35) thus leads to the Ag(c), AgCl(c), $Cl^-(aq)$ standard electrode potential:

$$Ag(c) + Cl^-(aq) = AgCl(c) + e; \qquad E°_{298} = -0.2225 \text{ volt} \qquad (9\text{-}2\text{-}50)$$

If this result is combined with the experimental result, $E°_{298} = 0.0455$ volt for the cell (9-2-1), we thus obtain

$$Hg(l) + Cl^-(aq) = \tfrac{1}{2}Hg_2Cl_2(c) + e; \qquad E°_{298} = -0.2680 \text{ volt} \qquad (9\text{-}2\text{-}51)$$

Or if it is combined with the experimental result, $E°_{298} = 1.1362$ volt for the cell (9-2-19), we obtain

$$Cl^-(aq) = \tfrac{1}{2}Cl_2(g) + e; \qquad E°_{298} = -1.3587 \text{ volts} \qquad (9\text{-}2\text{-}52)$$

The value of each standard electrode potential is equivalent to the standard free energy of the corresponding electrode reaction, by virtue of the general relationship

$$\Delta F° = -jE° \qquad (9\text{-}2\text{-}53)$$

The possibility of constructing a self-consistent table of standard electrode potentials rests in the independence of ionic thermodynamic properties at infinite dilution in the solvent, water. The numerical values are of course based on the convention represented by (9-2-46) and (9-2-49), and have no significance except in relation to each other, *i.e.*, except when recombined in the form of $E°$ for a complete oxidation-reduction reaction. Comprehensive and critical summaries of standard electrode potentials, or so-called "oxidation potentials," have been given by W. M. Latimer and by D. A. MacInnes; such information is implicit also in the extensive free-energy data being compiled by the National Bureau of Standards, under the direction of F. D. Rossini and his associates.[1]

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[1] W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, 1938; D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corporation, New York, 1939; F. D. Rossini *et al.*, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washingon, D.C. (issued quarterly since Dec. 31, 1947).

Example:

$$Pb(Hg)|PbCl_2(aq, m)|AgCl(c), Ag(c) \qquad (9\text{-}2\text{-}54)$$

The thermodynamics of this cell, studied by W. R. Carmody, is essentially similar to that of the cell (9-2-35).[1] The electrode reactions are

Anode reaction: $Pb(Hg) = Pb^{++}(aq) + 2e$
Cathode reaction: $AgCl(c) + e = Ag(c) + Cl^{-}(aq)$

so that the net cell reaction for $j = 2\mathfrak{F}$ is

$$Pb(Hg) + 2AgCl(c) = Ag(c) + PbCl_2(aq, m)$$

The corresponding free-energy change has the form [compare Eq. (7-4-23) for ϕ_{PbCl_2}]

$$\Delta F = \Delta F^\circ + 3RT \ln m\gamma_\pm + RT \ln 4$$

Therefore

$$E = E^\circ - \frac{3RT}{2 \text{ g-eq}} \ln m\gamma_\pm - \frac{RT}{2 \text{ g-eq}} \ln 4 \qquad (9\text{-}2\text{-}55)$$

where

$$\Delta F^\circ = -jE^\circ = F^\circ_{Ag(c)} + \phi'_{Pb^{++}(aq)} + 2\phi'_{Cl^{-}(aq)} - \phi_{Pb} - 2F^\circ_{AgCl(c)}$$

It has been found that saturated or two-phase amalgams of the metals lead, cadmium, zinc, copper, etc., give more reproducible results than sticks or sheets of the pure metals, which are subject to strains and gas occlusions. From measurements at $PbCl_2$ concentrations between $0.0002m$ and the saturated solution, $0.03905m$, at 25°C, Carmody found for E° the value $E^\circ_{298} = 0.3426$ volt. From the value of E for the saturated solution, 0.4842 volt, $\gamma_\pm = 0.408$.

Now, there is a small but significant potential difference between pure crystalline lead, and the two-phase lead amalgam, which Carmody measured by setting up the cell

$$Pb(c)|PbCl_2(aq)|Pb(Hg); \qquad E_{298} = E^\circ_{298} = 0.0058 \text{ volt} \qquad (9\text{-}2\text{-}56)$$

Therefore for the reaction

$$Pb(c) + 2AgCl(c) = 2Ag(c) + Pb^{++}(aq) + 2Cl^{-}(aq)$$
$$E^\circ_{298} = 0.3484 \text{ volt}$$

Combining this result with the standard potential (9-2-50) of the Ag(c), AgCl(c), Cl⁻(aq) electrode,

$$Pb(c) = Pb^{++}(aq) + 2e; \qquad E^\circ_{298} = 0.1259 \text{ volt} \qquad (9\text{-}2\text{-}57)$$

This statement is equivalent to

$$\begin{aligned} \phi'_{Pb^{++}(aq)} &= -2 \text{ g-eq} \times 0.1259 \text{ volt} \\ &= -5810 \text{ cal/mole} \qquad (9\text{-}2\text{-}58) \end{aligned}$$

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[1] W. R. Carmody, *J. Am. Chem. Soc.*, **51**, 2905–2909 (1929); see Prob. 9-3.

In a similar manner, the standard electrode potentials of many other metals have been determined.

Example:

$$(\mathrm{Pt}),\ \mathrm{H_2(g,\ 1\ atm)|H_2SO_4(aq},\ m)|\mathrm{PbSO_4(c),\ Pb(Hg)} \qquad (9\text{-}2\text{-}59)$$

This cell gives the thermodynamic potential of H_2SO_4 in aqueous solution, and also the standard potential of the Pb(Hg), $PbSO_4$(c), $SO_4^{=}$(aq) electrode. The cell reaction for $j = 2\mathfrak{F}$ is

$$\mathrm{H_2(g) + PbSO_4(c) = Pb(Hg) + H_2SO_4(aq},\ m) \qquad (9\text{-}2\text{-}60)$$

The emf has been measured over a wide range of concentrations and temperatures by J. Shrawder and I. A. Cowperthwaite; at 25°C,

$$E^\circ_{298} = -0.3505 \text{ volt}^1$$

Combining with (9-2-56),

$$\mathrm{H_2(g) + PbSO_4(c) = Pb(c) + H_2SO_4(aq)}; \qquad E^\circ_{298} = -0.3563 \text{ volt} \qquad (9\text{-}2\text{-}61)$$

$$\mathrm{Pb(c) + SO_4^{=}(aq) = PbSO_4(c)} + 2e; \qquad E^\circ_{298} = 0.3563 \text{ volt} \qquad (9\text{-}2\text{-}62)$$

The result (9-2-62) combined with (9-2-57) implies the thermodynamic solubility product of $PbSO_4$, for, by difference,

$$\mathrm{PbSO_4(c) = Pb^{++}(aq) + SO_4^{=}(aq)}; \qquad E^\circ_{298} = -0.2304 \text{ volt}$$

This corresponds to the standard free-energy change

$$\Delta F^\circ_{298} = -2 \text{ g-eq} \times (-0.2304 \text{ volt}) = 10{,}630 \text{ cal}$$

According to Eq. (7-4-37), ΔF° measures the thermodynamic solubility product K_s through the relationship

$$RT \ln K_s = -\Delta F^\circ \qquad (9\text{-}2\text{-}63)$$

Thus

$$\log K_s = -7.792$$
$$K_s = 1.61 \times 10^{-8}$$

This method of measuring solubility products is quite general, and its physical basis may perhaps be made clearer by the following remarks. The actual contribution of the lead electrode (9-2-57) to the emf of a cell of which it forms a part may be expressed in the form

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[1] J. Shrawder and I. A. Cowperthwaite, *J. Am. Chem. Soc.*, **56**, 2340–2345 (1934); the data have been analyzed critically by D. A. MacInnes, "The Principles of Electrochemistry," pp. 191–193, Reinhold Publishing Corporation, New York, 1939. See also H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **57**, 27–33 (1935), for the analogous cell based on Hg(l), Hg_2SO_4(c) instead of Pb(Hg), $PbSO_4$(c).

$$E_{\mathrm{Pb(c)},\mathrm{Pb^{++}(aq)}} = 0.1259 - \frac{RT}{2\ \text{g-eq}} \ln m_{\mathrm{Pb^{++}}}\gamma_{\mathrm{Pb^{++}}} \qquad (9\text{-}2\text{-}64)$$

where it is understood that this relationship has significance only in connection with some process taking place at the other electrode completing the cell. However, the lead electrode potential depends on the Pb^{++} concentration around the electrode, in the manner represented in general by (9-2-64). When this electrode is immersed in a solution saturated with $PbSO_4$, its potential then assumes a value determined in accordance with (9-2-64) by the Pb^{++} concentration in the saturated solution, and the difference between (9-2-57) and (9-2-62) is thus a measure of that concentration. The fact that the $E°$ values have been derived by extrapolations to infinitely dilute solution implies that deviation from ideal dilute-solution behavior has been taken into account. Thus, if one substitutes the result (9-2-62) in (9-2-64) in the ideal dilute-solution form,

$$0.3563\text{ volt} = 0.1259\text{ volt} - \frac{0.05916\text{ volt}}{2} \log m_{\mathrm{Pb^{++}}}$$

and solves for $m_{\mathrm{Pb^{++}}}$, one will obtain the Pb^{++} concentration in a hypothetical ideal dilute solution in which $m_{\mathrm{SO_4^{-}}} = 1$ mole/kg [the $SO_4^{=}$ state to which (9-2-62) applies]; this is the same as the thermodynamic solubility product of $PbSO_4$. A similar principle is used in the study of complex ion equilibria by emf measurements, except that it is usually more troublesome in a complex mixture to carry out the extrapolation to ideal dilute-solution behavior.

Example:

$$\mathrm{Zn(c)|ZnSO_4(aq,}m'\mathrm{)|Hg_2SO_4(c), Hg(l), Hg_2SO_4(c)|CuSO_4(aq,}m''\mathrm{)|Cu(c)} \qquad (9\text{-}2\text{-}65)$$

If we were to set up such a cell, then the net cell reaction accompanying the flow of $2\mathfrak{F}$ through the cell would be

$$\mathrm{Zn(c) + CuSO_4(aq,}\ m''\mathrm{) = Cu(c) + ZnSO_4(aq,}\ m'\mathrm{)} \qquad (9\text{-}2\text{-}66)$$

At the Zn anode, Zn^{++} ions would go into solution reversibly and would be accompanied by $SO_4^{=}$ ions from the $Hg_2SO_4(c)$ in the intermediate compartment of the cell, while simultaneously Cu^{++} ions would be reduced reversibly to Cu at the Cu cathode, the corresponding $SO_4^{=}$ ions combining with Hg(l) in the intermediate compartment to form $Hg_2SO_4(c)$. Exactly as much $Hg_2SO_4(c)$ would be formed by the process taking place in the right-hand half of the cell as would be consumed by the process taking place in the left-hand half of the cell. The cell reaction (9-2-66) is similar to the Daniell cell reaction (5-5) considered in Sec. 5-1, except that by the device of introducing the intermediate compartment containing materials behaving reversibly toward the deposition and liberation of the anion, $SO_4^{=}$, we have eliminated the irreversible feature of the actual Daniell cell associated with the migration of ions across the liquid junction between the two electrolytes.

It is not actually necessary for us to set up such a cell as (9-2-65), except in thought, because it consists merely of the two simple cells

$$\mathrm{Zn(c)|ZnSO_4(aq,}\ m')\mathrm{|Hg_2SO_4(c),\ Hg(l)} \qquad (9\text{-}2\text{-}67)$$
$$\mathrm{Cu(c)|CuSO_4(aq,}\ m'')\mathrm{|Hg_2SO_4(c),\ Hg(l)} \qquad (9\text{-}2\text{-}68)$$

connected in series, in opposition to each other.[1] Therefore if we merely subtract (algebraically) the emf of the cell (9-2-68) from that of the cell (9-2-67), we shall obtain the desired emf of the cell (9-2-65). The free energy of the reaction (9-2-66) has the form

$$\begin{aligned} \Delta F &= \bar{F}^\circ_{\mathrm{Cu(c)}} + \phi_{\mathrm{ZnSO_4}} - \bar{F}^\circ_{\mathrm{Zn(c)}} - \phi_{\mathrm{CuSO_4}} \\ &= \Delta F^\circ + 2RT \ln \frac{m'(\gamma_\pm)'}{m''(\gamma_\pm)''} \end{aligned}$$

Thus

$$E = E^\circ - \frac{2RT}{2\ \text{g-eq}} \ln \frac{m'(\gamma_\pm)'}{m''(\gamma_\pm)''} \qquad (9\text{-}2\text{-}69)$$

where

$$\Delta F^\circ = -jE^\circ = \bar{F}^\circ_{\mathrm{Cu(c)}} + \phi'_{\mathrm{Zn^{++}(aq)}} - \bar{F}^\circ_{\mathrm{Zn(c)}} - \phi'_{\mathrm{Cu^{++}(aq)}} \qquad (9\text{-}2\text{-}70)$$

The value of E° may be computed from the two standard electrode potentials

$$\mathrm{Zn(c)} = \mathrm{Zn^{++}(aq)}; \qquad E^\circ_{298} = 0.7611 \text{ volt} \qquad (9\text{-}2\text{-}71)$$
$$\mathrm{Cu(c)} = \mathrm{Cu^{++}(aq)}; \qquad E^\circ_{298} = -0.339 \text{ volt} \qquad (9\text{-}2\text{-}72)$$

Thus

$$E^\circ_{298} = 1.100 \text{ volts} \qquad (9\text{-}2\text{-}73)$$

Therefore the emf equation (9-2-69) has the form at 25°C

$$E = 1.100 - 0.05916 \log \frac{m_{\mathrm{ZnSO_4}}(\gamma_\pm)_{\mathrm{ZnSO_4}}}{m_{\mathrm{CuSO_4}}(\gamma_\pm)_{\mathrm{CuSO_4}}} \qquad (9\text{-}2\text{-}74)$$

It happens that when the concentrations of $ZnSO_4$ and $CuSO_4$ are equal, the mean ionic activity coefficients of these quite similar electrolytes are nearly equal; in that case, $E = 1.100$ volts. In a real Daniell cell, as ordinarily set up, the $CuSO_4$ concentration is usually made higher than

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[1] Compound cells similar to (9-2-65), containing a flowing amalgam in the center compartment, have been useful in the study of thermodynamic properties of the alkali metals and their compounds; see, for example, H. S. Harned, *J. Am. Chem. Soc.*. **47**, 676–684 (1925).

the $ZnSO_4$ concentration, but the emf is generally somewhat less than 1.10 volts.

The information (9-2-73) gives us essentially the equilibrium constant of the cell reaction (9-2-66); for if the concentrations of the two electrolytes were such that the system would be in a state of chemical equilibrium, then there would be no source of chemical free energy, and E would vanish. This condition implies that

$$E^\circ = \frac{RT}{2\text{ g-eq}} \ln \frac{m_{\mathrm{Zn}^{++}} m_{\mathrm{SO}_4^{-}}}{m_{\mathrm{Cu}^{++}} m_{\mathrm{SO}_4^{-}}} \frac{\gamma_{\mathrm{Zn}^{++}} \gamma_{\mathrm{SO}_4^{-}}}{\gamma_{\mathrm{Cu}^{++}} \gamma_{\mathrm{SO}_4^{-}}} \quad (E = 0) \qquad (9\text{-}2\text{-}75)$$

Therefore the expression on the right of Eq. (9-2-75) assumes a constant value for all equilibrium states of the chemical reaction

$$\frac{m_{\mathrm{Zn}^{++}} m_{\mathrm{SO}_4^{-}}}{m_{\mathrm{Cu}^{++}} m_{\mathrm{SO}_4^{-}}} \frac{\gamma_{\mathrm{Zn}^{++}} \gamma_{\mathrm{SO}_4^{-}}}{\gamma_{\mathrm{Cu}^{++}} \gamma_{\mathrm{SO}_4^{-}}} = K_m^\circ \qquad (9\text{-}2\text{-}76)$$

where, by definition,

$$E^\circ \equiv \frac{RT}{j} \ln K_m^\circ \qquad (9\text{-}2\text{-}77)$$

This relationship is quite general; for the cells we have previously considered, where the thermodynamic potential of only a single reactant or product depended on the electrolyte concentration, there was but a single concentration in principle (not necessarily an attainable one) at which the reaction would be in a state of equilibrium; *e.g.*, for the cell (9-2-35), and reaction (9-2-36), the equilibrium constant has the general form

$$K_m^\circ = \frac{m_{\mathrm{H}^+} m_{\mathrm{Cl}^-}}{(p_{\mathrm{H}_2})^{1/2}} \frac{\gamma_{\mathrm{H}^+} \gamma_{\mathrm{Cl}^-}}{(\nu_{\mathrm{H}_2})^{1/2}} \qquad (9\text{-}2\text{-}78)$$

so that at $p_{\mathrm{H}_2} = 1$ atm, there is in principle a unique concentration of HCl at which the reaction would be in a state of equilibrium. At lower concentrations, H_2(g) tends to reduce AgCl(c), but at higher concentrations, Ag(c) would tend to reduce HCl(aq). Calculation according to Eq. (9-2-77) from the observed value of E° shows that K_m° in Eq. (9-2-78) has the value 5.75×10^3; therefore it is impossible to attain a concentration of HCl high enough to attack silver (though complex ion formation between AgCl and Cl^- tends to favor this outcome). From the standard value of E° for the reaction (9-2-66), $\log K_m^\circ = 37.19$, $K_m^\circ = 1.6 \times 10^{37}$. This appears to be an astronomically large number, but it is measured quite precisely by Eq. (9-2-77) from the emf data. It implies that Zn will tend to displace Cu from aqueous Cu^{++} solution so long as $m_{\mathrm{Zn}^{++}}/m_{\mathrm{Cu}^{++}} < 1.6 \times 10^{37}$ (disregarding the effect of the two activity coefficients, which in this case practically cancel each other). It is quite possible, however, to reduce the free Cu^{++} concentration to such a low value through complex ion formation [*e.g.*, as $Cu(CN)_2^-$] that Zn cannot displace Cu from the solution; this principle is utilized in the electroplating of brass.

9-3. Cells with Liquid Junctions. It is not always possible for us to set up electrochemical reactions in which we are interested, in the form of galvanic cells without liquid junctions. For example, we cannot determine the important Ag(c), Ag^+(aq) standard electrode potential directly by means of cells without liquid junctions, because there are no sufficiently soluble silver salts for whose anions we have reversible electrodes. Therefore it is necessary for us to study liquid-junction effects, in order to understand how they may influence thermodynamic data based on cells with liquid junctions. Furthermore, the study of liquid-junction processes has proved to be extremely interesting in itself.

a. Transference Cells. Most of the cells we have considered in the preceding section have been based on chemical oxidation-reduction reactions, with the exception of (9-2-31) which was based on diffusion between the electrodes. We may construct cells comparable to (9-2-31), but based on diffusion of the electrolyte. Thus, the process

$$\mathrm{HCl}(\mathrm{aq}, m_1) = \mathrm{HCl}(\mathrm{aq}, m_2) \qquad (9\text{-}3\text{-}1)$$

involves a free-energy change having the form

$$\begin{aligned} \Delta F &= (\phi_{\mathrm{HCl}})_2 - (\phi_{\mathrm{HCl}})_1 \\ &= 2RT \ln \frac{m_2(\gamma_\pm)_2}{m_1(\gamma_\pm)_1} \end{aligned} \qquad (9\text{-}3\text{-}2)$$

which may be converted reversibly into electrical energy by means of such a compound cell as

$$\mathrm{Ag(c), AgCl(c)|HCl(aq}, m_1)|\mathrm{H_2(g), (Pt), H_2(g)|HCl(aq}, m_2)|\mathrm{AgCl(c), Ag(c)} \qquad (9\text{-}3\text{-}3)$$

The passage of 1$\mathfrak{F}$ of negative electricity through this cell from right to left results in the transfer of 1 mole of HCl from the left-hand compartment to the right, as represented by Eq. (9-3-1); it also results in the transfer of 1 mole of AgCl(c) from the right-hand electrode to the left-hand electrode, and the net gain of 1 mole of Ag(c) at the right and loss of 1 mole of Ag(c) at the left, but since no change of state of these substances is involved, these accompanying effects do not represent thermodynamic changes. We do not actually have to set up the cell (9-3-3), since it consists merely of two cells (9-2-35) coupled in series, back to back, and the emf will simply be the algebraic difference between the emf of (9-2-35) for

m_2 and the emf for m_1; if m_1 exceeds m_2, then the process (9-3-1) will tend spontaneously to take place as indicated, from left to right, and the left-hand electrode of the cell (9-3-3) will be the negative electrode (corresponding to a positive value of E). Thus, by interpolation of the data in Table 9-3, we find for $m_2 = 0.01$ mole/kg, $E_2 = 0.4643$ volt, and for $m_1 = 0.1$ mole/kg, $E_1 = 0.3525$ volt; therefore for the corresponding cell (9-3-3), $E = 0.1118$ volt.

Let us consider the cell

$$\text{Ag(c), AgCl(c)}|\text{HCl(aq, }m_1)||\text{HCl(aq, }m_2)|\text{AgCl(c), Ag(c)} \qquad (9\text{-}3\text{-}4)$$

in which the two electrolytes make direct physical contact with each other. Its electrical energy is derived basically from the same change of state (9-3-1) as that of the cell (9-3-3), but with $m_1 = 0.1$ mole/kg and $m_2 = 0.01$ mole/kg, we find at 25°C that E is only 0.0925 volt.[1] The reason for the difference rests in the fact that as the cell (9-3-4) is discharged, Cl^- ions can migrate across the boundary of the two electrolytes, from the right-hand compartment into the left. This cannot happen in the cell (9-3-3). Therefore the *net* quantity of HCl transferred by $1\mathfrak{F}$ from the left compartment of cell (9-3-4) to the right is *less* than 1 g-eq, by the number of gram-equivalents of Cl^- migrating across the liquid junction. The ionic migration is in this case a thermodynamically reversible process; it could be exactly reversed by the application to the cell (9-3-4) of a potential difference slightly greater than the cell's own emf.

Let t_+ represent the *transference number* of the cation, H^+, and t_-, the transference number of the anion, Cl^-; these numbers represent the respective *fractions* of the electricity transported through the electrolyte by the cation and by the anion, respectively, and they are determined by the relative rates of migration under a given potential gradient. They may be measured by methods independent of emf studies, such as by the original Hittorf method, based on straightforward analysis of the chemical changes taking place around the two electrodes during electrolysis, or by the elegant moving-boundary method, perfected by D. A. MacInnes, L. G. Longsworth, and their associates.[2] In general, the transference numbers vary slightly with concentration, so that they will differ on the two sides of the cell (9-3-4). In the present elementary treatment, we

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[1] Selected from a detailed investigation by T. Shedlovsky and D. A. MacInnes, *J. Am. Chem. Soc.*, **58**, 1970–1972 (1936). Their concentrations are expressed in moles per iter, but the difference is insignificant for our present purpose.

[2] J. W. Hittorf, *Pogg. Ann.*, **89**, 177 (1853), etc.

D. A. MacInnes and L. G. Longsworth, *Chem. Revs.*, **11**, 171–230 (1932); see also D. A. MacInnes, "The Principles of Electrochemistry," Chap. IV, Reinhold Publishing Corporation, New York, 1939.

shall assume that they are practically constant.[1] Thus, when $1\mathfrak{F}$ passes through the cell, the net quantity of HCl transferred from the more concentrated (left) to the less concentrated (right) solution is $1 - t_-$, or t_+ g-eq. Therefore in order to bring about the transfer of 1 mole, corresponding to the chemical equation (9-3-1) and the net free-energy change (9-3-2), it is necessary that $(1/t_+)\ \mathfrak{F}$ pass through the cell. Let E' represent the emf of the cell, which for thermodynamically reversible behavior will be related to ΔF by the general equation (9-1-10),

$$E' = -\frac{1}{j}\Delta F$$

Thus

$$E' = -2RTt_+ \ln \frac{m_2(\gamma_\pm)_2}{m_1(\gamma_\pm)_1} = t_+E \tag{9-3-5}$$

where E represents the emf of the corresponding cell (9-3-3) without the liquid junction. Thus, from the given data for the two cells,

$$\begin{aligned} t_+ &= \frac{0.0925 \text{ volt}}{0.1118 \text{ volt}} \\ &= 0.828 \end{aligned}$$

This result is in perfect agreement with the mean of $t_+ = 0.8251$ in $0.01M$ HCl and $t_+ = 0.8314$ in $0.1M$ HCl, found by Longsworth by the moving-boundary method.[2] If we were to set up the cell

$$(\text{Pt}), \text{H}_2(\text{g})|\text{HCl}(\text{aq}, m_2)||\text{HCl}(\text{aq}, m_1)|\text{H}_2(\text{g}), (\text{Pt}) \tag{9-3-6}$$

then we may show by similar reasoning that its emf, E'', is given approximately (ignoring the change of transference numbers with concentration) by the equation

$$E'' = -2RTt_- \ln \frac{m_2(\gamma_\pm)_2}{m_1(\gamma_\pm)_1} = t_-E \tag{9-3-7}$$

Since the transference numbers of many electrolytes may be measured independently with high precision, one may use cells such as (9-3-4) or (9-3-6) to measure the relative values of $\gamma_\pm$ at the two electrolyte concentrations; it is necessary for this purpose that one take into account the modification of the simple equations (9-3-5) and (9-3-7) resulting from the variation of the transference numbers with concentration. This method has been explored by MacInnes and his associates.[1]

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[1] For the exact treatment, in which one assumes that the transference number of the given ion changes continuously as one crosses the boundary, see D. A. MacInnes, "The Principles of Electrochemistry," pp. 156–165; see also Prob. 9-19.

[2] L. G. Longsworth, *J. Am. Chem. Soc.*, **54**, 2741–2758 (1932).

The differences: $E - E'$ and $E - E''$, constitute the so-called *liquid-junction potentials* of the cells (9-3-4) and (9-3-6), respectively.

b. Liquid-junction Potentials in General. The cells considered in Sec. 9-3*a* involved a comparatively simple process at the liquid-liquid boundary between the two electrolytes, because the ions involved were the same on either side. Even then, we neglected in the simple treatment to take into account the change of transference numbers with the concentration. Far more complicated changes may take place when different ions are present on either side of the boundary, and for this reason, one tries to eliminate liquid junctions altogether, wherever possible in precise thermodynamic investigation, by using cells of the types described in Sec. 9-2. This is not always possible, however, and furthermore the study of liquid junction processes is interesting in itself. We shall consider here only a single example, using certain drastic simplifications in order to effect a solution. For further discussion, the reader is referred to the excellent treatment given by D. A. MacInnes.[1]

Let us take the cell

$$\mathrm{Ag(c), AgCl(c)|HCl(aq,\ 0.1}M\mathrm{)||KCl(aq,\ 0.1}M\mathrm{)|AgCl(c), Ag(c)} \qquad (9\text{-}3\text{-}8)$$

This cell, and many others similar to it, has been studied by MacInnes and Yeh, who found for the particular concentrations given, at 25°C, $E = 0.02678$ volt.[2] They found incidentally that the emf depended on how the boundary was set up physically; this value was obtained by a "flowing-boundary" method, which ensures against changes in the boundary concentrations that may result from thermal diffusion, or from actual polarization of the cell as the emf is being measured. Presumably, the net change whose free energy gives rise to the electrical energy delivered by the cell is the migration of H^+ ions from the HCl into the boundary, and the migration of K^+ ions out of the boundary into the KCl; with the total ionic concentrations uniform throughout, and with the mean ionic activity coefficients for the two similar electrolytes at the given low ionic concentration practically the same on both sides, the production of Cl^- in the KCl electrolyte around the cathode and the disappearance of Cl^- from the HCl electrolyte around the anode must involve free-energy changes that practically cancel each other. If the process were to be continued indefinitely, then presumably the HCl would begin to diffuse throughout the KCl until ultimately the increase in Cl^- concentration in the right half of the cell and the decrease in the left half would compensate for the so-called liquid-junction potential at the boundary between them.

The precise nature and composition of the boundary region are of course

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[1] D. A. MacInnes, "The Principles of Electrochemistry," Chap. XIII.

[2] D. A. MacInnes and Y. L. Yeh, *J. Am. Chem. Soc.*, **43**, 2563–2573 (1921).

difficult if not impossible to describe exactly. Let us, however, introduce a simplifying assumption made originally by Henderson.[1] We shall suppose that the boundary consists of a region of finite width, over which there is a continuous and constant concentration gradient from one side to the other. If, therefore, we consider a layer of thickness dx located x fraction of the distance from one side of the boundary to the other, then we may assume that in this layer

$$\left.\begin{aligned} C_{\mathrm{H}^+} &= (1 - x)C_0 \\ C_{\mathrm{K}^+} &= xC_0 \\ C_{\mathrm{Cl}^-} &= C_0 \end{aligned}\right\} \tag{9-3-9}$$

where C_0 represents the uniform HCl and KCl concentration on either side of the boundary. The precise limits to the boundary region cannot of course be as sharply specified as these equations might imply; but it will be sufficient for our purpose if when $x = 0$, we are in a region essentially having the same composition as the bulk of the electrolyte in the anode half of the cell, and if when $x = 1$, we are in a region having the same composition as the bulk of the electrolyte in the cathode half of the cell. We need only suppose that the total distance represented by the range $x = 0$ to 1 is small in comparison with the dimensions of the cell, but yet large in comparison with molecular or ionic dimensions.

Now, within the region dx, the transference numbers of the three ions, representing the fractions of the electricity transported by them across this region as the cell discharges, will have the form

$$\left.\begin{aligned} t_{\mathrm{H}^+} &= \frac{C_{\mathrm{H}^+}u_{\mathrm{H}^+}}{C_{\mathrm{H}^+}u_{\mathrm{H}^+} + C_{\mathrm{K}^+}u_{\mathrm{K}^+} + C_{\mathrm{Cl}^-}u_{\mathrm{Cl}^-}} = \frac{(1 - x)u_{\mathrm{H}^+}}{(1 - x)u_{\mathrm{H}^+} + xu_{\mathrm{K}^+} + u_{\mathrm{Cl}^-}} \\ t_{\mathrm{K}^+} &= \frac{C_{\mathrm{K}^+}u_{\mathrm{K}^+}}{C_{\mathrm{H}^+}u_{\mathrm{H}^+} + C_{\mathrm{K}^+}u_{\mathrm{K}^+} + C_{\mathrm{Cl}^-}u_{\mathrm{Cl}^-}} = \frac{xu_{\mathrm{K}^+}}{(1 - x)u_{\mathrm{H}^+} + xu_{\mathrm{K}^+} + u_{\mathrm{Cl}^-}} \\ t_{\mathrm{Cl}^-} &= \frac{C_{\mathrm{Cl}^-}u_{\mathrm{Cl}^-}}{C_{\mathrm{H}^+}u_{\mathrm{H}^+} + C_{\mathrm{K}^+}u_{\mathrm{K}^+} + C_{\mathrm{Cl}^-}u_{\mathrm{Cl}^-}} = \frac{u_{\mathrm{Cl}^-}}{(1 - x)u_{\mathrm{H}^+} + xu_{\mathrm{K}^+} + u_{\mathrm{Cl}^-}} \end{aligned}\right\} \tag{9-3-10}$$

where u_{H^+}, u_{K^+}, and u_{Cl^-} denote, respectively, the ionic mobilities of H^+, K^+, and Cl^-. According to conductivity theory, we may suppose that these quantities are constant throughout the cell under the given conditions of uniform ionic strength throughout. Thus, when 1 faraday of electricity passes through the cell (the left-hand electrode, in the HCl solution, being the anode), the net free-energy change taking place in the region dx will be the result of t_{H^+} g-eq of H^+ migrating through a region in which its thermodynamic potential is falling with increasing x at the rate

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[1] P. Henderson, *Z. physik. Chem.*, **59**, 118–127 (1907); **63**, 325–345 (1908).

$$\frac{d\phi_{\mathrm{H}^+}}{dx} = RT\left(\frac{d\ln C_{\mathrm{H}^+}}{dx}\right)$$

t_{K^+} g-eq of K^+ migrating through a region in which its thermodynamic potential is rising with increasing x at the rate

$$\frac{d\phi_{\mathrm{K}^+}}{dx} = RT\left(\frac{d\ln C_{\mathrm{K}^+}}{dx}\right)$$

and t_- g-eq of Cl^- migrating in the opposite direction, in which its thermodynamic potential is presumably undergoing no change. We may assume that for these 1:1 electrolytes at uniform total electrolyte concentration throughout, the mean ionic activity coefficients are practically the same throughout. Thus, the net free-energy change through the element dx will have the form

$$\frac{dF}{dx} = t_{\mathrm{H}^+}RT\left(\frac{d\ln C_{\mathrm{H}^+}}{dx}\right) + t_{\mathrm{K}^+}RT\left(\frac{d\ln C_{\mathrm{K}^+}}{dx}\right)$$

Introducing (9-3-9) and (9-3-10),

$$\begin{aligned}\frac{dF}{dx} &= \frac{(1-x)u_{\mathrm{H}^+}}{(1-x)u_{\mathrm{H}^+} + xu_{\mathrm{K}^+} + u_{\mathrm{Cl}^-}}\left[\frac{-RT}{1-x}\right] + \frac{xu_{\mathrm{K}^+}}{(1-x)u_{\mathrm{H}^+} + xu_{\mathrm{K}^+} + u_{\mathrm{Cl}^-}}\left[\frac{RT}{x}\right]\\ &= RT\frac{(u_{\mathrm{K}^+} - u_{\mathrm{H}^+})}{(u_{\mathrm{H}^+} + u_{\mathrm{Cl}^-}) + x(u_{\mathrm{K}^+} - u_{\mathrm{H}^+})} \qquad (9\text{-}3\text{-}11)\end{aligned}$$

The net free-energy change taking place as a result of migration of the ions throughout the entire boundary is to be obtained by integrating the expression (9-3-11) from $x = 0$ to $x = 1$,

$$\begin{aligned}\Delta F &= \int_0^1 RT\frac{(u_{\mathrm{K}^+} - u_{\mathrm{H}^+})}{(u_{\mathrm{H}^+} + u_{\mathrm{Cl}^-}) + x(u_{\mathrm{K}^+} - u_{\mathrm{H}^+})}\,dx\\ &= RT\ln\frac{(u_{\mathrm{K}^+} + u_{\mathrm{Cl}^-})}{(u_{\mathrm{H}^+} + u_{\mathrm{Cl}^-})} \qquad (9\text{-}3\text{-}12)\end{aligned}$$

Now, the ratio of the sums, $(u_{\mathrm{K}^+} + u_{\mathrm{Cl}^-})$ and $(u_{\mathrm{H}^+} + u_{\mathrm{Cl}^-})$, represents simply the ratio of the equivalent conductivities, Λ_{KCl} and Λ_{HCl}, of the two electrolytes at the given concentration. Thus

$$\Delta F = RT\ln\frac{\Lambda_{\mathrm{KCl}}}{\Lambda_{\mathrm{HCl}}} \qquad (9\text{-}3\text{-}13)$$

This represents the net free-energy change taking place when 1 faraday of electricity passes through the cell, the left-hand electrode in (9-3-8) being regarded as the anode. The cell emf therefore results from the difference in the equivalent conductivities of the two electrolytes having the common ion, Cl^-, according to the equation

$$E = -\frac{RT}{1 \text{ g-eq}} \ln \frac{\Lambda_{KCl}}{\Lambda_{HCl}} \tag{9-3-14}$$

At 25°C and $0.1M$ concentration, the equivalent conductivities of KCl and HCl are, respectively,[1]

$$\Lambda_{KCl} = 128.96 \text{ ohm}^{-1}\text{cm}^2/\text{g-eq} \quad \text{and} \quad \Lambda_{HCl} = 391.32 \text{ ohm}^{-1}\text{cm}^2/\text{g-eq}$$

Therefore the value of E for the cell (9-3-8) according to Eq. (9-3-14) should be 0.02852 volt. This value is in reasonably good agreement with the observed value of 0.02678 volt, considering the simplifying assumptions made in the derivation. In Henderson's original treatment, he used the limiting equivalent conductivities at infinite dilution; the form (9-3-14) was proposed by Lewis and Sargent.[2] Equation (9-3-14), and the more general Henderson equation for electrolytes consisting of different pairs of ions at different concentrations on the two sides of the boundary, have been used in making approximate corrections for liquid-junction effects, for the purpose of drawing thermodynamic information from the study of galvanic cells with liquid junctions. The important thing to note is that the emf of a galvanic cell is a property of the actual chemical or physical change taking place in the cell, and unless we know precisely what the change is, the thermodynamic interpretation of the emf is quite uncertain; we are seldom in a position to define precisely what goes on at the interface between two different electrolytes at different concentrations when an electric current is flowing across the boundary, and to that extent, the interpretation of and correction for liquid-junction processes are uncertain.

In Jacques Loeb's famous controversial measurements of "membrane potentials," in which he obtained a potential difference between two identical $Hg(l)$, $Hg_2Cl_2(c)$,$KCl(aq, satd)$ electrodes immersed on either side of a Donnan system at equilibrium (Sec. 7-7), he was surely measuring a difference between the two liquid-junction potentials, where the saturated KCl of either electrode made contact with the respective "inside" or "outside" solution of the Donnan system. When $Ag(c)$,$AgCl(c)$ electrodes were introduced directly on either side, so that no liquid-liquid junctions were present except through the membrane itself (Cl^- being one of the ions unequally distributed as a consequence of the Donnan effect), no difference of potential could be detected, as one would expect for a system in a state of equilibrium, even though the equilibrium conditions in this case call for a difference between the concentrations of the diffusing electrolyte on either side. Equilibrium is not necessarily maintained, however, when a

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[1] D. A. MacInnes, "The Principles of Electrochemistry," p. 339, from measurements by T. Shedlovsky, A. S. Brown and D. A. MacInnes.

[2] G. N. Lewis and L. W. Sargent, *J. Am. Chem. Soc.*, **31**, 363–367 (1909).

saturated KCl salt bridge is introduced on either side, because there is then no barrier to prevent the giant ion that cannot pass through the membrane from migrating into the KCl solution on that side, while no comparable transference effect is present across the other liquid junction "outside" the membrane; this would remain true even if the thermodynamic potential of KCl were the same on either side of the membrane, so that there would be no difference between the diffusion tendencies of the KCl itself across the liquid junctions on either side. The physical interpretation of Loeb's "membrane potentials" is therefore probably much more complex than he realized. An interesting discussion of this problem is given by D. I. Hitchcock in R. Höber's "Physical Chemistry of Cells and Tissues," pp. 68*ff*., The Blakiston Company, Philadelphia, 1945.

c. Cells with Reference Electrode and Salt Bridge. Certain important applications of emf methods cannot be conveniently set up in galvanic cells without liquid junctions. This is the situation in the potentiometric measurement of pH, and in potentiometric titrations in general. It is common practice in such cases to use a standard reference electrode, coupled by means of a salt bridge to the "unknown" half of the cell where there is set up the electrode reaction in which we are interested.

Example:

$$(\mathrm{Pt}), \mathrm{H_2(g)}|\mathrm{H^+}(\mathrm{aq}, m)||\mathrm{KCl}(\mathrm{aq, satd})||\mathrm{KCl}(\mathrm{aq}, C)|\mathrm{Hg_2Cl_2(c)}, \mathrm{Hg(l)} \qquad (9\text{-}3\text{-}15)$$

This familiar cell is used in the measurement of pH. There will of course be some anion, and possibly other nonreacting cations, accompanying H^+ in the left-hand compartment. The main cell reaction, if we neglect for the moment the liquid-junction processes, may be expressed as follows:

$$\tfrac{1}{2}\mathrm{H_2(g)} + \tfrac{1}{2}\mathrm{Hg_2Cl_2(c)} = \mathrm{H^+}(\mathrm{aq}, m) + \mathrm{Cl^-}(\mathrm{aq}, C) + \mathrm{Hg(l)} \qquad (9\text{-}3\text{-}16)$$

from whose free-energy change we may infer an emf of the form

$$E = E^\circ - \frac{RT}{1\text{ g-eq}} \ln m_{\mathrm{H^+}}\gamma_{\mathrm{H^+}} - \frac{RT}{1\text{ g-eq}} \ln C\gamma_{\mathrm{Cl^-}} + \frac{RT}{1\text{ g-eq}} \ln (p_{\mathrm{H_2}})^{1/2} \qquad (9\text{-}3\text{-}17)$$

If it were not for liquid-junction effects, the value of E° in Eq. (9-3-17) would be the same as for the superficially similar cell without liquid junction

$$(\mathrm{Pt}), \mathrm{H_2(g)}|\mathrm{HCl}(\mathrm{aq}, m)|\mathrm{Hg_2Cl_2(c)}, \mathrm{Hg(l)}; \qquad E^\circ_{298} = 0.2680\text{ volt} \qquad (9\text{-}3\text{-}18)$$

The cell (9-3-18) is analogous to the cell (9-2-35), and its emf is given by Eq. (9-2-37), with the appropriate value of E° inserted [Eq. (9-2-51)]. The cell (9-3-15) thus differs materially from the cell (9-3-18) in several important respects; in the cell (9-3-15), Cl^- appears at the cathode always at the fixed concentration C, regardless of the composition of the electrolyte in the left-hand compartment, and independently of the anion present accompanying H^+, whereas in the cell (9-3-18), H^+ and Cl^- are formed simultaneously in the electrolyte at the same concentration, as the cell is discharged. For this reason, the emf of the cell (9-3-18) varies as $(2RT/1\text{ g-eq}) \ln m\gamma_\pm$, whereas the emf of the cell (9-3-15), if it happened to contain only HCl(aq) in the left-hand compartment, would vary only as $(RT/1\text{ g-eq}) \ln m\gamma_\pm$. There are, furthermore, changes taking place at the liquid junctions of the cell (9-3-15), which are not taken into account by the chemical equation (9-3-16) and the associated electrochemical equation (9-3-17).

There are three KCl concentrations commonly used for the setting up of calomel reference electrodes: tenth-normal ($C = 0.1$ mole/liter), normal ($C = 1$ mole/liter), and saturated ($m = 4.81$ mole/kg at 25°C). If we combine the first and third terms on the right of Eq. (9-3-17) into a single constant $E^{\circ\prime}$ characteristic of the particular KCl concentration employed in the reference electrode, then, still with neglect of liquid-junction effects,

$$E = E^{\circ\prime} + \frac{RT}{1\text{ g-eq}} \ln (p_{H_2})^{1/2} - \frac{RT}{1\text{ g-eq}} \ln m_{H^+}\gamma_{H^+} \qquad (9\text{-}3\text{-}19)$$

where the term $E^{\circ\prime}$ may be determined from the value of E° given by (9-3-18), and the following data for KCl solutions, assuming that we may equate γ_{Cl^-} to $\gamma_\pm$:

Calomel electrode	m_{KCl}	$\gamma_\pm$	$\frac{RT}{1\text{ g-eq}} \ln m\gamma_\pm$, volts	$E^{\circ\prime}$ at 25°C, volts
$N/10$..............	0.1006	0.770	−0.0657	0.3337
N.................	1.0327	0.607	−0.0120	0.2800
Saturated..........	4.81	0.590	+0.0268	0.2412

Equation (9-3-19) is presumably correct, with the appropriate value of $E^{\circ\prime}$, provided that we correct E separately for the liquid-junction potentials, according to the extended theory that we touched upon in Sec. 9-3*b*. As has been indicated, the correction is none too reliable, particularly when we are dealing with a complex electrolyte. Therefore a somewhat different procedure is generally employed, first proposed by S. P. L. Sørensen in 1909. Let us assume that within reasonable limits, the liquid-junction potentials of the cell (9-3-15) are independent of the exact composition of the electrolyte present in the left-hand compartment, so that they may be regarded as a property of the calomel electrode. This assumption appears to be fairly well supported by experiment. Then we may write Eq. (9-3-19) in the form

$$E = E^{\circ\prime\prime} + \frac{RT}{1 \text{ g-eq}} \ln (p_{H_2})^{1/2} - \frac{RT}{1 \text{ g-eq}} \ln m_{H^+}\gamma_{H^+} \qquad (9\text{-}3\text{-}20)$$

where the value of $E^{\circ\prime\prime}$ is determined empirically by observations with solutions of strong simple acids, such as HCl, HNO_3, $HClO_4$, etc., for which $\gamma_{\pm}$ has been determined independently, assuming that we may in such cases replace the expression $m_{H^+}\gamma_{H^+}$ by $m\gamma_{\pm}$, where m is the stoichiometric concentration. In this way, the following practical values of $E^{\circ\prime\prime}_{298}$ have been established:

Calomel Electrode	$E^{\circ\prime\prime}$ at 25°C, Volts
$N/10$	0.3378
N	0.2847
Saturated	0.2458

Thus, assuming that E has been corrected to $p_{H_2} = 1$ atm by means of Eq. (9-3-20), we may then write

$$E = E^{\circ\prime\prime} + 0.05916 \text{ pH} \quad (t = 25°\text{C}) \qquad (9\text{-}3\text{-}21)$$

where, by definition,

$$\text{pH} \equiv -\log m_{H^+}\gamma_{H^+} \qquad (9\text{-}3\text{-}22)$$

Equation (9-3-21) thus defines pH directly in terms of experimental operations, whatever its precise physical significance may be, with the understanding that no further attention is to be paid to liquid-junction effects. For such purposes as potentiometric titrations, where only the inflection point of E against the quantity of standard reagent added is required, this definition is of course entirely adequate.

We have expressed Eqs. (9-3-19) to (9-3-22) formally in terms of a hypothetical H^+-ion activity coefficient, which, as we have observed in Sec. 7-4, cannot be independently established except in relation to some particular anion. As a matter of fact, the relationship between pH, defined by the experimental operation (9-3-21), and the H^+-ion *concentration*, represented formally by Eq. (9-3-22), is not uniquely defined; *i.e.*, if one substitutes a mean ionic activity coefficient (which is the only kind of ionic activity coefficient one can actually measure independently by thermodynamic means) in place of the hypothetical factor γ_{H^+}, and measures m_{H^+} by some other independent chemical or physical method (*e.g.*, indicator equilibrium, acid or base catalysis, electrical conductivity, etc.), then the pH computed according to the assumed relationship (9-3-22) does not invariably agree precisely with the experimental value found by emf measurements according to (9-3-21), without regard to the anion or other presumably inert constituents of the solution. In other words, the thermodynamic basis of Sørensen's original procedure for evaluating the standard potentials of the calomel reference electrodes is not entirely sound, particularly for buffer mixtures which may contain high ionic strengths. For ordinary purposes, the discrepancies, which are of order 0.03 pH unit (2 mv), are not serious, but they become troublesome in work of high precision, particularly when one wishes to evaluate potentiometric pH data precisely for application to other types of investigation.

The source of the difficulty rests of course in the method used to dispose of the liquid-junction potentials, which are not completely independent of the electrolyte whose pH is being measured. A method of standardizing the pH scale so that the pH agrees closely with the quantity $m_{\mathrm{H}^+}\gamma_\pm$ has been proposed by E. J. Cohn, F. F. Heyroth, and M. F. Menkin;[1] the reference electrode is standardized by pH measurements on buffer solutions, instead of on strong acids, the buffers consisting of weak acids and their salts, for which the thermodynamic ionization constants have been precisely established by means of cells without liquid junctions.[2] Thus, for the weak acid HA,

$$\mathrm{HA} = \mathrm{H}^+ + \mathrm{Ac}^-$$

$$K_m^\circ = \frac{m_{\mathrm{H}^+} m_{\mathrm{A}^-}}{m_{\mathrm{HA}}} \frac{(\gamma_\pm)^2}{\gamma'_{\mathrm{HA}}}$$

[compare Eq. (8-1-36)]; therefore the quantity $m_{\mathrm{H}^+}\gamma_\pm$ may be computed from the buffer composition in the form

$$m_{\mathrm{H}^+}\gamma_\pm = K_m^\circ \frac{m_{\mathrm{HA}}}{m_{\mathrm{A}^-}} \frac{\gamma'_{\mathrm{HA}}}{\gamma_\pm} \qquad (9\text{-}3\text{-}22a)$$

The value of γ'_{HA} may be assumed to be practically equal to 1 in dilute solution, and the value of $\gamma_\pm$ in the term on the right may be estimated by a Debye-Hückel approximation. The value of $E^{\circ\prime\prime}$ in Eq. (9-3-21) has then been adjusted until the pH given by that equation agrees with $-\log m_{\mathrm{H}^+}\gamma_\pm$, as computed by Eq. (9-3-22*a*). In this way, MacInnes has derived a value of $E^{\circ\prime\prime} = 0.3358$ volt, instead of Sørensen's value of 0.3378 volt, for pH determinations with the hydrogen electrode against the $N/10$ calomel electrode at 25°C.

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[1] E. J. Cohn, F. F. Heyroth, and M. F. Menkin, *J. Am. Chem. Soc.*, **50**, 696–714 (1928); see also D. A. MacInnes, "The Principles of Electrochemistry," pp. 271–275.

[2] Such data have been obtained in the case of acetic acid, for example, by H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **54**, 1350–1357 (1932); **55**, 652–656 (1933), using the cell

$$(\mathrm{Pt}), \mathrm{H_2(g)}|\mathrm{HAc}(\mathrm{aq}, m), \mathrm{NaAc}(\mathrm{aq}, m), \mathrm{NaCl}(\mathrm{aq}, m)|\mathrm{AgCl(c)}, \mathrm{Ag(c)}$$

the concentrations of all three solutes being kept equal, and the data being extrapolated to $m = 0$ (see Prob. 9-14).

Example:

$$\text{(Au), Q·QH}_2\text{(c)}|\text{H}^+\text{(aq, }m)||\text{KCl(aq, satd)}||\text{KCl(aq, }C)|\text{Hg}_2\text{Cl}_2\text{(c), Hg(l)} \qquad (9\text{-}3\text{-}23)$$

The quinhydrone electrode is often used in combination with the calomel reference electrode for pH determinations; in a buffer solution at fixed pH, it may itself serve as a convenient reference electrode. Quinhydrone is a compound of quinone and hydroquinone in equimolal proportions. In an aqueous solution saturated with quinhydrone,

$$\text{Q·QH}_2\text{(c)} = \text{Q(aq)} + \text{QH}_2\text{(aq)}$$

$$\Delta F^\circ = \phi'_{\text{Q(aq)}} + \phi'_{\text{QH}_2\text{(aq)}} - \bar{F}^\circ_{\text{Q·QH}_2\text{(c)}} = -RT \ln a'_{\text{Q}} a'_{\text{QH}_2}$$

therefore

$$a'_{\text{Q}} a'_{\text{QH}_2} = (m_{\text{Q}}\gamma'_{\text{Q}})(m_{\text{QH}_2}\gamma'_{\text{QH}_2}) = K^\circ_m \qquad (9\text{-}3\text{-}24)$$

In dilute solutions, where each activity coefficient approaches 1, since $m_{\text{Q}} = m_{\text{QH}_2}$, therefore m_{Q} and m_{QH_2} are each separately constant. The oxidation potential

$$\text{QH}_2\text{(aq)} = \text{Q(aq)} + 2\text{H}^+\text{(aq)} + 2e; \qquad E^\circ_{298} = -0.6994 \text{ volt}$$

has been measured precisely by F. Hovorka and W. C. Dearing.[1]

The reaction taking place in the cell (9-3-23) for $j = 2\mathfrak{F}$, with neglect of liquid-junction potentials [which are the same as for the cell (9-3-15)], is $\text{QH}_2\text{(aq)} + \text{Hg}_2\text{Cl}_2\text{(c)} = 2\text{H}^+(\text{aq}, m) + \text{Q(aq)} + 2\text{Cl}^-(\text{aq}, C) + 2\text{Hg(l)}$ corresponding to the emf equation

$$E = E^\circ - \frac{RT}{2 \text{ g-eq}} \ln (C\gamma_{\text{Cl}^-})^2 - \frac{RT}{2 \text{ g-eq}} \ln \frac{a'_{\text{Q}}}{a'_{\text{QH}_2}} - \frac{RT}{2 \text{ g-eq}} \ln (m_{\text{H}^+}\gamma_{\text{H}^+})^2 \qquad (9\text{-}3\text{-}25)$$

Combining the first three constant terms on the right (for given C),

$$E = E^{\circ\prime} - \frac{RT}{1 \text{ g-eq}} \ln m_{\text{H}^+}\gamma_{\text{H}^+} \qquad (9\text{-}3\text{-}26)$$

where if liquid-junction effects could be ignored, $E^{\circ\prime}$ for the $N/10$ calomel electrode would have the following value: $-0.6994 + 0.3337 = -0.3657$ volt at 25°C. Using the same treatment as in the case of the hydrogen electrode, however, we may write

$$E = E^{\circ\prime\prime} + 0.05916 \text{ pH} \qquad (9\text{-}3\text{-}27)$$

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[1] F. Hovorka and W. C. Dearing, *J. Am. Chem. Soc.*, **57**, 446–453 (1935). For discussion of the mechanism of hydroquinone oxidations, see L. Michaelis, *Chem. Revs.*, **16**, 243–286 (1935).

where MacInnes has shown that $E^{\circ\prime\prime}_{298} = -0.3636$ volt, using buffer mixtures to define the pH scale.[1]

At high electrolyte concentrations, there is a slight "salt" effect on the value of $E^{\circ\prime\prime}$, which results from deviation of the ratio a'_{Q}/a'_{QH_2} in the third term on the right of Eq. (9-3-25) from 1; thus, in $1M$ HCl, the error in Eq. (9-3-27) amounts to 0.06 pH unit. The reason for the effect is evident in the solubility equilibrium relationship (9-3-24); at high solute concentrations, the values of γ'_{Q} and γ'_{QH_2} may deviate from 1 to different extents, so that while m_{Q} and m_{QH_2} necessarily remain equal to each other a'_{Q} and a'_{QH_2} may differ. The salt effect disappears if one saturates the solution with either quinone or hydroquinone, in addition to quinhydrone, the standard electrode potential shifting by about 0.07 volt in either direction; a'_{Q} and a'_{QH_2} are then no longer equal to each other, but fixing one by saturating the solution with the respective compound serves through the relationship (9-3-24) to fix the other. One may also eliminate the salt effect by using a quinone-hydroquinone couple that does not form a "quinhydrone" and then saturating the solution with both components. J. B. Conant and L. F. Fieser have shown, for example, that the quinone chloranil (2,3,5,6-tetrachloroquinone) and tetrachlorohydroquinone constitute such a couple; this couple is not practical for work in aqueous solutions, because of the low solubilities of the components and the slow rate of attainment of solubility equilibrium, but it has been used by N. F. Hall and J. B. Conant for pH measurements in the medium, glacial acetic acid.[2]

Example:

$$(\mathrm{Pt})|\mathrm{Fe}^{++}(\mathrm{aq},\, m_{\mathrm{Fe}^{++}}),\mathrm{Fe}^{+++}(\mathrm{aq},\, m_{\mathrm{Fe}^{+++}})||\mathrm{KCl}(\mathrm{aq, satd})||\mathrm{KCl}(\mathrm{aq},\, 0.1M)|\ \mathrm{Hg_2Cl_2(c)},\ \mathrm{Hg(l)} \qquad (9\text{-}3\text{-}28)$$

A cell of this general type is used in potentiometric oxidation-reduction titrations, and may be used also for the approximate measurement of oxidation potentials. The cell reaction for $j = 1\mathfrak{F}$ is

$$\mathrm{Fe}^{++}(\mathrm{aq},\, m_{\mathrm{Fe}^{++}}) + \tfrac{1}{2}\mathrm{Hg_2Cl_2(c)} = \mathrm{Fe}^{+++}(\mathrm{aq},\, m_{\mathrm{Fe}^{+++}}) + \mathrm{Cl}^{-}(0.1M\ \mathrm{KCl}) + \mathrm{Hg(l)} \qquad (9\text{-}3\text{-}29)$$

from which we may infer a reversible emf of the form

$$E = E^{\circ} - \frac{RT}{1\text{ g-eq}} \ln (0.1\gamma_{\mathrm{Cl}^-}) - \frac{RT}{1\text{ g-eq}} \ln \frac{m_{\mathrm{Fe}^{+++}}\gamma_{\mathrm{Fe}^{+++}}}{m_{\mathrm{Fe}^{++}}\gamma_{\mathrm{Fe}^{++}}} \qquad (9\text{-}3\text{-}30)$$

or combining the first two terms on the right and assuming a constant liquid-junction effect by using Sørensen's value for the electrode potential

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[1] D. A. MacInnes, "The Principles of Electrochemistry," p. 274.

[2] J. B. Conant and L. F. Fieser, *J. Am. Chem. Soc.*, **45**, 2194–2218 (1923); N. F. Hall and J. B. Conant, *ibid.*, **49**, 3047–3061 (1927).

of the $N/10$ calomel electrode,

$$E = E^{\circ\prime} - \frac{RT}{1\text{ g-eq}} \ln \frac{m_{\text{Fe}^{+++}}\gamma_{\text{Fe}^{+++}}}{m_{\text{Fe}^{++}}\gamma_{\text{Fe}^{++}}} \tag{9-3-31}$$

Thus, from the standard electrode potential,

$$\text{Fe}^{++}(\text{aq}) = \text{Fe}^{+++}(\text{aq}) + e; \qquad E^\circ = -0.783 \text{ volt} \tag{9-3-32}$$

combined with

$$\text{Hg(l)} + \text{Cl}^-(0.1M \text{ KCl}) = \tfrac{1}{2}\text{Hg}_2\text{Cl}_2(\text{c}) + e; \qquad E^{\circ\prime} = -0.3378 \text{ volt}$$

we obtain

$$E = -0.445 - 0.0592 \log \frac{m_{\text{Fe}^{+++}}\gamma_{\text{Fe}^{+++}}}{m_{\text{Fe}^{++}}\gamma_{\text{Fe}^{++}}} \qquad (t = 25°\text{C}) \tag{9-3-33}$$

The cell emf thus serves to measure the ratio of the Fe^{+++} to the Fe^{++} activity.

This property is utilized in potentiometric titration of Fe^{++}. Thus, suppose that we begin with a Fe^{++} solution in the left-hand compartment of the cell and add standardized $\text{Ce(SO}_4)_2$. Before any Ce^{++++} has been added, the emf will assume some unpredictable value, depending both on the total ionic strength, which determines the values of the activity coefficients, but also on the Fe^{+++} concentration that is always present, even though at low concentration, in any solution containing Fe^{++}. Let us assume that initially, $m_{\text{Fe}^{+++}} < 0.001\, m_{\text{Fe}^{++}}$, a condition that would be required if one is to determine iron analytically within a precision of 0.1 per cent by this method; then: $E > -0.267$ volt, in the algebraic sense, not including the effect of the activity coefficient ratio. As one adds Ce^{++++}, which oxidizes Fe^{++} in accordance with the chemical equation

$$\text{Ce}^{++++} + \text{Fe}^{++} = \text{Ce}^{+++} + \text{Fe}^{+++} \tag{9-3-34}$$

the changing proportion of Fe^{+++} to Fe^{++} is reflected by a change in E, in accordance with Eq. (9-3-33); in other words, E becomes increasingly negative.

At the same time, addition of Ce^{++++}, and production of Ce^{+++}, results in the possibility of the cell reaction

$$\begin{aligned}\text{Ce}^{+++}(\text{aq}, m_{\text{Ce}^{+++}}) + \tfrac{1}{2}\text{Hg}_2\text{Cl}_2(\text{c}) = {}& \text{Ce}^{++++}(\text{aq}, m_{\text{Ce}^{++++}}) \\ & + \text{Cl}^-(0.1M \text{ KCl}) + \text{Hg(l)}\end{aligned} \tag{9-3-35}$$

whose emf, in view of the standard oxidation potential,

$$\text{Ce}^{+++}(\text{aq}) = \text{Ce}^{++++}(\text{aq}) + e; \qquad E^\circ = -1.609 \text{ volts} \tag{9-3-36}$$

may be shown to have the form

$$E = -1.271 - 0.0592 \log \frac{m_{\mathrm{Ce}^{++++}}\gamma_{\mathrm{Ce}^{++++}}}{m_{\mathrm{Ce}^{+++}}\gamma_{\mathrm{Ce}^{+++}}} \qquad (9\text{-}3\text{-}37)$$

Of course, the value of E given by Eq. (9-3-37) is identical at all stages of the titration with the value of E given by Eq. (9-3-33), since the reaction, Eq. (9-3-34), taking place in the left-hand compartment of the cell comes rapidly to a state of equilibrium. We may readily infer the equilibrium conditions from the two standard electrode potentials, (9-3-32) and (9-3-36); thus

$$\mathrm{Ce}^{++++}(\mathrm{aq}) + \mathrm{Fe}^{++}(\mathrm{aq}) = \mathrm{Ce}^{+++}(\mathrm{aq}) + \mathrm{Fe}^{+++}(\mathrm{aq}); \qquad E^\circ = 0.826 \text{ volt}$$

$$E^\circ = -\frac{1}{j}\Delta F^\circ = \frac{RT}{j}\ln K^\circ_m$$

$$\log K^\circ_m = \frac{0.826 \text{ volt}}{0.0592 \text{ volt}} = 13.95$$

Thus

$$K^\circ_m = \frac{m_{\mathrm{Ce}^{+++}}m_{\mathrm{Fe}^{+++}}}{m_{\mathrm{Ce}^{++++}}m_{\mathrm{Fe}^{++}}}\,\frac{\gamma_{\mathrm{Ce}^{+++}}\gamma_{\mathrm{Fe}^{+++}}}{\gamma_{\mathrm{Ce}^{++++}}\gamma_{\mathrm{Fe}^{++}}} = 8.9 \times 10^{13} \qquad (9\text{-}3\text{-}38)$$

When precisely the equivalent quantity of Ce^{++++} has been added to correspond to the quantity of Fe^{++} originally present, let x represent the fraction of the iron still remaining in the Fe^{++} state; then x will represent also the fraction at that point of cerium remaining in the Ce^{++++} state. Thus approximately, with neglect of the activity coefficient terms,

$$\frac{(1-x)^2}{x^2} = 8.9 \times 10^{13}$$

$$x = 1 \times 10^{-7}$$

With either $m_{\mathrm{Fe}^{+++}}/m_{\mathrm{Fe}^{++}} \sim 10^7$ in (9-3-33), or $m_{\mathrm{Ce}^{++++}}/m_{\mathrm{Ce}^{+++}} \sim 10^{-7}$ in (9-3-37), we may infer an approximate value of $E = -0.859$ volt at the stoichiometric end point. The possibility of gauging the end point precisely depends on the sharpness with which E changes near the end point; thus, when all but 0.1 per cent of the stoichiometric quantity of $\mathrm{Ce(SO_4)_2}$ has been added, so that, approximately, $m_{\mathrm{Fe}^{+++}}/m_{\mathrm{Fe}^{++}} \sim 10^3$, the emf of the cell according to Eq. (9-3-33) has the approximate value -0.623 volt, whereas when one has added an excess of 0.1 per cent, so that $m_{\mathrm{Ce}^{++++}}/m_{\mathrm{Ce}^{+++}}$ jumps from 10^{-7} at the end point to 10^{-3}, then, according to Eq. (9-3-37), E assumes the approximate value -1.093 volts. The sharpness of the change depends on the magnitude of K°_m, that is, on the difference between the two standard electrode potentials, (9-3-32) and (9-3-36).

9-4. Theoretical Calculation of Electrode Potentials. Since the emf of a reversible galvanic cell represents the free-energy change of the cell reaction, it may be computed entirely from thermal data by means of the third law of thermodynamics, in accordance with the general principles outlined in Sec. 8-3. For the purpose of computing standard electrode potentials, the standard ionic entropies based on the convention (8-3-7), as developed by W. M. Latimer and his associates, are particularly valuable.[1] Thus, we may compute the standard potential of the Na(c), Na^+(aq) electrode from the following information. The third-law standard entropy of Na(c) at 25°C is 12.2 ± 0.1 eu/mole,[2] while that of Na^+(aq) is 14.0 ± 0.4 eu/mole; the latter result was computed from third-law entropies for NaCl(c) and $NaNO_3$(c), combined with their total heats and standard free energies of solution (solubilities and mean ionic activity coefficients in the saturated solutions), together of course with the ionic entropies of the corresponding anions, referred ultimately to the convention (8-3-7).[3] Using for H_2(g) the standard entropy, $\bar{S}^\circ_{298} = 31.23 \pm 0.01$ eu/mole, based on molecular spectroscopic data in relation to the third-law convention (Chap. 10),[4] we obtain as the standard entropy of the reaction

$$\mathrm{Na(c)} + \mathrm{H^+(aq)} = \mathrm{Na^+(aq)} + \tfrac{1}{2}\mathrm{H_2(g)}; \qquad \Delta S^\circ_{298} = 17.4 \text{ eu}$$

The calorimetrically determined standard enthalpy of this reaction has the value $\Delta H^\circ_{298} = -57{,}479$ cal; therefore

$$\begin{aligned}\Delta F^\circ_{298} &= \Delta H^\circ_{298} - T\,\Delta S^\circ_{298} \\ &= -57{,}479 \text{ cal} - (298.16)(17.4) \text{ cal} \\ &= -62{,}670 \text{ cal}\end{aligned}$$

In view of the convention (9-2-49), this quantity measures the standard electrode potential

$$\mathrm{Na(c)} = \mathrm{Na^+(aq)} + e; \qquad E^\circ_{298} = \frac{62{,}670 \text{ cal}}{1 \text{ g-eq}} = 2.718 \text{ volts}$$

in excellent agreement with the experimental value[5]

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[1] See Latimer, *op. cit.*

[2] K. K. Kelley, *U.S. Bur. Mines Bull.* 434 (1941), from data by F. Simon and W. Zeidler, *Z. physik. Chem.*, **123**, 383–404 (1926).

[3] W. M. Latimer, K. S. Pitzer, and W. V. Smith, *J. Am. Chem. Soc.*, **60**, 1829–1831 (1938).

[4] W. F. Giauque, *ibid.*, **52**, 4816–4831 (1930).

[5] The potentials of the alkali metal electrodes, which of course cannot be studied directly in aqueous solutions, were first measured by an ingenious method devised by G. N. Lewis. A sufficiently dilute sodium amalgam reacts slowly enough with water so that its potential in a solution containing Na^+ ions can be determined by ordinary

$$\mathrm{Na(c)} = \mathrm{Na^+(aq)} + e; \qquad E^\circ_{298} = 2.712 \text{ volts} \tag{9-4-1}$$

Such agreement constitutes experimental confirmation of the third law, as well as of the various assumptions underlying the concept of the independent behavior of the ions in ideal dilute solutions of electrolytes. It casts no new light, however, on the fundamental question of why the standard potential of the sodium electrode is so much higher than that, say, of the silver electrode in aqueous solution

$$\mathrm{Ag(c)} = \mathrm{Ag^+(aq)} + e; \qquad E^\circ_{298} = -0.800 \text{ volt} \tag{9-4-2}$$

The difference, 3.512 volts, measures of course the difference between the chemical "reactivities" of Na(c) and Ag(c) as reducing agents in aqueous solutions, in the sense that reactions in which Na(c) is a reactant have equilibrium points displaced correspondingly farther to the right than similar reactions in which Ag(c) is a reactant in place of Na(c). A table of standard electrode potentials, such as are represented by (9-4-1) and (9-4-2), is equivalent to a table of standard free energies of the corresponding electrode reactions, and this in turn is equivalent to a table of standard free energies and thermodynamic equilibrium constants of all conceivable oxidation-reduction reactions satisfying the requirement of conservation of electric charge that can be described by suitable combinations of the data included in the table, the quantitative relationship having the form

$$E^\circ = -\frac{\Delta F^\circ}{\mathfrak{J}} = \frac{RT}{\mathfrak{J}} \ln K^\circ_m \tag{9-4-3}$$

Provided that the experimental data have been obtained according to correct thermodynamic principles (*e.g.*, reversible galvanic cells, third-law data verified by independent thermodynamic measurements, etc.), Eq. (9-4-3) is entirely general, and is quite independent of the mechanism by which the electrical energy of the corresponding galvanic cell may be

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means, for example, from the standard emf of the reversible cell without liquid junctions

$$\mathrm{Na(Hg)|NaCl}(m_2 \text{ in } \mathrm{H_2O})|\mathrm{Hg_2Cl_2(c), Hg(l)}$$

The potential of the same amalgam against pure Na(c) may then be measured in a nonaqueous solution of a sodium salt, such as NaI in liquid ethyl amine, which does not react with the alkali metals,

$$\mathrm{Na(c)|NaI}(m_2 \text{ in } \mathrm{C_2H_5NH_2})|\mathrm{Na(Hg)}$$

By combining the data for the two cells, one may determine the standard potential of the Na(c), Na$^+$(aq) electrode. See G. N. Lewis and C. A. Kraus, *J. Am. Chem. Soc.*, **32**, 1459–1468 (1910); G. N. Lewis and F. G. Keyes, *ibid.*, **34**, 119–122 (1912); see also Prob. 9-6.

produced. The very generality of thermodynamic investigation, however, precludes the possibility of discovering by purely thermodynamic means why sodium is so much more powerful a reducing agent than silver, though it does provide a quantitative measure of their difference in reactivity, as well as a correlation with other thermodynamic properties. Nevertheless the question is well worth investigation for the insight it may give into the relative importance of the various factors originating in peculiarities of atomic or molecular structure that may influence thermodynamic behavior.

Now, it is well known that the alkali metals tend to lose electrons relatively easily, as compared with other metals, through various physical processes such as photoemission (as in the cesium phototube) and thermally or electrically induced ionization in the gaseous state. It is therefore natural for us to attempt to correlate this fact, which is consistent with the peculiar electronic structures of their atoms, with their extraordinary chemical reactivity. It is, furthermore, a fact that when two different metals whose surfaces are perfectly clean are brought in contact in a vacuum, electrons flow from one into the other until a definite difference of potential is established between them, a difference which is additive and transitive for a series of metals and which follows approximately, though not in exact detail, the familiar electromotive series. Table 9-4 presents observed contact potentials for various metals against platinum, as determined by O. W. Richardson and K. T. Compton,[1] together for comparison with the corresponding standard electrode potentials of the

TABLE 9-4. CONTACT POTENTIALS AND STANDARD ELECTRODE POTENTIALS

Metal	Contact potential* vs. Pt (metal positive with respect to Pt), volts	Standard electrode potential† in aqueous solution at 25°C, volts
Na	2.40	2.71 [$Na(c) = Na^+(aq) + e$]
Al	1.20	1.67 [$Al(c) = Al^{+++}(aq) + 3e$]
Mg	1.05	2.34 [$Mg(c) = Mg^{++}(aq) + 2e$]
Zn	0.90	0.76 [$Zn(c) = Zn^{++}(aq) + 2e$]
Sn	0.62	0.14 [$Sn(c) = Sn^{++}(aq) + 2e$]
Bi	0.35	−0.32 [$Bi(c) + H_2O(l) = BiO^+(aq) + 2H^+(aq) + 3e$]
Cu	0.13	−0.34 [$Cu(c) = Cu^{++}(aq) + 2e$]

* Values for contact potentials from O. W. Richardson and K. T. Compton, *Phil. Mag.*, (6) **24**, 575–594 (1912).

† Values for standard electrode potentials from W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, 1938.

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[1] O. W. Richardson and K. T. Compton, *Phil. Mag.*, (6) **24**, 575–594 (1912).

metals against their ions in aqueous solutions relative to the standard hydrogen electrode. It is surely significant that electrons tend to flow spontaneously, for example, from metallic zinc into metallic copper, and if we had further data on the relationships between Zn(c) and Zn^{++}(aq), and between Cu(c) and Cu^{++}(aq), we should be able to correlate the contact potential between Zn(c) and Cu(c) with the tendency for Zn(c) to reduce Cu^{++}(aq) in aqueous solution, the effect of the electrolyte concentration being governed by the general way in which the thermodynamic potentials of Cu^{++} and Zn^{++} in aqueous solution depend on the concentration.

Data for attempting a partial approximate solution to this kind of problem exist in the case of the halides of the univalent metals. The problem centers around the ionization potential of the metal, a physical property whose value may be derived from the spectrum, or may be measured directly by means of resonance potential measurements based on the electrical conductivity of the vapor.[1] Thus, for sodium,

$$\mathrm{Na(g)} = \mathrm{Na^+(g)} + e; \qquad I = 5.138 \text{ volts} = 118.5 \text{ kcal} \qquad (9\text{-}4\text{-}4)$$

This is a well-established property, determined in principle entirely by the structure of the atom. Ionization potentials for several other elements are given in Table 9-5; the first ionization potential represents the energy required to remove a single electron from the neutral atom to form the ion M^+(g); the second ionization potential represents the energy required to remove an electron from M^+(g) to form M^{++}(g), etc. One will note the characteristic periodic variation of the ionization potentials with the atomic number, and the marked effect of closed electron "shells." The energy required to remove an electron from Na(c) is rather different from that of the process of Eq. (9-4-4), and is measured independently by thermionic emission, photoelectric emission, and contact potential data; but for the process, Eq. (9-4-1), with which we are presently concerned, we are interested in the removal of the Na^+ ion, as well as the electron, from the metal electrode. In the process, Eq. (9-4-4), to which the ionization potential refers, the electron appears in the free gaseous state, whereas in a galvanic cell it might be liberated within the metallic electrode; this distinction need not disturb us, however, as its effect cancels out when one recombines data for one electrode with that for another in a complete cell. Now, the sublimation energy of the metal is another well-known property:

$$\mathrm{Na(c)} = \mathrm{Na(g)}; \qquad \bar{L}^\circ_{cg} = 26.2 \text{ kcal} \qquad (9\text{-}4\text{-}5)$$

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[1] For details, see, for example, M. N. Saha and N. K. Saha, "A Treatise on Modern Physics," Chap. XIII, The Indian Press, Ltd., Allahabad, 1934.

Table 9-5. Ionization Potentials of Selected Chemical Elements*

(In volts)

Atomic number	Element	I	II	III	IV	V
1	H	13.595				
2	He	24.580	54.403			
3	Li	5.390	75.619	122.420		
4	Be	9.320	18.206	153.850	217.657	
5	B	8.296	25.149	37.920	259.298	340.127
6	C	11.264	24.376	47.864	64.476	391.986
7	N	14.54	29.605	47.426	77.450	97.863
8	O	13.614	35.146	54.934	77.394	113.873
9	F	17.42	34.98	62.646	87.23	114.214
10	Ne	21.559	41.07	64	97.16	126.4
11	Na	5.138	47.29	71.65	98.88	138.60
12	Mg	7.644	15.03	80.12	109.29	141.23
13	Al	5.984	18.823	28.44	119.96	153.77
14	Si	8.149	16.34	33.46	45.13	166.73
15	P	11.0	19.65	30.156	51.354	65.007
16	S	10.357	23.4	35.0	47.29	72.5
17	Cl	13.01	23.80	39.90	53.5	67.80
18	A	15.755	27.62	40.90	59.79	75.0
19	K	4.339	31.81	46	60.90	
20	Ca	6.111	11.87	51.21	67	84.39
21	Sc	6.56	12.89	24.75	73.9	92
22	Ti	6.83	13.63	28.14	43.24	99.8
23	V	6.74	14.2	29.7	48	65.2
24	Cr	6.76	16.60	29.80	50.4	
25	Mn	7.430	15.637			
26	Fe	7.86	16.17	30.50		
27	Co	7.90	17.36			
28	Ni	7.633	18.22			
29	Cu	7.736	20.286			
30	Zn	9.456	18.024	39.7		
36	Kr	13.99	24.57	36.94		
37	Rb	4.240	27.564	39.74		
38	Sr	5.757	11.092			
47	Ag	7.574	21.478	36.1		
48	Cd	8.992	16.905	35.0		
49	In	5.849	18.930	28.10	58.0	
50	Sn	7.42	14.69	30.72	40.8	80.8
54	Xe	12.127	21.205	32.117	46.6	
55	Cs	3.957	23.52			
56	Ba	5.274	10.066			
57	La	5.68	11.502	19.232		
58	Ce	6.98	12.37	20.1	36.8	
78	Pt	8.95				
79	Au	9.294				
80	Hg	10.435	18.752			
81	Tl	6.171	20.468	29.89	50.6	
82	Pb	7.415	15.030	32.08	42.25	69.7
83	Bi	7.35	16.75	25.62	45.4	56.1

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* Values for elements 1 to 23 from C. E. Moore, Atomic Energy Levels, Vol. I, *Natl. Bur. Standards Circ.* C467 (1949); values for the remainder from "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D.C., as of March 31, 1950.

The value cited refers to 0°K, and has been derived by extrapolation from high-temperature vapor-pressure data, with the aid of spectroscopic data for Na(g) and calorimetric heat-capacity data for Na(c).[1] Combining with (9-4-4),

$$\text{Na(c)} = \text{Na}^+\text{(g)} + e; \qquad \Delta U_0^\circ = 144.7 \text{ kcal} \qquad (9\text{-}4\text{-}6)$$

The problem now is to get $Na^+(g)$ into solution. Unfortunately, this cannot be done without an accompanying anion.

The energy of the process

$$\text{Na}^+\text{(g)} + \text{Cl}^-\text{(g)} = \text{NaCl(c)} \qquad (9\text{-}4\text{-}7)$$

may be computed theoretically by the method of M. Born outlined in Sec. 4-4; it represents the negative of the crystal lattice energy, and in the simple Born-Landé treatment, one needs to know only the crystal geometry as established by X-ray analysis and the Born exponent, whose value may be established from the compressibility. Typical results are given in Table 4-6, but we shall use for (9-4-7), $\Delta U_0^\circ = -183.1$ kcal, as derived by J. E. Mayer and L. Helmholtz from a modification of the original theory by M. Born and J. E. Mayer taking into account Van der Waals' attraction energy between the ions and making use of an exponential rather than an inverse nth power repulsive potential-energy function of the interionic distance.[2] Furthermore, the total heat of solution of NaCl(c) in water has been determined by ordinary thermochemical means, leading to the conclusion (the volume change being negligible)

$$\text{NaCl(c)} = \text{Na}^+\text{(aq)} + \text{Cl}^-\text{(aq)}; \qquad \Delta U^\circ = 0.93 \text{ kcal} \qquad (9\text{-}4\text{-}8)$$

This result refers to room temperature, whereas the other data refer to a hypothetical temperature of 0°K [where the distinction between ΔF° and ΔU° for a process such as (9-4-1), whose volume change is negligible, vanishes], but we shall overlook the small corrections to 298°K. Thus, adding (9-4-7) and (9-4-8) to (9-4-6),

$$\text{Na(c)} + \text{Cl}^-\text{(g)} = \text{Na}^+\text{(aq)} + e + \text{Cl}^-\text{(aq)}; \qquad \Delta U^\circ = -37.5 \text{ kcal} \qquad (9\text{-}4\text{-}9)$$

This is not quite what we want for computing E° of the process (9-4-1), since the energy of the process

$$\text{Cl}^-\text{(g)} = \text{Cl}^-\text{(aq)} \qquad (9\text{-}4\text{-}10)$$

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[1] K. K. Kelley, Contributions to the Data on Theoretical Metallurgy. III. The Free Energies of Vaporization and Vapor Pressures of Inorganic Substances, *U.S. Bur. Mines Bull.* 383, p. 96 (1935).

[2] M. Born and J. E. Mayer, *Z. Physik*, **75**, 1–18 (1932); J. E. Mayer and L. Helmholtz, *ibid.*, 19–29.

is included; this cannot be independently measured. We may suppose, however, that the hydration energy of $Cl^-(g)$ is independent of the particular cation accompanying it, in the ultimately ideal dilute solution. The value of $E°$ in Eq. (9-4-1) is relative anyhow, being based on the arbitrary convention

$$\tfrac{1}{2}H_2(g) = H^+(aq) + e; \qquad E° \equiv 0.000 \tag{9-4-11}$$

Before continuing further, therefore, let us examine the results of the same sequence of calculations applied to the chlorides of other univalent metals, to see whether the calculated energies corresponding to the process

$$M(c) + Cl^-(g) = M^+(aq) + e + Cl^-(aq)$$

are in proportion to the relative standard electrode potentials. The data are summarized in Table 9-6. It is evident that the calculated energies listed in the last column of the table bear indeed the correct approximate relationships to each other. Thus, the difference between the values for Na and Ag, -93.6 kcal/g-eq, or 4.06 volts, may be compared with the actual difference, 3.51 volts, between the standard electrode potentials, (9-4-1) and (9-4-2).

Table 9-6 is instructive in demonstrating the influence of the various factors that contribute to the value of $E°$. Thus, it is well known that lithium has a higher standard electrode potential than any of the other alkali metals, with the possible exception of cesium, notwithstanding the fact that it has the highest ionization potential of the group, and might therefore be expected to be the least active of the metals. One perceives that its $E°$ value tends to be relatively high because of the relatively high lattice energy and heat of solution of the salt, which overshadow the effects of the relatively high ionization potential and sublimation energy; the lattice energy and the heat of solution are no doubt large because of the relatively small size of the Li^+ ion, which permits relatively close approach both of the accompanying anion in the crystal lattice, and of oriented polar water molecules in solution. One perceives also that the relatively "noble" character of Cu and Ag toward reactions in aqueous solutions is as much a consequence of their high sublimation energies (which are associated also with relatively high melting points and boiling points), as of their relatively high ionization potentials. The relatively endothermic character of the solution energy in the case of the silver salts in water is a further important factor in depressing the standard potential of the $Ag(c),Ag^+(aq)$ electrode below that of the $Cu(c),Cu^+(aq)$ electrode.

Data are available by which we may standardize the energy values given in the last column of Table 9-6 in terms of conventional $E°$ values with respect to the hydrogen electrode, though we must thereby forego efforts to determine "absolute" energies of processes such as (9-4-1), (9-4-2), (9-4-10), and (9-4-11) itself. The energies represented in the last column of Table 9-6 differ from the energies of the electrode processes

TABLE 9-6. ENERGY DATA FOR METAL CHLORIDES
(In kilocalories per gram-equivalent)

Metal	$\bar{L}^\circ_{cg}$,* $M(c) = M(g)$	I,† $M(g) = M^+(g) + e$	$(\Delta \bar{U}^\circ_0)_c$,‡ $M^+(g) + Cl^-(g) = MCl(c)$	$-\bar{Q}^\circ_s$,§ $MCl(c) = M^+(aq) + Cl^-(aq)$	Sum
Li	36.0	124.3	−199.2	− 8.9	−47.8
Na	26.2	118.5	−183.1	+ 0.9	−37.5
K	21.8	100.1	−165.4	+ 4.1	−39.4
Rb	20.6	97.8	−160.7	+ 4.0	−38.3
Cs	18.7	91.3	−152.2	+ 4.3	−37.9
Tl	43.0	142.3	−167	+10.3	+29
Cu	81.2	178.4	−216	+ 4.9	+49
Ag	69.4	174.7	−203.0	+15.0	+56.1

* Values for $\bar{L}_{cg}^\circ$ from K. K. Kelley, *U.S. Bur. Mines Bull.* 383 (1935).

† Values for I from Table 9-5.

‡ Values for $(\Delta\bar{U}_0^\circ)_c$ from J. E. Mayer and L. Helmholtz, *Z. Physik*, **75**, 19–29 (1932); J. E. Mayer, *J. Chem. Phys.*, **1**, 327–334 (1933); J. E. Mayer and R. B. Levy, *ibid.*, 647–648.

§ Values for $-\bar{Q}_s^\circ$ from "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D.C., 1950.

$$M(c) = M^+(aq) + e$$

by the energy of the process (9-4-10), which may be broken down as follows:

$$\frac{1}{2}\,Cl_2(g) = Cl(g); \qquad \Delta U_0^\circ = \frac{D_0}{2} = 28.6 \text{ kcal} \qquad (9\text{-}4\text{-}12)$$

$$Cl(g) + e = Cl^-(g); \qquad \Delta U_0^\circ = -\epsilon_{Cl} = -85.8 \text{ kcal} \qquad (9\text{-}4\text{-}13)$$

The dissociation energy D_0 of the $Cl_2(g)$ molecule is known from a variety of sources, including thermal equilibrium data at high temperatures and also analysis of the molecular spectrum (see Sec. 10-5*d*). The electron affinity of Cl(g), ϵ_{Cl}, has been established by the experimental work of J. E. Mayer described in Sec. 4-4, as well as by inference from theoretically calculated lattice energies of ionic chlorides (Table 4-6). Both experimental quantities given in (9-4-12) and (9-4-13) refer to 0°K. Thus, adding these terms to (9-4-9), we obtain

$$Na(c) + \tfrac{1}{2}Cl_2(g) = Na^+(aq) + Cl^-(aq); \qquad \Delta U^\circ = -94.7 \text{ kcal} \qquad (9\text{-}4\text{-}14)$$

This quantity would represent the difference between the Na(c), $Na^+(aq)$ and the $Cl^-(aq)$, $Cl_2(g)$ standard electrode potentials at the hypothetical temperature 0°K, except that the solution energy (9-4-8) refers to room temperature. Let us in a similar manner add the quantity

$$D_0/2 - \epsilon_{\mathrm{Cl}} = -57.2 \text{ kcal}$$

to each of the energies in the last column of Table 9-6, and convert to volts by dividing through by the conversion factor −23.06 kcal/volt g-eq, as shown in the second and third columns of Table 9-7; we may then derive conventional standard electrode potentials for the metals [based on (9-4-11)] by adding algebraically the potential

$$\mathrm{Cl^-(aq)} = \tfrac{1}{2}\mathrm{Cl_2(g)} + e; \qquad E^\circ = -1.36 \text{ volts}$$

whose experimental determination has been described in Sec. 9-2 [see Eq. (9-2-52)]. The resulting calculated potentials are given in the fourth column of Table 9-7, while the experimental values are given in the fifth column. One should note that the only actual emf data entering the calculated potentials are those pertaining to the establishment of the chlorine electrode potential. The terms $\bar{L}^\circ_{cg}$ and I are properties solely of the metal, the terms $D_0/2$ and $-\epsilon_{\mathrm{Cl}}$ are properties solely of chlorine, while the term $(\Delta \bar{U}^\circ_0)_c$ is a property of the chloride, *i.e.*, of both the metal and chlorine in combination; the effect of the solvent enters through the term $-\bar{Q}^\circ_s$, which of course is also a property of the particular chloride. The calculated potentials show the proper order of magnitude, though the values for Tl, Cu, and Ag are about 0.5 volt more negative than the observed values. One should note in this connection that the theoretical lattice energy of CuCl(c) is about 6 kcal smaller in magnitude than the experimental value based on thermochemical data, a difference that has

TABLE 9-7. CALCULATED STANDARD ELECTRODE POTENTIALS

Metal	$\mathrm{M(c)} + \frac{1}{2}\mathrm{Cl_2(g)} = \mathrm{M^+(aq)} + \mathrm{Cl^-(aq)}$		$\mathrm{M(c)} = \mathrm{M^+(aq)} + e$	
	Kcal/g-eq	Volts	E° (calc), volts	E° (exp), volts
Li	−105.0	4.55	3.19	3.02
Na	− 94.7	4.10	2.74	2.71
K	− 96.6	4.19	2.83	2.92
Rb	− 95.5	4.14	2.78	2.99
Cs	− 95.1	4.12	2.76	3.02
Tl	− 28	1.21	−0.15	0.34
Cu	− 8	0.35	−1.01	−0.52
Ag	− 1.1	0.05	−1.25	−0.80

been interpreted to indicate a partially covalent character of the bonding energy in this compound;[1] the thermochemical lattice energy, 221.9 kcal/g-eq, would yield a calculated value of E° less negative by 0.26 volt than the value given in Table 9-7.

Table 9-8 presents similar data for fluorides of divalent metals. These results are surely indicative, considering the simplicity of the theoretical treatment. Thus, one perceives that the effect of decreasing ionization potential in the series Ca, Sr, and Ba is practically neutralized by the effect of decreasing lattice energy of the salts, both effects resulting from the increasing size of the cation; the net effect is a leveling of the standard electrode potentials of the three metals in aqueous solution. In the case of Mg, however, the cation has become so small that the fluoride crystallizes in the rutile structure, with Mg^{++} coordination number of only 6 instead of 8 as in the fluorite structure; the increase in lattice energy from $CaF_2(c)$ to $MgF_2(c)$ therefore does not keep pace with the quite large increase of ionization potential from Ca to Mg, and despite the relatively exothermic solution energy of the magnesium salt, one finds a lower standard electrode potential for Mg in aqueous solution than for Ca (compare Li and Na in Tables 9-6 and 9-7). One also perceives that in the case of Pb, whose ionization potential is actually slightly less than that of Mg, the much lower standard electrode potential is associated with the relatively low crystal lattice energy, a consequence of the large

TABLE 9-8. ENERGY DATA FOR METAL FLUORIDES*

Metal	$\bar{L}^\circ_{cg}$, kcal	I, $M(g) = M^{++}(g) + 2e$, kcal	$(\Delta\bar{U}^\circ_0)_c$, kcal	$-\bar{Q}^\circ_s$, kcal	Sum, kcal/mole	$M(c) = M^{++}(aq) + 2e$	
						E° (calc), volts	E° (exp), volts
Mg	35.9	522.8	−699.2	− 2.8	−143.3	3.03	2.34
Ca	45.9	414.6	−620.2	+ 3.2	−156.5	3.32	2.87
Sr	39.2	385.6	−581.8	+ 2.6	−154.4	3.27	2.89
Ba	42.0	350.8	−558.9	+ 0.9	−165.2	3.51	2.90
Mn	68.0	531.9	−654.5	−20	− 75	1.55	1.05
Cd	27.0	597.2	−626.9	− 8.7	− 11.4	0.17	0.40
Ni	101.1	596.3	−699.5	−12.0	− 14.1	0.23	0.25
Pb	46.5	517.6	−589.4	+ 2.8	− 22.5	0.42	0.13
Cu	81.2	646.2	−691.8	−15.0	+ 20.6	−0.52	−0.34

* Values for $(\Delta\bar{U}_0^\circ)_c$ from Table 4-8 and also from J. Sherman, *Chem. Rev.*, **11**, 153 (1932). Calculated E° values are based on the following:

$F_2(g) = 2F^-(g)$; $\Delta U_0^\circ = -129.0$ kcal

$F^-(aq) = \frac{1}{2}F_2(g) + e$; $E^\circ = -2.87$ volts

Note that for the divalent metals, $j = 2$g-eq/mole.

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[1] J. E. Mayer and R. B. Levy, *J. Chem. Phys.*, **1**, 647–648 (1933).

size of the Pb^{++} ion. On the other hand, the relatively low standard electrode potential of Ni is as much a consequence of its high sublimation energy (associated with high melting point and boiling point) as of its relatively high ionization potential. The comparison between Cd and Ni is interesting; both metals have practically identical ionization potentials, but the much higher sublimation energy of Ni(c) is offset by the relatively high lattice energy of its salt. This is a consequence of the smaller size of the Ni^{++} ion, reflected also in the fact that NiF_2(c) crystallizes in the rutile structure, which accommodates only 6 F^- ions about each Ni^{++} ion, whereas CdF_2(c) crystallizes in the fluorite structure, which accommodates 8 F^- ions about each Cd^{++} ion.

It is interesting for us to examine the relative magnitudes of the factors influencing the H_2(g), H^+(aq) standard electrode potential, although of course we cannot calculate independently its absolute magnitude. The following energies (0°K) are involved:

$$\tfrac{1}{2}H_2(g) = H(g); \qquad \Delta U_0^\circ = \tfrac{1}{2}D_0 = 51.6 \text{ kcal} \qquad (9\text{-}4\text{-}15)$$

$$H(g) = H^+(g) + e; \qquad \Delta U_0^\circ = I = 313.5 \text{ kcal} \qquad (9\text{-}4\text{-}16)$$

These may be combined with (9-4-12) and (9-4-13) to give

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) = H^+(g) + Cl^-(g); \qquad \Delta U_0^\circ = 307.9 \text{ kcal} \qquad (9\text{-}4\text{-}17)$$

Now, the energies of the processes

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) = HCl(g); \qquad \Delta U_0^\circ = -22.0 \text{ kcal}$$

$$HCl(g) = H^+(aq) + Cl^-(aq); \qquad \Delta U^\circ = -17.4 \text{ kcal}$$

are well known from thermochemical sources (the solution energy refers to room temperature, however, whereas the other data refer to 0°K). Therefore we may infer for the process

$$H^+(g) + Cl^-(g) = H^+(aq) + Cl^-(aq) \qquad (9\text{-}4\text{-}18)$$

an energy of $\Delta U^\circ = -347.3$ kcal/g-eq. This quantity is much larger in magnitude than the corresponding quantities for the other metal chlorides listed in Table 9-6 $[(\Delta \bar{U}_0^\circ)_c - \bar{Q}_s^\circ]$, and we may therefore attribute most of it to solvation energy of the H^+ ion. This exceptionally large solvation energy is apparently responsible for the fairly high effectiveness of H_2(g) as a reducing agent toward substances in aqueous solution, particularly under the influence of a catalytic agent that will accelerate the progress of reaction (9-4-15); the large dissociation energy of the extremely stable H_2(g) molecule and particularly the high ionization potential of the H(g) atom, which is nearly twice that of the Ag(g) atom, tend to depress the standard electrode potential.

An attempt has been made to measure single electrode potentials, or what amounts to the same thing, the free-energy changes of single electrode processes such as (9-4-1), (9-4-2), (9-4-11), etc., by taking advantage of the curious fact that the surface tension of mercury is sensitive to the electric charge it bears. Thus, if one assumes that the surface tension is a maximum when the mercury bears no charge, one may set up a galvanic cell with one of the electrodes consisting of mercury making contact with the electrolyte in a capillary tube so that its surface tension can be observed; by applying such a difference of potential that the surface tension of the mercury attains the maximum value, one may then assign the entire potential difference to the process taking place at the other electrode. Results so derived are discussed by W. M. Latimer;[1] thus, with two mercury electrodes in an aqueous KCl electrolyte saturated with Hg_2Cl_2(c), the surface tension of the mercury in the capillary electrode reaches a maximum when that electrode is made negative with respect to the other by 0.56 volt. On the basis of this type of evidence, one may separate the hydration energy (9-4-18) into approximately -260 kcal/g-eq for H^+(g) and -90 kcal/g-eq for Cl^-(g). The interpretation of the behavior of the capillary electrometer is certainly open to question, however, and one would like a sounder theoretical basis for its operation.

R. W. Gurney has given a stimulating discussion of electrode processes from the point of view of the quantum theory of metallic and ionic structures.[2] One of the fundamental principles of quantum mechanics is that no two electrons in a given system can be in identical states (a special case of the general exclusion principle proposed by W. Pauli). Furthermore, according to the statistical theory developed by E. Fermi and A. Sommerfeld, the energy distribution of electrons in condensed phases (liquids or solids) is such that at all temperatures from 0°K to ordinary room temperature, almost all the electrons remain in the states of lowest energy open to them consistently with the exclusion principle.[3] Now, for the electrons associated with a given atom, these states occur in groups or bands of closely spaced energy, the bands themselves being relatively widely separated. The states for an atom constituting part of a solid or a liquid are comparable to those of an isolated gas atom or molecule, in so far as one can identify such local states at all, but they are of course modified by the presence of the neighboring atoms. The theory of metallic conductors is that the highest occupied electronic states (practically all states of lower energy being completely filled by electrons) hap-

[1] Latimer, *op. cit.*, pp. 21–22.

[2] R. W. Gurney, "Ions in Solution," Cambridge University Press, New York, 1936.

[3] E. Fermi, *Z. Physik*, **36**, 902–912 (1926); A. Sommerfeld, *ibid.*, **47**, 1–32, 43–60 (1928); see Sec. 10–2.

pen to lie within a band that includes some unoccupied states of but slightly different (higher) energy; in a nonconductor, on the other hand, a band has been completely filled, so that the next higher unoccupied states lie in the next band at a considerably higher energy level. Thus, in the metallic conductor, it is relatively easy for the outermost or so-called *valence electrons* of the atoms to shift about within the metal; in fact, the metal atoms are to a considerable extent bonded through sharing of these overlapping electrons. In a nonconductor or dielectric, on the other hand, ordinarily few electrons can get into the higher energy states through which they must pass if they are to escape from one particular atom or molecule with which they happen to be associated to another. The distinction between conductors and dielectrics is thus regarded as one of degree, rather than of kind.

When two different metals are brought into contact, if the highest occupied energy level of the one metal happens to overlap unoccupied energy levels of the other (as will generally be the case), electrons will tend to flow from the first metal into the second until they fill up to equal levels in both. This gives rise to a contact potential, which can be directly measured, with results as shown in Table 9-4. Where sufficiently precise data have been available, the contact potential between two metals, which measures the energy required to transfer an electron from one to the other, has been found to be approximately equal to the difference between their threshold voltages for photoelectronic emission; it should also equal approximately the difference between the work functions for thermionic emission, but it is generally difficult to measure these quantities for a given pair of metals at the same temperature.[1]

In Gurney's treatment, the metallic contact effect is considered to be a primary factor in the mechanism of discharge of a galvanic cell. The further processes whereby electrons are exchanged between the electrodes and ions or molecules in solution are then treated in terms of the relative energies of the atoms in the metal and their ions in solution, on the basis of essentially the same type of data we have just been considering. The stability of certain ions and the instability of others also calls for discussion. For free gas atoms, the removal of each successive electron as the atom is ionized calls for increasingly greater energy (Table 9-5). Thus, in the case of Na(g), there is an extremely large difference between the ionization potential of Na(g) and that of Na^+(g), a difference inherent of course in the peculiar structure of the sodium atom (and of the other alkali metal atoms). We have no difficulty therefore in understanding why Na^+ and only Na^+ exists in aqueous solution. It is not so obvious

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[1] See K. T. Compton and I. Langmuir, *Rev. Modern Phys.*, **2**, 123–242 (1930); S. Dushman, *ibid.*, 381–476; J. A. Becker, *ibid.*, **7**, 95–128 (1935).

why an ion such as Mg^+, which can certainly exist in the gaseous state, as does the molecule MgCl, does not exist in aqueous solution or in the crystalline state. The reason here is to be sought in the relationship between the successive ionization potentials and those other factors that we have seen may influence the relative energies of the various ions in solution; for example, one may show that the lattice energy of such a hypothetical crystalline compound as MgCl(c), based on reasonably assumed structures, would be much smaller per gram-equivalent than that of the actual compound, $MgCl_2$(c),[1] so that in spite of the higher ionization energy, $MgCl_2$(c) is much more stable than MgCl(c). The stability of certain ions in solution, particularly of the transitional elements, is no doubt conditioned by the relative stability of the bond configurations that can be set up between the metal ion and solvent molecules, or possibly other ions or molecules that may be present in the solution. Pauling has described, for example, in terms of available electronic orbitals why the covalent octahedral complex ions of Co^{+++} are far more stable than those of Co^{++}, whereas Co^{+++}(aq) is much less stable than Co^{++}(aq).[2]

9-5. Overvoltage. A brief discussion is in order concerning the nonreversible phenomenon of *overvoltage*.[3] If an electrolytic conductor such as HCl(aq,1*M*) is electrolyzed between a reversible anode, such as the Hg(l),Hg_2Cl_2(c) electrode, and a *reversible cathode*, such as platinized platinum saturated with H_2(g), then a current begins to flow and hydrogen is evolved at the cathode, according to the reaction

$$H^+(aq) + e = \tfrac{1}{2}H_2(g),$$

just as soon as the applied potential difference exceeds even by a fraction of a millivolt that of the corresponding galvanic cell, in this case, about 0.27 volt. The current and the corresponding rate of evolution of H_2(g) increase with the applied potential difference approximately in proportion to the excess of the applied potential difference over the reversible cell potential difference. This excess, or net potential difference across the electrodes, is called the *overvoltage* at which the electrochemical reaction is being run.

Now, if other metallic electrodes are substituted for the platinized platinum cathode, for example, bright platinum, copper, mercury, etc.,

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[1] H. G. Grimm and K. F. Herzfeld, *Z. Physik*, **19**, 141–166 (1923); recall also Prob. 4-24.

[2] L. Pauling, "The Nature of the Chemical Bond," pp. 93–95, Cornell University Press, Ithaca, New York, 1939.

[3] The reader will find excellent recent reviews of this subject in *Faraday Society Discussion*, **1** (1947), and also by J. O'M. Bockris, *Chem. Revs.*, **43**, 525–577 (1948), and by A. Hickling, *Quart. Revs.*, **3**, 95–125 (1949).

then one finds that considerably higher overvoltages are required to produce the same current density (current per unit area of electrode surface), or what amounts to the same thing, smaller currents and rates of reduction of $H^+(aq)$ are obtained at given overvoltage. Hydrogen overvoltages on a number of different metals at a current density of 0.001 amp/cm^2 are given in Table 9-9. It should be noted that these data are not perfectly reproducible, the values tending to increase with time of polarization; there is no doubt, however, concerning the approximate relative magnitudes.

TABLE 9-9. HYDROGEN OVERVOLTAGES IN 1*M* HCl AT 0.001 AMPERE PER SQUARE CENTIMETER*

Cathode	Overvoltage, volts	Cathode	Overvoltage, volts
Tl	1.05	Cu	0.54
Hg	1.04	Ag	0.46
Cd	0.99	Ta	0.41
Pb	0.88	Fe	0.40
Sn	0.85	Ni	0.33
In	0.80	Mo	0.30
Bi	0.69	W	0.27
Nb	0.65	Pt	0.25
Be	0.63	Au	0.17
Al	0.58	Pt (platinized)	0.01

* A. Hickling, *Quart. Revs.*, **3**, 108 (1949).

The existence of hydrogen overvoltage is partly responsible for the fact that we may readily plate by electrolysis from aqueous solution several metals such as Ni and Cd whose reversible oxidation potentials are higher than that of $H_2(g)$ without simultaneously reducing $H^+(aq)$.[1] Hydrogen overvoltage accounts, moreover, for the fact that the "active" metal, zinc, in the pure state is attacked quite slowly by dilute acids, whereas evolution of hydrogen is promptly speeded up by the addition of a small quantity of copper salt to the electrolyte; the hydrogen overvoltage on a zinc cathode at 0.001 amp/cm^2 is about 0.72 volt,[2] but copper, by depositing on the zinc through ordinary chemical displacement, apparently provides spots of lower hydrogen overvoltage. Amalgamation of

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[1] The reversible potential of the hydrogen electrode may be increased of course by the use of alkaline solutions; for many of the metals this involves an increase in their reversible potentials as well, through engagement of most of the metal ions in solution as amphoteric anions, complex cyanides, etc.

[2] "International Critical Tables," Vol. VI, p. 339, McGraw-Hill Book Company, Inc., New York, 1929.

the zinc surface with mercury, on the other hand, still further desensitizes it to the action of dilute acids.

The slowness of the reduction of $H^+(aq)$ on most metal surfaces must be at least in part a consequence of the high potential of the intermediate step

$$H^+(aq) + e = H(g)$$

From the dissociation energy (9-4-15) of the $H_2(g)$ molecule, we may calculate as the theoretical reversible standard potential of the reaction

$$H(g) = H^+(aq) + e; \qquad E^\circ = 2.26 \text{ volts} \tag{9-4-19}$$

The subsequent process

$$2H(g) = H_2(g) \tag{9-4-20}$$

makes up of course for this energy in the net electrode reaction, but it would evidently take a considerably higher potential to reduce $H^+(aq)$ to $H(g)$ than to $H_2(g)$. Therefore, if there were any delay in the establishment of equilibrium in the reaction (9-4-20), a potential significantly higher than the equilibrium value might be required for the progress of hydrogen evolution. It is noteworthy that platinized platinum, which is an excellent general catalyst for hydrogenations and dehydrogenations, apparently through accelerating the attainment of equilibrium in the reaction (9-4-20), behaves practically reversibly toward the electrolytic reduction of $H^+(aq)$.

While this theory is fairly satisfactory at high current densities, and can be further developed along quantitative lines,[1] it fails to account for the existence of finite limiting overvoltages at low current densities approaching zero. Possibly gas polarization is responsible for the overvoltage at low current densities. Thus, we noted in Eq. (6-66) how much higher the pressure may be within a tiny gas bubble than within a gas bubble of larger radius, as an effect of surface tension. The physical formation of the initial gas bubbles may therefore require higher energy than one would suppose from ordinary equilibrium measurements with the reversible hydrogen electrode. In this connection, D. A. MacInnes and L. Adler made some extremely interesting observations with small platinized platinum electrodes at low current densities.[2] As the overvoltage was increased from zero, the current gradually increased, with no

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[1] See, for example, J. Tafel, *Z. physik. Chem.*, **50**, 641–712 (1905); G. N. Lewis and R. F. Jackson, *ibid.*, **56**, 193–211 (1906); J. A. V. Butler, *Trans. Faraday Soc.*, **19**, 734–739 (1924); **28**, 379–382 (1932); L. P. Hammett, *ibid.*, **29**, 770–775 (1933).

[2] D. A. MacInnes and L. Adler, *J. Am. Chem. Soc.*, **41**, 194–207 (1919); see also D. A. MacInnes and A. W. Contieri, *ibid.*, 2013–2019.

observed evolution of gas, until an overvoltage of about 16 mv was reached, whereupon gas bubbles appeared all over the electrode; as the exciting current was then gradually decreased, the overvoltage decreased, with decreasing evolution of gas, until at about 1.5 mv the potential was observed to fluctuate by about ±0.5 mv. The fluctuations coincided with the cycle of growth of a single bubble of hydrogen, occurring always at the same point on the electrode; just after the detachment of a bubble, leaving a tiny nucleus, the potential was at its highest, decreasing gradually as the new bubble grew in size. These experiments would indicate that when the gas phase is not already present, a quite high degree of supersaturation of hydrogen may develop in the electrolyte surrounding the cathode; once gas bubbles have formed, the evolution of gas may then proceed at much lower overvoltages, but since it takes a higher pressure to develop a bubble of smaller radius, there remains an overvoltage varying with the bubble size. It is indeed remarkable in these experiments that the potential over the entire electrode, even though the electrodes were small, was apparently determined by a gas bubble located at a single point on it. However, less energy is required to put more hydrogen into the small bubble already present than to put it into a new bubble of smaller radius; therefore, at sufficiently low current densities, the bubble already present apparently receives all the gas being generated, in much the same manner by which a large crystal tends to grow through slow evaporation of the saturated solution. The low hydrogen overvoltage at low current densities on platinized platinum as compared with other metals may be related to the ease with which hydrogen dissolves in platinized platinum, whose surface may take up the gas readily from the saturated aqueous solution. This explanation does not account for the differences in limiting overvoltages at low current densities observed with different metals.

Overvoltages have been measured also for anodic oxidation of $Cl^-(aq)$ to $Cl_2(g)$, $OH^-(aq)$ to $O_2(g)$, and for many other electrode reactions, including the depositions of metals from solutions of their salts. Really large overvoltages, however, are practically always associated with the evolution of some gas.

General References for Chapter 9

HARNED, H. S., and B. B. OWEN: "The Physical Chemistry of Electrolytic Solutions," 2d ed., Reinhold Publishing Corporation, New York, 1950.

LATIMER, W. M.: "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, 1938.

LEWIS, G. N., and M. RANDALL: "Thermodynamics and the Free Energy of Chemical Substances," Chaps. XXIX and XXX, McGraw-Hill Book Company, Inc., New York, 1923.

MacInnes, D. A.: "The Principles of Electrochemistry," Reinhold Publishing Corporation, New York, 1939.

Problems

9-1. The cell

$$(\mathrm{Pt})\ H_2(g)|HCl(0.1M)|Hg_2Cl_2(c),\ Hg(l)$$

has been studied at high hydrogen pressures by W. R. Hainsworth, H. J. Rowley, and D. A. MacInnes [*J. Am. Chem. Soc.*, **46**, 1437–1443 (1924)], with the following (selected) results at 25°C:

p, atm	E_{298}, volts
1.0	0.3990
110.2	0.4596
204.7	0.4683
386.6	0.4784
556.8	0.4844
701.8	0.4891
754.4	0.4903
862.2	0.4932
974.5	0.4963
1035.2	0.4975

The effect of pressure on all the reactants and products except $H_2(g)$ is small, and tends to be compensating, though at the highest pressures, hydrogen is appreciably soluble in the electrolyte. Plot E vs. log $p\nu$, taking ν at each pressure from the generalized fugacity coefficient chart (Fig. 6-4), and test the validity of the theoretical relationship between E and ϕ_{H_2} in the form

$$E = \left(E^\circ - \frac{2RT}{1\ \text{g-eq}} \ln m\gamma_\pm\right) + \frac{RT}{1\ \text{g-eq}} \ln (p_{H_2}\nu_{H_2})^{1/2}$$

(the first term on the right being constant, if we may disregard the effect of dissolved hydrogen on $\gamma_\pm$ of HCl).

9-2. E. Cohen and E. J. Joss [*J. Am. Chem. Soc.*, **50**, 727–733 (1928)] used the cell

$$Pb(c),\ PbI_2(c)|CaCl_2\cdot 6H_2O(l)|AgI(c),\ Ag(c)$$

to study the transition between AgI(c, α) (the form stable at room temperature) and AgI(c, β) (the high-temperature form). A typical set of results for one of the cells tested follows:

t, °C	E, int volts	t, °C	E, int volts
130.70	0.2610	137.30	0.2646
141.97	0.2673	134.28	0.2631
144.30	0.2687	147.30	0.2705
152.70	0.2726	149.00	0.2710
155.95	0.2740	158.20	0.2750
124.13	0.2573	159.25	0.2756
128.28	0.2596	161.80	0.2765

Plot E vs. t, and from the discontinuity in slope determine the transition temperature. From the slope $(dE/dT)_p$, on either side of the transition temperature, determine $\Delta S°$ for the cell reaction above and below the transition point, and by difference calculate $\Delta S°$ and $\Delta H°$ for the transition itself

$$\mathrm{AgI(c,\ \alpha) = AgI(c,\ \beta)}$$

at the transition point.

9-3. The following (selected) results were obtained by W. R. Carmody [*J. Am. Chem. Soc.*, **51,** 2905–2909 (1929)] for the cell

$$\mathrm{Pb(Hg)|PbCl_2}(m)\mathrm{|AgCl(c),\ Ag(c)}$$

at 25°C:

m, moles/kg	E, int volts
0.03905 (satd)	0.4842
0.01039	0.5205
0.00516	0.5419
0.00262	0.5639
0.001337	0.5870
0.0006197	0.6143
0.0002116	0.6537

In accordance with the theoretical equation (9-2-55) for this cell, plot

$$\left(E + \frac{3RT}{2\ \text{g-eq}} \ln m + \frac{RT}{2\ \text{g-eq}} \ln 4\right) \text{ vs. } m^{1/2}$$

and determine $E°$ by extrapolation. Compare the limiting slope with that predicted by the Debye-Hückel limiting law for a strong 1:2 electrolyte.

From the value of $E°$, and the value of E for the saturated solution, calculate $\gamma_{\pm}$ for the saturated solution, and determine the standard free energy of solution of $PbCl_2$: $\phi'_{PbCl_2(aq)} - \bar{F}°_{PbCl_2(c)}$. Using the ϕ' values for $Pb^{++}(aq)$ and $Cl^-(aq)$ given by Eqs. (9-2-52) and (9-2-58), calculate the standard free energy of formation of $PbCl_2(c)$. Express these results also in terms of the thermodynamic solubility product of $PbCl_2(c)$.

9-4. (*a*) The cell

$$\mathrm{(Pt)\ H_2(g,\ 1\ atm)|HClO_4}(m)\mathrm{,\ Pb(ClO_4)_2}(m)\mathrm{|PbO_2(c),\ Pb(c)}$$

has been studied by D. J. Brown and J. C. Zimmer [*J. Am. Chem. Soc.*, **52,** 1–6 (1930)] and found to behave reversibly. They obtained the following results at 25°C:

m, moles/kg	E, int volts
0.100	1.432
0.025	1.417
0.0100	1.407
0.0025	1.389
0.0010	1.378

Write the cell reaction, express E as a function of the electrolyte concentration, and by means of an appropriate extrapolation to zero electrolyte concentration determine the standard emf, $E°$.

(*b*) The standard enthalpy of formation of $PbO_2(c)$ at 25°C and 1 atm is −66,120 cal/mole, and its third-law entropy is 18.3 eu/mole. Using for Pb(c) the third-law entropy, 15.49 eu/mole, and for $O_2(g)$ the spectroscopically determined entropy, 49.003 eu/mole, calculate the standard free energy of formation of $PbO_2(c)$, and combining with the result of part (*a*) [using the $\bar{F}°$ value for $H_2O(l)$ found in Appendix 2], calculate a value for $\phi'_{Pb^{++}(aq)}$, and compare with that given by Eq. (9-2-58).

9-5. (*a*) A. W. Hutchison [*J. Am. Chem. Soc.*, **69**, 3051–3054 (1947)] has made measurements at 25°C with the cell

$$\text{(Pt), } H_2(\text{g, 1 atm})|HClO_4(m),\ Mn(ClO_4)_2(m)|MnO_2(\text{c}), \text{ (Pt)}$$

From the following results, using for each electrolyte the Debye-Hückel approximation,

$$-\log \gamma_{\pm} = \frac{0.5091 z_+ z_- \sqrt{\mu}}{1 + 2\sqrt{\mu}}$$

calculate the standard potential of the Mn^{++}(aq), MnO_2(c) electrode

$$Mn^{++}(\text{aq}) + 2H_2O(\text{l}) = 4H^+(\text{aq}) + MnO_2(\text{c}) + 2e$$

$m_{HClO_4} = m_{Mn(ClO_4)_2}$, moles/kg	E, int volts
0.5000	1.234
0.2000	1.220
0.1000	1.209
0.0500	1.199
0.0250	1.191
0.0125	1.181

(*b*) The standard thermochemical enthalpy of formation of MnO_2(c) is −124,500 cal/mole, and of Mn^{++}(aq), −52,300 cal/mole. The third-law entropies of MnO_2(c) and Mn(c) are, respectively, 13.9 and 7.61 eu/mole at 25°C; the entropy of O_2(g) at 25°C is given in the preceding problem. Using this information with the result of part (*a*) [together with thermodynamic data for H_2O(l) found in Appendix 2], calculate $\phi'_{Mn^{++}(aq)}$ and $\sigma'_{Mn^{++}(aq)}$.

9-6. (*a*) The potential of the Cs(c), Cs^+(aq) electrode has been investigated by H. E. Bent, G. S. Forbes, and A. F. Forziati [*J. Am. Chem. Soc.*, **61**, 709–715 (1939)]. For the cell

$$Cs(\text{c})|CsI \text{ in } (CH_3)_2NH(\text{l})|Cs(Hg)$$

they obtained the following at 25°C: $E = 1.119$ int volt, with $x_{Cs} = 0.2827$ in the amalgam. Using the same amalgam concentration, they then studied the cell

$$Cs(Hg)|CsOH(0.02109m \text{ in } H_2O)|HgO(\text{c}), Hg(\text{l})$$

obtaining at 25°C a "best" value of 2.1058 int volts. Using for CsOH at the given concentration the mean activity coefficient $\gamma_{\pm} = 0.877$ [H. S. Harned and O. E. Schupp, *J. Am. Chem. Soc.*, **52**, 3886–3900 (1930)], calculate $E°$ for the hypothetical cell

$$Cs(\text{c})|CsOH(\text{aq}, m\gamma_{\pm} = 1)|HgO(\text{c}), Hg(\text{l}) \qquad \text{(I)}$$

and using for the standard potential of the Hg(l), HgO(c), OH^-(aq) electrode the value −0.0976 int volt [compare cell (9-2-22)], calculate the standard potential of the cesium electrode

$$Cs(\text{c}) = Cs^+(\text{aq}) + e$$

(*b*) From measurements at other temperatures, they found as the mean temperature coefficient of $E°$ for the hypothetical cell (I) $(dE°/dT) = -0.00128$ int volt/deg.

Calculate the standard enthalpy of the cell reaction, and using for HgO(c) the standard enthalpy of formation, $\bar{H}^\circ_{298} = -21{,}680$ cal/mole [compare Eq. (8-1-27) for formation from Hg(g)], calculate the standard enthalpy of reaction between Cs(c) and H_2O(l).

9-7. The following cell has been studied by H. S. Harned and H. R. Copson [*J. Am. Chem. Soc.*, **55,** 2206–2215 (1933)]:

$$(\text{Pt})\text{H}_2(\text{g, 1 atm})|\text{LiOH}(0.01m), \text{LiCl}(m)|\text{AgCl(c), Ag(c)}$$

Write the cell reaction, and show that E may be represented by the formula

$$E = E^\circ - \frac{RT}{1\text{ g-eq}} \ln K^\circ_w \frac{m_{\text{Cl}^-}}{m_{\text{OH}^-}} \frac{(\gamma_\pm)_{\text{LiCl}}}{(\gamma_\pm)_{\text{LiOH}}} a_{\text{H}_2\text{O}}$$

where E° is the same as for the cell (9-2-35), and K°_w represents the thermodynamic ion product of water. From the following experimental data at 25°C, construct a graph of $E + (RT/1\text{ g-eq}) \ln (m_{\text{Cl}^-}/m_{\text{OH}^-})$ vs. μ ($= m + 0.01$ in this case, using molal in place of molar concentration units), and determine by extrapolation to zero ionic strength the value of $E^\circ + 0.059161\ pK^\circ_w$. Using the value of E° given in the text (see Table 9-3), calculate pK°_w and K°_w at 25°C.

m_{LiCl}, moles/kg	E_{298}, int volts
0.01	1.04979
0.02	1.03175
0.05	1.00755
0.1	0.98883
0.2	0.96957
0.5	0.94277
1.0	0.91992

9-8. The ion product of water has been determined also by straightforward equilibrium measurements for the reaction

$$\tfrac{1}{2}\text{HgO(c)} + \tfrac{1}{2}\text{Hg(l)} + \tfrac{1}{2}\text{H}_2\text{O(l)} + \text{Br}^-(\text{aq}) = \tfrac{1}{2}\text{Hg}_2\text{Br}_2(\text{c}) + \text{OH}^-(\text{aq}) \qquad \text{(I)}$$

combined with the emf data

$$(\text{Pt})\text{H}_2(\text{g, 1 atm})|\text{NaOH(aq)}|\text{HgO(c) Hg(l)}; \qquad E^\circ_{298} = 0.9255 \text{ int volt}$$
$$(\text{Pt})\text{H}_2(\text{g, 1 atm})|\text{HBr(aq)}|\text{Hg}_2\text{Br}_2(\text{c}) \text{ Hg(l)}; \qquad E^\circ_{298} = 0.1396 \text{ int volt}$$

[Y. Kobayashi and H. Wang, *J. Sci. Hiroshima Univ.*, (A) **5,** 71–82 (1934); R. H. Gerke and J. R. Geddes, *J. Phys. Chem.*, **31,** 886–889 (1927)]. Thus, in a typical equilibrium experiment, R. F. Newton and M. G. Bolinger [*J. Am. Chem. Soc.*, **52,** 921–925 (1930)] found that when a mixture of HgO(c), Hg_2Br_2(c), and Hg(l) was agitated with a solution of KBr at 25°C, the solution upon analysis was found to contain 0.01370 mole OH^-/liter and 0.0689 mole Br^-/liter. Taking for KOH the mean ionic activity coefficient 0.770 and for KBr, 0.791, as estimated from activity-coefficient data for the pure electrolytes at the same total ionic strength (Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIIc, pp. 2147, 2149, 1936), calculate the thermodynamic equilibrium constant and standard free-energy change of the reaction (I), and combining with the standard free-energy data represented by the emf measurements, calculate ΔF°_{298} for the reaction

$$H_2O(l) = H^+(aq) + OH^-(aq)$$

Calculate accordingly the value of K_w°: $RT \ln K_w^\circ = -\Delta F^\circ$.

9-9. Given the value of K_w°, the thermodynamic ion product of water, what further information is needed in order to fix the entropy of $OH^-(aq)$ (relative to the third-law convention)? Look up this information, and using the value of K_w° derived in Prob. 9-7, calculate $\sigma'_{OH^-(aq)}$.

9-10. Calculate the standard electrode potential of the hydrogen electrode in basic solution,

$$\tfrac{1}{2}H_2(g) + OH^-(aq) = H_2O(l) + e$$

from the ion product and the standard free energy of formation of $H_2O(l)$. Calculate also the potential of the hydrogen electrode in neutral solution.

9-11. (*a*) The potential of the Cu(c), CuCl(c), $Cl^-(aq)$ electrode has been studied by R. F. Nielsen and D. J. Brown [*J. Am. Chem. Soc.*, **50**, 9–19 (1928)] who used the cell

$$(Pt)H_2(g)|HCl(m)|CuCl(c),\ Cu(Hg)$$

Write the cell reaction, and write an equation for the emf as a function of the electrolyte concentration and the hydrogen partial pressure. In typical measurements at 25°C, they obtained the following results:

m_{HCl}, moles/kg	p_{H_2}, *mm* Hg	*E*, int volts
0.00757	695	0.3825
0.02029	700	0.3362
0.03564	697	0.3083

Taking $\gamma_\pm$ for HCl from Fig. 7-19 (see also Table 9-3), calculate a value of E° from each result. Combining the average with the information,

$$Cu(Hg)|CuSO_4(aq)|Cu(c); \qquad E_{298} = 0.0051 \text{ int volt}$$

[M. Oka, *Science Repts. Tôhoku Imp. Univ.*, (1) **22**, 288 (1933)], calculate the standard electrode potential corresponding to the process

$$Cu(c) + Cl^-(aq) = CuCl(c) + e$$

(*b*) Using the value of $\phi'_{Cl^-(aq)}$ given by Eq. (9-2-47), calculate from the result of part (*a*) the standard free energy of formation of CuCl(c) at 25°C, and compare with the value of −28,490 cal/mole derived by M. Watanabe (*ibid.*, 423–435) from high-temperature equilibrium measurements for the reduction of CuCl(c) by $H_2(g)$.

9-12. (*a*) The equilibrium constant for the reaction

$$2Cu^+(aq) = Cu^{++}(aq) + Cu(c)$$

has been measured by E. Heinerth [*Z. Elektrochem.*, **37**, 61–76 (1931)] who determined the concentrations of Cu_2SO_4 and $CuSO_4$ in equilibrium with Cu(c) at various temperatures. He found at 25°C, $K_m^\circ = 1.190 \times 10^6$, the effects of the two activity coefficients apparently canceling. Using the Cu(c),Cu^{++}(aq) standard potential given in Eq. (9-2-72), calculate the value of the Cu(c), Cu^+(aq) standard potential

$$\mathrm{Cu(c)} = \mathrm{Cu^+(aq)} + e$$

(compare D. A. MacInnes, "The Principles of Electrochemistry," pp. 286–287, Reinhold Publishing Corporation, New York, 1939).

(*b*) Combining with the information derived in Prob. 9-11, calculate the thermodynamic solubility product of CuCl(c) and the solubility of CuCl(c) in water, neglecting hydrolysis of Cu^+ and complex ion formation between Cu^+ and Cl^- (which is no doubt appreciable at high Cl^- concentrations).

9-13. (*a*) The emf of the normal Weston cell

$$\mathrm{Cd(Hg)|CdSO_4{\cdot}\tfrac{8}{3}H_2O(satd,\ in\ H_2O)|Hg_2SO_4(c),\ Hg(l)}$$

is 1.0181 int volts at 25°C. Using the standard electrode potentials

$$\mathrm{Cd(Hg)} = \mathrm{Cd^{++}(aq)} + 2e; \qquad E^\circ_{298} = 0.3516 \text{ int volt}$$
$$\mathrm{2Hg(l)} + \mathrm{SO_4^=(aq)} = \mathrm{Hg_2SO_4(c)} + 2e; \qquad E^\circ_{298} = -0.6141 \text{ int volt}$$

(D. A. MacInnes, "The Principles of Electrochemistry," p. 201), calculate $\gamma_\pm$ of $CdSO_4$ in the saturated solution, whose concentration is 3.683*m*.

(*b*) The vapor pressure of water from the saturated solution at 25°C is 21.17 mm Hg. Calculate a_{H_2O}, and using the result of part (*a*), calculate the standard free energy of solution $\phi'_{CdSO_4(aq)} - \bar{F}^\circ_{CdSO_4\cdot\frac{8}{3}H_2O(c)}$, corresponding to the process:

$$\mathrm{CdSO_4{\cdot}\tfrac{8}{3}H_2O(c)} = \mathrm{CdSO_4(aq)} + \tfrac{8}{3}\mathrm{H_2O(l)}$$

(*c*) The emf of the cell

$$\mathrm{Cd(c)|CdSO_4(aq{,}0.05\mathit{m})|Cd(Hg)}$$

was measured by W. G. Parks and V. K. LaMer [*J. Am. Chem. Soc.*, **56**, 90–91 (1934)] who obtained $E_{298} = 0.0505$ int volt. Using the information given in part (*a*), calculate $\phi'_{Cd^{++}(aq)}$, and from the independently derived value of $\phi'_{SO_4^=(aq)} = -177{,}340$ cal/mole [*e.g.*, from (9-2-61), combined with thermal entropy and enthalpy data for $PbSO_4$(c)], calculate the standard free energy of formation of $CdSO_4\cdot\frac{8}{3}H_2O$(c).

9-14. H. S. Harned and R. W. Ehlers [*J. Am. Chem. Soc.*, **54**, 1350–1357 (1932)] have used the cell

$$\mathrm{(Pt)H_2(g,\ 1\ atm)}\left|\begin{array}{ll}\mathrm{CH_3COOH} & (m_1)\\ \mathrm{CH_3COONa} & (m_2)\\ \mathrm{NaCl} & (m_3)\end{array}\right|\mathrm{AgCl(c),\ Ag(c)}$$

to measure the thermodynamic ionization constant of acetic acid. Write the equation for the cell reaction, and show that

$$E = E^\circ - \frac{RT}{1\text{ g-eq}}\ln\left[K^\circ_m\,\frac{m_1m_3}{m_2}\,\frac{\gamma'_{\mathrm{HAc}}(\gamma_\pm)_{\mathrm{NaCl}}}{(\gamma_\pm)_{\mathrm{NaAc}}}\right]$$

where E° is the same as for the cell (9-2-35). **From the following data, construct a graph of** $\left(E + \frac{RT}{1\text{ g-eq}}\ln\frac{m_1m_3}{m_2}\right)$ **vs.** μ**, and by extrapolating to zero ionic strength, determine the value of** $E^\circ + 0.059161\,pK^\circ_m$**. Using the value of** E°_{298} **given in the text,** calculate the value of pK°_m at 25°C.

m_1, HAc	m_2, NaAc	m_3, NaCl	μ	E_{298}, int volts
0.004779	0.004599	0.004896	0.00951	0.63959
0.012035	0.011582	0.012426	0.02403	0.61583
0.021006	0.020216	0.021516	0.04175	0.60154
0.04922	0.04737	0.05042	0.09781	0.57977
0.08101	0.07796	0.08297	0.16095	0.56712
0.09056	0.08716	0.09276	0.17994	0.56423

9-15. From the following data obtained by L. F. Nims [*J. Am. Chem. Soc.*, **55**, 1946–1951 (1933)] for the cell:

$$(\mathrm{Pt})\mathrm{H_2}(\mathrm{g},\ 1\ \mathrm{atm})\left|\begin{matrix}\mathrm{NaH_2PO_4}\ (m_1)\\ \mathrm{Na_2HPO_4}\ (m_2)\\ \mathrm{NaCl}\qquad (m_3)\end{matrix}\right|\mathrm{AgCl(c),\ Ag(c)}$$

the concentrations of the three salts being practically equal, determine the secondary ionization constant of phosphoric acid. Show that a suitable extrapolating function, taking advantage of the Debye-Hückel limiting law, is

$$E + \frac{RT}{1\ \text{g-eq}} \ln \frac{m_3 m_1}{m_2} + \frac{2.303\,RT}{1\ \text{g-eq}}\, 2A\sqrt{\mu}$$

[compare Eqs. (7-4-28) and (7-4-31) and also Prob. 9-14], and plot this function against μ to obtain in the zero-concentration limit, $E^\circ - \dfrac{RT}{1\ \text{g-eq}} \ln K_m^\circ$.

m_1, NaH_2PO_4	m_2, Na_2HPO_4	m_3, NaCl	μ	E_{298}, int volts
0.002689	0.002698	0.002689	0.01347	0.7943
0.005468	0.005486	0.005468	0.02739	0.7738
0.006272	0.006292	0.006272	0.03142	0.7697
0.008750	0.008778	0.008750	0.04383	0.7599
0.01190	0.01193	0.01190	0.05959	0.7506
0.02087	0.02094	0.02087	0.10458	0.7333
0.02874	0.02882	0.02874	0.14393	0.7233

9-16. (*a*) N. Elliot and D. M. Yost [*J. Am. Chem. Soc.*, **56**, 1057–1060, 2797–2798 (1934)] measured the emfs at 25°C of cells in liquid ammonia, of the type

$$\mathrm{Zn(c),\ ZnCl_2{\cdot}6NH_3(c)|NH_4Cl}(m \text{ in } \mathrm{NH_3})|\mathrm{TlCl(c),\ Tl(c)}$$

The actual cells contained amalgam electrodes, but the standard emf, corrected to the pure metals from independent data, had the mean value $E_{298}^\circ = 0.8293$ int volt. Write the cell reaction and calculate its standard free-energy change.

(*b*) From the following data for $NH_3(g)$ at 25°C (Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIIa, p. 100, 1935), determine by graphical integration the fugacity coefficient and fugacity at the vapor pressure, 9.895 atm, and using for $NH_3(g)$ $\bar{F}_{298}^\circ = -3976$ cal/mole (compare Sec. 8-1), calculate $\bar{F}_{298}$ for $NH_3(l)$ under its own vapor pressure.

v, cm^3/g	p, atm	$p\bar{V}$, l atm/mole
	0	(24.465)
1300	1.092	24.179
500	2.786	23.726
300	4.549	23.244
200	6.645	22.636
150	8.618	22.017
128.3	9.895	21.623

(*c*) Using for TlCl(c) $\bar{F}^\circ_{298} = -44{,}190$ cal/mole, calculate from the results of parts (*a*) and (*b*) the standard free energy of formation of $ZnCl_2 \cdot 6NH_3$(c) at 25°C.

(*d*) In a subsequent investigation, C. S. Garner, E. W. Green, and D. M. Yost [*J. Am. Chem. Soc.*, **57**, 2055–2058 (1935)] found for the cell

$$\mathrm{Zn(c),\ ZnCl_2{\cdot}6NH_3(c)|NH_4Cl(}m\mathrm{\ in\ NH_3)|CdCl_2{\cdot}6NH_3(c),\ Cd(c)}$$

the standard emf: $E^\circ_{298} = 0.3605$ int volt. Calculate the standard free energy of formation of $CdCl_2 \cdot 6NH_3$(c).

9-17. The emf of the cell

$$\mathrm{(Pt)H_2(g)|H_2SO_4(}m\mathrm{\ in\ CH_3OH)|Hg_2SO_4(c),\ Hg(l)}$$

has been measured at 25°C by E. W. Kanning and M. G. Bowman [*J. Am. Chem. Soc.*, **68**, 2042–2046 (1946)] with the following results:

m, moles/kg CH_3OH	E'_{298}, corrected to $p_{H_2} = 1$ atm
0.0006999	0.7289
0.0011184	0.7174
0.002412	0.6996
0.005475	0.6805
0.006778	0.6756
0.008111	0.6711
0.022385	0.6509
0.043217	0.6388
0.09688	0.6249
0.24099	0.6098
0.39613	0.6032
0.46964	0.6009

By plotting $(E' + 0.05916 \log m - 0.05916\, A\rho_0^{1/2}\sqrt{m})$ against m for the lower concentrations, where $A = 1.99$ for CH_3OH(l) ($D = 31.5$ at 25°C), and $\rho_0 = 0.787$ kg/liter, show that H_2SO_4 behaves as a strong 1:1 electrolyte in dilute solution in methanol, and determine by extrapolation the value of E°. (Compare Table 9-3, but for this cell reaction, $j = 2$ g-eq/mole H_2SO_4.)

Comparing with $E^\circ = 0.61515$ int volt obtained by H. S. Harned and W. J. Hamer [*J. Am. Chem. Soc.*, **57**, 27–33 (1935)] for the corresponding cell in water, where H_2SO_4 behaves in dilute solution as a 2:1 electrolyte, calculate ΔF°_{298} for the process

$$\mathrm{H_2SO_4(CH_3OH) = H_2SO_4(aq)}$$

where the standard state of H_2SO_4 in $CH_3OH(l)$ is regarded as that of a hypothetical ideal 1:1 electrolyte at 1*m* concentration, and the standard state of H_2SO_4 in $H_2O(l)$ is regarded as that of a hypothetical ideal 2:1 electrolyte at 1*m* concentration. From the fact that at $m = 0.1$ mole/kg in H_2O, the actual emf of the cell is 0.7371 int volt, calculate also (by interpolation) the value of ΔF_{298} for the actual process

$$H_2SO_4(0.1m \text{ in } CH_3OH) = H_2SO_4(0.1m \text{ in } H_2O)$$

(Kanning and Bowman found evidence that the 1:1 dissociation of H_2SO_4 in CH_3OH is incomplete at the higher solute concentrations.)

9-18. The emf of the cell

$$(Pt)H_2(g)|H_2SO_4(m \text{ in HAc})|Hg_2SO_4(c), Hg(l)$$

has been measured at concentrations between 0.002 and 0.87*m* by A. W. Hutchison and G. C. Chandlee [*J. Am. Chem. Soc.*, **53**, 2881–2888 (1931)]. By interpolation of their data, $E_{298} = 0.484$ int volt at $m = 0.1$ mole/kg. Using the data for the corresponding cell in water as solvent, given in the preceding problem, calculate the difference between the thermodynamic potential of H_2SO_4 at 0.1*m* concentration in glacial acetic acid and at 0.1*m* concentration in H_2O. (Because of the low dielectric constant of acetic acid, interionic attraction is relatively large at low ionic concentrations in this medium, and it is not easy to determine $E°$ with precision; apparently H_2SO_4 behaves as a 1:1 electrolyte, but ionization is not necessarily complete; see V. K. LaMer and W. C. Eichelberger [*J. Am. Chem. Soc.*, **54**, 2763–2766 (1932).]

9-19. The exact expression for the cation transference number at a particular concentration m_2 from emf measurements on cells of the type (9-3-4), where m_1 is regarded as constant for the series, has the form

$$t_+ = \frac{dE_t}{dE}$$

where E_t represents the emf of the given cell, with the liquid junction, and E represents the emf of the corresponding cell (9-3-3), without the liquid junction, both E_t and E being taken at the same value of m_2. For convenience, this relationship may be put in the equivalent form

$$t_+ = \frac{(dE_t/d \log m_2)}{(dE/d \log m_2)}$$

From the following selected data obtained for the cell (9-3-4) by T. Shedlovsky and D. A. MacInnes [*J. Am. Chem. Soc.*, **58**, 1970–1972 (1936)]:

m_2, moles/kg	E_{298}(with m_1 = 0.10048 mole/kg), int volts
0.0034572	0.136264
0.0052590	0.118815
0.07844	0.009948
0.10048	0.000000

calculate $(\Delta E_t/\Delta \log m_2)$ between the first and between the second pair of concentrations, and using the data between 0.003215 and 0.005619*m* and between 0.05391 and 0.1238*m* from Table 9-3, calculate likewise $(\Delta E/\Delta \log m_2)$. In this way, calculate mean values of t_+ between 0.003 and 0.006*m* and between 0.08 and 0.10*m*. (Still greater precision in the "instantaneous" value of t_+ could be obtained from a graphical plot of E_t vs. E, constructed on a large scale, but the moving-boundary method is superior for the direct measurement of transference numbers.)

9-20. The emf of the cell

$$\mathrm{Zn(Hg)}|\mathrm{ZnI_2}(0.3m)||\mathrm{ZnI_2}(m)|\mathrm{Zn(Hg)}$$

has been measured at 25°C by R. H. Stokes and B. J. Levien [*J. Am. Chem. Soc.*, **68,** 1852–1854 (1946)], who obtained for $m = 0.1$ mole/kg, $E = -0.02689$ int volt, and for $m = 1.0$ mole/kg, $E = +0.04090$ int volt. They also measured $\gamma_\pm$ for aqueous ZnI_2 solutions by means of an isopiestic vapor-pressure method (equilibration of the vapor phase with standard sulfuric acid solutions having established vapor pressures), with the following results:

m, moles/kg	$\gamma_\pm$
0.1	0.581
0.3	0.564
1.0	0.800

Calculate the mean value of t_+ between 0.1 and $0.3m$ and between 0.3 and $1.0m$ concentrations. (They found that at concentrations greater than $1m$, the value of t_+ decreases abnormally rapidly with increasing concentration, becoming negative above $3.53m$; this indicates complex-ion formation at the higher I^- concentrations.)

9-21. (*a*) The entropy of $KClO_3(c)$ was found to be 34.17 eu/mole at 298.16°K by W. M. Latimer, P. W. Schutz, and J. F. G. Hicks [*J. Am. Chem. Soc.*, **56,** 88–89 (1934)] from low-temperature thermal data. The standard enthalpy of solution at 298.16°K is 9,960 cal/mole, and the solubility is $0.715m$, the activity coefficient in the saturated solution having the estimated value $\gamma_\pm = 0.476$ (by analogy with that of KNO_3). Calculate $\Delta F°$ and $\Delta S°$ for the process

$$\mathrm{KClO_3(c) = KClO_3(aq)}$$

and using for $K^+(aq)$ the independently established value $\sigma_{K^+(aq)} = 24.5$ eu/mole, calculate the entropy of $ClO_3^-(aq)$.

(*b*) The entropies of K(c), $Cl_2(g)$, and $O_2(g)$ are, respectively, 15.2, 53.286, and 49.003 eu/mole, and the enthalpy of formation of $KClO_3(c)$ is $-93{,}500$ cal/mole at 25°C. Combining with the information given in part (*a*), calculate the standard free energy of formation of $KClO_3(aq)$, and using for $K^+(aq)$ the independently established value $\phi'_{K^+(aq)} = -67{,}466$ cal/mole, calculate $\phi'_{ClO_3^-(aq)}$. Combining with information found in the text, calculate the standard oxidation potential of the $ClO_3^-(aq)$, $Cl^-(aq)$ couple in acid and in basic solution

$$\mathrm{3H_2O(l) + Cl^-(aq) = ClO_3^-(aq) + 6H^+(aq) + 6}e$$
$$\mathrm{6OH^-(aq) + Cl^-(aq) = ClO_3^-(aq) + 3H_2O(l) + 6}e$$

9-22. From the standard electrode potentials

$$\mathrm{Mn^{++}(aq) + 4H_2O(l) = MnO_4^-(aq) + 8H^+(aq) + 5}e; \qquad E° = -1.52 \text{ volts}$$
$$\mathrm{MnO_2(c) + 2H_2O(l) = MnO_4^-(aq) + 4H^+(aq) + 3}e; \qquad E° = -1.67 \text{ volts}$$

(W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, 1938), calculate the standard oxidation potentials of the $MnO_4^-(aq)$, $Mn^{++}(aq)$ and the $MnO_4^-(aq)$, $MnO_2(c)$ couples in neutral solution, and also in $OH^-(aq)$ solution at unit activity. Calculate also the standard oxidation potential in acid, neutral, and basic solution of the $MnO_2(c)$, $Mn^{++}(aq)$ couple

$$\mathrm{Mn^{++}(aq) + 2H_2O(l) = MnO_2(c) + 4H^+(aq) + 2}e$$

9-23. Using the data in the preceding problem, calculate the thermodynamic equilibrium constant for the reaction

$$3Mn^{++}(aq) + 2MnO_4^-(aq) + 2H_2O(l) = 5MnO_2(c) + 4H^+(aq)$$

and discuss the effect of pH on the equilibrium.

9-24. Calculate the approximate potential of a platinum electrode in a solution containing 1*m* $HClO_4$ and 0.01*m* $FeSO_4$, at the 50 per cent, the 99 per cent, the 99.9 per cent, and the 100 per cent points as the solution is titrated with standardized $KMnO_4$(aq). (Neglect the activity-coefficient effects, which would remain approximately constant during the titration, and neglect also the dilution effect of the added reagent; $HClO_4$ is an extremely slow oxidizing agent in 1*m* solution, and it does not react with Fe^{++}; it is a useful strong acid because of its relatively slight tendency to form complex ions with the metal ions.) What would be the actual cell emfs if the system were coupled with a saturated calomel reference electrode? What would be the potential of the platinum electrode at the end point if the (final) concentration of $HClO_4$ were 0.1*m* instead of 1*m*?

9-25. The effect of a centrifugal field of force has been investigated by R. C. Tolman [*Proc. Am. Acad. Arts Sci.*, **46**, 109–146 (1910); *J. Am. Chem. Soc.*, **33**, 121–147 (1911)]. Using the cell

$$\begin{array}{ll} (Pt)|I_2(0.01m);\ LiI(1m);\ & I_2(0.01m)|(Pt) \\ (r_2 = 29.5\text{ cm}) & (r_1 = 4.2\text{ cm}) \end{array}$$

where r_1 and r_2 denote the distances of the electrodes from the axis of rotation, he obtained the following results at different speeds of rotation, the leads from the cell being taken through mercury contacts, so that the emf could be measured while the cell was rotating:

ν, rps	E, volts
52.3	0.00323
56.2	0.00372
59.2	0.00416
63.8	0.00480
68.3	0.00551
72.4	0.00622

(the highest speed represents a force at the outer electrode equivalent to more than 6000 times ordinary gravity). The passage of 1$\mathfrak{F}$ of electricity through the cell is equivalent to the following net change:

$$\tfrac{1}{2}I_2(0.01m,\text{ at } r_1) = \tfrac{1}{2}I_2(0.01m,\text{ at } r_2)$$
$$t_+LiI(1m,\text{ at } r_2) = t_+LiI(1m,\text{ at } r_1)$$

The centrifugal force per unit mass at the radius r having the well-known form $4\pi^2\nu^2r$, the thermodynamic potential of any component of the solution at given fixed temperature therefore has the form

$$d\phi_i = v_i\,dp - 4\pi^2\nu^2\bar{M}_i r\,dr$$

or since the hydrostatic pressure increases with r at the rate $dp = 4\pi^2\nu^2\rho r\,dr$, where ρ is the density of the solution

$$d\phi_i = -4\pi^2\nu^2(\bar{M}_i - v_i\rho)r\,dr$$
$$(\phi_i)_{r_2} - (\phi_i)_{r_1} = -2\pi^2\nu^2(\bar{M}_i - v_i\rho)(r_2^2 - r_1^2)$$

Write the net free-energy change for the cell reaction, and show that E is given by the theoretical equation (to be expressed in consistent units)

$$jE = 2\pi^2\nu^2(r_2^2 - r_1^2)[\tfrac{1}{2}(\bar{M}_{\mathrm{I}_2} - v_{\mathrm{I}_2}\rho) - t_+(\bar{M}_{\mathrm{LiI}} - v_{\mathrm{LiI}}\rho)]$$

where $j = 1$ g-eq = 96,485 coulombs. Calculate E/ν^2 at each of the given experimental rotational speeds, and show that this quantity is actually constant for the cell. From the mean value, calculate a value of t_+, using the following information for the particular solution: $\rho = 1.096$ g/cm³; $v_{\mathrm{I}_2}/\bar{M}_{\mathrm{I}_2} = 0.2376$ cm³/g; $v_{\mathrm{LiI}}/\bar{M}_{\mathrm{LiI}} = 0.2605$ cm³/g, as determined by Tolman. [In time, the centrifugal force would presumably set up an equilibrium concentration gradient throughout the cell, whereupon the emf would become zero, the ultimate equilibrium state calling for constant thermodynamic potential of each component throughout the system; for solutes of such low molecular weights, however, equilibrium in this sense, between mechanical potential energy and ordinary molecular thermal energy, would not be established for a long time under a force of the magnitude described here. For a recent investigation of this problem, see D. A. MacInnes and B. R. Ray, *J. Am. Chem. Soc.*, **71,** 2987–2992 (1949).]

9-26. $SrCl_2$(c) has the fluorite structure, and according to J. Sherman [*Chem. Revs.*, **11,** 153 (1932)], its lattice energy is 491.8 kcal/mole. Using data found in the text, calculate a theoretical value of the standard electrode potential of the Sr(c), Sr^{++}(aq) electrode, and compare with the observed value.

9-27. (*a*) The dissociation constant for the zinc-cyanide complex ion was measured by H. Euler [*Ber.*, **36,** 3400–3406 (1903)] who obtained

$$\mathrm{Zn(CN)_4^{=}(aq) = Zn^{++}(aq) + 4CN^{-}(aq)}; \qquad K_m = 1.3 \times 10^{-17}$$

Calculate the standard potential of the zinc electrode in an alkaline cyanide solution:

$$\mathrm{Zn(c) + 4CN^{-}(aq) = Zn(CN)_4^{=}(aq)} + 2e$$

(*b*) What must be the least value of the hydrogen overvoltage on zinc so that Zn(c) may be electroplated from a hypothetical ideal solution containing 1*m* CN^-, 1*m* $Zn(CN)_4^{=}$, and 1*m* OH^-, without simultaneous evolution of H_2(g)?

9-28. The standard enthalpy of solution of Ca(c) in acid

$$\mathrm{Ca(c) + 2H^{+}(aq) = Ca^{++}(aq) + H_2(g)}$$

has the value $\Delta H^\circ_{298} = -129.74$ kcal. Using the standard entropy values given in Appendix 2, calculate the corresponding standard entropy of the reaction, and calculate therefrom the standard free-energy change. Use this result to calculate the standard potential of the calcium electrode

$$\mathrm{Ca(c) = Ca^{++}(aq)} + 2e$$

(Compare W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," p. 274, Prentice-Hall, Inc., New York, 1938.)

9-29. Using the free-energy data given in Appendix 2, calculate E° at 25°C for the cell

$$\mathrm{Zn(c)|ZnSO_4(aq,}\ m_2\mathrm{)|Hg_2SO_4(c),Hg(l)}$$

For $m_2 = 1.000$ mole/kg H_2O, the observed emf was found to be 1.4560 int volts (K. Masaki and T. Ikkatai, as reported in Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIIc, p. 1850, 1936); calculate $\gamma_\pm$ for $ZnSO_4$ at that concentration.

9-30. From the entropy data given in Appendix 2, calculate the rate of change at 25°C of E° with temperature for the cell described in the preceding problem.

CHAPTER 10

STATISTICAL MOLECULAR THEORY OF THERMODYNAMICS

The three laws of thermodynamics and the system of relationships logically implied by them contain no assumptions whatever concerning the ultimate structure of matter, and consequently can by themselves give no information on that subject. For example, equation-of-state and heat-capacity data must be introduced into the theory as empirically determined quantities, whose values cannot be deduced by purely thermodynamic reasoning. Nevertheless, the molecular hypothesis, introduced originally in chemistry by Amadeo Avogadro in 1811 and later applied by S. Cannizzaro in 1860 with great success to account for the integral relationships implied by the laws of combining weights and combining volumes in the case of gas reactions, provided a possible mechanical basis for Joule's law in terms of molecular motion. R. J. E. Clausius and James Clerk Maxwell were among the first to ascribe definite mechanical properties to the tiny molecules of a gas, so small as to be invisible, and thus to lay the foundations of the kinetic theory of gases (about 1860). This concept was brilliantly developed along statistical lines by Ludwig Boltzmann during the latter part of the nineteenth century. Boltzmann came eventually to the conclusion that the thermal or internal energy of a material substance consists of nothing more nor less than mechanical energy, kinetic and potential, of the molecules or atoms of which the substance is composed. This energy he supposed to differ from ordinary gross or macroscopic mechanical energy in that the molecules, extremely tiny in size and enormous in number, are moving in random directions, so that no motion of the material substance is perceived by ordinary macroscopic methods of investigation. Such an idea, expressed in general form, is of course quite ancient in origin; but Boltzmann succeeded in deriving quantitative conclusions, such as the correct equation of state of an ideal gas and the correct value for the heat capacity of a monatomic gas. Where Boltzmann's original theory failed, as in the formulas for the heat capacities of diatomic and polyatomic gases, we have since found it necessary to revise the mechanical principles (Newton's laws of motion) that he naturally tried to apply.

The reality of molecular motion, a pure speculation during Boltzmann's time (though it was supported indirectly by the observed broadening of spectral lines resulting from the Döppler effect), was first demonstrated in J. Perrin's quantitative studies of Brownian motion beginning in 1908, following up A. Einstein's theoretical treatment of this problem a few years previously. Experiments with molecular beams, initiated by O. Stern in 1920, have since provided a direct means of measuring molecular velocities and of confirming the velocity-distribution law predicted many years earlier by Maxwell and by Boltzmann.

The quantum theory of atomic and molecular structure was proposed originally by Niels Bohr in 1913, in order to account for the stability of the electronic-nuclear model of the atom stemming from the work of E. Rutherford and for the origin of the characteristic atomic and molecular spectra. It was put on a rational though radically new mathematical foundation in the form of quantum mechanics, beginning in 1926 with the independent work of E. Schrödinger and W. Heisenberg. Quantum mechanics has given us insight into the nature of the internal motions of atoms and molecules, where classical mechanics has failed completely. The thermodynamic methods stemming from Boltzmann's original treatment have thereby become immensely more powerful, so that spectroscopic analyses of atomic and molecular structures have now become the source of some of the most precise modern thermodynamic data. In turn, data derived from purely thermodynamic sources may now be applied to give us valuable information concerning molecular structure; the existence of nuclear spin isomerism in the case of ortho- and parahydrogen, for example, was first indicated by the lack of agreement between the observed heat capacity and the original theoretical calculations for $H_2(g)$ at low temperatures.

Even more significant, however, from the general theoretical point of view has been the interpretation in terms of statistical properties of a many-molecule system of such thermodynamic concepts as temperature and entropy. We suppose that a system consisting of an enormous number of molecules must have an enormous number of different detailed states that pass for a given thermodynamic state, in view of the relative coarseness of thermodynamic methods of investigation. The second law of thermodynamics then turns out to be a statistical law, whose reliability rests on the enormous sizes of the populations with which thermodynamics is concerned. The thermodynamic equilibrium state corresponding to a given set of externally imposed conditions is merely that apparent or thermodynamically sensible state to which the greatest number of detailed states corresponds, with a probability that becomes all but a certainty when the detailed state is as complex as we have reason to believe it must be for ordinary material systems, containing the order of 10^{23} molecules in random motion.

The treatment of our subject falls into two general parts. First, there is the development of the statistics of a material system having a complex structure, from which we may derive statistical analogues of the fundamental thermodynamic relationships (Sec. 10-1), with particular application to certain classes of systems (Sec. 10-2); then comes the introduction of specific mechanical properties for the constituent molecules, from which, within certain limitations, the statistical laws permit us to calculate the values of the thermodynamic properties (Secs. 10-3 to 10-5). Within the range of this chapter, we cannot attempt a rigorous discussion of the physics underlying the statistical method; such discussion comes properly within the scope of statistical mechanics, for which a number of excellent reference works are cited at the end of the chapter. We shall confine ourselves here to the development in a reasonably logical order of the fundamental principles used directly in chemical thermodynamic calculations and their application to some of the simpler types of molecular systems. This necessarily brief treatment may well serve as an introduction to further study of one of the most brilliant intellectual achievements in the entire realm of scientific thought.

10-1. The Gibbs Assembly. The most generally satisfactory approach to the statistical problem is one conceived originally by J. Willard Gibbs.[1] Let us imagine an assembly of a large number N of replicas of the system in which we are interested, loosely coupled with constant total energy E. In using the term "system" in this sense, we mean generally the entire thermodynamic or macroscopic system, complete with all its constituent parts; for example, the system might consist of a sample of nitrogen gas, containing a specified number of molecules confined within a volume of specified size, the same for all systems of the assembly during any given investigation. The loose coupling implies that the systems are free to exchange energy, without other specific effects on each other; for example, the cylinders containing the different samples of nitrogen gas might be brought in thermal contact with each other, without mixing of their material contents. In such circumstances, the behavior of any one system will be the same as though it were in a "heat bath" or thermostat, consisting of the other $N - 1$ systems. Its energy and other properties may fluctuate as it interacts with the other members of the assembly, but so long as we provide that only thermal interchange takes place among them, then the behavior of the individual system will be independent of the nature of the heat bath and of the particular interchange mechanism,

[1] J. Willard Gibbs, "Elementary Principles in Statistical Mechanics Developed with Especial Reference to the Rational Foundation of Thermodynamics," Charles Scribner's Sons, New York, 1902; reprinted in "The Collected Works of J. Willard Gibbs," Vol. II, Longmans, Green & Co., Inc., New York, 1928.

in accord with our experience in dealing with the behavior of ordinary thermodynamic systems. In fact, we may suppose that the entire assembly, which constitutes essentially an isolated supersystem, will tend toward a state of thermodynamic equilibrium, whose attainment we may hasten in principle by starting the systems off initially distributed with respect to individual system energies according to the ultimate equilibrium law for the assembly which we now propose to investigate. It is our basic premise that the statistics of such an assembly determines the probability of our finding the actual system in any particular one of its system states, when it is in thermal equilibrium with a thermostat of specified temperature. Since there is no limit to the number of virtual systems we may include in the assembly, the statistical treatment will give us *statistical* results whose reliability may be made as high as we please, within statistical limitations; we must necessarily abandon the hopelessly complex task of following the behavior in molecular detail of an individual material system.

We shall suppose that an individual system of the particular type under consideration may exist in any one of a number of *system states*, which we may enumerate; let the corresponding *system energies* be represented by $E_1, E_2, E_3, \ldots, E_j, \ldots$.[1] Then a particular state of the *assembly* will be defined by a statement of the particular system state in which each individual system happens to be (*e.g.*, system 1 in system state E_7, system 2 in system state E_1, system 3 in system state $E_4, \ldots$, system N in system state E_j). Now, in a strict quantum-mechanical sense, this statement is meaningless. If the systems are allowed to interact with each other, then the system states of the individual systems lose their identity, and become merged in states that can be identified only as belonging to the assembly as a whole. However, if the assumed interaction is sufficiently weak (thermal contact among the systems might be maintained, for example, by bathing them in an inert gas, serving merely as a convective heat interchanger), then the situation we have assumed leads to practically the same results as one would obtain by a more rigorous quantum-mechanical treatment;[2] we shall suppose that no harm is done in the

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[1] Where several different system states happen to have the same energy (a so-called degenerate energy value), we shall nevertheless consider them all to be numbered serially, assigning them for the present different symbols to represent their equal energy values, so that to each different state, there will correspond a different value of the running integer j. The generalization for the case of a series of states whose energies differ by continuous degrees is straightforward, the sums appearing in the following argument being replaced by appropriate integrals, but in order to avoid complicating the discussion, we shall not take this case into consideration specifically at this point.

[2] One might set up the assembly in rigorous terms by first examining the behavior

present instance when we speak of localized system energies, whose sum over all members of the assembly is equal to the fixed total assembly energy E.

Let us proceed to classify the assembly states according to the numbers of systems occupying the various system-energy levels. A particular class of states is represented by the set of numbers, N_1, N_2, N_3, . . . , N_j, . . . denoting, respectively, the numbers of systems occupying the system states whose energy levels are represented by E_1, E_2, E_3, . . . , E_j, ... Each state of the assembly is included within some one of the different classes corresponding to different sets of the numbers N_1, N_2, N_3, . . . , N_j, . . . consistent with the general conditions

$$N_1 + N_2 + N_3 + \cdots + N_j + \cdots = \sum_j N_j = N \qquad (10\text{-}1)$$

$$N_1E_1 + N_2E_2 + N_3E_3 + \cdots + N_jE_j + \cdots = \sum_j N_jE_j = E \qquad (10\text{-}2)$$

The *number of assembly states* P belonging to the class (N_1, N_2, N_3, . . . , N_j, . . .) is given by the well-known combination law

$$P = \frac{N!}{N_1!\,N_2!\,N_3! \cdots N_j! \cdots} \qquad (10\text{-}3)$$

We have introduced no restrictions whatever of a mechanical nature on the system state that an individual system may occupy, except for the automatic restriction implied by Eq. (10-2). We are supposing indeed that at a given moment, individual members of the assembly may be found occupying states of widely differing system energies, but we are hopeful that the *average* system energy, E/N, when the assembly is at equilibrium, may be identified with the system energy given by thermodynamic measurements on the individual system in some corresponding thermodynamic state. In fact, *any* system state whose energy is not so large as to exceed the total energy E ascribed to the assembly is theoretically accessible at any time to any individual system, though as a result of chance and the general limitations imposed by conditions (10-1) and (10-2), some states may turn out to be more frequently or more densely occupied than others; the determination of the relative frequencies or probabilities of the various system states constitutes of course the key

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of N completely independent systems, and then introducing the weak interaction as a second-order perturbation of the first-order equations of motion for N independent systems. Fundamental questions of this kind have been explored in advanced theoretical treatises, such as that of J. von Neumann, "Mathematische Grundlagen der Quantenmechanik," Springer-Verlag, Berlin, 1932; reprinted by Dover Publications, Inc., New York, 1943.

to the problem we have undertaken to solve. How then does chance enter the picture? We make the *fundamental statistical assumption* that *each different assembly state is equally likely*. This assumption is inherently plausible, since if an individual system is capable of falling in any system state accessible under the given conditions, then there is no a priori reason why one particular disposition of individual systems among the system states should be preferred over any other particular disposition; the greater likelihood of one *system state* over another is supposed to be the result merely of statistical pressure, as we shall presently see.[1]

In principle, we should be able to derive such a postulate from the general mechanical laws governing the motion of the systems and the assembly. In practice, however, even the three-body problem can be solved only by means of approximation methods, and the mechanics of a many-system assembly (or of a many-molecule system) is far too complicated for its detailed state to be predicted from one moment to the next. In abandoning any effort to plot the detailed state of the assembly by making use of the established mechanical equations of motion (classical or quantal, as the case may be), we require a statistical postulate to make up for the deficiency in our state of knowledge. The essential correctness of the postulate chosen is judged not so much by its inherent plausibility as by the correctness of the statistical results that follow from it. The statistical properties of the assembly are therefore to be derived by *averaging over all accessible assembly states*, each different assembly state (consisting of a detailed account of the particular system state each individual system occupies) being counted as *equally likely*. The average properties of a system in such an assembly are then taken in accordance with the underlying philosophy of the Gibbs assembly to represent the time-average behavior of the actual prototype system when in thermal equilibrium with a large thermostat or heat bath.

The problem of averaging over all accessible states of the assembly when N is large (and one should bear in mind that since the assembly is

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[1] The situation is not unlike that encountered in the dealing of a poker hand, where any combination of five *particular* cards is as likely as any other (assuming an honest deal, unbiased by preceding runs). We recognize in poker certain conventional classes of hands as having special values, and we may calculate the probabilities of their occurrence (*e.g.*, the probability of drawing three of a kind) by straightforward counting methods, counting the number of favorable combinations in relation to the total number of different possible hands. If we should happen to hold three kings and draw an additional card, then the chance of drawing the fourth king is precisely the same as the chance of drawing any other *particular* card, such as the seven of spades, but the chance of drawing the king is obviously different from the chance of *not* drawing the king; there are many more unfavorable cards than the one favorable card, although each individual card is equally likely.

purely mentally conceived, one may always let $N \to \infty$ when necessary, without having to worry about the expense of the project) has been solved in an elegant manner by C. G. Darwin and R. H. Fowler.[1] It turns out that as N is increased without limit, an extremely sharp maximum develops in P as a function of the numbers $(N_1, N_2, N_3, \ldots, N_j \ldots)$, so that an overwhelming fraction of the total number of assembly states comes to be included within classes whose numbers $(N_1, N_2, N_3, \ldots, N_j, \ldots)$ differ but slightly from the set for which P assumes its maximum value, consistent with N and E. Therefore, average properties of the assembly, or of systems as members of the assembly, may be computed with insignificant error for most purposes on the assumption that the systems are distributed among the system states according to whatever set of numbers $(N_1, N_2, N_3, \ldots, N_j, \ldots)$ gives rise to maximum P in Eq. (10-3), subject to the conditions (10-1) and (10-2). The mathematics for computing this distribution corresponding to maximum P is relatively simple, whereas that of Darwin and Fowler for computing directly the true average properties of the assembly is highly abstract. Therefore we shall derive the conditions for maximum P, and thereafter assume that assembly states differing significantly from the class of assembly states corresponding to maximum P contribute inappreciably to the average properties of the assembly. This procedure is legitimized a posteriori by the results of the rigorous Darwin-Fowler treatment of the problem.

We seek the set of numbers $(N_1, N_2, N_3, \ldots, N_j, \ldots)$ that make P a maximum, subject to conditions (10-1) and (10-2). Let δN_1, δN_2, $\delta N_3, \ldots, \delta N_j, \ldots$ represent variations in the numbers N_1, N_2, $N_3, \ldots, N_j, \ldots,$ introduced in order to test the behavior of P; then conditions (10-1) and (10-2) may be put in the form

$$\sum_j \delta N_j = 0 \qquad (10\text{-}4)$$

$$\sum_j E_j\, \delta N_j = 0 \qquad (10\text{-}5)$$

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[1] C. G. Darwin and R. H. Fowler, *Phil. Mag.*, (6) **44**, 450–479, 823–842 (1922); R. H. Fowler, *ibid.*, **45**, 1–33, 497–516 (1923). Their method constitutes the logical foundation of the general treatise by R. H. Fowler, "Statistical Mechanics," 2d ed., Cambridge University Press, New York, 1936. In order to follow the mathematics, the student needs some familiarity with contour integration of functions of a complex variable, as treated, for example, by N. W. McLachlan, "Complex Variable and Operational Calculus with Technical Applications," Part I, The Macmillan Company, New York, 1947. See also the lucid discussion of the method given by E. Schrödinger, "Statistical Thermodynamics," Chap. VI, Cambridge University Press, New York, 1946.

Instead of seeking the maximum in P itself, it is more convenient mathematically to seek the maximum in ln P

$$\ln P = \ln N! - \sum_j \ln N_j! \tag{10-6}$$

for then we may introduce Stirling's approximation for the logarithms of the large factorial numbers appearing in the theory[1]

$$\ln N_j! \sim N_j \ln N_j - N_j \qquad (N_j \text{ large}) \tag{10-7}$$

In view of (10-7), Eq. (10-6) assumes the approximate form (exact in the limit as $N \rightarrow \infty$)

$$\ln P = N \ln N - \sum_j N_j \ln N_j \tag{10-8}$$

Therefore for maximum P or ln P subject to the conditions (10-4) and (10-5), we are to solve the equation

$$\delta \ln P = -\sum_j \ln N_j \, \delta N_j = 0 \quad (E, N \text{ const}) \tag{10-9}$$

or

$$\sum_j \ln N_j \, \delta N_j = 0 \qquad (E, N \text{ const}) \tag{10-10}$$

We may solve the system of simultaneous linear equations (10-10), (10-4), and (10-5) most conveniently by means of Lagrange's method of undetermined multipliers.[2] Let us multiply Eq. (10-4) by an arbitrary constant A and Eq. (10-5) by another arbitrary constant B, whose values are subsequently to be determined, and then add the resulting equations

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[1] This approximation formula, which follows from the series expansion

$$N! = \left(\frac{N}{e}\right)^N (2\pi N)^{1/2} \left(1 + \frac{1}{12N} + \frac{1}{288N^2} - \cdots\right)$$

when N is sufficiently large, was published by James Stirling during the eighteenth century. A rigorous proof is given by E. T. Whittaker and G. N. Watson, "A Course in Modern Analysis," pp. 251–253, The Macmillan Company, New York, 1943 (see also T. C. Fry, "Probability and Its Engineering Uses," pp. 103–107, D. Van Nostrand Company, Inc., New York, 1928), but the reader may convince himself of the accuracy of the approximation (10-7) by empirical test. One should recall in connection with the use of the approximation (10-7) that the number of systems in the assembly, and the proportional numbers of systems occupying the various system states, may be made as large as one pleases. The Darwin-Fowler treatment does not require the use of Stirling's approximation, but nevertheless calls for indefinitely large N, or, more precisely, an indefinitely large number of different accessible assembly states.

[2] Compare the use of this method in Sec. 7-1.

to (10-10); we thus obtain

$$\sum_j (A + BE + \ln N_j)\delta N_j = 0 \qquad (10\text{-}11)$$

where the variations δN_1, δN_2, δN_3, . . . , δN_j, . . . are now freed from restrictions, because the values of A and B may be adjusted so as to take up the conditions imposed by Eqs. (10-4) and (10-5); *i.e.*, in view of the two conditions (10-4) and (10-5), we were free anyhow to assign arbitrary values to all but two of the variations δN_1, δN_2, δN_3, . . . , δN_j, . . . , seeking the conditions for maximum P by solving Eq. (10-11) accordingly; while the remaining two variations, say δN_1 and δN_2, would then no longer be arbitrary, but would have to satisfy Eqs. (10-4) and (10-5) in relation to the other δN_j's, we still have at our disposal the two arbitrary constants A and B to complete the solution of Eq. (10-11). Thus, if the variations δN_3, . . . , δN_j, . . . are to be regarded as entirely arbitrary, and independent of each other, then Eq. (10-11) can be satisfied generally only if their coefficients in that equation are each separately equal to zero:

$$A + BE_j + \ln N_j = 0 \qquad (j = 3, 4, 5, \ldots)$$

Equation (10-11) then reduces to

$$(A + BE_1 + \ln N_1)\delta N_1 + (A + BE_2 + \ln N_2)\delta N_2 = 0$$

and while the quantities δN_1 and δN_2 are no longer arbitrary, but have to be adjusted so that Eqs. (10-4) and (10-5) are satisfied, this equation may finally be satisfied if the quantities A and B are so adjusted that the coefficients of δN_1 and δN_2 likewise vanish; in principle, with two such conditions and two adjustable parameters, the adjustment can always be made. Thus, the general solution of Eq. (10-11), and of the simultaneous equations (10-4), (10-5), and (10-10), has the form

$$A + BE_j + \ln N_j = 0 \qquad (j = 1, 2, 3, \ldots, j, \ldots) \qquad (10\text{-}12)$$

In other words, the numbers of systems in the various system states characteristic of the class of assembly states having *maximum probability* are given by the formula

$$N_j = C \exp(-BE_j) \qquad (j = 1, 2, 3, \ldots, j, \ldots) \qquad (10\text{-}13)$$

where we have replaced A by an equivalent constant $C \equiv \exp(-A)$.

We may readily eliminate C by the substitution of (10-13) back in (10-1):

$$\sum_j N_j = C \sum_j \exp(-BE_j) = N$$

Thus

$$N_j = N \frac{\exp(-BE_j)}{\sum_j \exp(-BE_j)} \quad (j = 1, 2, 3, \ldots, j, \ldots) \tag{10-14}$$

The *average* number of systems in the system-energy state E_j is evidently given by the expression

$$\bar{N}_j = \frac{N_j}{N} = \frac{\exp(-BE_j)}{\sum_j \exp(-BE_j)} \tag{10-15}$$

To speak more precisely, Eq. (10-15) represents the average number of systems in the system-energy state E_j when the assembly as a whole is in some one of the assembly states belonging to the class giving rise to maximum P; but as we stated at the outset (without proof, relying on the results of the more rigorous analysis of the problem by Darwin and Fowler), this class turns out to include an overwhelmingly large fraction of all the possible assembly states, when N is made sufficiently large. We may therefore tentatively interpret Eq. (10-15) as representing the frequency or *probability* with which an individual system of the given type, in thermal equilibrium with a relatively large heat bath of specified temperature, will be found in the particular system state E_j. Its *average energy*, $U = E/N$, in these circumstances is represented in a similar sense by the formula

$$U = \frac{E}{N} = \frac{\sum_j E_j \exp(-BE_j)}{\sum_j \exp(-BE_j)} \tag{10-16}$$

The summation over system states

$$Z \equiv \sum_j \exp(-BE_j) \tag{10-17}$$

which recurs throughout our theory, is evidently a property of the particular type of system; it is known as the *partition function* or *state sum* (German: *Zustandsumme;* hence the origin of the symbol Z) for the system. We may thus rewrite Eqs. (10-15) and (10-17) in the compact forms

$$\bar{N}_j = \frac{1}{Z} \exp(-BE_j) = -\frac{1}{B}\left[\frac{d \ln Z}{dE_j}\right]_{B,E_i'} \tag{10-18}$$

$$U = \frac{1}{Z} \sum_j E_j \exp(-BE_j) = -\left[\frac{d \ln Z}{dB}\right]_{E_i} \tag{10-19}$$

where for short, we have introduced subscript E'_j to indicate constant $E_1, E_2, E_3, \ldots, E_{j-1}, E_{j+1}, \ldots$ except E_j itself in the partial derivative represented in Eq. (10-18), and subscript E_j to indicate that *all* E_j's are to be held constant in the partial derivative represented in Eq. (10-19).

Equation (10-16), or Eq. (10-19), presumably determines the value of the parameter B in terms of the average system energy U. We may, however, obtain insight into the physical significance of B more directly by considering an assembly consisting of two different kinds of systems, loosely coupled so that they may exchange energy, but having no other explicit effect on each other's properties. The different pairs of systems in such an assembly might represent, for example, a thermodynamic system consisting of a sample of argon gas in contact with a sample of solid copper (neglecting the effect of surface adsorption on the thermodynamic properties of the copper), or a sample of nitrogen gas separated by a heat-conducting partition from a sample of hydrogen gas; each pair of systems in the assembly would represent the thermodynamic system in some one of its detailed states, these detailed states (*e.g.*, the positions, velocities, energies, etc., of the argon molecules and the copper atoms, or of their own constituent parts) being hidden by the relative coarseness of ordinary thermodynamic methods of investigation. Let the system states of the one kind of system be represented by the corresponding system-energy values $E'_1, E'_2, E'_3, \ldots, E'_i, \ldots$, and let the total number of systems of this kind in the assembly be represented by N'; let the system states of the other kind of system be represented by the system-energy values $E''_1, E''_2, E''_3, \ldots, E''_j, \ldots$, and let the total number of systems of the second kind in the assembly be represented by N''. By the hypothesis of loose coupling (*e.g.*, purely thermal interaction), we suppose that the system states of the one type of system in the case under consideration are not significantly disturbed by the interaction with the other type of system, so that if an individual system of the one type is coupled with an individual system of the other type, then the various possible energy levels for the combined systems are given simply by the sums $(E'_i + E''_j)$ for $i = 1, 2, 3, \ldots, j = 1, 2, 3, \ldots$ of the possible energy levels of the separate systems, where E'_i and E''_j are assumed to be quite independent of each other. A detailed state of such an assembly is now given by a specification of the particular system state occupied by each individual system of both kinds, but the number of such assembly states belonging to the class represented by the distribution $N'_1, N'_2, N'_3, \ldots, N'_i, \ldots, N''_1, N''_2, N''_3, \ldots, N''_j, \ldots$ of the numbers of systems in the various system states is given by the expression

$$P = \frac{N'!}{N'_1!\,N'_2!\,N'_3!\cdots N'_i!\cdots} \cdot \frac{N''!}{N''_1!\,N''_2!\,N''_3!\cdots N''_j!\cdots} \qquad (10\text{-}20)$$

since each different assembly state of the one kind of system may be combined with each different assembly state of the other kind of system to produce a distinct state of the combined assembly. The assembly is subject to the conditions

$$\left.\begin{aligned}\sum_i N'_i &= N'\\ \sum_j N''_j &= N''\end{aligned}\right\} \tag{10-21}$$

$$\sum_i N'_iE'_i + \sum_j N''_jE''_j = E \tag{10-22}$$

As before, it turns out that an overwhelmingly large fraction of all the assembly states consistent with (10-21) and (10-22) when N' and N'' are sufficiently large is included within classes for which $N'_1, N'_2, N'_3, \ldots, N'_i, \ldots, N''_1, N''_2, N''_3, \ldots, N''_j, \ldots$ differ inappreciably from the set of values corresponding to maximum P. Solving for this condition by the same method used previously, but taking cognizance of the fact that while there are two independent material conditions, Eqs. (10-21), there is but a single energy condition, Eq. (10-22), we obtain for the average numbers of systems in the respective system states

$$\left.\begin{aligned}\bar{N}'_i &= \frac{1}{Z'}\exp(-BE'_i) \qquad (i = 1,2,3, \ldots)\\ \bar{N}''_j &= \frac{1}{Z''}\exp(-BE''_j) \qquad (j = 1,2,3, \ldots)\end{aligned}\right\} \tag{10-23}$$

where $Z' \equiv \sum_i \exp(-BE'_i)$ and $Z'' \equiv \sum_j \exp(-BE''_j)$. In other words, the systems tend to be distributed among their respective system states on the average just as though they constituted two independent assemblies, but because of the single energy condition, Eq. (10-22), the value of the parameter B is common to both distributions.

Now, when two different thermodynamic systems are actually brought into loose coupling, so that they may exchange energy in thermal form without otherwise interacting, the most characteristic feature of their behavior is that they tend to reach a *common temperature* (compare Sec. 1-1). Temperature as a precise scientific concept is in fact founded on this idea of ultimate thermal equilibrium, which underlies the use of thermometers for the comparison of different temperatures. The fact that the quantity B, which evidently governs in a general way the statistical behavior of the system when it is loosely coupled to a thermostat, is likewise the same for two different kinds of systems free to exchange thermal energy suggests a functional relationship between B and the temperature. Furthermore, this relationship must necessarily be universal in character, since one may always select some particular kind of system to serve as thermometer and B-meter; its B vs. T relationship, once empirically established, would serve as the standard for other systems with which it might be brought to states of thermal equilibrium (equal B and equal T).

The formal relationship between B and the thermodynamic temperature may be established by the examination of how a general thermodynamic change of state may be interpreted in terms of the statistical behavior of the corresponding Gibbs assembly. The absolute thermodynamic temperature T has uniquely among all other conceivable temperature scales the property that when divided into the element of thermal energy $d'Q_r$ absorbed by the system during any thermodynamically reversible change of state, it yields the differential, dS, of a function (the entropy) whose value depends solely on the state of the system. This unique property of the Kelvin scale has of course given it immense practical advantages over other universal temperature scales, such, for example, as might be based in principle on $\ln T$ instead of T itself.[1] Now, we are obviously going to interpret U, the mean system energy of the members of the assembly, as represented by Eqs. (10-16) and (10-19), to be identical with the thermodynamic internal energy of an individual system in the condition of thermal equilibrium with a relatively large thermostat (represented by the other members of the assembly), assuming that we need not make correction for ordinary mechanical kinetic or potential energy that the system may possess as a whole. How may we establish statistical analogues of such thermodynamic quantities as $d'Q$ and $d'W$? We may evidently write formally

$$U = \sum_j E_j \bar{N}_j \tag{10-24}$$

whence corresponding to a general change of state influencing the average energy of members of the assembly

$$dU = \sum_j E_j \, d\bar{N}_j + \sum_j \bar{N}_j \, dE_j \tag{10-25}$$

We have supposed that the energy levels $E_1, E_2, E_3, \ldots, E_j, \ldots$ may be identified as properties of the individual systems, the same for all members of the assembly. Thus, we are to suppose that the changes dE_1,

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[1] Temperature scales differing from the Kelvin scale merely by a constant proportionality factor, depending on the arbitrary number of degrees assigned to the fundamental interval, belong of course to the same class; thus, the Rankine, or absolute Fahrenheit, scale is equivalent to the Kelvin scale in this respect.

dE_2, dE_3, . . . , dE_j, . . . represented in the second term on the right of Eq. (10-25) correspond to changes in the respective system-energy levels affecting all the systems. If, for example, the individual system were to consist of a sample of nitrogen gas, containing a specified mass or number of molecules, then we might imagine each system to be equipped with a piston by means of which its volume could be adjusted. As we shall observe later, the energy levels open to a gas sample depend in particular on its volume; therefore in setting up the assembly, we should require that each identical sample be adjusted to the same volume, in order that the statistical behavior of the assembly may represent correctly the time-average behavior of an individual sample having that volume. A change such as is represented by the second term on the right of Eq. (10-25) would thus be effected by a change in the setting of each piston, the setting being changed by the same amount throughout all the systems of the assembly. Clearly, we may interpret this term as the *average work* done on the members of the assembly during the change under consideration:

$$-d'W_r = \sum_j \bar{N}_j \, dE_j \tag{10-26}$$

This interpretation is quite general, and does not depend on the particular form in which the energy is introduced. We are entitled to suppose, however, that it takes energy introduced in *nonthermal* form, through the agency of external forces acting on the system, to produce changes in its system-energy levels.

Comparing Eq. (10-25) with the general thermodynamic equation (2-20),

$$dU = d'Q - d'W$$

representing the first law of thermodynamics, we may evidently identify the first term on the right of Eq. (10-25) with the *average heat* absorbed by the members of the assembly during the change under consideration:

$$d'Q_r = \sum_j E_j \, d\bar{N}_j \tag{10-27}$$

In other words, thermal energy is represented in statistical theory as energy absorbed not in changing the properties of the individual system but in changing the relative probabilities of its states, *i.e.*, the relative frequencies with which the system will be found in them under a given set of conditions (given temperature and volume). We have expressed Eqs. (10-26) and (10-27) as applicable to reversible changes of state, in view of the fact that the theory of Eqs. (10-15) and (10-16) is presumably based on average or thermodynamic equilibrium states of the system under statistical investigation.

If these analogies, tentatively advanced, are correct, then it should be possible for us by dividing $d'Q_r$ by T to construct a perfect differential of some statistical property of the assembly that will correspond to the entropy of an individual system. According to Eqs. (10-26) and (10-18),

$$\frac{d'Q_r}{T} = \frac{dU - \sum_j \bar{N}_j \, dE_j}{T} = \frac{dU}{T} + \frac{1}{BT} \sum_j \left(\frac{d \ln Z}{dE_j}\right)_{B, E_i'} dE_j$$

Now, Z is itself a function of B and the E_j's, defined by Eq. (10-17); the change of $\ln Z$ with changes in these variables is given in general by

$$d \ln Z = \left(\frac{d \ln Z}{dB}\right)_{E_i} dB + \sum_j \left(\frac{d \ln Z}{dE_j}\right)_{B, E_i'} dE_j$$

or, in view of Eq. (10-19),

$$d \ln Z = -U \, dB + \sum_j \left(\frac{d \ln Z}{dE_j}\right)_{B, E_i'} dE_j$$

Thus

$$\frac{d'Q_r}{T} = \frac{dU}{T} + \frac{1}{BT} (U \, dB + d \ln Z)$$

Evidently, our objective of creating a perfect differential out of $d'Q_r/T$ is attained if and only if B *is inversely proportional to* T,

$$B = \frac{1}{kT} \tag{10-28}$$

For if B satisfies (10-28) in relation to the absolute thermodynamic temperature T, then

$$\frac{d'Q_r}{T} = d\left(\frac{U}{T}\right) + k \, d \ln Z = d\left(\frac{U}{T} + k \ln Z\right)$$

The proportionality factor k is known as *Boltzmann's constant;* its magnitude depends merely on the relative numerical scale used for the measurement of T, and may be determined by application of the theory to some particular system whose properties have already been established in terms of the thermodynamic temperature T. We shall later demonstrate by applying the theory to a system consisting of an ideal gas [Eq. (10-73) or (10-92)] that k is equal to the molal ideal-gas constant R divided by Avogadro's number N_0

$$k = \frac{R}{N_0} = (1.38048 \pm 0.00050) \times 10^{-16} \text{ erg/deg} \tag{10-29}$$

We may therefore rewrite the fundamental equations (10-17), (10-18), and (10-19) in the forms

$$Z = \sum_j \exp\left(-\frac{E_j}{kT}\right) \tag{10-30}$$

$$\bar{N}_j = \frac{1}{Z}\exp\left(-\frac{E_j}{kT}\right) \tag{10-31}$$

$$U = \frac{1}{Z}\sum_j E_j \exp\left(-\frac{E_j}{kT}\right) = -k\left[\frac{d\ln Z}{d(1/T)}\right]_{E_i} \tag{10-32}$$

We may furthermore identify the entropy function S with the expression

$$S = \frac{U}{T} + k\ln Z \tag{10-33}$$

We may obtain further insight into the statistical interpretation of the entropy function by substituting back in the general formula (10-8) for $\ln P$ the numbers of systems occupying the various system-energy levels $E_1, E_2, E_3, \ldots, E_j, \ldots$ when the assembly as a whole is in one of the assembly states corresponding to maximum P, as given by Eqs. (10-14) [compare also Eq. (10-31) which gives the *average* numbers],

$$\begin{aligned} \ln P_{\max} &= N\ln N - \sum_j \left(\ln\frac{N}{Z} - \frac{E_j}{kT}\right)\frac{N}{Z}\exp\left(-\frac{E_j}{kT}\right) \\ &= N\ln Z + \frac{NU}{kT} \end{aligned}$$

Multiplying through by k/N, and comparing with (10-33),

$$S = \frac{k}{N}\ln P_{\max} \tag{10-34}$$

The entropy of the system thus appears as a measure of how many different assembly states, each supposed to be equally likely, correspond to the class of assembly states giving rise to maximum P. We have already noted (without proof) that this class includes an overwhelming fraction of *all* the accessible assembly states consistent with E and N, when N is sufficiently large. Therefore we may equally correctly state that the entropy of the individual system is identified with a measure of the total number of different assembly states accessible to the assembly under the given set of conditions (fixed N and E). Now, each assembly state is made up from some particular combination of the various system states the individual system may occupy under the given set of conditions (given T, as established by interaction with other members of the assembly, or with a thermostat, and given values of the system-energy levels, $E_1, E_2, E_3, \ldots, E_j, \ldots$). Evidently, the greater the *range* of states that may be occupied simultaneously by members of the assembly (*i.e.*, in view of our basic statistical premise, the greater the range of states that may be covered in the course of time by an individual system, while it is sensibly in the one particular thermodynamic equilibrium state), the greater will be the number of different combinations giving rise to different assembly states, and the greater according to Eq. (10-34) will then be the entropy of the corresponding thermodynamic state, which the statistical behavior of the assembly presumably represents. In this sense, the entropy of the system measures the relative extent to which its detailed states, hidden to ordinary thermodynamic investigation, are mixed up or involved in the given thermodynamic state.

We may express (10-34) also in the equivalent form

$$S = -k \sum_j \bar{N}_j \ln \bar{N}_j \tag{10-35}$$

where $\bar{N}_j = N_j/N$, given by Eq. (10-31), represents the *average* number of systems in the system state j, when the assembly as a whole is in one of the assembly states corresponding to maximum P. Applied to the behavior of an individual system, we may interpret N_j as the *probability* of the system state j, when the system is sensibly in a given thermodynamic equilibrium state; we may suppose that this probability refers to the time-average behavior of the system, as its detailed state undergoes changes imperceptible to the relatively coarse methods of thermodynamic investigation. Using probability P_j in this sense, we may express (10-35) in the form

$$\left.\begin{aligned} S &= -k \sum_j P_j \ln P_j \\ P_j &= \frac{1}{Z} e^{-E_j/kT} \end{aligned}\right\} \tag{10-35a}$$

Equations (10-33) and (10-35) could of course contain an arbitrary additive integration constant, whose value, however, would necessarily be independent of T and of $E_1, E_2, E_3, \ldots, E_j, \ldots$, from the manner in which these relationships were derived [B or T, and the quantities $E_1, E_2, E_3, \ldots, E_j, \ldots$ having been treated as the variables in the initial equation, Eq. (10-24)]. Since we are always concerned with entropy *differences* between states of a thermodynamic system, the particular value assigned to this constant is immaterial, since it will drop out of any self-consistent set of calculations based on Eq. (10-33) that may be subjected to direct experimental verification. We have therefore assigned it for convenience the value 0 for any kind of system, and have left it out of Eqs. (10-33) and (10-35*a*) altogether. This convention is equivalent, however, to Planck's proposal to assign zero entropies to regular crystalline solids at $T = 0$ on the basis of Nernst's empirical generalization (8-3-16); *i.e.*, having set the integration constant in (10-33) and (10-35*a*) equal to zero, we may now prove that under certain general conditions, these equations lead actually to a zero value of S as $T \rightarrow 0$, thereby establishing a logical foundation in statistical theory for the third law of thermodynamics [Eq. (10-24) embodies the first law, and the identification of the statistical quantity B with $1/kT$ in Eq. (10-28) has established the second law]. Thus, suppose that under a given set of original conditions, there are r system states of equal lowest energy[1] open to the system as $T \rightarrow 0$, but that a finite difference exists between their common energy and the energy level associated with the next higher state or group of states; note that this is essentially a quantum theoretical concept. Then when T has become sufficiently small, the exponential factor $\exp(-E_j/kT)$ will become negligibly small for all states except the group of r lowest energy states, for each of which P_j will become equal to $1/r$.[2] Thus

$$\begin{aligned}\lim_{T\rightarrow 0} S &= -k \sum_{j=1}^{r} \frac{1}{r} \ln \frac{1}{r} \\ &= k \ln r \qquad (10\text{-}36)\end{aligned}$$

Now, S is an additive property of the system, and for a system consisting of N_0 molecules, its order of magnitude at ordinary temperatures is kN_0 (*i.e.*, R per mole). Therefore even if r were of order N_0, so that the system had as many different states of the same lowest energy as it has molecules, the value of $k \ln N_0$ would be vanishingly small in comparison with kN_0 (*e.g.*, compare log 10^{23} with 10^{23} itself). Thus, if there is but a single state of the system, or even a single distinguishable state per funda-

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[1] The lowest energy level open to the system may depend on circumstances. For example, if one cools down a sample of silver and a sample of chlorine in chemically equivalent proportions, separated from each other by a partition, then at 0°K this system may settle down into a "lowest" energy state different from that of a sample consisting of the equivalent quantity of AgCl(c), which constitutes essentially a different thermodynamic state of the same system. Under either set of conditions, however, the following argument shows that according to (10-33) or (10-35*a*), the entropy has the same terminal value at $T = 0$.

[2] This proposition may be demonstrated rigorously; see Schrödinger, *op. cit.*, Chap. III.

mental particle present, corresponding to the lowest energy level into which the system may pass as $T \rightarrow 0$, then S given by the statistical formulas (10-33) or (10-35a) vanishes at $T = 0$, in agreement with the empirical evidence summarized in the third law. If, however, each individual molecule may assume either of two different configurations of equal or practically equal energy, so that the system as a whole has 2^{N_0} distinguishable states of lowest equal energy, then $\lim\limits_{T\rightarrow 0} S = kN_0 \ln 2$. In general, if there are g different molecule states of equal lowest energy, then for a system of N_0 independent molecules,

$$\lim_{T\rightarrow 0} S = kN_0 \ln g \tag{10-37}$$

This consideration accounts for certain of the apparent exceptions to Nernst's law, such as N_2O, where apparently the linear but almost symmetrical *NNO* molecules retain random orientation in either of the two positions: *NNO* or *ONN* throughout the crystal lattice as $T \rightarrow 0$. In this case, the third-law entropy is about $R \ln 2$ (actually, 1.14 eu/mole) lower than the value obtained by other experimental and theoretical methods;[1] similarly, a randomness in the orientation of hydrogen bonds in ice crystals has been assumed to account for the discrepancy in the third-law entropy of water.[2] In these cases, the system at 0°K is not necessarily in the state of lowest energy it could conceivably get into, which might be the state of perfect order for which S would be zero; but the slowness with which diffusion and rearrangement of the molecules takes place at the extremely low temperatures for which the small energy differences among the different configurations would become significant [according to the second of Eqs. (10-35a)], effectively freezes in the randomness of orientation that occurs normally [because of the relatively small magnitude of the energy differences among different configurations in cases such as $N_2O(c)$ and ice] at higher temperatures. One sees therefore that the third law of thermodynamics lacks in practice, if not in principle, the generality of the first and second laws; one must always subject third-law entropies based on low-temperature thermal data to independent experimental test, whether in the form of equilibrium measurements involving the particular substance or in the form of calculations based on its spectroscopic properties, as shown in Sec. 10-5.

In the case of an ideal solid solution, we may suppose that the lowest energy state into which the crystal actually gets as it is cooled to zero (not necessarily the lowest state into which it could conceivably get, if it were not for the slowing down of processes such as diffusion under the influence

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[1] R. W. Blue and W. F. Giauque, *J. Am. Chem. Soc.*, **57**, 991–997 (1935).

[2] L. Pauling, *ibid.*, pp. 2680–2684.

of gravity, and other processes which tend to differentiate among the different kinds of particles) is one in which the randomness of distribution of the different kinds of particles throughout the crystal lattice, characteristic of higher temperatures, is retained. Therefore there will be as many distinguishable states (distinguishable in principle, though indistinguishable by the methods of thermodynamic investigation) belonging to this lowest energy level as there are different ways of distributing N_1 identical particles of the one kind and N_2 identical particles of the second kind among the $N_0 = (N_1 + N_2)$ lattice points, assuming that we are concerned with a binary solution. Thus $r = N_0!/N_1!N_2!$, and introducing Stirling's approximation for the logarithms of the large factorial numbers in (10-36),

$$\begin{aligned}\lim_{T\to 0} S &= k(N_0 \ln N_0 - N_1 \ln N_1 - N_2 \ln N_2)\\ &= -kN_0(x_1 \ln x_1 + x_2 \ln x_2) \qquad (10\text{-}37a)\end{aligned}$$

In view of (10-29), this result is identical with the ideal entropy of solution at ordinary temperatures (7-3-32). The relation (10-37*a*) has been confirmed experimentally by E. D. Eastman and R. T. Milner, who showed that a solid solution of AgCl and AgBr containing $x_{\text{AgCl}} = 0.27$ had a third-law entropy from low-temperature heat-capacity measurements 1.03 eu/mole lower than that found by means of emf measurements;[1] if one assumes for the solid solution

$$\bar{S}_0^\circ = -R(0.27 \ln 0.27 + 0.73 \ln 0.73) = 1.16 \text{ eu/mole}$$

instead of zero, then the agreement between the two sets of data becomes excellent.

It remains for us to show that the assembly states in which the individual systems are distributed among system states in a manner differing significantly from the law (10-31) characteristic of maximum P are relatively insignificant in number, *i.e.*, that the laws (10-30)–(10-34) represent accurately the statistical properties of the assembly. As we have previously mentioned, this fact is confirmed most elegantly by means of the rigorous treatment of average properties given by Darwin and Fowler. However, we may readily prove that the maximum in P is indeed extremely sharp when N is taken sufficiently large. Let us introduce in Eq. (10-8) for $\ln P$ the set of N_j values corresponding to maximum P [Eq. (10-14)], and consider the effect of varying all the N_j's slightly; the first-order variation of P or of $\ln P$ of course vanishes, in view of condition (10-10) for maximum P; let us, however, retain the second-order terms. Thus

$$\ln P - \ln P_{\max} = -\sum_j (N_j + \delta N_j) \ln (N_j + \delta N_j) + \sum_j N_j \ln N_j$$

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[1] E. D. Eastman and R. T. Milner, *J. Chem. Phys.*, **1**, 444–456 (1933).

where P represents the number of assembly states belonging to the varied class, whose occupation numbers for the system states are represented by $N_1 + \delta N_1, N_2 + \delta N_2, N_3 + \delta N_3, \ldots, N_j + \delta N_j, \ldots$, subject to the condition $\sum_j \delta N_j = 0$. Taking this condition into consideration, and using also Eq. (10-10),

$$\begin{aligned} \ln \frac{P}{P_{\max}} &= -\sum_j \left\{ (N_j + \delta N_j) \left[\ln N_j + \ln \left(1 + \frac{\delta N_j}{N_j} \right) \right] - N_j \ln N_j \right\} \\ &= -\sum_j (N_j + \delta N_j) \ln \left(1 + \frac{\delta N_j}{N_j} \right) \\ &= -\sum_j (N_j + \delta N_j) \left[\frac{\delta N_j}{N_j} - \frac{1}{2} \left(\frac{\delta N_j}{N_j} \right)^2 + \cdots \right] \\ &= -\sum_j \left\{ \frac{1}{2} N_j \left(\frac{\delta N_j}{N_j} \right)^2 - \cdots \right\} \qquad (10\text{-}38) \end{aligned}$$

Higher terms in the series are of order $N_j\,(\delta N_j/N_j)^3$, and may be neglected for our immediate purpose. Let us consider, for example, a class of assembly states for which each N_j differs from the "most probable" value, as given in Eq. (10-36), by at least the small amount ± 0.01 per cent, so that $(\delta N_j/N_j)^2 \geqq 10^{-8}$ for each value of j; then, according to Eq. (10-38),

$$\ln \frac{P}{P_{\max}} \leqq -\frac{N}{2} \times 10^{-8}$$

Evidently, by taking N sufficiently large we may make $P/P_{\max}$ as small as we please; if, for example, we were to take $N = 10^{10}$, then, in the present example, $P/P_{\max} < 2 \times 10^{-22}$. This represents a vanishingly small probability for the varied class of assembly states, as compared with the "most probable" class. In order to complete the argument, we should want to sum expressions such as this over other classes of assembly states differing from the most numerous class by other arbitrary small amounts, but it is evident that an assembly containing a sufficiently large number of systems can hardly ever get into a state in which the individual systems are distributed among the system states in any other manner than that described by Eq. (10-36), or its equivalent, Eq. (10-31). Therefore we may regard Eqs. (10-30) to (10-33) as accurately describing the average properties of a thermodynamic system in thermal equilibrium with a constant-temperature heat bath. Equation (10-38) may be used for the estimation of fluctuations from average behavior in real assemblies containing finite numbers of "systems," such as the molecular assemblies (actual gases) described in the following section.

It should be emphasized that the statistical method described in this section is entirely general, and may be applied in principle to any kind of system, however complex. In order for us to obtain practical results, of course, it is necessary for us to be able to evaluate the system-energy levels E_1, E_2, E_3, . . . , E_j, ... This may be done accurately only for the simplest types of thermodynamic systems, such as the ideal gas, as we shall observe in the following sections. If we can establish the system-energy levels from some theoretical knowledge of the system's structure, then we are in a position to evaluate the statistical function Z [given by Eq. (10-30)], from which the other thermodynamic properties of the system may be readily derived. One will note that, from Eq. (10-33),

$$kT \ln Z = -(U - TS) = -A \tag{10-39}$$

where A represents the Helmholtz free-energy function, introduced originally by means of Eq. (5-49).

10-2. Statistics of the Ideal Gas. An ideal gas is itself apparently a working model of an assembly of many loosely coupled identical systems, *i.e.*, the molecules comprising it. In real gases at finite pressures, the coupling is presumably not so loose, the energy of a given molecule depending to some extent on the relative locations of its neighbors. While N is finite, so that fluctuations in the average behavior may appear, it is so enormous for the quantities of gas ordinarily under consideration that significant fluctuations may be observed only in minute samples or in highly rarefied gases. If throughout the argument given in the preceding section we regard the "systems" as gas molecules, and the "assembly" as an actual sample of the gas, consisting of N molecules exchanging energy by virtue of elastic collisions of relatively short duration (the precise mechanism being unimportant for our present purpose), then we may obtain formally the following results:

$$\frac{N_j}{N} = \frac{1}{\zeta} \exp\left(-\frac{\epsilon_j}{kT}\right) \tag{10-40}$$

where

$$\zeta \equiv \sum_j \exp\left(-\frac{\epsilon_j}{kT}\right) \tag{10-41}$$

(ζ is not to be confused with Z for the entire gas sample considered as a thermodynamic system, such as we were discussing in the preceding section); furthermore,

$$\bar{\epsilon} = \frac{1}{\zeta} \sum_j \epsilon_j \exp\left(-\frac{\epsilon_j}{kT}\right) = -k\left[\frac{d \ln \zeta}{d(1/T)}\right]_{\epsilon_j} \qquad (10\text{-}42)$$

In these equations, ϵ_j denotes a typical *molecule-energy level* for molecules of the given type, N_j/N denotes the average fraction of all the *molecules* in the particular *molecule state* ϵ_j (what we may regard as the probability of that state compared with all other states under the same general set of conditions), and $\bar{\epsilon}$ denotes the *average molecule energy.* The thermodynamic internal energy of the gas in this case is presumably given by

$$U = N\bar{\epsilon} \qquad (10\text{-}43)$$

corresponding to the assembly energy E in the previous discussion. The temperature of the gas enters the theory essentially in the same way as in our discussion of the Gibbs assembly.

Equation (10-40) is known as *Boltzmann's law.* It was conceived originally by Ludwig Boltzmann during the latter part of the nineteenth century in terms of the concrete physical picture we have just presented, prior to Gibbs' powerful generalization. While there is a formal resemblance between Eqs. (10-40) and (10-31), one should realize that in (10-40) we are presumably discussing the distribution of actual molecules in an actual sample of gas in some one of its thermodynamic equilibrium states, whereas (10-31) represents abstractly the time-average behavior of an entire thermodynamic system (*e.g.*, the gas sample itself) as its detailed internal state undergoes changes imperceptible by the relatively coarse-grained methods of thermodynamic investigation, while it is apparently in a stationary equilibrium state. The difference between the two points of view is reflected in the difference between the thermodynamic interpretations of Eqs. (10-42) and (10-32); the former gives the average energy of a single molecule, whereas the latter gives directly the thermodynamic internal energy of the entire thermodynamic system (which itself is supposed to be an average of a system energy that may fluctuate as the system interacts with a thermostatic heat bath). In order to pass from Boltzmann's view to the thermodynamic properties of the gas, one must introduce an additional hypothesis such as (10-43), which represents the thermodynamic internal energy essentially as the sum of the individual molecule energies. In assigning individual molecule energies whose possible values are constants throughout the gas, Boltzmann's theory is necessarily confined to situations in which molecular interaction is weak, *e.g.*, as in a dilute gas; since the interaction between the systems of a Gibbs assembly, however, is purely mentally conceived (though in principle not beyond the scope of feasible experimentation), the application of Eqs. (10-30) to (10-33) is entirely general, *provided* that we can evaluate in some way the system-energy levels E_1, E_2, E_3, . . . , E_j, . . . of the entire thermodynamic system. Boltzmann's theory suggests how in the case of a dilute gas, at least, we may be able to calculate the thermodynamic properties from a theoretical or empirical knowledge of the energy levels ϵ_1, ϵ_2, ϵ_3, . . . , ϵ_j, . . . of the *individual molecules*, for example, such as by Eqs. (10-42) and (10-43). Boltzmann's theory exploits the molecular hypothesis by ascribing ordinary mechanical properties to the molecules, thereby putting thermodynamics on a purely mechanical foundation from the molecular point of view. At the time of its conception, Boltzmann's theory was a startlingly bold innovation, which met with sharp criticism and considerable opposition; direct experimental evidence for the reality of molecular motion came many years later.

If we push our analogies one step further, and attempt to write an equation for the entropy of the gas, by analogy with Eq. (10-33), we obtain

$$S = \frac{U}{T} + Nk \ln \zeta \quad \text{(wrong equation!)} \qquad (10\text{-}44)$$

At this point, trouble begins; for when we attempt to apply this equation, using proper mechanical laws for evaluating the energy levels ϵ_1, ϵ_2, ϵ_3, . . . , ϵ_j, . . . which enter Eq. (10-41) for ζ (as we shall do in the following sections), while we obtain the proper form for the dependence of S on T and p [see Eqs. (6-39) and (6-41)], the results turn out to be totally inconsistent with those derived experimentally on the basis of the third law of thermodynamics (as described in Sec. 8-3). The source of the difficulty is appreciated when one reviews the situation in the light of concepts inherent in modern quantum theory. The molecular model of a gas differs from a Gibbs assembly in at least one fundamental respect: while the systems of a Gibbs assembly have been conceived as copies of an ordinary macroscopic thermodynamic system, which may be enumerated in principle so that a distinct state of the assembly is properly represented by a statement of the system state each individual system is in, the analogous statement in the case of a molecular assembly is false. No operation is at present known whereby on an atomic or a molecular scale we can tag individual particles without disturbing them otherwise; therefore there is no way of distinguishing even in principle between two "states" of a molecular assembly differing only by the interchange of two identical molecules between molecule states. Quantum mechanics has of course actually capitalized on this cardinal operational principle, with results too well known to call for further comment at this point. But when we speak of identical molecules in quantum-mechanical terms, we really mean it; that is to say, the molecules under consideration are to be regarded as completely indistinguishable from one another, in principle.

We may rescue Boltzmann's theory satisfactorily for our present purpose by returning to Gibb's general point of view, as represented by Eqs. (10-30) to (10-33). Let us consider an assembly consisting of a huge number of samples of the ideal gas under consideration, each containing the same number of molecules N (we used this symbol in Sec. 10-1 to denote the number of samples in the assembly, but let us disregard this previous use, which we now no longer need). Now, in the case of an ideal gas, we may presumably represent the energy E_j of the gas in any one of its system states as the sum of the individual energies of the N molecules (this would not be true of a real gas at finite pressure, where mutual interaction energy represented by van der Waals' forces would have to be taken into consideration; but we may always use standard thermodynamic methods to correct our calculations later for deviations from ideal-gas behavior). If we were to adopt the naïve classical point of view, we might write

$$E_j = \epsilon' + \epsilon'' + \epsilon''' + \cdots + \epsilon^{(N)} \tag{10-45}$$

where ϵ' denotes the energy of the first molecule, which might have any one of the molecule-energy values $\epsilon_1, \epsilon_2, \epsilon_3, \ldots, \epsilon_j, \ldots$, ϵ'' denotes the energy of the second, which might also have any one of the values $\epsilon_1, \epsilon_2, \epsilon_3, \ldots, \epsilon_j, \ldots$, etc. A distinct state of the gas as a whole would then be represented by a set of N particular values drawn from among $\epsilon_1, \epsilon_2, \epsilon_3, \ldots, \epsilon_j, \ldots$ and assigned, respectively, to $\epsilon', \epsilon'', \epsilon''', \ldots, \epsilon^{(N)}$. If it be assumed that any molecule can get into any molecule state, independently of the molecule states occupied by the other molecules (and we make this assumption warily, subject to further discussion later), then the sum over system states, Z, given by Eq. (10-30) would assume the form

$$\begin{aligned} Z &= \sum_j \exp\left(-\frac{E_j}{kT}\right) \\ &= \sum_a \sum_b \sum_c \cdots \sum_s \exp\left(-\frac{\epsilon_a' + \epsilon_b'' + \epsilon_c''' + \cdots + \epsilon_s^{(N)}}{kT}\right) \end{aligned}$$

$$\begin{aligned} \text{where } a &= 1, 2, 3, \ldots, j, \ldots \\ b &= 1, 2, 3, \ldots, j, \ldots \\ c &= 1, 2, 3, \ldots, j, \ldots \\ &\cdots\cdots\cdots\cdots \\ s &= 1, 2, 3, \ldots, j, \ldots \end{aligned}$$

$$\begin{aligned} Z &= \left[\sum_j \exp\left(-\frac{\epsilon_j}{kT}\right)\right]^N \\ &= \zeta^N \end{aligned}$$

Substitution of this result in Eq. (10-33) leads of course to the wrong entropy formula (10-44). We have, however, counted each permutation of the molecule-energy values appearing in an equation of the form (10-45), for a particular set of N such values, as constituting a separate system state of the gas. In view of the indistinguishability of the molecules, each set of N particular molecule-energy values (which in general may possibly include duplications) may be permuted among the N molecules *without* giving rise to a different state of the gas. In the formula for Z given above, we have therefore counted the system states $N!$ too many times. The correct expression for Z should thus have the form

$$Z = \frac{1}{N!}\zeta^N \qquad \text{(ideal gas)} \qquad (10\text{-}46)$$

This amendment does not affect the formula for U [compare Eq. (10-32) with Eqs. (10-42) and (10-43)], which involves only the derivative of $\ln Z$ with respect to $1/T$; the factor $1/N!$ in that case disappears during the differentiation. But it does affect the formula for S, which upon substitution of (10-46) in (10-33) and introduction of Stirling's approximation for $\ln N!$ assumes the form

$$S = \frac{U}{T} + Nk \ln \zeta - Nk(\ln N - 1) \qquad \text{(ideal gas)} \qquad (10\text{-}47)$$

This equation, as we shall see later, gives theoretical results in excellent agreement with experiment.

It is important that we understand clearly the relationship between Eqs. (10-33) and (10-47). We have seen that Eq. (10-33), which presumably applies to any kind of thermodynamic system, in a thermodynamic equilibrium state at any temperature, leads to a zero entropy at $T = 0$, provided that the lowest energy level open to the system as a whole is not highly degenerate. For ordinary material systems, the energy level attained at $T = 0$ belongs to some condensed state of the system, *i.e.*, the crystalline solid for most pure chemical substances.[1] It is to the system in such a state that the limiting value, $\lim_{T\to 0} S = 0$ [described more precisely by Eq. (10-36)], applies; this theoretical result is in agreement (1) with Nernst's empirical law that entropy differences between the various thermodynamic states of the system vanish at $T = 0$ and (2) with Planck's subsequent proposal to assign this common 0°K entropy the conventional value of zero in all cases where degeneracy does not have to be taken into consideration [we have met the requirements of

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[1] Liquid helium-II, which comes into existence below 2.2°K at atmospheric pressure, is anomalous in this respect, and shows other associated remarkable properties.

this convention, which contributes nothing essential to the physical content of Nernst's law, by setting the arbitrary integration constant that might have appeared in Eq. (10-33) equal to zero]. Now, in Eq. (10-47), we have applied Eq. (10-33) to a material system consisting of a dilute gas, having introduced certain assumptions not implied by the general statistical theory concerning the way in which the system energy depends on properties of the constituent molecules. Equation (10-47) then permits us to calculate S for the gas in any thermodynamic state from a knowledge solely of the molecular-energy levels $\epsilon_1, \epsilon_2, \epsilon_3, \ldots, \epsilon_j, \ldots$ through Eq. (10-41) defining the quantity ζ; the value of U may also be calculated for the gas from ζ by means of Eqs. (10-42) and (10-43). Since in originally setting up Eq. (10-33), we provided by suitable adjustment of the integration constant (*i.e.*, by setting it equal to zero) that all entropies should be based on the standard third-law convention, $S_{0°\text{K}} = 0$ for the system in any of its 0°K (crystalline) states, therefore if Eq. (10-47) is correct, it should give us directly entropy values for the gas in agreement with those derived experimentally from heat-capacity and heat-of-transition data by standard thermodynamic means based on the third-law convention (Sec. 8-3).[1]

Equation (10-47) contains terms depending on the thermodynamic state of the gas (as we shall see more explicitly after we have actually evaluated ζ) and also a constant term independent of the thermodynamic state (including the last term on the right, which appeared when we adopted the quantal conception of distinguishing the system states of a molecular system, plus additional constants that appear later when we evaluate ζ). The constant part of S in Eq. (10-47) is *not* to be regarded merely as an integration constant in the ordinary sense; we settled the question of the integration constant once and for all when we set it equal to zero in Eq. (10-33). The constant appearing in Eq. (10-47) enters as a term theoretically demanded by general statistical considerations in order that entropy values computed for the gas, based on a certain physical conception of its structure, should bear the proper numerical relation to the entropy at 0°K of the corresponding crystalline solid (*i.e.*, in the standard third-law entropy reference state). If we know its value, then we can compute, for example, the entire vapor-pressure curve for the solid from purely thermal data (heat capacities and heat of sublimation), without requiring a single equilibrium measurement. One of the most brilliant achievements of quantum mechanics has been the correct evaluation of this constant from general theoretical principles, as we shall presently see.

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[1] Caution! Equation (10-47) itself is not valid at temperatures approaching 0°K for reasons that we shall presently explain.

In deriving Eq. (10-46), we implicitly assumed that each molecule could get into any molecule state independently of the molecule states occupied by other molecules. At sufficiently high temperatures, where it turns out that there are many more molecule states available consistently with the total energy than there are molecules (as we shall confirm later), this assumption turns out to be quite justified, and it has permitted us to derive our theoretical equations, particularly the important equation (10-47), by quite simple mathematics. Even though we include formally in the sum, Eq. (10-41), molecule states running up to indefinitely high energies, no harm is done, because the factor kT appearing in the denominator of each exponential term in the sum serves automatically to cut down the effect on Z of all states with energy values much greater than kT; for example, the term contributed to Z by a state for which $\epsilon_j > 10kT$ is less than 0.00005, as compared with terms of order 1 contributed by each low-energy state. At sufficiently low temperatures, however, where kT gets to be of the order of the lowest molecule-energy values, our assumption may break down, and with it, the validity of formulas such as (10-40), (10-46), and (10-47). For when the total energy is so low that most of the molecules are confined to the lowest energy levels, then the energy required for a molecule to get from a lower to a higher level may be not at all insignificant in comparison with the average energy. This condition may therefore serve to limit the freedom of access of the molecules to the higher states theoretically available to them; *i.e.*, a few molecules in the higher states may account for all the energy, and thereby serve to block other molecules from entering higher states. This is of course a purely quantal notion, for if the molecule energies could vary by continuous degrees, then as the temperature fell, the average energy could decrease indefinitely while individual molecules could still have energies not specifically dependent on those of other molecules; the molecules lose this freedom, however, under conditions such that the only energy values open to them differ by amounts constituting significant fractions of the total energy. Another kind of difficulty arises for certain kinds of particles when at low temperatures their low total energy confines them to the lowest particle states; for certain kinds of particles (including electrons, in particular), the occupancy of a given state excludes other particles from occupying the same state (W. Pauli's exclusion principle).

The statistical problem may be treated generally in the following way: Let $N_1, N_2, N_3, \ldots, N_s, \ldots$ denote, respectively, the numbers of molecules occupying the molecule-energy levels $\epsilon_1, \epsilon_2, \epsilon_3, \ldots, \epsilon_s, \ldots$ for a given state of the gas. Then by the ideal-gas hypothesis, if we assume no specific interaction between the particles, the corresponding energy level of the gas as a whole (the "system" in the sense of Sec. 10-1) is given by

$$E_j = N_1\epsilon_1 + N_2\epsilon_2 + N_3\epsilon_3 + \cdots + N_s\epsilon_s + \cdots$$

Each different set of numbers $N_1, N_2, N_3, \ldots, N_s, \ldots$ gives rise to a different state of the gas, but in view of the indistinguishability of the molecules, a given set corresponds to but a single state of the gas. Substituting in Eq. (10-30),

$$Z = \sum \exp\left[-\frac{1}{kT}(N_1\epsilon_1 + N_2\epsilon_2 + N_3\epsilon_3 + \cdots + N_s\epsilon_s + \cdots)\right] \qquad (10\text{-}48)$$

This expression may be abbreviated to

$$Z = \Sigma z_1^{N_1} z_2^{N_2} z_3^{N_3} \cdots z_s^{N_s} \cdots \qquad (10\text{-}49)$$

where

$$z_s \equiv \exp\left(-\frac{\epsilon_s}{kT}\right) \qquad (10\text{-}50)$$

The sum in Eq. (10-48) or in Eq. (10-49), which represents an accurate generalization of Eq. (10-46) presumably valid at any temperature, is to be taken over all sets of numbers $N_1, N_2, N_3, \ldots, N_s, \ldots$ satisfying the condition

$$N_1 + N_2 + N_3 + \cdots + N_s \cdots = N \qquad (10\text{-}51)$$

The Pauli exclusion case may be taken into consideration by the introduction of the further condition

$$N_s = 0, 1 \qquad (10\text{-}52a)$$

Otherwise, the N_s values may be regarded as unrestricted except for the general condition (10-51); *i.e.*,

$$N_s = 0, 1, 2, 3, \ldots \qquad (10\text{-}52b)$$

The set of equations represented by Eqs. (10-49) to (10-52) is extremely general, and it covers several other important classes of systems consisting of loosely coupled particles besides ordinary material gases. Systems satisfying condition (10-52*a*) are called *Fermi-Dirac gases;* their statistics were developed originally by E. Fermi specifically to take account of Pauli's empirical exclusion principle, but they were discovered independently by P. A. M. Dirac from a somewhat more general point of view.[1] It appears in general that systems consisting of *fundamental material particles*, such as electrons, protons, or neutrons, or of molecules contain-

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[1] E. Fermi, *Z. Physik*, **36**, 902–912 (1926); P. A. M. Dirac, *Proc. Roy. Soc.* (*London*), (A)**112**, 661–677 (1926).

ing *odd numbers of fundamental particles* (*e.g.*, D atoms, but not D_2 molecules, H_2 molecules, or H atoms), satisfy Fermi-Dirac statistics. Systems satisfying condition (10-52*b*) are called *Bose-Einstein* gases; their statistics were developed originally by S. N. Bose, who succeeded in deriving Planck's thermal radiation law by treating radiation as a "gas" consisting of photons; the extension of the statistical treatment to material gases was developed by A. Einstein.[1] It appears that systems consisting of *photons* in particular, and of molecules containing *even numbers of fundamental particles*, such as H_2 molecules, He molecules, H atoms, etc., satisfy Bose-Einstein statistics. There are general theoretical reasons in quantum mechanics for the distinction between the two cases.

Equations (10-49) to (10-52) may be solved by application of the so-called method of steepest descent, as shown by E. Schrödinger.[2] One obtains as a result

$$\ln Z = -N \ln C \mp \sum_s \ln \left[1 \mp Ce^{-(\epsilon_s/kT)}\right] \quad \text{(ideal "gas")} \quad (10\text{-}53)$$

where the upper sign refers to the Bose-Einstein case and the lower sign to the Fermi-Dirac case. The average numbers of "molecules" in the various "molecule" states are given by

$$\bar{N}_s = \frac{1}{\dfrac{1}{C} e^{\epsilon_s/kT} \mp 1} \quad \text{(ideal "gas")} \quad (10\text{-}54)$$

where the quantity C, which is a constant over the system (the "gas") in a given thermodynamic state, is determined by the condition

$$N = \sum_s \frac{1}{\dfrac{1}{C} e^{\epsilon_s/kT} \mp 1} \quad (10\text{-}55)$$

Equation (10-53) represents the generalization of Eq. (10-46), and Eq. (10-54) represents the generalization of Boltzmann's law [Eq. (10-40)]. Evidently, Eq. (10-53) reduces to Eq. (10-46), and Eq. (10-54) reduces to Eq. (10-40), whenever most of the molecules are in molecule states satisfying the condition

$$Ce^{-(\epsilon_s/kT)} \ll 1 \quad (10\text{-}56)$$

[1] S. N. Bose, *Z. Physik*, **26**, 178–181 (1924); A. Einstein, *Sitzber. preuss. Akad. Wiss., Physik.-math. Klasse*, 261–267 (1924); 3–14 (1925).

[2] Schrödinger, *op. cit.*, Chap. VII; the mathematics is similar to that used by Darwin and Fowler in their treatment of the statistical properties of the assembly in general. For a quite different mathematical development of the statistics of Bose-Einstein and Fermi-Dirac gases, see E. H. Kennard, "Kinetic Theory of Gases," Chap. X, McGraw-Hill Book Company, Inc., New York, 1938.

For in that case, condition (10-55) reduces to

$$N \sim \sum_s Ce^{-\epsilon_s/kT} = C\zeta \quad (Ce^{-\epsilon_s/kT} \ll 1) \qquad (10\text{-}57)$$

where ζ is defined as before, by Eq. (10-41).[1] In the general case, however, we cannot solve Eq. (10-55) explicitly for C in terms of familiar analytical functions of N and the quantities ϵ_s; instead, given the energy-level values $\epsilon_1, \epsilon_2, \epsilon_3, \ldots, \epsilon_s, \ldots$ in particular cases, we are then compelled to rely on approximation methods involving some degree of complexity.[2]

Fortunately for our present purpose, condition (10-56) turns out to be satisfied by all known material gases at ordinary temperatures, as we shall see in Sec. 10-4. Only helium and hydrogen remain gases under ordinary pressures at temperatures sufficiently low so that deviation from the "classical" Boltzmann distribution law (10-40) and the "semiclassical" entropy law (10-47) has any chance of becoming detectable; even in those cases, the predicted effect at the respective normal boiling points of the liquids turns out to have the order of magnitude only of the van der Waals deviation from ideal-gas behavior. We may therefore proceed with confidence on the basis of Boltzmann's distribution law, Eq. (10-40), as representing correctly the average distribution of the molecules among molecule states in material gases, and Eqs. (10-42), (10-43), and (10-47) as representing the statistical foundation of the thermodynamic properties, in all ordinary applications except possibly at the lowest attainable temperatures for those gases having the lowest molecular weights.

The general statistical theory of the ideal "gas" represented by Eqs. (10-53) to (10-55) has, however, met with conspicuous success in the cor-

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[1] The terms ln $(1 \mp Ce^{-\epsilon_s/kT})$ in Eq. (10-53) then reduce approximately to $\mp Ce^{-\epsilon_s/kT}$; upon the substitution of (10-57), the resulting expression for ln Z then becomes the same as that derived from (10-46) upon introduction of Stirling's approximation for ln $N!$.

[2] See Schrödinger, *op. cit.*, Chap. VIII; see also Kennard, *loc. cit.* Equation (10-55) may be expanded in the form of the series

$$N = C\zeta\left[1 \pm \frac{C}{\zeta}\sum_s e^{-2\epsilon_s/kT} + \frac{C^2}{\zeta}\sum_s e^{-3\epsilon_s/kT} \pm \cdots\right] \qquad (10\text{-}55a)$$

Since each series of exponential terms is going to have the order of magnitude of ζ itself, we can readily see that condition (10-57) will be met if $C \ll 1$; this condition in turn will follow if $\zeta/N \gg 1$, which may be taken as equivalent to (10-56). We shall show in Sec. 10-4 that this condition is in fact satisfied by all known material gases at ordinary temperatures.

relation of several diverse classes of problems where Boltzmann's law fails. Three cases may be noted. As we have already indicated, S. N. Bose, by treating thermal radiation within a hollow enclosure whose walls are maintained at constant temperature as a photon "gas," succeeded in deriving Planck's black-body thermal radiation law in a most elegant manner;[1] in this case, it is assumed that $C = 1$ and $\epsilon_s = h\tilde{\nu}_s$ in Eq. (10-54), the upper (minus) sign applying. The condition $C = 1$ corresponds to the presence of an indefinite number of photons within the enclosure, since it is supposed that the number may change by reaction with the walls; h represents Planck's constant, and ϵ_s the energy of a photon corresponding to radiation of frequency $\tilde{\nu}_s$. Equation (10-54) then represents the average numbers of photons corresponding to radiation with various frequencies $\tilde{\nu}_s$, from which one may readily derive Planck's law for the distribution of radiant energy with frequency.[2] The second important case treated successfully by the methods of quantum statistics is that of the relatively dense electron "gas" in metals. Although metals contain electrons more or less free to move independently of each other, as shown by the electrical conductivity (and indirectly by the related thermal conductivity), it is a well-known fact that these "free" electrons contribute negligibly to the thermodynamic properties at ordinary temperatures; the heat capacity of a metal, for example, can be calculated accurately by theoretical methods (*e.g.*, Debye's method) that ignore completely the presence of the electrons. A. Sommerfeld first solved this problem by treating the free electrons in a metal as a Fermi-Dirac gas, which on account of the relatively small mass of the electron and the high electron density in the metallic state turns out to be in a highly degenerate state at ordinary temperatures; *i.e.*, most of the "free" electrons are in the lowest energy levels consistent with the exclusion principle.[3] This first successful theory of the metallic state has had far-reaching consequences in the development of the general theory of the solid state.[4] The third case to which nonclassical statistics has been applied is that of liquid helium-II. F. London has shown that certain properties of this remarkable fluid are in agreement with what one would expect of a Bose-Einstein gas in the completely degenerate

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[1] Bose, *loc. cit.*

[2] See Shrödinger, *op. cit.*, Chap. IX.

[3] A. Sommerfeld, *Z. Physik*, **47**, 1–32, 43–60 (1928). See also the reviews of the theory by A. Sommerfeld and H. A. Bethe, Elektronentheorie der Metalle, "Handbuch der Physik," Vol. XXIV/2, Springer-Verlag, Berlin, 1933; K. K. Darrow, *Rev. Modern Phys.*, **1**, 90–155 (1929); J. C. Slater, *ibid.*, **6**, 209–280 (1934).

[4] See, for example, N. F. Mott and H. Jones, "Theory of the Properties of Metals and Alloys," Oxford University Press, New York, 1936; F. Seitz, "The Modern Theory of Solids," McGraw-Hill Book Company, Inc., New York, 1940.

state; the strange behavior of such a "gas" (superfluidity, second sound, etc.) apparently results from the presence of many molecules in the ground state of zero translational velocity.[1] It has recently been shown that liquid He^3, which should obey Fermi-Dirac rather than Bose-Einstein statistics, fails to pass into a superfluid state at temperatures down to 1.05°K, well below the temperature of 2.19°K at which He^4-II comes into existence at atmospheric pressure,[2] but it is still too soon for anyone to know what the actual behavior of such a fluid is like. It is beyond our present scope to discuss further the properties of these extraordinarily interesting nonclassical systems. The reader will find an excellent account by J. E. Mayer and M. G. Mayer in their "Statistical Mechanics."[3]

We may recapitulate the results of this section for the thermodynamic properties of ordinary material gases in the ideal-gas state by means of the following formulas:

$$\zeta \equiv \sum_j e^{-\epsilon_j/kT} \qquad \text{(definition of } \zeta) \qquad (10\text{-}58)$$

$$\bar{U}^\circ - \bar{U}_0^\circ = \frac{N_0}{\zeta} \sum_j \epsilon_j e^{-\epsilon_j/kT} = -R \left[\frac{d \ln \zeta}{d(1/T)} \right]_{\epsilon_j} \qquad \text{(internal energy relative to hypothetical ideal-gas state at 0°K)} \qquad (10\text{-}59)$$

$$\bar{S}^\circ = \frac{\bar{U}^\circ - \bar{U}_0^\circ}{T} + R \ln \zeta - R(\ln N_0 - 1) \qquad \text{(entropy relative to crystalline state at 0°K)} \qquad (10\text{-}60)$$

Equation (10-58) merely defines the molecular partition function ζ. In Eq. (10-59) [compare Eqs. (10-42) and (10-43)], we have introduced explicitly a term $\bar{U}_0^\circ$ to take account of the fact that the implied reference base for *energy* calculations on the gas consists of the *gas molecules* in their state of lowest energy; no account has previously been taken of sublimation energy from the crystalline state (which obviously cannot be calculated purely from gas theory), nor of chemical reaction energy from possible constituents. On the other hand, the entropy value given by Eq. (10-60) [compare Eq. (10-47)] refers for the reasons previously noted to the standard third-law convention. To these equations, we may now add the following:

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[1] F. London, *Nature*, **141**, 643–644 (1938); *J. Phys. Chem.*, **43**, 49–69 (1939). See also L. Tisza, *Compt. rend.*, **207**, 1035–1037, 1186–1189 (1938).

[2] D. W. Osborne, B. Wienstock, and B. M. Abraham, *Phys. Rev.*, **75**, 988 (1949).

[3] J. E. Mayer and M. G. Mayer, "Statistical Mechanics," John Wiley & Sons, Inc., New York, 1940.

$$\bar{C}_v^\circ = \left(\frac{d\bar{U}^\circ}{dT}\right)_{\epsilon_j} = \frac{N_0^2}{\zeta RT^2}\left[\sum_j \epsilon_j{}^2\, e^{-\epsilon_j/kT} - \left(\sum_j \epsilon_j e^{-\epsilon_j/kT}\right)^2\right] \tag{10-61}$$

$$= \frac{R}{T^2}\left[\frac{d^2\ln\zeta}{d(1/T)^2}\right]_{\epsilon_j} \tag{10-62}$$

We may derive a theoretical equation for the pressure of the gas by introducing (10-46) in (10-39), and taking advantage of the general thermodynamic relation (6-56),

$$p = -\left(\frac{dA}{dV}\right)_T = NkT\left[\frac{d\ln\zeta}{dV}\right]_T \tag{10-63}$$

We shall use this equation later to derive the ideal-gas equation of state from purely mechanical principles; so far, the only physical assumption concerning the nature of the gas has been that its molecules have independent energy values. The generalization of (10-63) for a Bose-Einstein gas or a Fermi-Dirac gas including the nonclassical temperature range is obtained by substituting (10-53), in place of (10-46), in Eq. (10-39).

The following relations are also useful:

$$\bar{H}^\circ - \bar{H}_0^\circ = \bar{U}^\circ - \bar{U}_0^\circ + RT \tag{10-64}$$

$$\bar{C}_p^\circ = \bar{C}_v^\circ + R \tag{10-65}$$

$$\frac{\bar{F}^\circ - \bar{H}_0^\circ}{T} = \frac{\bar{H}^\circ - \bar{H}_0^\circ}{T} - \bar{S}^\circ = -R\ln\zeta + R\ln N_0 \tag{10-66}$$

Equation (10-64) merely represents the ideal-gas enthalpy, given in general by $\bar{H} \equiv \bar{U} + p\bar{V} = \bar{U} + RT$, in terms of the theoretical internal energy determined by (10-59). The constant $\bar{H}_0^\circ$ is of course the same as $\bar{U}_0^\circ$, and from the standpoint of statistical theory, must be regarded as empirically determined, *i.e.*, by standard thermochemical means; it is the only arbitrary constant entering the statistical theory of the ideal gas. Actually, its value is significant only in relation to a ΔH° for some chemical transformation or phase transition of the gas; ΔH_0° for the change in question is then determined by comparing ΔH° deduced from theory according to Eqs. (10-59) and (10-64), involving the unknown constant, ΔH_0° or ΔU_0°, with the experimental value of ΔH° as determined by conventional thermochemical methods at some one particular temperature (*e.g.*, the standard temperature: $T = 298.16°\text{K}$). It is customary to assign to each chemical element in whatever happens to be the stable modification at 298.16°K the value $\bar{H}_0^\circ = \bar{U}_0^\circ = 0$;[1] if that modification

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[1] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D.C., Dec. 31, 1947.

happens itself to be the gas, then that value applies directly in Eq. (10-64); if not, then $\bar{H}_0^\circ$ for the gas [*e.g.*, for $I_2(g)$] must be established essentially from a measurement of $\Delta\bar{H}^\circ$ for the phase transition from the standard form to the gas at some one temperature (as we shall see later). There is no conflict in assigning one and the same element, in a particular allotropic modification, an arbitrary zero enthalpy at both 0°K and 298.16°K (and in fact, at all temperatures), since the "absolute" value of H has significance only in relation to chemical or physical transformations to other forms that may have a separate existence (stable, metastable, or even hypothetical) at the same temperature and pressure. Any change of $\bar{H}^\circ$ for the element in its standard allotropic modification with temperature may therefore simply be cast into the change of $\bar{H}^\circ$ for its compounds and other allotropic forms.

Equation (10-66) represents the simplest and most useful form in which to cast free-energy data derived from statistical molecular sources. Since, in general, $\bar{F} \equiv \bar{H} - T\bar{S}$, the value assigned to $\bar{F}^\circ$ necessarily involves the value assigned to the constant $\bar{H}_0^\circ$; Eq. (10-66) therefore permits us to calculate $\bar{F}^\circ$ in relation to $\bar{H}_0^\circ$ directly in terms of the statistical function ζ. The thermodynamic function $(\bar{F}^\circ - \bar{H}_0^\circ)/T$ is always used in combination with similar functions for other substances for computing standard free-energy *changes* of chemical transformations or phase transitions, *i.e.*, as a term in an expression of the form $(\Delta F^\circ - \Delta H_0^\circ)/T$; therefore it does no harm that the $\bar{H}^\circ$ value [Eqs. (10-64) and (10-59)] and the $\bar{S}^\circ$ value [Eq. (10-60)] implicitly entering its computation according to Eq. (10-66) are based on two different reference states, because in view of the third law, the ΔS_0° value implied in the calculations vanishes, leaving only the ΔH_0° value as an empirical constant for the reaction. In view of Eq. (8-2-1), Eq. (10-66) leads to an elegant theoretical expression for the thermodynamic equilibrium constant of a gas reaction:

$$\ln K_p^\circ = \frac{\Delta H_0^\circ}{RT} - \Delta \ln \frac{\zeta}{N_0} \quad \text{(gas reaction)} \qquad (10\text{-}67)$$

For reactions involving liquid or solid substances with gases, the corresponding $(\bar{F}^\circ - \bar{H}_0^\circ)/T$ values for the condensed phases cannot, of course, be evaluated by the theoretical method for ideal gases outlined in this section. Instead, we must use the thermodynamic formula

$$\frac{\bar{F}^\circ - \bar{H}_0^\circ}{T} = \frac{\bar{H}^\circ - \bar{H}_0^\circ}{T} - \bar{S}^\circ \qquad (10\text{-}68)$$

where, for a substance undergoing no phase transition between 0°K and T,

$$\frac{\bar{H}^\circ - \bar{H}^\circ_0}{T} = \frac{1}{T}\int_{0^\circ\mathrm{K}}^{T} \bar{C}^\circ_p \, dT \tag{10-69a}$$

$$\bar{S}^\circ = \int_{0^\circ\mathrm{K}}^{T} \frac{\bar{C}^\circ_p}{T} \, dT \tag{10-69b}$$

The two integrals may be evaluated graphically from low-temperature heat-capacity data, Eq. (10-69*b*) representing simply the conventional third-law entropy at the temperature T (Sec. 8-3). The modification for a substance that undergoes one or more phase transitions between 0°K and T is sufficiently obvious to call for no special comment.

One further point should be noted before we undertake the evaluation of ζ. If the molecule-energy levels can be represented as sums of several entirely independent contributing terms, then on account of the exponential form in which ϵ_j enters ζ [Eq. (10-58)], ζ separates into a product of several independent factors; since, furthermore, the only form in which ζ then enters any of the thermodynamic functions, Eqs. (10-59) to (10-66), is as $\ln \zeta$, each independent molecule-energy term therefore contributes independently an additive term to each thermodynamic function. In particular, the energy of a free body (*e.g.*, an ideal-gas molecule) in either classical or quantum mechanics is always separable into a translational-energy term, corresponding to the motion of the center of mass, plus an "internal-energy" term, corresponding to relative motion about the center of mass (*e.g.*, relative motions of the constituent atoms, or of their fundamental particles).[1] Thus

$$\epsilon_j = (\epsilon_{tr})_l + (\epsilon_{\mathrm{int}})_m \tag{10-70}$$

where any translational-energy value $(\epsilon_{tr})_l$ may combine with any "internal-energy" value $(\epsilon_{\mathrm{int}})_m$ to produce a characteristic energy level for the molecule. Therefore

$$\zeta = \sum_l \sum_m e^{-\frac{(\epsilon_{tr})_l + (\epsilon_{\mathrm{int}})_m}{kT}} = \zeta_{tr}\zeta_{\mathrm{int}}$$

or

$$\ln \zeta = \ln \zeta_{tr} + \ln \zeta_{\mathrm{int}} \tag{10-71}$$

where

$$\zeta_{tr} \equiv \sum_l e^{-(\epsilon_{tr})_l/kT} \tag{10-71a}$$

$$\zeta_{\mathrm{int}} \equiv \sum_m e^{-(\epsilon_{\mathrm{int}})_m/kT} \tag{10-71b}$$

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[1] The thermodynamic internal energy of the gas as a whole includes of course both these forms of molecular energy.

These equations may be substituted in any of the foregoing formulas for the thermodynamic functions; we may therefore speak of the translational entropy, the translational heat capacity, etc., and later, when we have analyzed ϵ_{int} further, of the vibrational entropy, the rotational heat capacity, etc., meaning by such an expression the additive term contributed to the thermodynamic function by the corresponding form of molecular motion. Since the internal motions of the molecules presumably depend in no way on the volume, in a gas at ordinary pressures, we may put Eq. (10-63) immediately in the form

$$p = NkT \left[\frac{d \ln \zeta_{tr}}{dV} \right]_T \tag{10-72}$$

10-3. Classical Mechanics of the Ideal Gas. So far, our discussion has been almost purely statistical in nature. No mechanical properties of the molecules have been introduced, except extremely general ones, such as the concept of independent molecule energies in the ideal-gas model and the quantum-mechanical method of distinguishing the different states of a molecular system. In this section, we shall describe essentially how Boltzmann treated the mechanical problem in the case of translational motion according to Newton's classical equations of motion. Classical mechanics broke down completely, of course, in the case of internal molecular motions, this collapse being one of the stimuli that led to the creation of quantum mechanics. While the classical treatment of translational molecular energy also has been superseded by the general quantum-mechanical treatment to be described in Sec. 10-4, nevertheless it retains considerable interest, and it leads to correct results in all respects except those bearing on the entropy constant for an ideal gas consistent with the third law of thermodynamics. It is indeed a remarkable fact that the one point in the classical theory that gave rise to the greatest conceptual difficulty turned out to foreshadow the third law, whose experimental foundation was not established until after Boltzmann's death.

The major theoretical problem arising in the classical treatment of translational molecular motion is how to define the molecule states in a proper manner. As a consequence of Newton's general equations of motion, we may express the energy of an independent molecule in the form

$$\epsilon_{tr} = \epsilon_p(x, y, z) + \frac{p^2}{2m} \tag{10-73}$$

where $\epsilon_p(x, y, z)$ denotes the mechanical potential energy, a function of the coordinates (x, y, z) of the molecule's center of mass (*e.g.*, as in a gravitational field), and $p^2/2m = (p_x^2 + p_y^2 + p_z^2)/2m$ denotes the kinetic energy, represented as a function of the components of momentum: $p_x = mu_x$, $p_y = mu_y$, $p_z = mu_z$.[1] If, however, the variables x, y, z, p_x, p_y, p_z, which describe the instantaneous state of motion, may assume any of a continuous series of values, then the question arises how to convert the sum represented in Eq. (10-71*a*) into an integral. This question, of course, does not arise in quantum mechanics, as we shall see in Sec. 10-4.

Formally, we may proceed as follows:

$$\zeta_{tr} = \frac{\Sigma e^{-\epsilon_{tr}/kT}\,\Delta x\,\Delta y\,\Delta z\,\Delta p_x\,\Delta p_y\,\Delta p_z}{\Delta x\,\Delta y\,\Delta z\,\Delta p_x\,\Delta p_y\,\Delta p_z} \tag{10-74}$$

where we have divided up the range of the variables x, y, z, p_x, p_y, p_z into little "equal" units of extension: $s = \Delta x\,\Delta y\,\Delta z\,\Delta p_x\,\Delta p_y\,\Delta p_z$. If we may now suppose that this element of "volume," s, in (x, y, z, p_x, p_y, p_z) "space" can be made sufficiently small so that throughout its extension, when located at a given "point" (x, y, z, p_x, p_y, p_z), the value of the function $\exp\,(-\epsilon_{tr}/kT)$ will be sensibly constant, then we may replace the sum in the numerator of Eq. (10-74) by an integral, taken over the entire ranges of the variables accessible to the individual molecules:

$$\zeta_{tr} = \frac{1}{s}\int\!\!\int\!\!\int\!\!\int\!\!\int\!\!\int e^{-\frac{\epsilon_p(x,y,z)+p^2/2m}{kT}}\,dx\,dy\,dz\,dp_x\,dp_y\,dp_z \tag{10-75}$$

It is precisely at this point that the conceptual difficulty to which we have previously referred arises, for we cannot actually pass to the limit $s \rightarrow 0$, without wrecking ζ_{tr}; yet there is no clue as to how small s ought to be, if it is to remain finite. If we suppose that s can be taken as a sufficiently small but arbitrary number, short of zero, then upon our examining the thermodynamic formulas (10-59) to (10-66), it becomes clear that only those involving the entropy [*i.e.*, Eqs. (10-60) and (10-66)] are affected by the precise value assigned to s, the effect there being the addition of a constant of the form $-R \ln s$ to the value of $\bar{S}^\circ$. The internal energy and the heat-capacity functions, and also Eq. (10-72) for the pressure, involve only derivatives of $\ln \zeta_{tr}$, from which the value assigned to s disappears. Obviously, however, we cannot reconcile such a haphazard procedure with the great generality represented by the third law of thermodynamics, which of course was unknown to Clausius, Boltzmann, Maxwell, and the

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[1] Compare Sec. 2-1. For reasons of symmetry, as represented by Sir William Rowan Hamilton's generalization of the equations of motion, the coordinates and the corresponding components of momenta are superior to the coordinates and the corresponding components of velocity as variables defining the state of motion. Equation (10-73) is of course a nonrelativistic expression for the translational energy, which breaks down at extremely high velocities approaching the speed of light.

other early investigators of statistical mechanics. After Nernst's establishment of the third law as an empirical principle, it became increasingly clear that the quantity s had to have a universal value, imposed by nature. This embarrassment disappears in the quantum-mechanical treatment of translational energy (Sec. 10-4), where it turns out on the basis of general theoretical principles that the translational-energy levels are discrete, even though extremely closely spaced.

Let us proceed, however, along classical lines to evaluate the integral appearing in Eq. (10-75). We shall suppose that we are dealing with a situation in which $\epsilon_p(x, y, z)$ equals 0 for all values of (x, y, z) falling within the region containing the gas but assumes an extremely large positive value for regions outside the container; this is merely a convenient mathematical device for keeping the gas within its container, whose volume we shall represent by V. Then the exponential factor $e^{-\epsilon_p(x,y,z)/kT}$ in the integrand of Eq. (10-75) will equal 1 for all values of (x, y, z) falling within the range represented by the volume V of the container, and will equal 0 for all values outside the container.[1] The other factor of the integrand, $e^{-p^2/2mkT}$, is independent of (x, y, z), and hence we may integrate over all values of x, y, and z, obtaining the factor V,[2]

$$\zeta_{tr} = \frac{V}{s} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-p^2/2mkT}\, dp_x\, dp_y\, dp_z$$

We may continue as follows:

$$\begin{aligned} \zeta_{tr} &= \frac{V}{s} \int_{-\infty}^{\infty} e^{-p_x^2/2mkT}\, dp_x \int_{-\infty}^{\infty} e^{-p_y^2/2mkT}\, dp_y \int_{-\infty}^{\infty} e^{-p_z^2/2mkT}\, dp_z \\ &= \frac{V}{s} \left(\int_{-\infty}^{\infty} e^{-p_x^2/2mkT}\, dp_x \right)^3 \\ &= \frac{V}{s} (2\pi mkT)^{3/2} \end{aligned} \tag{10-76}$$

Let us introduce this result directly in Eq. (10-72); we thus obtain

$$p = \frac{NkT}{V} \tag{10-77}$$

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[1] The thermodynamic equilibrium of a gas column in the earth's field of gravity could be studied by letting $\epsilon_p = mgz$ everywhere within the container, where z is the coordinate representing the altitude; similarly, by introducing for ϵ_p an appropriate function of the intermolecular distance, we could at this point digress into the theory of real gases subject to van der Waals' interaction.

[2] No conceptual difficulty arises in our extending the ranges of integration of p_x, p_y, and p_z from $-\infty$ to $+\infty$, because the integrand practically vanishes before the value of p^2 gets to be many times larger than $2mkT$.

Equation (10-77) represents the ideal-gas equation of state, which has here been derived from straightforward statistical-mechanical principles. This result illustrates the power of the statistical molecular approach; in purely thermodynamic theory, the equation of state enters only as an empirical or an assumed relationship, which cannot be deduced from general theoretical principles. In deriving an equation such as (10-77), it was of course necessary for us to create a molecular model that had sufficiently simple properties; this has involved an attendant loss of generality, and we find that the range of validity of Eq. (10-77) is confined to the low-pressure ideal-gas region. Comparing Eq. (10-77) with experiment, where p, V, and T are measured in conventional units, we establish the relationship $k = R/N_0$, anticipated in Eq. (10-29).

Substituting Eq. (10-76) in Eq. (10-59), we may deduce for the translational contribution to the thermodynamic internal energy

$$\bar{U}^\circ_{tr} - \bar{U}^\circ_0 = RT^2\left(\frac{d \ln \zeta_{tr}}{dT}\right)_V = \frac{3}{2}RT \qquad (10\text{-}78)$$

Thus

$$(\bar{C}^\circ_v)_{tr} = \tfrac{3}{2}R \qquad (10\text{-}79)$$

These calculated expressions are in agreement with the well-known experimental results for monatomic gases, where presumably all the molecular energy at ordinary temperatures is in translational form.[1]

Using on Eq. (10-40) similar reasoning to that advanced for Eq. (10-74), we may derive laws for the distributions of molecular velocities and kinetic energies. Thus, we may interpret the equation

$$\frac{\overline{\Delta N}}{N} = \frac{1}{\zeta_{tr}} e^{-\epsilon_{tr}/kT} \frac{\Delta x\, \Delta y\, \Delta z\, \Delta p_x\, \Delta p_y\, \Delta p_z}{s}$$

as representing the average fraction of the molecules having coordinates in the range x to $x + \Delta x$, y to $y + \Delta y$, z to $z + \Delta z$, and momentum components in the range p_x to $p_x + \Delta p_x$, p_y to $p_y + \Delta p_y$, p_z to $p_z + \Delta p_z$. One should note that since N is finite, though huge, this fraction may show fluctuations, which may be investigated on the general basis of Eq. (10-38). Substituting Eq. (10-76), going over to infinitesimal notation, and integrating over (x, y, z),

$$\frac{\overline{dN}(p_x, p_y, p_z)}{N} = \frac{1}{(2\pi mkT)^{3/2}} e^{-p^2/2mkT}\, dp_x\, dp_y\, dp_z$$

This equation now represents the average fraction of the molecules with

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[1] At sufficiently high temperatures, electronic excitation may contribute significantly to the thermodynamic properties.

momentum components in the range p_x to $p_x + dp_x$, p_y to $p_y + dp_y$, p_z to $p_z + dp_z$, without regard to spatial distribution (which tends on the average to be uniform, so long as $\epsilon_p = 0$ everywhere within the container). In order to obtain the average fraction, $\overline{dN}(p)/N$ with momentum in the range p to $p + dp$ without regard to direction, we may introduce the polar transformation

$$dp_x\, dp_y\, dp_z = p^2 \sin\theta\, dp\, d\theta\, d\varphi$$

and integrate over the entire range 0 to 2π of the polar angle φ and over the entire range 0 to π of the azimuthal angle θ, with the result

$$\frac{\overline{dN}(p)}{N} = \frac{4}{\pi^{1/2}} \frac{1}{(2\pi mkT)^{3/2}} e^{-p^2/2mkT} p^2\, dp \qquad (10\text{-}80)$$

If we replace p by its equivalent, mu,

$$\frac{\overline{dN}(u)}{N} = \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{m}{kT}\right)^{3/2} e^{-mu^2/2kT} u^2\, du \qquad (10\text{-}81)$$

This famous law was first deduced in 1859 by J. C. Maxwell, from a less general point of view than the one developed here. It received direct experimental confirmation in the ingenious molecular beam experiments initiated by O. Stern in 1920.[1] The corresponding equation for the distribution of molecular kinetic energy ($\epsilon_k = mu^2/2$) has the form

$$\frac{\overline{dN}(\epsilon_k)}{N} = \frac{2}{\pi^{1/2}} \frac{1}{(kT)^{3/2}} e^{-\epsilon_k/kT} \epsilon_k^{1/2}\, d\epsilon_k \qquad (10\text{-}82)$$

These molecular distribution equations have no particular bearing on the thermodynamic properties of the gas, all of which represent average molecular properties, but they constitute the foundation of the kinetic theory of gases, and the collision theory of gas reactions.

10-4. Quantum Mechanics and Molecular Translational Energy. Quantum mechanics arose mainly through the need to have a satisfactory theory of atomic and molecular spectra. After the electron had been discovered by J. J. Thomson in 1897 and the existence of atomic nuclei demonstrated by E. Rutherford shortly thereafter, the nuclear theory of the atom that was at once suggested called for a model fundamentally unstable according to classical electrodynamics; an electron centrally accelerated by a positively charged nucleus should emit radiation, accord-

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[1] O. Stern, *Z. Physik*, **2**, 49–56 (1920); **3**, 417–421 (1920). See also J. L. Costa, H. D. Smyth, and K. T. Compton, *Phys. Rev.*, **30**, 349–353 (1923); I. F. Zartman, *ibid.*, **37**, 383–389 (1931); C. C. Ko, *J. Franklin Inst.*, **217**, 173–199 (1934). Some of this work has been reviewed by R. G. J. Fraser, "Molecular Rays," The Macmillan Company, New York, 1932.

ing to classical theory, thereby continually losing energy, and its ultimate fate should be to spiral into the nucleus. At the same time, there is nothing in classical theory to account for the wonderfully complex and characteristic spectra that can be excited by appropriate methods in gases, and for the even more remarkable series relationships discovered among the observed spectral wavelengths of the simpler gases, such as in the Balmer series and the Lyman series of the atomic hydrogen spectrum.

The problem was resolved by a radically new departure from classical ideas proposed by Niels Bohr in 1913. Bohr proposed the following scheme:

1. Each atomic or molecular system has a series of characteristic *stationary states* in which it can remain indefinitely *without* emitting radiation.
2. Radiation is emitted or absorbed when the system undergoes a transition from one stationary state to another.
3. The frequency $\tilde{\nu}$ of the radiation emitted or absorbed during a transition between two states is proportional to the energy difference between the states:

$$\epsilon_2 - \epsilon_1 = h\tilde{\nu} \tag{10-83}$$

Equation (10-83) was an adaptation of a principle that had been introduced in 1900 by Max Planck in order to account for the spectral distribution of the thermal energy radiated by a hot body (which is quite different from the characteristic line or band spectra that can be excited in gases). Planck had had to assume that thermal energy radiated at a given frequency came in discrete units or *quanta*, whose size was proportional to the frequency; the proportionality constant h in (10-83) is known as *Planck's constant*, and it has the experimentally established value of $(6.624 \pm 0.004) \times 10^{-27}$ erg sec. Since in spectroscopy, one generally measures directly the wavelength λ rather than the frequency ($\tilde{\nu} = c/\lambda$, where c is the speed of light), Eq. (10-73) is commonly used in the form

$$\epsilon_2 - \epsilon_1 = hc\nu \tag{10-84}$$

where ν represents the *wave number* or reciprocal of the wavelength of the radiation, $\nu = 1/\lambda$; the universal constant, hc, appearing in (10-84) has the value $(1.9857 \pm 0.0006) \times 10^{-16}$ erg cm; $N_0hc = 2.8585 \pm 0.0009$ cal cm/mole.

Each spectral line thus represents an energy difference between two characteristic stationary states of the corresponding atomic or molecular system. The absorption spectrum corresponds of course to transitions from states of lower to states of higher energy, while the emission spectrum corresponds to transitions from states of higher to states of lower energy.

If conditions are such that it is feasible to observe either absorption or emission over the same wavelength range, then the observed absorption and emission lines coincide in wavelength; more generally, however, absorption and emission data overlap or supplement each other. A low-frequency line, such as may be observed in the microwave or in the infrared region corresponds to a transition between states differing relatively slightly in energy (*e.g.*, rotational-vibrational states of molecules); a high-frequency line, such as may appear in the visible or in the ultraviolet, corresponds to a transition between states relatively far apart in energy (electronic transitions of atoms and molecules), while lines in the X-ray spectrum, which have extremely high frequencies, correspond to transitions between states extremely far apart in energy (transitions involving the innermost electrons of atoms). By intercomparing the spectral lines, taking advantage of certain empirical selection rules which fortunately restrict the numbers and types of transitions ordinarily observed, the energies of the various states can be sorted out through direct application of Eq. (10-84), and an energy-level diagram for the atom or molecule can be constructed. With energies represented as *term values*, ϵ_j/hc, in wave-number units (cm^{-1}), the difference between term values for two given states represents directly the wave number of the spectral line corresponding to a transition between the two states. For converting energies expressed in term values to calories per mole, one may use the conversion factor, $N_0hc = 2.8585 \pm 0.0009$ cal/mole cm^{-1}, previously given.

Without the help of a comprehensive theory of atomic and molecular structure, the problem of unraveling the information furnished by the spectra of even the simpler atoms and molecules would be a hopelessly difficult task. Bohr's original theory was supplemented by certain more or less empirical rules characterizing the stationary states. Beginning in 1925, however, a new mathematical technique known as *quantum mechanics* was developed for coping with the problems presented by the dynamics of submicroscopic particles. Two different logically equivalent systems were worked out, one by W. Heisenberg known as *matrix mechanics* and the other by E. Schrödinger known as *wave mechanics*. Quantum mechanics has the logical status of a generalization of Newton's mechanics, to which it reduces when the masses in the mechanical system are sufficiently large.

In quantum mechanics, all attempt to define with precision the positions and momenta of the particles comprising an atomic or molecular system is abandoned. There is a fundamental difficulty in the way of applying classical concepts to particles of molecular and submolecular size, first pointed out by Heisenberg; in observing the properties of particles this small, the observation itself may introduce a disturbance in the state of the system, so that while experiments can be designed that will fix either the positions or the momenta in a given state, both cannot be determined simultaneously with that exactness associated with the classical concept of a trajectory or orbit; therefore the classical concept of an electron moving like a planet in a centrally accelerated orbit about the nucleus is meaningless. If there are s constituent particles in the system, then instead of having $3s$ pairs of coordinates and momenta, one solves the quantum-mechanical equation of motion for a certain function $\Psi(q_1, q_2, \ldots, q_{3s}, \tau)$ of the $3s$ coordinates, which is generally also an explicit function of the time (in nonrelativistic treatment); Ψ will also depend on s different spin coordinates, one for each particle, but it can generally be separated into a space-time factor and a spin factor; we shall postpone for the present the consideration of the effect of electron and nuclear spins. The value of this function Ψ itself has no special significance, but the square of its absolute magnitude $\bar{\Psi}\Psi$ (in general, Ψ may assume complex values and $\bar{\Psi}$ is taken to represent the function conjugate complex to Ψ) is interpreted as a probability distribution function, representing the probability when the system is in a state of motion represented by a particular function Ψ of finding the coordinates lying within the ranges q_1 to $q_1 + dq_1$, q_2 to $q_2 + dq_2$, . . . , q_{3s} to $q_{3s} + dq_{3s}$ during the time interval τ to $\tau + d\tau$. We are using the notation q_1, q_2, . . . , q_{3s} to denote generalized coordinates, three for each independent constituent particle of the system; *e.g.*, in Cartesian coordinates, q_1, q_2, q_3 might represent, respectively, the x, y, z coordinates of one particle, q_4, q_5, q_6 those of a second, etc.

In Schrödinger's formulation of quantum mechanics, the fundamental equation of motion satisfied by Ψ has the form

$$\sum_{i=1}^{s} \frac{1}{m_i} \nabla_i^2 \Psi - \frac{8\pi^2}{h^2} \epsilon_p \Psi = - \frac{4\pi i}{h} \frac{\partial \Psi}{\partial \tau} \tag{10-85}$$

where m_i denotes the mass of the ith particle, ∇_i^2 the Laplacian differential operator for the ith particle, which in Cartesian coordinates has the form

$$\nabla_i^2(\ \ ) = \frac{\partial^2(\ \ )}{\partial x_i^2} + \frac{\partial^2(\ \ )}{\partial y_i^2} + \frac{\partial^2(\ \ )}{\partial z_i^2}$$

and ϵ_p is a function of the coordinates and possibly also of time, representing the potential energy of the system; in many applications, this can be given the same functional form as in the corresponding classical problem (*e.g.*, in the hydrogen-atom problem, where the system consists of two charged particles, a proton and an electron, ϵ_p is given simply by Coulomb's law). It is assumed in (10-85) that the s particles are all independent, being coupled only through the common potential-energy term. Equation (10-85) has the logical status of a pure postulate replacing Newton's laws of motion; its justification rests in the fact that it correctly represents the mechanical properties of an atomic or molecular system using familiar potential-energy forms and with no other *ad hoc* assumptions aside from that of the physical interpretation of Ψ itself. Because Eq. (10-85) bears a formal resemblance, though not a very close one, to the familiar wave equations of classical physics and because in solving it we generally look for stationary solutions (corresponding to the stationary states of the system) analogous to the standing-wave solutions of the wave equations, Schrödinger's mechanics is often referred to as wave mechanics, and Eq. (10-85) is called the wave equation (including the time). The wavelike character of Eq. (10-85) is by no means without real physical significance, for in the case of particles having tiny masses and high energies, one is able to infer from (10-85) the wavelike character of the state of motion that has become familiar to us in such experimental forms as electron diffraction and interactions between material particles and radiation generally.

Under certain conditions, Eq. (10-85) may have solutions of the form

$$\Psi(q_1, q_2, \ldots, q_{3s}, \tau) = \psi(q_1, q_2, \ldots, q_{3s})F(\tau) \tag{10-86}$$

that is to say, separable in the space and time variables. This is generally possible only if ϵ_p does not depend explicitly on τ. By substituting the form (10-86) in (10-85) and separating the variables, one finds that solutions of this form are possible when $F(\tau)$ has the form

$$F(\tau) = \exp\left(-2\pi i \frac{\epsilon}{h} \tau\right) \tag{10-87}$$

and $\psi(q_1, q_2, \ldots, q_{3s})$ simultaneously satisfies the equation

$$\sum_{i=1}^{s} \frac{1}{m_i} \nabla_i^2 \psi + \frac{8\pi^2}{h^2} (\epsilon - \epsilon_p)\psi = 0 \tag{10-88}$$

where ϵ is a real constant (if it were complex, $\bar{F}F$ would not remain finite for all values of τ). In this case, Ψ oscillates in value everywhere periodically with frequency ϵ/h, but since $\bar{F}F = 1$, the physically significant quantity $\bar{\Psi}\Psi$ is independent of τ, and is in fact equal to the value of $\bar{\psi}\psi$ satisfying (10-88). We therefore interpret such solutions to represent stationary states of the system, as postulated by Bohr. For such solutions, we need concern ourselves only with Eq. (10-88), which is in fact commonly known as Schrödinger's wave equation, or amplitude equation.

An equation of the form (10-88), when ψ is subjected to certain boundary conditions, such as that it be single-valued, continuous, and finite for all values open to the coordinates of the system (conditions required in order that $\bar{\psi}\psi$ should be capable of serving its stated purpose as a probability distribution function), admits of solutions generally only for certain specific values of the parameter ϵ. The problem is in this respect analogous to the familiar problem of standing waves in a stretched elastic string, subject to the boundary conditions that the amplitude of vibration is zero at the two fixed ends; in that case, standing waves can exist only if their wavelengths are integral submultiples of twice the length of the string. The values of ϵ for which Eq. (10-88) has proper solutions are known as *eigenvalues* of ϵ. They are taken to represent the various possible energy levels that the system can assume in stationary states; in some cases, they may include a continuous range of values, but in others, all the values may be discrete. Solutions $\psi(q_1, q_2, \ldots, q_{3s})$ satisfying (10-88) for a given eigenvalue ϵ_n are known as *eigenfunctions* belonging to the eigenvalue ϵ_n. In general, different eigenfunctions are taken to represent different stationary states or eigenstates of the system; *i.e.*, if ψ_{jn} represents an eigen-ψ belonging to the eigenvalue ϵ_n, then $\bar{\psi}_{jn}\psi_{jn}$ (a function of the coordinates $q_1, q_2, \ldots, q_{3s}$) represents the probability when the system is in the particular stationary state represented by ψ_{jn} of finding the coordinates within the ranges q_1 to $q_1 + dq_1$, q_2 to $q_2 + dq_2$, $\ldots$, q_{3s} to $q_{3s} + dq_{3s}$, the energy of the system in this state having the definite value ϵ_n. From the form of (10-88), the eigen-ψ's are obviously undetermined to the extent of arbitrary constant multipliers having the character of integration constants; by convention, the absolute value of each eigen-ψ is adjusted to a scale on which

$$\int\int \cdots \int \bar{\psi}\psi \, dq_1 \, dq_2 \cdots dq_{3s} = 1 \tag{10-89}$$

where the integration extends over the entire range of the coordinates open to the system; ψ is then said to be *normalized*, which merely means that the probability of finding the coordinates anywhere at all is conventionally taken as 1; the probability of finding them within a specified finite range is then always represented by a fraction smaller than 1.

If to a given eigenvalue there corresponds only one normalized eigen-ψ, then the energy level, or in this case state, represented by that eigenvalue is said to be nondegenerate. If two or more different eigen-ψ's belong to a given eigenvalue ϵ_n, then the corresponding energy level is said to be degenerate. Let ψ_{1n}, ψ_{2n}, ψ_{3n}, . . . represent normalized eigen-ψ's belonging to the eigenvalue ϵ_n. Then since (10-88) is linear in ψ, any linear combination of eigen-ψ's belonging to the eigenvalue ϵ_n with arbitrary constant coefficients

$$\psi = c_1\psi_{1n} + c_2\psi_{2n} + c_3\psi_{3n} + \cdots \tag{10-90}$$

is also a solution of (10-88) (this can be seen by applying (10-88) term by term), and is therefore also an eigen-ψ belonging to the eigenvalue ϵ_n. Such an eigen-ψ would be interpreted to represent a state intermediate in properties between the states represented by ψ_{1n}, ψ_{2n}, ψ_{3n}, ... Now, eigenfunctions belonging to different eigenvalues may be shown to have a property known as orthogonality: if ψ_i and ψ_j represent two such eigenfunctions, then

$$\int\int \cdots \int \bar{\psi}_i\psi_j \, dq_1 \, dq_2 \cdots dq_{3s} = 0$$

Obviously, an eigenfunction cannot be represented as a linear combination of the form (10-90) in terms of other eigenfunctions with respect to each of which it is orthogonal, for taking $\int\int \cdots \int \bar{\psi}\psi \, dq_1 \, dq_2 \cdots dq_{3s}$ would then lead to the result 0. From among the eigen-ψ's belonging to a common eigenvalue, however, one can always construct a set that are mutually orthogonal, and such that all other eigen-ψ's belonging to the same eigenvalue can be represented by means of such a linear combination in terms of members of the set. The least number of mutually orthogonal or so-called linearly independent eigenfunctions is known as the degree of degeneracy of the corresponding energy level. The coefficients c_1, c_2, c_3, . . . in an expression such as (10-90) (if ψ_{1n}, ψ_{2n}, ψ_{3n}, . . . are orthogonal normalized eigen-ψ's, and if ψ is itself normalized, then it is easy to show that $c_1^2 + c_2^2 + c_3^2 + \cdots = 1$, so that each of the coefficients is a fractional number) denote the relative contributions of the states represented by ψ_{1n}, ψ_{2n}, ψ_{3n}, . . . to the intermediate state represented by ψ; that is to say, if one makes repeated observations of some property G of the system, which has the definite value G_1 when the system is in the state represented by ψ_{1n}, G_2 when the system is in the state represented by ψ_{2n}, G_3 when the system is in the state represented by ψ_{3n}, . . . , then if the system should be in the intermediate state represented by ψ, one would obtain the result G_1 in the fraction c_1 of the observations, G_2 in the fraction c_2, G_3 in the fraction c_3, ... This idea of a system's existing in a state made up of contributions from other states having the same energy is a purely quantum-mechanical concept, which has been of great value in interpreting the behavior of many atomic and molecular systems.

The principal dynamic problem in Schrödinger's mechanics, then, is to set up properly the potential energy ϵ_p in Eq. (10-88) as a function of the coordinates. The solution of (10-88) yields a set of eigenvalues of ϵ or energy levels, to each of which one or more linearly independent eigen-ψ's belong; these eigen-ψ's represent the stationary states of the system, in the sense that $\bar{\psi}\psi$ gives the system's coordinates in the form of a probability distribution function for the particular state represented by ψ.

Heisenberg's formulation of quantum mechanics is rather more abstract. In Heisenberg's method, each state of the system is represented by a vectorlike quantity ψ; multiplying ψ by a constant factor is presumed not to change the state that it represents, and thus one can always normalize ψ by dividing by its absolute magnitude (ψ differs from an ordinary vector in that it may assume complex values). Observable properties of the system, such as its energy, are represented by linear operators which transform the ψ's one into another. This principle corresponds to the fact that in an atomic or molecular system, the taking of an observation generally disturbs the state of the system under observation, because the tools available (light quanta, electron beams, molecular beams, etc.) cannot be much finer than the system itself. The linear operators have the character known in the algebra of transformations as matrices; a matrix is a set of numbers arranged in a particular way which defines how each component of a vector or of another matrix on which the given matrix operates is transformed (in general, each successive component is transformed differently, but according to a definite law of matrix multiplication). It is assumed that if the operation of a matrix H representing some particular observable, such as the energy, on a vector ψ representing some particular state merely multiplies that vector by a number ϵ, without changing its components relatively to each other, so that symbolically

$$H\psi = \epsilon\psi \tag{10-91}$$

then if one makes the observation corresponding to H on the system when it is in the state represented by ψ, one is sure to obtain the definite result ϵ; otherwise, the outcome of the observation is in general uncertain. Values of ϵ for which Eq. (10-91) is satisfied are called eigenvalues of the observable H, and when H is the matrix operator corresponding to the energy, these eigenvalues are taken to represent energy levels of the stationary states. Values of ψ satisfying (10-91) for a given eigenvalue ϵ_n are called eigen-ψ's belonging to the eigenvalue ϵ_n, and they are then supposed to represent the stationary states of the system. Heisenberg's scheme includes certain general properties satisfied by the particular operators representing the coordinates and the momenta of the system, and the dynamic problem consists of setting up properly the matrix components that are to represent the energy operator for a given dynamic system. By the use of standard rules of matrix algebra, one then solves (10-91) to find the eigenvalues of H and the corresponding eigenfunctions representing the states.

For further discussion, the reader is referred to any of the standard treatises on quantum mechanics.[1] It is sufficient for our present purpose that we take for granted some of the results.

Now, for a free particle moving in a rectangular box whose edges are a, b, and c, the various energy levels are given by the expression

$$\epsilon_{tr} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \quad \begin{cases} n_x = 0, 1, 2, 3, \ldots \\ n_y = 0, 1, 2, 3, \ldots \\ n_z = 0, 1, 2, 3, \ldots \end{cases} \tag{10-92}$$

These values are derived by solving Eq. (10-88) in the three coordinate variables (x, y, z), with $\epsilon_p = 0$ everywhere within the box but increasing rapidly to an infinitely large value at the boundaries.[2] Each different set of integers: (n_x, n_y, n_z) represents a different possible state of translational motion, with kinetic energy represented by (10-92). For a complex "particle" having a potential energy that depends on the relative distances between its constituent particles, the equation of motion (10-88) separates as in classical mechanics into an equation of motion for the center of mass, behaving like a free particle with the entire mass concentrated in it, and an equation of relative motion of the constituent particles with respect to the center of mass. The energy is then the sum, as represented in Eq. (10-70), of a translational-energy term, which may assume any of the values such as are represented by Eq. (10-92), plus an "internal-energy" term, whose general nature we shall consider later. Thus, upon substitution of (10-92) in (10-71*a*),

$$\zeta_{tr} = \sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty} e^{-\frac{h^2}{8mkT}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)} \tag{10-93}$$

If any two of the edges of the container happen to have a common factor, then some of the energy levels will be degenerate; for example, if $a = b$, then for each pair of different integers, n_x and n_y, there will exist two different states belonging to the same energy (with the values of n_x and n_y interchanged). We shall assume for mathematical convenience that the edges are incommensurable, so that we do not have to take explicit account of such degeneracy in the evaluation of (10-93); this involves no loss of generality, since we know that the thermodynamic properties of the gas are not sensitive to the precise shape of the container. We may then separate ζ_{tr} into a product of three independent sums:

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[1] L. Pauling and E. B. Wilson, "Introduction to Quantum Mechanics," McGraw-Hill Book Company, Inc., New York, 1935; P. A. M. Dirac, "Quantum Mechanics," 3d ed., Oxford University Press, New York, 1947.

[2] Pauling and Wilson, *op. cit.*, pp. 95–100.

$$\zeta_{tr} = \sum_{n_x=0}^{\infty} e^{-\frac{h^2}{8mkT}\frac{n_x^2}{a^2}} \sum_{n_y=0}^{\infty} e^{-\frac{h^2}{8mkT}\frac{n_y^2}{b^2}} \sum_{n_z=0}^{\infty} e^{-\frac{h^2}{8mkT}\frac{n_z^2}{c^2}}$$

Now, the increment of the running integer as one proceeds from term to term in each of these sums is 1; therefore the sums may be put in the typical form

$$\sum_{n_x=0}^{\infty} e^{-\frac{h^2}{8mkT}\frac{n_x^2}{a^2}} = \sum_{n_x=0}^{\infty} e^{-\frac{h^2}{8mkT}\frac{n_x^2}{a^2}} \Delta n_x$$

where $\Delta n_x = 1$. In this sum, significant terms are present, even at low values of T, up to values of n_x enormously greater than $\Delta n_x = 1$; for the factor $h^2/8mk$, with m of order 10^{-24} g (the H atom having a mass of 1.6734×10^{-24} g), is of order 10^{-14} cm²/deg, and if we are considering a gas sample with a having the order 1 cm, then n_x may run up to values of order 10^6 even at $T = 0.01$°K before the terms begin to decrease appreciably from 1. The series consists in other words of a huge number of 1's, followed by terms gradually diminishing with increasing n_x from 1 to 0.[1] Therefore the sum may be computed with more than satisfactory precision as the integral

$$\begin{aligned}\sum_{n_x=0}^{\infty} e^{-\frac{h^2}{8mkT}\frac{n_x^2}{a^2}} &= \int_0^{\infty} e^{-\frac{h^2}{8mkT}\frac{n_x^2}{a^2}}\, dn_x \\ &= (8mkT)^{1/2}\frac{a}{h}\int_0^{\infty} e^{-x^2}\, dx \\ &= (2\pi mkT)^{1/2}\frac{a}{h}\end{aligned}$$

The other two factor sums in ζ_{tr} may be evaluated similarly, leading finally to the result

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[1] This statement does *not* necessarily imply that all such molecule states are actually occupied at a given moment; there are in fact many more accessible translational-energy states than there are molecules in a material gas at ordinary temperatures. The statement merely implies that each state counted has a finite, even if relatively minute, chance of being occupied. Nor does it imply that at low temperatures, the value of ζ_{tr} given by (10-93) necessarily gives correct thermodynamic results when substituted in Eq. (10-46) for Z, on which the formulas (10-59) to (10-66) depend; the value of Z for deriving exact thermodynamic formulas valid even at the lowest temperatures is given by Eq. (10-53), where the quantity C is related to ζ by means of Eq. (10-55*a*). The conditions under which Eq. (10-55*a*) reduces to (10-57), thereby justifying our derivation of the thermodynamic formulas (10-59) to (10-66) and the validity of Boltzmann's distribution law, we are about to examine [Eq. (10-96)].

$$\begin{aligned}\zeta_{tr} &= (2\pi mkT)^{3/2}\frac{abc}{h^3}\\ &= (2\pi mkT)^{3/2}\frac{V}{h^3} \qquad (10\text{-}94)\end{aligned}$$

Comparing with Eq. (10-76), we see that the quantum-mechanical treatment has led to assignment of the definite value h^3 to the indefinite constant $s = \Delta x\, \Delta y\, \Delta z\, \Delta p_x\, \Delta p_y\, \Delta p_z$ appearing in Boltzmann's classical treatment. One may easily verify that (10-94) leads to the ideal-gas equation of state (10-77) and the classical value (10-78) for the translational thermodynamic internal energy.

Before we proceed to evaluate the contribution of translational molecular motion to the entropy, let us test condition (10-56), or its equivalent, (10-57), on which the validity of the "semiclassical" approximations (10-46) and (10-47) depend. If we substitute the translational-energy levels (10-92) in the sums over states appearing in Eq. (10-55*a*), we may evaluate those sums in the same manner in which we have just evaluated the sum ζ_{tr} itself. We obtain as a result

$$N = C\zeta_{tr}\left[1 \pm \frac{C}{2^{3/2}} + \frac{C^2}{3^{3/2}} \pm \cdot \cdot \cdot\right] \qquad (10\text{-}95)$$

where the upper (+) sign refers to the Bose-Einstein case, and the lower (−) sign to the Fermi-Dirac case. Now, for 1 mole of gas,

$$\begin{aligned}\frac{N_0}{\zeta_{tr}} &= \frac{N_0}{\bar{V}}\frac{h^3}{(2\pi mkT)^{3/2}}\\ &= \frac{N_0^4}{\bar{V}}\frac{h^3}{(2\pi \bar{M}RT)^{3/2}} = \frac{3200(\text{g deg/mole})^{3/2}\ \text{cm}^3/\text{mole}}{(\bar{M}T)^{3/2}\bar{V}} \qquad (10\text{-}96)\end{aligned}$$

Thus, at 0°C and 1 atm, with $\bar{V} = 22{,}400\ \text{cm}^3/\text{mole}$ for all known material gases, $N_0/\zeta_{tr} \sim 3.2 \times 10^{-5}/\bar{M}^{3/2}$; even for hydrogen, the material gas having the smallest molecular weight, this number is only about 10^{-5}, and according to Eq. (10-95), C itself under this condition must have the same order of magnitude. Therefore condition (10-57) is satisfied, justifying rigorously our set of thermodynamic equations (10-58) to (10-66). The only material gases for which there is any chance for C to differ from N/ζ_{tr} are hydrogen and helium at extremely low temperatures; thus, for H_2 at its normal boiling point (20.4°K), $N_0/\zeta_{tr} \sim 0.0074$, while for He at its normal boiling point (4.2°K), $N_0/\zeta_{tr} \sim 0.14$; even under these conditions, as previously mentioned, the expected effect on the thermodynamic properties is hardly any greater than that of van der

Waals' deviation from ideal-gas behavior.[1] The reason for Fermi-Dirac degeneracy in the case of the electron "gas" in metals at ordinary temperatures appears to be the relatively small value of the electron mass ($\bar{M} = 0.00055$ g/mole on the atomic-weight scale), combined with the high electron density in metals ($\bar{V} \sim 10$ cm^3/mole typically, on the assumption that there is at least one "free" electron per atom); the electrons emitted thermally from a heated metal filament satisfy the Maxwell-Boltzmann velocity distribution law, as shown originally by experiments of O. W. Richardson, a consequence no doubt of their much lower density outside the metal. Likewise, Bose-Einstein degeneracy in liquid He-II may be associated with the relatively high density of the liquid as compared with the gaseous state, though in that case, the ideal-gas theory undoubtedly has to be supplemented by the consideration of intermolecular forces.

Let us now substitute Eq. (10-94) in Eq. (10-60) to obtain the formula for the translational entropy of an ideal gas:

$$\bar{S}_{tr} = \frac{3}{2} R + R \ln (2\pi mkT)^{3/2} \frac{\bar{V}}{h^3} - R \ln N_0 + R$$

Replacing $\bar{V}$ by RT/p and rearranging terms,

$$\bar{S}_{tr} = \frac{5}{2} R \ln T - R \ln p + \frac{3}{2} R \ln \bar{M} + R \left[\frac{5}{2} + \ln \left(\frac{2\pi}{N_0} \right)^{3/2} \frac{k^{5/2}}{h^3} \right] \tag{10-97}$$

Equation (10-97) is known as the *Sackur-Tetrode equation*;[2] the last term in it represents a universal constant, which with the inclusion of a factor to convert p from cgs to atmosphere units has the value -2.314 ± 0.005 eu/mole.[3] Therefore the standard ideal-gas entropy contributed by

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[1] There is no point in considering lower temperatures, because the lower pressures required in order to maintain the gaseous state below the normal boiling point result in increase of the value of $\bar{V}$ in the denominator of Eq. (10-96); both high gas density and low temperature concurrently are required for the appearance of Bose-Einstein or Fermi-Dirac degeneracy.

[2] O. Sackur, "Nernst-Festschrift," pp. 405–423, W. Knapp, Halle, 1912; *Ann. Physik*, **40**, 67–86 (1913); H. Tetrode, *ibid.*, **38**, 434–442 (1912); **39**, 255–256 (1912). Tetrode was actually the first to succeed in deriving the correct value for the constant appearing as the last term in the equation. The method of Sackur and Tetrode consisted essentially of arbitrarily assuming Eq. (10-46) and then assigning to s in Eq. (10-76) the value h^3 on semiempirical grounds. They obviously did not have the benefit of modern quantum mechanics, which has justified both steps on general theoretical grounds, as part of a comprehensive system of atomic physics.

[3] Based on the values of the natural constants given in Appendix 2, as adopted by the National Bureau of Standards for "Selected Values of Chemical Thermodynamic Properties," Dec. 31, 1947.

molecular translational motion at $p = 1$ atm is given by the formula

$$\bar{S}^\circ_{tr} = \tfrac{5}{2}R \ln T + \tfrac{3}{2}R \ln \bar{M} - 2.314 \text{ eu/mole} \qquad (10\text{-}97a)$$

In particular, at the standard reference temperature $T = 298.16°\text{K}$,

$$(\bar{S}^\circ_{tr})_{298.16} = (6.864 \log \bar{M} + 25.992) \text{ eu/mole} \qquad (10\text{-}97b)$$

In Table 10-1, ideal-gas entropy values calculated according to Eq. (10-97*b*) are compared with third-law entropy values determined according to the method described in Sec. 8-3 from experimental heat-capacity data for the solid, the liquid, and the gas, together with the latent heats of fusion and vaporization at the respective transition points for the monatomic gases: Ne, A, Kr, and Xe. For these gases, the contributions of internal states of motion, such as of excited electronic states, are entirely negligible at room temperature. The third-law results given in the table pertain to an actual pressure of 1 atm; correction to the ideal-gas state could be made by the method described in Sec. 6-2 [see, for example, Eq. (6-45)], but it is insignificant in comparison with the experimental error attending the third-law results. The agreement between the experimental and the theoretically calculated values is as complete as could be desired. The correct theoretical evaluation of the entropy constant appearing in Eq. (10-97*a*) represents a brilliant achievement of the molecular approach to thermodynamics.

TABLE 10-1. EXPERIMENTAL AND THEORETICAL ENTROPIES OF MONATOMIC GASES AT 25°C*

Monatomic gas	$\bar{M}$, g/mole	$\bar{S}_{1\text{ atm}}$ (3d law), eu/mole	$\bar{S}^\circ_{tr}$ [Eq. (10-97*b*)], eu/mole
Ne	20.183	35.0 ± 0.1	34.949 ± 0.005
A	39.944	37.0 ± 0.2	36.984 ± 0.005
Kr	83.7	39.0 ± 0.3	39.19 ± 0.01
Xe	131.3	40.7 ± 0.3	40.53 ± 0.01

* Third-law entropies from the 1940 compilation by K. K. Kelley, *U.S. Bur. Mines Bull.* 434 (1941).

We may now express our important thermodynamic functions for gases in the hypothetical ideal-gas state at 1 atm in the general forms

$$\bar{H}^\circ - \bar{H}^\circ_0 = \frac{5}{2}RT + RT^2 \frac{d \ln \zeta_{\text{int}}}{dT} \qquad (10\text{-}98)$$

$$= \frac{5}{2}RT + \frac{RT}{\zeta_{\text{int}}} \sum \frac{\epsilon_{\text{int}}}{kT} e^{-\epsilon_{\text{int}}/kT} \qquad (10\text{-}98a)$$

$$\bar{C}^\circ_p = \frac{d\bar{H}^\circ}{dT} = \frac{5}{2}R + \frac{R}{T^2} \frac{d^2 \ln \zeta_{\text{int}}}{d(1/T)^2} \qquad (10\text{-}99)$$

$$\bar{C}_p^\circ = \frac{5}{2}R + \frac{R}{\zeta_{\text{int}}}\left[\sum\left(\frac{\epsilon_{\text{int}}}{kT}\right)^2 e^{-\epsilon_{\text{int}}/kT} - \left(\sum \frac{\epsilon_{\text{int}}}{kT} e^{-\epsilon_{\text{int}}/kT}\right)^2\right] \tag{10-99a}$$

$$\bar{S}^\circ = -2.314 \text{ eu/mole} + \frac{3}{2}R \ln \bar{M} + \frac{5}{2}R \ln T + R \ln \zeta_{\text{int}} + RT\frac{d \ln \zeta_{\text{int}}}{dT} \tag{10-100}$$

$$= -2.314 \text{ eu/mole} + \frac{3}{2}R \ln \bar{M} + \frac{5}{2}R \ln T + R \ln \zeta_{\text{int}} + \frac{R}{\zeta_{\text{int}}}\sum \frac{\epsilon_{\text{int}}}{kT} e^{-\epsilon_{\text{int}}/kT} \tag{10-100a}$$

$$\frac{\bar{F}^\circ - \bar{H}_0^\circ}{T} = 7.282 \text{ cal/mole deg} - \frac{3}{2}R \ln \bar{M} - \frac{5}{2}R \ln T - R \ln \zeta_{\text{int}} \tag{10-101}$$

where ζ_{int} is defined by Eq. (10-71), the summations being taken over all molecular internal-energy states. It is evident that of all these functions, the last one is the simplest to evaluate, since it involves only ζ_{int} itself; this is fortunate for chemical applications, since the free-energy function is the thermodynamic function most directly related to the conventional chemical equilibrium constant for reactions involving the gas.

We may list for convenience the following values of the natural constants appearing in applications of these formulas:

$$\begin{aligned} R &= 1.98719 \pm 0.00013 \text{ cal/mole deg} \\ \tfrac{5}{2}R &= 4.9680 \text{ cal/mole deg} \\ R \ln (\quad) &= 4.5757 \text{ (cal/mole deg) } \log (\quad) \\ \tfrac{3}{2}R \ln \bar{M} &= 6.8635 \text{ (cal/mole deg) } \log \bar{M} \\ \tfrac{5}{2}R \ln T &= 11.4392 \text{ (cal/mole deg) } \log T \end{aligned}$$

In particular, at $T = 298.16$°K,

$$\begin{aligned} (\bar{H}^\circ - \bar{H}_0^\circ)_{tr} &= 1481.25 \text{ cal/mole} \\ (\bar{C}_p^\circ)_{tr} &= 4.9680 \text{ cal/mole deg} \\ (\bar{S}^\circ)_{tr} &= (25.992 + 6.8635 \log \bar{M}) \text{ eu/mole} \\ \left(\frac{\bar{F}^\circ - \bar{H}_0^\circ}{T}\right)_{tr} &= -(21.024 + 6.8635 \log \bar{M}) \text{ cal/mole deg} \end{aligned}$$

10-5. Energy Levels from Spectroscopic Data. The "internal-energy" levels of gas molecules are revealed by analysis of their spectra, as we have already observed in connection with Eq. (10-84). The possibility of using such molecular data for the precise calculation of thermodynamic properties was suggested originally by H. C. Urey, and also by R. C.

Tolman and R. M. Badger.[1] The method has been described in detail by W. F. Giauque, who first applied it correctly to the molecular spectrum of hydrogen.[2] It has since become an invaluable source of thermodynamic information. Part of its value rests in the possibility afforded for the thermodynamic investigation of such ordinarily transient molecules as OH(g), N(g), CN(g), Cu(g), etc., which may constitute intermediates in gas reactions at high temperatures; such information is important in the investigation of reaction mechanisms. Even for ordinary gases, however, the precision of the data obtained from spectroscopic sources, when properly interpreted, generally exceeds that of data derived by conventional thermodynamic methods.

a. Electronic-energy Terms. We shall illustrate the method first by applying it to a comparatively simple case, that of C(g). The lowest energy levels (term values) of the C(g) atom, together with the number of states (g_i) belonging to each, are given in Table 10-2.[3] The term values are taken by convention with respect to the lowest state of the C(g) atom, to which therefore the value of $\bar{H}_0^\circ$ applies; this thermochemical constant, representing the hypothetical enthalpy of formation of C(g) from C(graphite) at 0°K, is not obtainable from purely statistical calculations. In the fifth column of Table 10-2, each term value has been multiplied by the conversion factor

$$\frac{hc}{k} = 1.43847 \pm 0.00045 \text{ cm deg} \qquad (10\text{-}102)$$

which converts them directly into ϵ/k values, expressed in degrees. The number of states g_i belonging to the energy level ϵ_i is given according to quantum theory by $(2J + 1)$, where J represents the angular momentum quantum number of the electronic system corresponding to the energy value in question.[4] In the seventh, ninth, and eleventh columns of Table 10-2,

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[1] H. C. Urey, *J. Am. Chem. Soc.*, **45**, 1445–1455 (1923); R. C. Tolman and R. M. Badger, *ibid.*, 2277–2285.

[2] W. F. Giauque, *J. Am. Chem. Soc.*, **52**, 4808–4815, 4816–4831 (1930). Excellent descriptions have been given also by K. K. Kelley, *U.S. Bur. Mines Bull.* 434 (1941), and by G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Chap. V, D. Van Nostrand Company, Inc., New York, 1945.

[3] C. E. Moore, Atomic Energy Levels, Vol. I, *Natl. Bur. Standards Circ.* 467 (1949).

[4] These states actually separate when the gas is in a magnetic or an electric field, giving rise, respectively, to the Zeeman or the Stark splitting of the spectral lines corresponding to transitions involving them. The number $(2J + 1)$ (*e.g.*, 1 when $J = 0$, 2 when $J = \frac{1}{2}$, 3 when $J = 1$, etc.) then represents the number of different orientations the angular momentum may assume with respect to the direction of the field; J itself may assume integral or half-integral values, depending on the nature of the state in question. For a general description of atomic-energy terms, the reader

referring, respectively, to temperatures of 298.16, 2500, and 5000°K, the value of exp $(-\epsilon_i/kT)$ for each energy level has therefore been counted g_i times. It is evident that even at 5000°K, only the first six levels contribute significantly to ζ_{int}, while at 298.16°K, only the first three, constituting actually the components of a triplet ground state, are significant.

TABLE 10-2. ATOMIC-ENERGY LEVELS AND THERMODYNAMIC PROPERTIES OF C(g) (At 298.16, 2500, and 5000°K)

Term	J	g_i	ϵ_i, cm^{-1}	$\frac{\epsilon_i}{k}$, deg	T = 298.16°K		T = 2500°K		T = 5000°K	
					$\frac{\epsilon_i}{kT}$	$g_ie^{-\epsilon_i/kT}$	$\frac{\epsilon_i}{kT}$	$g_ie^{-\epsilon_i/kT}$	$\frac{\epsilon_i}{kT}$	$g_ie^{-\epsilon_i/kT}$
$^3P_0$	0	1	0.0	0.0	0	1.0000	0	1.0000	0	1.0000
$^3P_1$	1	3	16.4	23.6	0.0792	2.7714	0.00944	2.9717	0.00472	2.9858
$^3P_2$	2	5	43.5	62.6	0.2100	4.0529	0.02504	4.8764	0.01252	4.9378
$^1D_2$	2	5	10193.70	14663.33	49.2	0.0000	5.865	0.0141	2.9327	0.2664
$^1S_0$	0	1	21648.4	31140.6	......	......	12.5	0.0000	6.23	0.0019
$^5S_2$	2	5	33735.2	48527.1	......	......	....	....	9.71	0.0003
$^3P_0$	0	1	60333.80	86788.36	......	......	....	....	17.4	0.0000
$^3P_1$	1	3	60353.00	86815.98	......	......	....	....	17.4	0.0000
$^3P_2$	2	5	60393.52	86874.27	......	......	....	....	17.4	0.0000
Totals:										
ζ_{int}					....	7.8243	....	8.8622	....	9.1922
$\log \zeta_{\text{int}}$					....	0.89345	....	0.94754	....	0.96342
Calculation of free-energy function:										
$-R \ln \zeta_{\text{int}}$					....	−4.088	....	−4.336	....	−4.408
$\left(\frac{\bar{F}^\circ - \bar{H}_0^\circ}{T}\right)_{tr}$					....	−28.433	....	−38.997	....	−42.440
$\frac{\bar{F}^\circ - \bar{H}_0^\circ}{T}$, cal/mole deg					....	−32.521	....	−43.333	....	−46.848
Calculation of enthalpy function:										
$\sum \frac{\epsilon_i}{kT} g_ie^{-\epsilon_i/kT}$					....	1.0706	....	0.2329	....	0.8719
$\frac{1}{\zeta_{\text{int}}} \sum \frac{\epsilon_i}{kT} g_ie^{-\epsilon_i/kT}$					....	0.1368	....	0.0263	....	0.09468
$(\bar{H}^\circ - \bar{H}_0^\circ)_{\text{int}} = \frac{RT}{\zeta_{\text{int}}} \sum \frac{\epsilon_i}{kT} g_ie^{-\epsilon_i/kT}$					....	81.0	....	130.7	....	942.4
$(\bar{H}^\circ - \bar{H}_0^\circ)_{tr} = \frac{5}{2}RT$					....	1481.3	....	12,419.9	....	24,839.9
$\bar{H}^\circ - \bar{H}_0^\circ$, cal/mole					....	1562.3	....	12,550.6	....	25,782.3

From the values of ζ_{int} calculated by the addition of the entries in the respective columns, the values of $(\bar{F} - \bar{H}_0^\circ)/T$ have been calculated at the three temperatures according to Eq. (10-101). In the lower part of Table 10-2, the values of $(\bar{H}^\circ - \bar{H}_0^\circ)$ for C(g) have also been calculated at the three temperatures by means of Eq. (10-98a), the sum called for by that equation being obtained at each temperature by multiplying the

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is referred to G. Herzberg, "Atomic Spectra and Atomic Structure," 2d ed., Dover Publications, Inc., New York, 1944.

entries in the sixth, eighth, or tenth column by the corresponding entry in the seventh, ninth, or eleventh column, respectively, and adding; this operation is readily performed directly on a simple calculating machine.

The values of $(\bar{F}^\circ - \bar{H}_0^\circ)/T$ for C(graphite) at the three temperatures, obtained from the experimentally determined heat capacity by means of Eqs. (10-68) and (10-69), are, respectively, −0.517, −6.39, and −10.02 cal/mole deg.[1] Comparing with the values for C(g) computed in Table 10-2, we obtain for the process

$$\begin{aligned} \text{C(graphite)} &= \text{C(g)} \\ \Delta F^\circ_{298.16} &= \Delta H^\circ_0 - 9.542 \text{ kcal} \\ \Delta F^\circ_{2500} &= \Delta H^\circ_0 - 92.35 \text{ kcal} \\ \Delta F^\circ_{5000} &= \Delta H^\circ_0 - 184.2 \text{ kcal} \end{aligned}$$

If we accept A. G. Gaydon's value of $\Delta H^\circ_0 = 170.6 \pm 0.2$ kcal/mole as the zero-point heat of sublimation of graphite, then we obtain the following values of ΔF°:

$$\text{C(graphite)} = \text{C(g)}; \qquad \begin{aligned} \Delta F^\circ_{298.16} &= 161.1 \text{ kcal} \\ \Delta F^\circ_{2500} &= 78.2 \text{ kcal} \\ \Delta F^\circ_{5000} &= -13.6 \text{ kcal} \end{aligned}$$

Gaydon's value of ΔH°_0 has been derived indirectly from the spectroscopically determined dissociation energy of CO(g), combined with its standard enthalpy of formation.[2] There has been considerable controversy concerning the heat of sublimation of carbon; the vapor pressure is extremely difficult to measure precisely because of the unusually high temperatures, and its interpretation is obscured by the presence of C_2(g), whose equilibrium conditions with C(g) have not until recently been satisfactorily established.[3] If it were not for the known presence of C_2 molecules in the gas phase (detected spectroscopically), the above ΔF° values would give us the ideal-gas vapor pressure of graphite, through Eq. (6-76). Conversely, a measurement of the vapor pressure at any one temperature (*e.g.*, measurement of the normal sublimation point) would

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[1] "Selected Values of Chemical Thermodynamic Properties," Series III, National Bureau of Standards, Washington, D.C., June 30, 1948; the value at 5000°K, which is above the normal sublimation point of graphite, has been estimated by extrapolation from data given in the table up to 4000°K; results based on it should be regarded as indicative only.

[2] A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," pp. 184–186, John Wiley & Sons, Inc., New York, 1947.

[3] See L. Brewer, P. W. Gilles, and F. A. Jenkins, *J. Chem. Phys.*, **16**, 797–807 (1948); they report $\Delta H^\circ_0 = 170.39 \pm 0.20$ kcal/mole from vapor-pressure measurements corrected for the presence of C_2(g); see also A. L. Marshall and F. J. Norton, *J. Am. Chem. Soc.*, **72**, 2166–2171 (1950).

enable us to calculate the value of ΔH_0° independently. This procedure has in fact been applied to many other vaporization equilibria, where either the vapor consists of a single species of molecule whose spectroscopic properties have been established or the equilibrium conditions among the various species present are known.

b. Molecular Rotation. When we come to consider diatomic and polyatomic molecules, the number of energy levels significant at ordinary temperatures is enormously increased, because of the possibility of molecular rotation and vibration. These energy levels lie much lower than the energy levels associated with excited electronic states of atoms and molecules; K. K. Kelley has given a sample calculation in the case of CO(g) showing that at 298.16°K no fewer than 40 rotational term values have to be taken into consideration in order to fix the thermodynamic functions with ordinary precision.[1] Fortunately, the calculations may be made with quite satisfactory precision in many cases on the basis of approximate theoretical equations based on quantum mechanics, which call for only a general knowledge of the spectroscopic data. In the first place, we may usually ignore the effect at ordinary temperatures of excited electronic states for the majority of diatomic and polyatomic molecules, except for a very few that happen to have multiplet ground states (*e.g.*, NO_2, NOCl, ClO_2). The lowest excited electronic state in most cases lies so far above the ground state that such terms give rise to significant Boltzmann factors only at quite high temperatures. Furthermore, while the rotational and vibrational levels are coupled (a molecule in a high rotational state is stretched, so to speak, by centrifugal force, with a corresponding effect on the vibrational energy), relatively little error is introduced in many cases if we neglect the interaction at ordinary temperatures. Therefore we may write as an approximation

$$\begin{aligned} \zeta_{\text{int}} &= \zeta_{\text{rot}}\,\zeta_{\text{vibr}} \\ \ln \zeta_{\text{int}} &= \ln \zeta_{\text{rot}} + \ln \zeta_{\text{vibr}} \end{aligned} \qquad (10\text{-}103)$$

where each term may be calculated separately by summing the Boltzmann factors over the respective rotational- and vibrational-energy levels.

Now, for a *diatomic molecule*, or as it turns out, for a *linear molecule* in general, the rotational-energy levels are given by the formula

$$\epsilon_{\text{rot}} = K(K+1)\,\frac{h^2}{8\pi^2 I} \quad (K = 0, 1, 2, 3, \ldots) \qquad (10\text{-}104)$$

if we assume as an approximation that the atoms are rigidly connected (*i.e.*, if we ignore the effect of centrifugal stretching on the higher rota-

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[1] K. K. Kelley, *U.S. Bur. Mines Bull.* 434, p. 14 (1941).

tional levels). In this equation, I represents the *moment of inertia*, which for a diatomic molecule has the form

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2 \quad \text{(diatomic molecule)} \qquad (10\text{-}105)$$

where r represents the internuclear distance (the mean or equilibrium value, about which vibration takes place), and m_1 and m_2 represent the masses of the two atoms, which may be regarded as concentrated in the two nuclei; for a linear molecule in general,

$$I = m_1 r_1^2 + m_2 r_2^2 + \cdots \quad \text{(linear molecule)} \qquad (10\text{-}105a)$$

where m_1 denotes the mass and r_1 the distance from the center of mass for the first atom, m_2 the mass and r_2 the distance from the center of mass for the second atom, etc.; $r_1, r_2, \ldots$ satisfy the condition

$$m_1 r_1 + m_2 r_2 + \cdots = 0$$

The energy levels (10-104) each contain $(2K + 1)$ different rotational states, and this of course has to be taken into consideration when one sums over the rotational states.[1]

It turns out according to quantum-mechanical theory that transitions between rotational states associated with actual absorption or emission of radiation are confined to those for which $\Delta K = \pm 1$. Therefore the pure rotational spectrum, if one exists, consists of a series of lines satisfying the relationship

$$\Delta\epsilon_{\text{rot}} = hc\nu = \frac{h^2}{8\pi^2 I}(2K) \quad (K = 1, 2, 3, \ldots) \qquad (10\text{-}106)$$

i.e., lines equally spaced in frequency or wave number [compare Eq.

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[1] The levels given by (10-104) are derived when one solves the Schrödinger equation (10-88) for a system of two "particles" (*i.e.*, the nuclei of the two atoms), with ϵ_p a function only of the interparticle distance; the equation separates into an equation of motion for the center of mass, from which one derives the translational-energy levels (10-92), and an equation for relative motion about the center of mass; if in this latter equation, one treats r as fixed, then the equation may be solved with eigenvalues having the form (10-104). More generally, when r is treated as a variable on which ϵ_p depends, the equation yields combined rotational-vibrational energy levels. See Pauling and Wilson, *op. cit.*, Chap. X. The number K indicates the amount of rotational angular momentum of the molecule, according to a form analogous to that by which J in Table 10-2 represents the amount of *electronic* angular momentum (which is zero for the majority of diatomic and polyatomic molecules in their ground states at ordinary temperatures), and the $(2K + 1)$ states corresponding to the particular rotational-energy level represented by the quantum number K describe different possible orientations of the rotational angular momentum with respect to an arbitrary direction in space.

(10-84)].[1] Since I is typically of order 10^{-40} g cm^2, therefore Eq. (10-106) places these lines at wave numbers of order 100 cm^{-1}, or wavelengths of order 0.01 cm, in the far infrared region of the spectrum. The pure rotational absorption spectra of the hydrogen halides, corresponding to transitions between rotational-energy levels unaccompanied by any change in the vibrational state, were actually detected in this region by M. Czerny, using a wire grating to diffract the transmitted radiation.[2] The lines observed in the case of HCl(g) are given in Table 10-3, together with the assumed value of K; one will note that the value of K in Eq. (10-106) represents the quantum number K of the upper rotational level to which the molecule passes by the absorption of the given frequency of radiation. The third column of Table 10-3 gives the value of $\nu/2K$, and the last column, the mean value of I between the upper and lower states, as given by Eq. (10-106); the rotational constant $h/8\pi^2c$ has the value $(2.7986 \pm 0.0018) \times 10^{-39}$ g cm. The slight increase observed in the value of I with increasing K may be attributed to centrifugal stretching

TABLE 10-3. ROTATIONAL SPECTRUM OF HCl(g)*

K	ν, cm^{-1}	$\nu/2K$, cm^{-1}	I, 10^{-40} g cm^2
4	83.03	10.379	2.6964
5			
6	124.30	10.358	2.7019
7	145.03	10.359	2.7016
8	165.63	10.352	2.7034
9	185.86	10.326	2.7102
10	206.38	10.319	2.7121
11	226.50	10.295	2.7184

* M. Czerny, *Z. Physik,* **34,** 227–244 (1925). The "lines" in the rotational spectrum are actually narrow bands; the presence of the isotopic forms, HCl^{35} and HCl^{37}, whose moments of inertia are slightly different, results in a broadening of the lines.

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[1] According to general theory, a change of dipole moment is necessary in order that the molecule absorb or emit radiation. Therefore homopolar molecules such as N_2 and H_2 show no infrared absorption spectra. The conditions for Raman absorption or emission call for a change in the polarizability of the molecule, but Raman spectra are more generally used for the study of molecular vibrations. See G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., New York, 1945; G. R. Harrison, R. C. Lord, and J. R. Loofbourow, "Practical Spectroscopy," Prentice-Hall, Inc., New York, 1948.

[2] M. Czerny, *Z. Physik*, **34,** 227–244 (1925); **44,** 235–255 (1927); **45,** 476–483 (1927). The hydrogen halides were particularly favorable for this purpose, because of their comparatively small moments of inertia resulting from the great disparity between the masses of the two atoms. Modern microwave spectroscopy, at wavelengths of order 1 cm, has made accessible the entire region just beyond the extreme range of Czerny's measurements; see D. H. Whiffen, *Quart. Revs.*, **4,** 131–152 (1950).

at the higher rotational-energy levels. In order to obtain I_0 for the lowest rotational state of the molecule, we may extrapolate to $K = \frac{1}{2}$, thereby obtaining $I_0 = 2.686 \times 10^{-40}$ g cm^2; this spectroscopic result corresponds to $r_0 = 1.285 \times 10^{-8}$ cm as the mean internuclear distance. This example shows how the value of I may be determined with high precision from spectroscopic data, in a favorable case; if one can measure the internuclear distances independently, such as by electron diffraction for the gas, or X-ray diffraction for the crystalline state (assuming no change on vaporization), then one may compute I geometrically by means of Eq. (10-105) or Eq. (10-105*a*). One may also determine I from independent spectroscopic sources, such as the fine structure of the rotational-vibrational absorption band, or of the electronic transition bands, corresponding to simultaneous changes in the vibrational or the electronic-vibrational states coupled with change in the rotational state.

It thus turns out that for molecules whose I values are at least as great as that of HCl, the value of ϵ_{rot}/kT is at most of order $K(K+1)/T$, and therefore at ordinary and high temperatures, significant contributions are made to ζ_{rot} by energy levels with K values extending beyond 20. While we could evaluate ζ_{rot} precisely by introducing the actual rotational-energy levels as established by detailed spectroscopic information such as is contained in Table 10-3 (supplemented by additional information derived from the rotational-vibrational absorption bands), or by actually summing the expression

$$\zeta_{\text{rot}} = \sum_{K=0}^{\infty} (2K+1)e^{-K(K+1)h^2/8\pi^2 IkT} \tag{10-107}$$

we may derive an approximate expression quite satisfactory at 298.16°K and higher temperatures for all diatomic and linear polyatomic gases with the exception of hydrogen, by means of the integral

$$\zeta_{\text{rot}} \sim \int_0^{\infty} (2K+1)e^{-(h^2/8\pi^2 IkT)K(K+1)}\,dK$$

since the increment by which K increases from term to term in the sum (10-107) equals 1. Letting $x = K(K+1)h^2/8\pi^2 IkT$, and neglecting the slight change of I with K,

$$\begin{aligned}\zeta_{\text{rot}} &= \frac{8\pi^2 IkT}{h^2}\int_0^{\infty} e^{-x}\,dx \\ &= \frac{8\pi^2 IkT}{h^2}\end{aligned} \tag{10-108}$$

An additional factor must be taken into consideration if the molecule has symmetry, as in the case of N_2 or CO_2. If the molecule has two or more identical atoms whose positions are exactly interchanged by a rigid rotation to produce identical states, then only part of the rotational-energy levels are occupied. For homopolar diatomic or for symmetric linear molecules in general, there are two indistinguishable positions assumed during the course of a single rotation, and it turns out in such cases that either only the odd or only the even rotational levels are occupied, depending on the nuclear spin (this situation is a general consequence of Pauli's exclusion principle). At temperatures sufficiently high so that Eq. (10-108) is a satisfactory approximation to Eq. (10-107), it is evident that the odd and the even rotational levels contribute approximately equally to ζ_{rot}. Therefore we may take account of this effect of molecular symmetry by introducing into Eq. (10-108) for ζ_{rot} the factor $\frac{1}{2}$ in such cases, or in general, the factor $1/s$, where s represents the *symmetry number;* the symmetry number of the molecule is defined as the number of indistinguishable positions into which the molecule can be turned by simple rigid rotations (for example, $s = 2$ for N_2, CO_2, and C_2H_2, but $s = 1$ for HCl, HD, and CO).[1] Thus, we may express Eq. (10-108) in the form

$$\zeta_{\text{rot}} = \frac{8\pi^2 IkT}{h^2}\,\frac{1}{s} \quad \text{(linear molecules)} \qquad (10\text{-}109)$$

For nonlinear molecules, the value of ζ_{rot} in the limiting case of sufficiently high temperatures is given by the formula

$$\zeta_{\text{rot}} = \left(\frac{8\pi^2 kT}{h^2}\right)^{3/2} \pi^{1/2}(I_1 I_2 I_3)^{1/2}\,\frac{1}{s} \quad \text{(nonlinear molecules)} \qquad (10\text{-}110)$$

where I_1, I_2, and I_3 represent moments of inertia with respect to the three principal axes of inertia. This equation embraces three cases: the *spherical top* molecule, where $I_1 = I_2 = I_3$ (*e.g.*, CH_4; in this particular exam-

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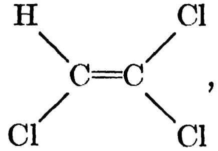
[1] E. B. Wilson, *Chem. Revs.*, **27**, 17–38 (1940). Nuclear spin may introduce further degeneracy in the rotational levels, but since each atomic nucleus apparently retains its spin unchanged throughout all its chemical combinations, this effect cancels out of all calculations of *changes* in the thermodynamic functions, except at extremely low temperatures. It is therefore generally ignored in statistical calculations of chemical thermodynamic properties. The case of H_2 (and also of D_2) presents special complications because of the existence of stable spin isomers, as shown originally by D. M. Dennison, *Proc. Roy. Soc.* (*London*), (A)**115**, 483–486 (1927). Ordinary hydrogen is a mixture of $\frac{1}{4}$ parahydrogen, in which the nuclear spins cancel ($j_s = 0$, the hydrogen nucleus itself having spin: $j_s = \frac{1}{2}$), and $\frac{3}{4}$ orthohydrogen, in which the nuclear spins are parallel ($j_s = 1$, giving rise to $2j_s + 1 = 3$ nuclear spin states for each molecular energy level). Parahydrogen can exist only in the even rotational states, while orthohydrogen can exist only in the odd rotational states. The statistical calculations for hydrogen have been described by W. F. Giauque, *J. Am. Chem. Soc.*, **52**, 4816–4831 (1930). A comprehensive treatment of the thermodynamic properties of hydrogen in its various isotopic and ortho-para modifications has been given by H. W. Wolley, R. B. Scott, and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **41**, 379–475 (1948).

ple, the moment of inertia may be calculated by multiplying the mass of each H atom by the square of its distance from the central C atom, and adding, that is, $I = 4m_{\text{H}}r^2_{\text{C-H}}$; for this and other symmetric tetrahedral molecules, $s = 12$); the *symmetric top* molecule, where $I_1 \neq I_2 = I_3$ (*e.g.*, the pyramidal molecule, NH_3, where $s = 3$, and the planar molecule, BF_3, where $s = 6$); and the *asymmetric top* molecule, where all three moments of inertia are different (*e.g.*, H_2O, where $s = 2$, and  , where $s = 1$). Equation (10-110) is readily derived for the spherical top molecule (with $I_1 = I_2 = I_3 = I$) from the quantum-mechanical energy levels of the rigid spherical rotator by means of an integral approximation similar to the one used in the derivation of Eq. (10-109); the energy levels are given actually by the same formula (10-104) as for the linear molecule, but the number of states belonging to each energy value is given by $(2K + 1)^2$ instead of by $(2K + 1)$.[1] The energy levels of the symmetric top molecule are given by the formula

$$\epsilon_{\text{rot}} = \frac{h^2}{8\pi^2}\left[\frac{K(K+1)}{I_1} + L^2\left(\frac{1}{I_2} - \frac{1}{I_1}\right)\right]$$

where the degree of degeneracy of each energy level is given by $(2K + 1)$, but L may assume any of the $(2K + 1)$ values, $-K$, $-(K - 1)$, . . . , -1, 0, $+1$, . . . , $(K - 1)$, K, each giving rise to a different energy value under the given value of K; L. S. Kassel has given a series approximation for ζ_{rot} in this case, which reduces to Eq. (10-110) at sufficiently high temperatures (I_3 in that equation being of course equal to I_2); for most polyatomic molecules, actually, Eq. (10-110) is a fairly close approximation even at quite low temperatures.[2] For the asymmetric top molecule, the rotational-energy levels cannot be represented exactly by means of an explicit formula, because the equations of motion are too difficult; the generalization (10-110) is believed, however, to be a good approximation for ζ_{rot} at ordinary and high temperatures.[3]

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[1] Make the substitution $x^2 = K(K + 1)h^2/8\pi^2IkT$ in the integral expression for ζ_{rot}, and assume that for most of the significant values of K, one may make the approximation $(2K + 1) \sim 2\sqrt{K(K + 1)} = 2(8\pi^2IkT/h^2)^{1/2}$.

[2] L. S. Kassel, *J. Chem. Phys.*, **1**, 576–585 (1933); *Chem. Revs.*, **18**, 277–313 (1936). The derivation of the eigenvalues of the rigid symmetric top molecule is given by Pauling and Wilson, *op. cit.*, pp. 275–280.

[3] See A. R. Gordon, *J. Chem. Phys.*, **2**, 65–72 (1934); see also G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," pp. 506–507, D. Van Nostrand Company, Inc., New York, 1945.

We may summarize the rotational contributions to the thermodynamic functions [Eqs. (10-98) to (10-101)] in the form of the following table:

LINEAR MOLECULES

$$\bar{H}_{\text{rot}} = RT \tag{10-111a}$$

$$(\bar{C}_p)_{\text{rot}} = R \tag{10-111b}$$

$$\begin{aligned} \bar{S}_{\text{rot}} &= R + R\ln\frac{8\pi^2 k}{h^2} + R\ln\frac{I}{s} + R\ln T \\ &= 177.671 \text{ eu/mole} + R\ln\frac{I}{s} + R\ln T \end{aligned} \tag{10-111c}$$

$$\begin{aligned} \frac{\bar{F}_{\text{rot}}}{T} &= -R\ln\frac{8\pi^2 k}{h^2} - R\ln\frac{I}{s} - R\ln T \\ &= -175.684 \text{ cal/mole deg} - R\ln\frac{I}{s} - R\ln T \end{aligned} \tag{10-111d}$$

NONLINEAR MOLECULES

$$\bar{H}_{\text{rot}} = \tfrac{3}{2}RT \tag{10-112a}$$

$$(\bar{C}_p)_{\text{rot}} = \tfrac{3}{2}R \tag{10-112b}$$

$$\begin{aligned} \bar{S}_{\text{rot}} &= \frac{3}{2}R + \frac{1}{2}R\ln\pi + \frac{3}{2}R\ln\frac{8\pi^2 k}{h^2} + R\ln\frac{(I_1I_2I_3)^{1/2}}{s} + \frac{3}{2}R\ln T \\ &= 267.643 \text{ eu/mole} + R\ln\frac{(I_1I_2I_3)^{1/2}}{s} + \frac{3}{2}R\ln T \end{aligned} \tag{10-112c}$$

$$\begin{aligned} \frac{\bar{F}_{\text{rot}}}{T} &= -\frac{1}{2}R\ln\pi - \frac{3}{2}R\ln\frac{8\pi^2 k}{h^2} - R\ln\frac{(I_1I_2I_3)^{1/2}}{s} - \frac{3}{2}R\ln T \\ &= -264.663 \text{ cal/mole deg} - R\ln\frac{(I_1I_2I_3)^{1/2}}{s} - \frac{3}{2}R\ln T \end{aligned} \tag{10-112d}$$

In particular, at $T = 298.16°\text{K}$,

	LINEAR MOLECULES	NONLINEAR MOLECULES
$\bar{H}_{\text{rot}}$:	592.5 cal/mole	888.8 cal/mole
$(\bar{C}_p)_{\text{rot}}$:	1.987 cal/mole deg	2.981 cal/mole deg
$\bar{S}_{\text{rot}}$:	$\left(188.994 + 4.5757\log\frac{I}{s}\right)$ eu/mole	$\left(284.628 + 4.5757\log\frac{(I_1I_2I_3)^{1/2}}{s}\right)$ eu/mole
$\frac{\bar{F}_{\text{rot}}}{T}$:	$\left(-187.007 - 4.5757\log\frac{I}{s}\right)$ cal/mole deg	$\left(-281.648 - 4.5757\log\frac{(I_1I_2I_3)^{1/2}}{s}\right)$ cal/mole deg

The numerical constants in these equations apply with the moments of inertia represented in g cm².

Introducing now for HCl(g) the value of $I = 2.686 \times 10^{-40}$ g cm² derived from the rotational absorption spectrum, we obtain

$$R\ln I = -181.063 \text{ eu/mole}$$

whence according to Eqs. (10-112c) and (10-112d) at $T = 298.16°\text{K}$,

$$\left.\begin{aligned} \bar{S}_{\text{rot}} &= 7.930 \text{ eu/mole} \\ \frac{\bar{F}_{\text{rot}}}{T} &= -5.943 \text{ cal/mole deg} \end{aligned}\right\} \quad \text{HCl(g) at } 298.16°\text{K}$$

One will note that according to the "high-temperature" approximations represented by Eqs. (10-111) and (10-112), the rotational contributions to $\bar{H}^\circ$ and $\bar{C}_p^\circ$ have the "classical" values corresponding to a quasi-continuous distribution of molecules among rotational states (compare Sec. 3-4); these values are independent of the particular internal structure of the molecule, except in so far as a linear molecule has only two dimensions of rotational motion (rotation about the line of centers being inhibited by the exceedingly small moment of inertia about this axis), while a nonlinear molecule has three.

c. Vibration of Diatomic Molecules. Molecules also show vibrational motions. For most of the *diatomic* gases at ordinary and at low temperatures, this motion may be treated with sufficient accuracy on the assumption that it is *simple harmonic* in nature, *i.e.*, that ϵ_p in the Schrödinger equation (10-88) has the form

$$\epsilon_p = \frac{\varkappa}{2}(r - r_0)^2$$

where r represents the instantaneous distance and r_0 the equilibrium distance between the two nuclei and $\varkappa$ represents a characteristic proportionality factor for the molecule, known as the *force constant;* such a potential-energy function is equivalent to a Hooke's law restoring force, directly proportional in magnitude to the displacement: $(r - r_0)$ (see Sec. 2-1). In this case, the solution of Eq. (10-88) leads to the vibrational-energy levels

$$\epsilon_{\text{vibr}} = (n + \tfrac{1}{2})h\tilde{\nu}_0 \quad (n = 0, 1, 2, 3, \ldots) \tag{10-113}$$

where $\tilde{\nu}_0$, called the *fundamental vibration frequency,* is a constant for the particular kind of molecule related to $\varkappa$ by

$$\tilde{\nu}_0 = \frac{1}{2\pi}\sqrt{\varkappa\left(\frac{m_1 + m_2}{m_1 m_2}\right)} \tag{10-114}$$

Equation (10-113) neglects the interaction between rotation and vibration (*i.e.*, the effect of centrifugal stretching at the higher rotational levels); more serious, however, is the failure of the simple harmonic law, particularly for the higher vibrational levels; these effects are usually not important at ordinary temperatures, but they may have to be taken into account in precise thermodynamic calculations at high temperatures.[1]

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[1] The derivation of Eq. (10-113) in the case of the idealized simple harmonic oscillator, without regard to rotation, is given by Pauling and Wilson, *op. cit.*, pp. 67–82; the general treatment of the rotation and vibration of diatomic molecules is given by them in Chap. X. See also, G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," 2d ed., D. Van Nostrand Company, Inc., New York, 1950.

Now, the selection rule for the absorption or emission of radiation during a transition between states turns out to be $\Delta n = \pm 1$, or 0. The latter condition permits the existence of the pure rotational spectrum, which as we have noted, may occur in the far infrared or the microwave region. If it were not for simultaneous change in the rotational quantum number K, we should thus expect the vibrational spectrum of a diatomic molecule to consist of a single line [compare Eq. (10-83)]:

$$\Delta\epsilon_{\text{vibr}} = h\tilde{\nu}_0 = h\tilde{\nu}$$

with frequency equal to the fundamental vibration frequency. Actually, however, ΔK is at the same time restricted to ± 1. Since the energy difference between successive vibrational states of all diatomic molecules is much greater than the energy differences between the lower rotational levels, we therefore observe a relatively narrow rotational-vibrational band, consisting of two series of approximately equally spaced lines on either side of the fundamental vibration frequency. In the case of HCl(g), this band is detected in the infrared absorption spectrum around a wavelength of 3.46μ (ν = 2886 cm^{-1}).[1] The band components on the high-frequency side (the so-called R branch) correspond to changes for which $\Delta n = 1$ and $\Delta K = +1$, while those on the low-frequency side (the so-called P branch) correspond to changes for which $\Delta n = 1$ and $\Delta K = -1$; the central frequency itself is missing, in agreement with the selection rules, which forbid transitions such that $\Delta K \neq \pm 1$ (ΔK would be 0 for the central frequency). The spacing of the components with respect to frequency is essentially the same as one observes in the pure rotational spectrum, and the fine structure of the rotational-vibrational band therefore yields the same information concerning the moment of inertia and the rotational-energy levels in the case of a diatomic molecule as the pure rotational spectrum, which for molecules whose moments of inertia exceed those of the hydrogen halides occurs in the microwave spectral region.

Vibration frequencies have been investigated extensively also by means of Raman spectra.[2] These consist of lines or bands observed in light scattered by the substance. The *displacements* from the exciting frequency, which is usually in the visible region of the spectrum (*e.g.*, one of the prominent lines in the mercury spectrum), and therefore accessible

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[1] See Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," pp. 53–57.

[2] Discovered by the eminent Indian physicist, C. V. Raman, *Indian J. Phys.*, **2**, 387–398 (1928). For a general description of experimental methods and results, see J. H. Hibben, "The Raman Effect and Its Chemical Applications," Reinhold Publishing Corporation, New York, 1939; Harrison, Lord, and Loofbourow, *op. cit.*

to an ordinary precise spectrograph with suitable adaptations, satisfy Eq. (10-84), ν in that equation representing the *difference* between the exciting and the Raman line wave numbers, and $\epsilon_2 - \epsilon_1$ the corresponding difference between the energy levels of the molecule for the transition responsible for the particular Raman line. Thus, the Raman spectrum gives essentially the same kind of information as the infrared spectrum, with certain differences for polyatomic molecules resulting from a difference between the selection rules for the two types of interaction with radiation.[1] For HCl(g), the displacement of the one observed Raman line (it is actually a band, whose fine structure corresponds to simultaneous changes in n and K) in wave-number units is 2886 cm^{-1}, in agreement with the wave number of the infrared absorption band.[2]

Let us now construct ζ_{vibr} for a diatomic molecule, using the simple harmonic-law approximation (10-113) for the vibrational-energy levels. Let us note at the outset that Eq. (10-113) implies a zero-point energy: $h\tilde{\nu}_0/2$ per molecule in the lowest vibrational state ($n = 0$). It is customary to refer the thermodynamic functions of the gas to this lowest vibrational state (*i.e.*, to include any zero-point energy by implication in the term $\bar{H}_0^\circ$), and we shall therefore subtract out the zero-point energy from the vibrational-energy value of each level. Since according to the theory of the one-dimensional oscillator, each of the vibrational levels is nondegenerate, we may form ζ_{vibr} by means of the equation

$$\zeta_{\text{vibr}} = \sum_{n=0}^{\infty} e^{-(hc\nu_0/kT)n} \tag{10-115}$$

where in accord with standard practice, we have replaced the fundamental vibration frequency $\tilde{\nu}_0$ by the corresponding wave number: $\nu_0 \equiv \tilde{\nu}_0/c$. The sum in Eq. (10-115) is actually a simple power series of the form

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[1] Raman radiation calls for a change in the *polarizability* of the molecule during the transition giving rise to the radiation; ordinary infrared absorption depends on a change in the *dipole moment*. Homopolar diatomic molecules, such as N_2 and O_2, may show rotational-vibrational bands for transitions that involve a simultaneous change in the electronic state, these normally occurring in the visible (or near infrared) and ultraviolet region. For polyatomic molecules having certain types of symmetry, certain Raman lines cannot appear in the infrared absorption spectrum, and vice versa, certain infrared absorption lines cannot appear in the Raman spectrum; therefore a comparison of the two spectra may serve to establish the symmetry, for example, that CO_2 is linear but SO_2 is not, that BF_3 is planar, but NH_3 pyramidal, etc. See G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., New York, 1945.

[2] Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," p. 62.

$$\zeta_{\text{vibr}} = 1 + (e^{-hc\nu_0/kT}) + (e^{-hc\nu_0/kT})^2 + (e^{-hc\nu_0/kT})^3 + \cdots$$

which, since $e^{-hc\nu_0/kT}$ invariably satisfies the condition of not exceeding 1, represents the series expansion of the function

$$\zeta_{\text{vibr}} = \frac{1}{1 - e^{-hc\nu_0/kT}} \tag{10-116}$$

Since $hc\nu_0/kT$ is quite evidently *not* small at ordinary temperatures, judging by the value of ν_0 for HCl, we must *not* attempt to reduce the sum appearing in Eq. (10-115) to an integral, according to the technique that provided us with such an excellent approximation to ζ_{tr} and such a good approximation in most cases at ordinary temperatures to ζ_{rot}. It turns out that for many diatomic gases, most of the molecules at ordinary temperatures are in the ground state of vibrational energy. This represents a distinctive feature of quantum mechanics, as contrasted with classical mechanics, where if *any* vibrational-energy value were available [instead of the restricted set of discrete values represented by Eq. (10-113)], we should expect an equalization on the average between the vibrational kinetic and potential energies and the energies located in other degrees of freedom, including the translational and the rotational motions. Thus

$$\ln \zeta_{\text{vibr}} = -\ln(1 - e^{-hc\nu_0/kT}) \tag{10-117}$$

We may now summarize the vibrational contributions to the thermodynamic functions of a diatomic gas in the form of the following table [bearing in mind Eqs. (10-98) to (10-101) and (10-103)]:

DIATOMIC MOLECULES

$$x \equiv \frac{hc\nu_0}{kT} = \frac{\nu_0}{T} \times (1.43847 \pm 0.00045 \text{ cm deg}) \tag{10-118}$$

$$\bar{H}_{\text{vibr}} = RT\frac{x}{e^x - 1} \tag{10-118a}$$

$$(\bar{C}_p)_{\text{vibr}} = R\frac{x^2e^x}{(e^x - 1)^2} \tag{10-118b}$$

$$\bar{S}_{\text{vibr}} = -R\ln(1 - e^{-x}) + R\frac{x}{e^x - 1} \tag{10-118c}$$

$$\frac{\bar{F}_{\text{vibr}}}{T} = R\ln(1 - e^{-x}) \tag{10-118d}$$

The functions $Rx^2e^x/(e^x - 1)^2$, $Rx/(e^x - 1)$, and $-R\ln(1 - e^{-x})$ appearing in these formulas are known as *Einstein functions;* their values have been tabulated in terms of the variable x, and are given in Appendix 5.[1]

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[1] They appeared originally in A. Einstein's theory of the heat capacity of solids, *Ann. Physik,* **22,** 180–190, 800 (1907). Einstein treated the monatomic crystalline solid essentially as a system of N independent three-dimensional harmonic oscillators, having the uniform fundamental frequency $\tilde{\nu}_0$; with characteristic boldness, he applied

Now, in the case of HCl(g), from the fundamental vibration frequency $\nu_0 = 2886.2$ cm^{-1}, one obtains at 298.16°K, $\nu_0/T = 9.68$ cm^{-1}/deg. Therefore one may conclude that at that temperature, the vibrational contributions to the thermodynamic properties are altogether negligible. This is in accord with the fact that the observed value of $\bar{C}_p^\circ$, 6.96 cal/mole deg at 298.16°K, is entirely accounted for by the translational and rotational terms ($\frac{7}{2}R$). Table 10-4 summarizes the thermodynamic properties computed at 298.16, 500, and 1000°K according to the approximate molecular theory represented by Eqs. (10-111) and (10-118). The entropy calculated at 298.16°K is in excellent agreement with the third-

TABLE 10-4. THERMODYNAMIC PROPERTIES OF HCl(g)*
$I = 2.686 \times 10^{-40}$ g cm^2
$\nu_0 = 2886.2$ cm^{-1}

Temperature	$\bar{H}^\circ - \bar{H}_0^\circ$, cal/mole	$\bar{C}_p^\circ$, cal/mole deg	$\bar{S}^\circ$, eu/mole	$\frac{\bar{F}^\circ - \bar{H}_0^\circ}{T}$, cal/mole deg
298.16°K:				
Translational	1481.3	4.968	36.712	−31.744
Rotational	592.5	1.987	7.930	− 5.943
Vibrational	0.0	0.000	0.000	− 0.000
Total	2073.8	6.955	44.642	−37.687
500°K:				
Translational	2484.0	4.968	39.280	−34.312
Rotational	993.6	1.987	8.958	− 6.971
Vibrational	2.0	0.034	0.004	− 0.000
Total	3479.6	6.989	48.242	−41.283
1000°K:				
Translational	4968.0	4.968	42.724	−37.756
Rotational	1987.2	1.987	10.335	− 8.348
Vibrational	132.	0.557	0.163	− 0.031
Total	7087.	7.512	53.222	−46.135

* Calculations based on rigid-rotator simple-harmonic-oscillator approximations.

Planck's quantum formula to the increments of energy between atomic vibrational levels, and derived for the thermodynamic properties of the solid the formulas (10-118), each multiplied by the factor 3 (because of the three-dimensional character of the atomic vibrations in the crystal lattice). While Einstein's formulas were later superseded by those of Debye, this was the first application of quantum theory to material substances, and represents a truly outstanding contribution by Einstein to modern scientific thought. Planck had introduced his quantum idea originally (in 1900) almost with reluctance, as an inexplicable hypothesis forced on him by the experimental facts connected with the spectral distribution of black-body radiation only.

law entropy: $\bar{S}^\circ_{298.16} = 44.5 \pm 0.15$ eu/mole derived from low-temperature heat-capacity data.[1]

In the case of $Cl_2(g)$, the fundamental vibration frequency, $\nu_0 = 561 \text{ cm}^{-1}$, is considerably lower than in the case of HCl(g), and molecular vibration contributes significantly to the thermodynamic properties at 298.16°K ($\nu_0/T = 1.88$). Precise calculation in this case calls for a consideration of the isotopic molecules, $Cl^{35}Cl^{35}$ and $Cl^{35}Cl^{37}$, of which the gas mainly consists, but fairly precise results, at least as good as those obtained by classical thermodynamic methods, may be derived by the use of average molecular properties. Thus, using $I = 115.2 \times 10^{-40}$ g cm², with $s = 2$, we obtain the data presented in Table 10-5.[2] The third-law entropy

TABLE 10-5. THERMODYNAMIC PROPERTIES OF $Cl_2(g)$*

$I = 115.2 \times 10^{-40}$ g cm²
$\nu_0 = 561$ cm⁻¹
(averages for isotopes)

Temperature	$\bar{H}^\circ - \bar{H}^\circ_0$, cal/mole	$\bar{C}^\circ_p$, cal/mole deg	$\bar{S}^\circ$, eu/mole	$(\bar{F}^\circ - \bar{H}^\circ_0)/T$, cal/mole deg
298.16°K:				
Translational	1481.3	4.968	38.694	−33.726
Rotational	592.5	1.987	14.021	−12.034
Vibrational	114.9	1.117	0.523	− 0.138
Total	2188.6	8.072	53.238	−45.898

* Calculations based on rigid-rotator simple-harmonic-oscillator approximations, using average molecular properties for the isotopes $Cl^{35}Cl^{35}$ and $Cl^{35}Cl^{37}$ weighted according to natural isotopic distribution.

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[1] W. F. Giauque and R. Wiebe, *J. Am. Chem. Soc.*, **50**, 101–122 (1928); the thermodynamic properties at high temperatures have been calculated precisely from the spectroscopically determined energy levels by W. F. Giauque and R. Overstreet, *ibid.*, **54**, 1731–1744 (1932). F. D. Rossini *et al.* in "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D.C., June 30, 1948, report $\bar{S}^\circ_{298.16} = 44.617$ eu/mole, from spectroscopic calculations based on currently accepted values of the natural constants; the values of h and N_0 in particular were revised about 1941 [R. T. Birge, *Rev. Modern Phys.*, **13**, 233–239 (1941)]. The value in Table 10-4 is slightly higher because we have neglected the increase of I with K, and have used the integral approximation (10-108) instead of the actual sum (10-107) over rotational states.

[2] M. Trautz and H. Ader, *Z. Physik*, **89**, 15–23 (1934), have given the precise calculation of $\bar{C}^\circ_p$ for the normal isotopic mixture; Giauque and Overstreet, *loc. cit.*, have calculated the entropy and other thermodynamic properties; the value of $\bar{S}^\circ_{298.16} = 53.286$ eu/mole has been accepted in "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D.C., June 30, 1948. A table of molecular constants (fundamental vibration frequencies and moments of inertia) for many kinds of molecules has been assembled by K. Wohl and H. Zeise in Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIIc, pp. 2341–2364, 1936; one should multiply the moments of inertia, most of

as determined by low-temperature heat-capacity measurements is $\bar{S}^\circ_{298.16} = 53.32 \pm 0.10$ eu/mole.[1]

In order to illustrate the determination of the constant $\bar{H}^\circ_0$ in the case of HCl(g) relative to the elements, let us use the spectroscopically determined values of $(\bar{H}^\circ - \bar{H}^\circ_0)$ reported in "Selected Values of Chemical Thermodynamic Properties":[2]

$$\begin{aligned} \mathrm{HCl(g)}: (\bar{H}_{298.16} - \bar{H}^\circ_0) &= 2064.8 \text{ cal/mole} \\ \mathrm{H_2(g)}: (\bar{H}_{298.16} - \bar{H}^\circ_0) &= 2023.8 \text{ cal/mole} \\ \mathrm{Cl_2(g)}: (\bar{H}_{298.16} - \bar{H}^\circ_0) &= 2193.9 \text{ cal/mole} \end{aligned}$$

Therefore for the reaction

$$\tfrac{1}{2}\mathrm{H_2(g)} + \tfrac{1}{2}\mathrm{Cl_2(g)} = \mathrm{HCl(g)}; \qquad \Delta(\bar{H}^\circ_{298.16} - \bar{H}^\circ_0) = -44.0 \text{ cal}$$

This figure has been derived entirely from spectroscopic data for the three gases, without the need for any thermal or low-temperature measurements; it could have been obtained, with somewhat lower precision, from low-temperature heat-capacity data and heat-of-transition measurements for the three separate substances. Now, the heat of reaction has been measured directly by F. D. Rossini, using an adiabatic flame calorimeter;[3] he obtained the result: $\Delta H^\circ_{298.16} = -22{,}063 \pm 12$ cal. Thus

$$\begin{aligned} \tfrac{1}{2}\mathrm{H_2(g)} + \tfrac{1}{2}\mathrm{Cl_2(g)} = \mathrm{HCl(g)}; \qquad \Delta H^\circ_0 &= -22{,}063 \text{ cal} + 44 \text{ cal} \\ &= -22{,}019 \text{ cal} \end{aligned}$$

---

which were derived from spectral frequencies by means of an equation such as (10-106), by the factor 1.0118, in order to correct for revision in the value of h.

[1] W. F. Giauque and T. M. Powell, *J. Am. Chem. Soc.*, **61**, 1970–1974 (1939). The heat capacity of the gas cannot be measured with anything approaching the precision of the statistical calculations, except with extraordinary experimental difficulty. Therefore the procedure usually followed by Giauque and other investigators in this field has been to measure the heat capacity of the solid and liquid up to the normal boiling point, together with the latent heats of phase transitions. The third-law entropy of the gas at the normal boiling point of the liquid, corrected to the ideal-gas state, is then compared with the value calculated at that temperature from the spectroscopic data. In this way, any discrepancy of theoretical origin may be detected (*e.g.*, random orientation of CO molecules in the crystalline state, affecting the third-law entropy). The above third-law entropy of Cl_2(g) at 298.16°K thus includes a term, 1.76 eu/mole, for the gas between the normal boiling point and 298.16°K, actually based on the spectroscopic data; see Table 8-8, page 512.

[2] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D.C., June 30, 1948. The approximate value for diatomic molecules with sufficiently excited rotational motion, but negligible excitation of vibrational motion, according to Eqs. (10-98) and (10-111*a*), would be $\frac{7}{2}RT = 2073.8$ cal/mole at 298.16°K. Because of the comparatively small moments of inertia of H_2 and HCl molecules, this classical limit has not quite been reached by 298.16°K; for Cl_2, however, the vibrational contribution is significant at that temperature.

[3] F. D. Rossini, *J. Research Natl. Bur. Standards*, **9**, 679–702 (1932).

Had this piece of thermochemical information not been available, we could have derived the value of ΔH_0° alternatively from a single measurement of ΔF° or the equilibrium constant for the reaction at any one temperature [compare Eq. (10-67)]. As it is, we may now proceed to calculate ΔF° at any temperature, using only the one calorimetric measurement and spectroscopic data for the three gases. Thus, the spectroscopically determined values of $(\bar{F}^\circ - \bar{H}_0^\circ)/T$ for the three gases, from precise evaluations of ζ_{int} according to the actual rotational-vibrational energy levels [Eq. (10-101)], are[1]

$$\left.\begin{aligned} \text{HCl(g)}: \frac{\bar{F}^\circ - \bar{H}_0^\circ}{T} &= -37.692 \text{ cal/mole deg} \\ \text{H}_2\text{(g)}: \frac{\bar{F}^\circ - \bar{H}_0^\circ}{T} &= -24.423 \text{ cal/mole deg} \\ \text{Cl}_2\text{(g)}: \frac{\bar{F}^\circ - \bar{H}_0^\circ}{T} &= -45.928 \text{ cal/mole deg} \end{aligned}\right\} T = 298.16^\circ\text{K}$$

Therefore

$$\frac{1}{2}\text{H}_2\text{(g)} + \frac{1}{2}\text{Cl}_2\text{(g)} = \text{HCl(g)}; \qquad \Delta\left(\frac{\bar{F}^\circ - \bar{H}_0^\circ}{T}\right)_{298.16} = -2.516 \text{ cal/mole deg}$$

Introducing the thermochemically derived value of ΔH_0° given above,

$$\begin{aligned} \Delta F_{298.16}^\circ &= -22{,}019 \text{ cal} - (2.516 \times 298.16) \text{ cal} \\ &= -22{,}769 \text{ cal} \end{aligned}$$

This result represents the standard molal free energy of formation of HCl(g) at 298.16°K, and is of course equivalent to the thermodynamic equilibrium constant for the gas reaction, in accordance with the general relationship [Eq. (8-2-1)],

$$\Delta F_T^\circ = -RT \ln K_p^\circ$$

Extension of the calculations to higher temperatures, the value of ΔH_0° being fixed, is straightforward in principle.[2] While the precise treatment calls for introduction of the actual energy levels for the three kinds of molecules, as derived from detailed spectroscopic analysis, the approximate treatment summarized in Eqs. (10-111) and (10-118) in many cases gives results at least as precise as those obtainable from actual equilibrium measurements, and is quite simple to apply.

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[1] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D.C., June 30, 1948.

[2] This reaction has been analyzed in detail by Giauque and Overstreet, *loc. cit.*

d. Dissociation Energies of Diatomic Molecules. The simple harmonic law

$$\epsilon_p = \tfrac{1}{2}\kappa(r - r_0)^2 \tag{10-119}$$

which led to the vibrational-energy levels represented by Eq. (10-113), is a sufficiently accurate approximation for most purposes at ordinary temperatures, but it is unsatisfactory in two respects: it fails to indicate any state beyond which the molecule could be regarded as completely dissociated, and furthermore, there is evidence from the electronic-vibrational band spectra (corresponding to simultaneous changes in the electronic and in the vibrational states, so to speak) that the vibrational-energy levels actually converge with increasing n. Thus, instead of single bands corresponding to each electronic transition (the band structure consisting of a group of closely spaced lines representing rotational transitions), one observes sets of bands, which may appear in the near infrared, visible, or ultraviolet spectral regions, whose wavelengths for the members of a given set converge in the direction of high frequencies, leading ultimately into a region of continuous absorption or emission. If the vibrational levels were all equally spaced, as demanded by the simple harmonic

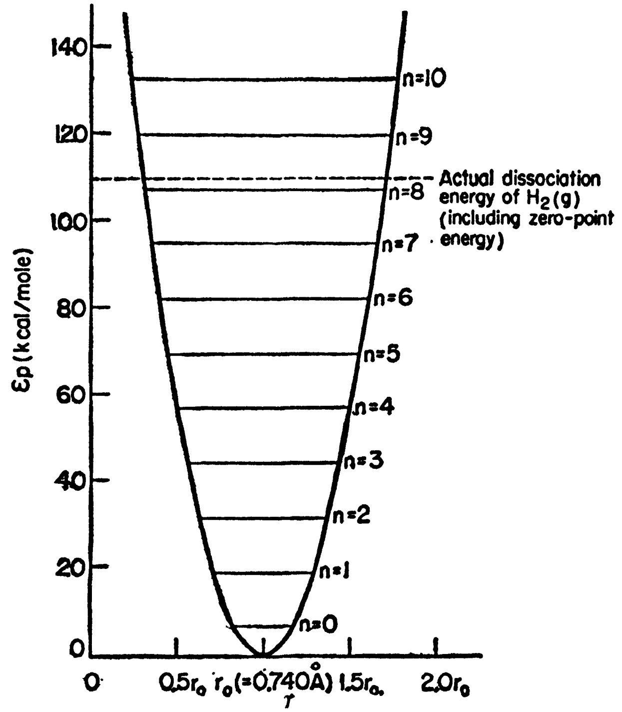

FIG. 10-1. Simple harmonic oscillator potential-energy function and vibrational-energy levels, drawn approximately to scale for constants of the hydrogen molecule.

oscillator model, then we should expect but a single band (with rotational fine structure) corresponding to each different electronic transition, or at most, a set of bands with frequencies some multiple of the fundamental frequency.[1]

It would lead us too far afield to consider the effect of anharmonicity on the vibrational contributions to the thermodynamic functions, though actually this is one of the more serious sources of error in the application of Eqs. (10-118) at high temperatures; but the deviation from the simple harmonic law does constitute an important means of establishing dissociation energies from spectroscopic information. Let us therefore consider this subject briefly, noting, however, that it has nothing to do with

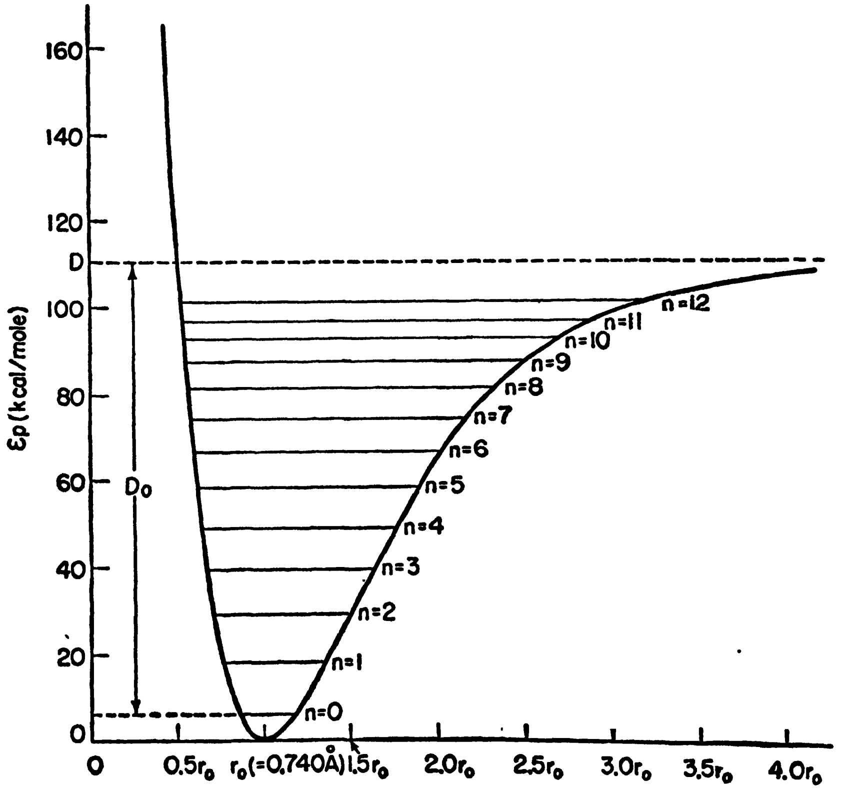

FIG. 10-2. Morse potential-energy function and vibrational-energy levels, drawn approximately to scale for constants of the hydrogen molecule.

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[1] The selection rules for vibrational transitions accompanying electronic transitions are not as restrictive as for pure rotational-vibrational transitions, but are governed by the Franck-Condon principle [J. Franck, *Trans. Faraday Soc.*, **21**, 536–542 (1926); E. U. Condon, *Phys. Rev.*, **28**, 1182–1201 (1926); **32**, 858–872 (1928)]. See E. U. Condon and P. M. Morse, "Quantum Mechanics," Chap. V, McGraw-Hill Book Company, Inc., New York, 1929.

general statistical theory; for further details, the reader is referred to the excellent monographs by Herzberg and by Gaydon.[1]

Figure 10-1 illustrates the general form of the potential-energy curve and energy levels for the simple harmonic oscillator [Eq. (10-119)]. A better approximation to the actual situation is obtained in most cases by means of a potential-energy function proposed by P. M. Morse:[2]

$$\epsilon_p = D\{1 - e^{-a(r-r_0)}\}^2 \tag{10-120}$$

This function has the form shown in Fig. 10-2; with increasing r, ϵ_p approaches the value D, which therefore represents the difference between the energy of the completely dissociated atoms and the energy minimum for the molecule corresponding to $r = r_0$; in order to obtain the true dissociation energy, one must subtract from D the zero-point energy in the lowest actual vibrational state.

Now, if we substitute Eq. (10-120) in the Schrödinger equation (10-88) for the two-body system, and solve for the eigenvalues, we obtain

$$\epsilon_{\text{vibr}} = h\tilde{\nu}_0\left(n + \frac{1}{2}\right) - \frac{h^2\tilde{\nu}_0^2}{4D}\left(n + \frac{1}{2}\right)^2 \qquad (n = 0, 1, 2, 3, \ldots) \tag{10-121}$$

neglecting higher terms representing the interaction between rotation and vibration [the term identified as ϵ_{rot} then has the same form (10-104) as before].[3] The quantity $\tilde{\nu}_0$, which is identified as the fundamental vibration frequency, happens to be related to the constant a in Eq. (10-120) by $\tilde{\nu}_0 = \dfrac{a}{2\pi}\sqrt{2D\left(\dfrac{m_1 + m_2}{m_1 m_2}\right)}$, but this relationship is immaterial for our present purpose, since we have no independent means of establishing the value of a. The vibrational term values [compare Eq. (10-84)] may therefore be put in the form

$$\frac{\epsilon_{\text{vibr}}}{hc} = \nu_0\left(n + \frac{1}{2}\right) - \frac{hc\nu_0^2}{4D}\left(n + \frac{1}{2}\right)^2 \qquad (n = 0, 1, 2, 3, \ldots) \tag{10-122}$$

An empirical relationship of this form is found actually to represent the experimentally determined vibrational terms, as derived from electronic-vibrational band sequences, with a fairly high degree of accuracy in many

---

[1] G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," 2d ed., D. Van Nostrand Company, Inc., New York, 1950. A. G. Gaydon, *op. cit.*

[2] P. M. Morse, *Phys. Rev.*, **34**, 57–64 (1929).

[3] See Pauling and Wilson, *op. cit.*, pp. 271–274.

cases. In the case of $H_2(g)$, for example, the vibrational term values are represented by the following empirical formula:[1]

$$\frac{\epsilon_{\text{vibr}}}{hc} = 4405.3\left(n + \frac{1}{2}\right) - 125.3\left(n + \frac{1}{2}\right)^2 \qquad (10\text{-}123)$$

The coefficient x_0 in the general empirical approximation of the form (10-123)

$$\frac{\epsilon_{\text{vibr}}}{hc} = \nu_0\left(n + \frac{1}{2}\right) - x_0\nu_0\left(n + \frac{1}{2}\right)^2 \qquad (10\text{-}124)$$

is called the *anharmonicity coefficient;* its magnitude measures the extent to which the molecular vibration deviates from the simple harmonic law. In general there is no direct connection between the magnitudes of ν_0 and x_0.

Thus, comparing (10-124) with (10-122),

$$\frac{D}{hc} = \frac{\nu_0}{4x_0} \qquad (10\text{-}125)$$

In order to obtain the dissociation energy relatively to the ground state of vibration ($n = 0$), we must subtract the zero-point energy, $\nu_0/2$ (in wave-number units; the term $x_0\nu_0/4$ may be neglected by comparison); thus

$$\frac{D_0}{hc} = \nu_0\left(\frac{1}{4x_0} - \frac{1}{2}\right) \qquad (10\text{-}126)$$

Therefore from the experimentally established value of x_0, we may calculate approximately the value of D_0, the dissociation energy of the diatomic molecule. Ordinarily, we wish to determine the dissociation energy with respect to the ground state of the atoms produced by the dissociation; in some cases, there is evidence to show that one of the atoms, at least, is produced in an electronically excited state; in such cases, D_0 given by Eq. (10-126) has to be corrected by subtraction of the electronic energy of the excited atom relative to its ground state.

Equation (10-125) may be derived from Eq. (10-124), considered as an empirical relation, without reference to the Morse equation. The terms given by (10-124) converge with increasing n, and we may equate D with the value of ϵ_{vibr} at the convergence limit. In a few cases, the band sequence can be followed spectroscopically all the way up to the convergence limit, or wave number (on the low-frequency side) marking the beginning of continuous absorption or emission. More commonly, however, this region lies beyond the ordinary ultraviolet spectroscopic range.

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[1] Gaydon, *op. cit.*, p. 78.

If one has established a sufficient number of terms (corresponding to the lower values of n) to determine ν_0 and x_0 in Eq. (10-124) accurately, then, as shown by Birge and Sponer, this equation may be used with fair accuracy in many cases to extrapolate the data to the convergence limit.[1] Thus, the difference between successive terms, according to (10-124), is given by

$$\Delta\left(\frac{\epsilon_{\text{vibr}}}{hc}\right) = \nu_0[1 - 2x_0(n + 1)]$$

and therefore the value of n at the convergence limit, if Eq. (10-124) continues to apply, will be

$$n = \frac{1}{2x_0} - 1$$

Substituting in (10-124), and neglecting $x_0\nu_0/4$ in comparison with $\nu_0/4x_0$, we obtain (10-125) as the value of $\epsilon_{\text{vibr}}/hc$ at the convergence limit.

Let us substitute the data for H_2, represented by the empirical equation (10-123), in Eq. (10-126),

$$\begin{aligned}\frac{D_0}{hc} &= 4405.3 \text{ cm}^{-1}\left(\frac{4405.3}{4 \times 125.3} - \frac{1}{2}\right)\\ &= 36{,}520 \text{ cm}^{-1}\end{aligned}$$

A more accurate extrapolation of the actual term values than is possible with the "linear" equation (10-126) results in $D_0/hc = 36{,}100 \pm 40 \text{ cm}^{-1}$.[2] In this case, the atoms produced by the dissociation as a consequence of radiation absorbed at the convergence limit are certainly in their ground states, inasmuch as the lowest electronically excited term of the H atom lies 82,259 cm^{-1} above the ground level. Since D_0 includes no consideration of translational terms, it therefore represents ΔH_0° for the dissociation reaction; using the conversion factor

$$N_0hc = 2.8585 \pm 0.0009 \text{ (cal/mole)/cm}^{-1}$$

to convert from wave-number units to calories per mole:

$$\begin{aligned}H_2(g) = 2H(g); \qquad \Delta H_0^\circ &= 2.8585 \times 36{,}100 \text{ cal}\\ &= 103{,}200 \text{ cal}\end{aligned}$$

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[1] R. T. Birge and H. Sponer, *Phys. Rev.*, **28**, 259–283 (1926). Instead of using Eq. (10-124), which is equivalent to an assumed linear relationship between $\epsilon_{\text{vibr}}/(n + \frac{1}{2})$ and $(n + \frac{1}{2})$, one may use an actual graphical extrapolation to obtain D with higher precision. For illustrations and criticism of the Birge-Sponer extrapolation, see Gaydon, *op. cit.*, Chap. V.

[2] Gaydon, *op. cit.*, p. 78.

In this way, we obtain for H(g), $\bar{H}^\circ_0 = 51{,}600$ cal/mole. We may find $\bar{H}^\circ_{298.16}$ by making use of spectroscopically determined values of $(\bar{H}^\circ_{298.16} - \bar{H}^\circ_0)$ for $H_2(g)$ and H(g), as previously shown; thus

$$
\begin{aligned}
H_2(g)\colon (\bar{H}^\circ_{298.16} - \bar{H}^\circ_0) &= 2023.8 \text{ cal/mole} \\
H(g)\colon (\bar{H}^\circ_{298.16} - \bar{H}^\circ_0) &= \tfrac{5}{2}RT = 1481.2 \text{ cal/mole} \\
\tfrac{1}{2}H_2(g) = H(g); \qquad \Delta(\bar{H}^\circ_{298.16} - \bar{H}^\circ_0) &= 469.3 \text{ cal}
\end{aligned}
$$

Therefore for H(g), $\bar{H}^\circ_{298.16} = 52{,}070$ cal/mole. The other thermodynamic properties of H(g) are readily derived from the statistical theory of the monatomic gas; electronic terms contribute negligibly until extremely high temperatures are reached.

The greatest source of uncertainty in the calculation of dissociation energies by the method just outlined, aside from general uncertainty when a long extrapolation is required from the observed band sequence to its convergence limit, is the identification of the electronic states of the molecule and of the dissociated atoms, corresponding to the given band system. The example we have given happens to be a relatively simple one. Other cases may be far more complex; thus, for N_2, Gaydon has reported a dissociation energy of 225.1 kcal, whereas during the same year, the value accepted by F. D. Rossini and staff for "Selected Values of Chemical Thermodynamic Properties" is 170.2 kcal;[1] there has been considerable difficulty also in the analysis of the spectrum of CO.[2] However, the spectroscopic method has undoubtedly yielded data of considerable value, that would otherwise be all but inaccessible.

e. Vibrations of Polyatomic Molecules. The detailed internal motion of a molecule consisting of more than two atoms is extremely complex, but the molecular vibration may be resolved into a number of so-called *fundamental modes of vibration,* such that the total vibrational energy may be treated approximately as the sum of independent terms associated with the various modes.[3] The fundamental frequencies, together with various overtones and combinations, appear in the infrared absorption and Raman spectra (under certain restrictive selection rules), which constitute the most useful source of such information. In most cases, we do not have to take into consideration electronic-energy terms except at extremely high temperatures; information concerning electronically excited states may be derived from the electronic-vibrational band

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[1] Gaydon, *op. cit.,* Chap. IX; "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D.C., Dec. 31, 1947.

[2] See, for example, G. Glockler, *J. Chem. Phys.,* **18,** 1517–1518 (1950).

[3] See G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Chap. II, D. Van Nostrand Company, Inc., New York, 1945, for an excellent and comprehensive treatment of this subject.

spectra, but generally, the lowest electronically excited state lies well above the excited vibrational states associated with the ground electronic state.

We may assume to a first order of approximation that each fundamental mode of vibration satisfies the simple harmonic law (10-113), with its own characteristic frequency. Therefore the expression for the total vibrational energy may be cast in the form

$$\epsilon_{\text{vibr}} = (n_1 + \tfrac{1}{2})hc\nu_1 + (n_2 + \tfrac{1}{2})hc\nu_2 + (n_3 + \tfrac{1}{2})hc\nu_3 + \cdots \qquad \begin{cases} n_1 = 0, 1, 2, 3, \ldots \\ n_2 = 0, 1, 2, 3, \ldots \\ n_3 = 0, 1, 2, 3, \ldots \\ \ldots\ldots\ldots\ldots \end{cases}$$

Thus

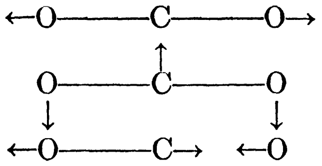
$$\ln \zeta_{\text{vibr}} = -\ln (1 - e^{-hc\nu_1/kT}) - \ln (1 - e^{-hc\nu_2/kT}) - \ln (1 - e^{-hc\nu_3/kT}) - \cdots$$

The thermodynamic functions contain an additive term of the form (10-118) for each fundamental vibration frequency.

Now, the number of fundamental modes of vibration is determined by the number of atoms in the molecule. Thus, if there are N atoms, then it takes $3N$ coordinates to describe its complete state of motion (three for each atom, neglecting the electronic structure). We are not interested, however, in translational motion of the molecule as a whole, or in rotation, which we have already considered separately. If we use three coordinates to describe the motion of the center of mass, then three more are sufficient to describe the rotational motion about the center of mass if the molecule is not linear, or two if it is linear. This leaves $3N - 6$ or $3N - 5$, respectively, depending on whether the molecule is nonlinear or linear, to describe the state of vibration; for example, in the case of a nonlinear triatomic molecule such as H_2O, the three vibrational coordinates may be the three interatomic distances. There are thus $3N - 6$ fundamental vibration frequencies for molecules in general, or $3N - 5$ for linear molecules. These may conveniently be represented as "stretching" frequencies and "bending" frequencies, the former corresponding to oscillations in internuclear distances, and the latter to oscillations in bond angles. The identification of the various fundamental frequencies is the task of the spectroscopist.

In certain cases, there may be internal rotations, such as the relative rotation of the CH_3— and the —OH groups about the C—O bond in methanol. When this internal rotation is entirely free, then an additional rotational term should be included in the rotational partition function, involving the moments of inertia of the rotating groups, and a corresponding fundamental vibration frequency is omitted from the computation of ln $\zeta_{\text{vibr.}}$[1] More generally, however, particularly in the hydrocarbon chains, internal rotation is not free, but is more or less hindered. This was shown in the case of ethane by J. D. Kemp and K. S. Pitzer, who found a small but significant difference between the observed heat capacity and the value calculated on the basis of free internal rotation.[2] Pitzer treated this situation by introducing a potential-energy function depending on the angular displacement of the two groups in relation to each other; this torsional type of internal motion gives rise to a rather complicated expression for the partition function, which may be expressed as a function of temperature in terms of a parameter, the so-called *potential barrier* hindering free rotation. The potential barrier may be estimated from theoretical principles, or from analogies with other similar structures, or it may be obtained empirically from the difference between the observed $\bar{C}_p^\circ$ vs. T curve and the curve calculated without taking the potential barrier into consideration. Tables have been prepared from which accurate corrections to the thermodynamic functions may be computed for this effect.[3] It will serve our present purpose, however, to confine our attention to the simpler types of molecules, in which the complexities associated with internal rotations do not occur.

Now, in the case of the linear CO_2(g) molecule, the fundamental vibration frequencies are represented in the following diagrams:[4]



$\nu_1 = 1337 \text{ cm}^{-1}$

$\nu_2 = 667 \text{ cm}^{-1}$

$\nu_3 = 2349 \text{ cm}^{-1}$

The frequency ν_2 counts twice, since this bending displacement may take place in two equivalent mutually perpendicular directions. The corresponding contributions to the thermodynamic functions at 298.16°K [Eqs. (10-118)], together with the translational and rotational contribu-

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[1] M. L. Eidinoff and J. G. Aston, *J. Chem. Phys.*, **3**, 379–383 (1935). L. S. Kassel, *ibid.*, **4**, 276–282, 435–441, 493–496 (1936), has prepared tables giving the contributions to the rotational partition function for free internal rotations in various types of molecular structures.

[2] J. D. Kemp and K. S. Pitzer, *J. Chem. Phys.*, **4**, 749 (1936); *J. Am. Chem. Soc.*, **59**, 276–279 (1937). See also G. B. Kistiakowsky, J. R. Lacher, and F. Stitt, *J. Chem. Phys.*, **7**, 289–296 (1939).

[3] K. S. Pitzer, *J. Chem. Phys.*, **5**, 469–472 (1937); B. L. Crawford, *ibid.*, **8**, 273–281 (1940); K. S. Pitzer and W. D. Gwinn, *ibid.*, **9**, 485–486 (1941); B. L. Crawford and E. B. Wilson, *ibid.*, 323–329; D. Price, *ibid.*, 807–815; **10**, 80 (1942).

[4] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," p. 173.

tions ($I = 71.87 \times 10^{-40}$ g cm^2; $s = 2$), are presented in Table 10-6. The entropy at 298.16°K is in excellent agreement with the third-law calorimetric value of $\bar{S}^\circ_{298.16} = 51.1 \pm 0.1$ eu/mole reported by K. K. Kelley.[1]

TABLE 10-6. THERMODYNAMIC PROPERTIES OF CO_2(g) AT 298.16°K

	$\bar{H}^\circ - \bar{H}^\circ_0$, cal/mole	$\bar{C}^\circ_p$, cal/mole deg	$\bar{S}^\circ$, eu/mole	$\dfrac{\bar{F}^\circ - \bar{H}^\circ_0}{T}$, cal/mole deg
Translational	1481.2	4.968	37.272	−32.304
Rotational	592.5	1.987	13.105	−11.118
Vibrational:				
ν_1	6.1	0.131	0.025	− 0.003
ν_2	79.6	0.895	0.348	− 0.081
	79.6	0.895	0.348	− 0.081
ν_3	0.1	0.003	0.000	0.000
Total	2239.1	8.879	51.098	−43.587

TABLE 10-7. THERMODYNAMIC PROPERTIES OF H_2CO(g) AT 298.16°K

	$\bar{H}^\circ - \bar{H}^\circ_0$, cal/mole	$\bar{C}^\circ_p$, cal/mole deg	$\bar{S}^\circ$, eu/mole	$\dfrac{\bar{F}^\circ - \bar{H}^\circ_0}{T}$, cal/mole deg
Translational	1481.2	4.968	36.135	−31.167
Rotational	888.8	2.981	16.007	−13.027
Vibrational:				
1167 cm^{-1} (ν_6)	12.1	0.229	0.048	− 0.007
1280 cm^{-1} (ν_5)	7.5	0.156	0.029	− 0.004
1503 cm^{-1} (ν_3)	3.0	0.074	0.012	− 0.001
1744 cm^{-1} (ν_2)	1.1	0.031	0.004	0.000
2780 cm^{-1} (ν_1)	0.2	0.001	0.000	0.000
2874 cm^{-1} (ν_4)	0.1	0.000	0.000	0.000
Total	2394.0	8.440	52.235	−44.206

In Table 10-7, similar data are presented for H_2CO(g). The formaldehyde molecule is supposed to consist of a planar Y structure, with principal moments of inertia: $I_1 = 2.977 \times 10^{-40}$ g cm^2, $I_2 = 21.65 \times 10^{-40}$ g cm^2, $I_3 = 24.62 \times 10^{-40}$ g cm^2, and $s = 2$. The smallest of these quantities represents the moment of inertia about the C—O axis; the other two

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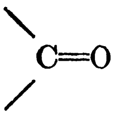
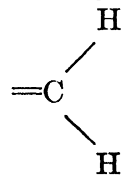
[1] K. K. Kelley, *U.S. Bur. Mines Bull.* 434 (1941). The thermodynamic properties of CO_2(g) at high temperatures have been computed by D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer, and F. D. Rossini, *J. Research Natl. Bur. Standards,* **34,** 143–161 (1945).

represent the moments of inertia about axes normal to the C—O axis, in the plane of the molecule, and normal to the plane of the molecule, respectively. The molecule has six fundamental vibration frequencies, which have been identified approximately as follows: ν_1 and ν_4 correspond, respectively, to symmetrical and antisymmetrical stretching of the two C—H bond distances; ν_2 corresponds to stretching of the C—O bond; ν_3 corresponds to bending of the H—C—H angle; ν_5 and ν_6 correspond to bending of the H—C—O angle in the plane and normal to the plane of the molecule, respectively.[1] The entropy of formaldehyde has apparently never been measured by the third-law calorimetric method, but the spectroscopic method is more precise, and the calculated entropy is in excellent agreement with chemical equilibrium data for this substance.[2]

The $\bar{H}_0^\circ$ values of $CO_2(g)$ and $H_2CO(g)$ may be readily established from their standard enthalpies of formation at 25°C, based on their heats of combustion; one has to know the $(\bar{H}_{298.16}^\circ - \bar{H}_0^\circ)$ values for the elements as well; for the gases, O_2 and H_2, these have been established from spectroscopic data, whereas for C(graphite), the value is known from heat-capacity data extending down to temperatures below which the Debye T^3 law may be used for the extrapolation to 0°K.

When exact spectroscopic data are lacking, but the general shape and dimensions of the molecule are known, one may estimate the fundamental vibration frequencies from characteristic group frequencies that are apparently associated with the presence of certain groups of atoms in the molecule. Herzberg has given a table of such group frequencies;[3] for example, molecules containing the  $>C{=}O$ group generally show a fundamental vibration frequency of about 1700 cm^{-1} associated with bond stretching of this group (compare ν_2 in Table 10-7), and molecules containing the  $=C\begin{matrix}H\\H\end{matrix}$ group generally show a fundamental vibration frequency of about 1100 cm^{-1} associated with bending of the =C—H angle (compare ν_5 and ν_6 in Table 10-7). But when exact spectroscopic data

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[1] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," pp. 300–301; the moments of inertia are given on p. 437.

[2] G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," Reinhold Publishing Corporation, New York, 1932, estimated $\bar{S}_{298}^\circ = 51$ eu/mole, by rough analogy between the structures of formaldehyde and ethylene.

[3] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," p. 195.

are available, the spectroscopic method is far more precise than any other method of establishing the thermodynamic properties of gases; it is essential, of course, that one have a correct interpretation of the spectroscopic data; this depends on a knowledge of general quantum-mechanical principles, together with a certain insight, such as led to the concept of hindered group rotations, in order to account successfully for the comparatively small discrepancies that turned up in the thermodynamic properties of ethane, etc.

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Problems

10-1. Show according to Eq. (10-82) that the average molecular translational kinetic energy in a gas is $\frac{3}{2}kT$. (Multiply by ϵ_k, and integrate from $\epsilon_k = 0$ to ∞; the definite integral involved is of a well-known form, and may be found in tables of integrals, if you are not familiar with it.)

10-2. Calculate according to Eq. (10-92) the value of $(n_x^2 + n_y^2 + n_z^2)$ corresponding to the state of average molecular translational energy: $\frac{3}{2}kT$ in a cube 1 cm on edge of O_2(g) at 298.16°K.

10-3. The lowest term values of the Na(g) atom are as follows:

Term	Number of states	Energy, cm^{-1}
$3s\ ^2S_{1/2}$	2	(0.000)
$3p\ ^2P_{1/2}$	2	16,956.183
$3p\ ^2P_{3/2}$	4	16,973.379
$4s\ ^2S_{1/2}$	2	25,739.86

(Transitions from the $^2P_{1/2}$ and $^2P_{3/2}$ levels to the ground level are responsible for the well-known sodium D "line.") Calculate according to Boltzmann's law, Eq. (10-40), the approximate fractions of the atoms in each of these excited energy levels in sodium vapor at 1000, 1500, and 2000°K.

10-4. The third-law entropy of argon gas at its normal boiling point, 87.29 ± 0.02°K, has recently been redetermined from low-temperature thermal data by K. Clusius and A. Frank [*Z. Elektrochem.*, **49**, 308–309 (1943)], with the following result:

$$\bar{S}^\circ = 30.850 \pm 0.10 \text{ eu/mole}$$

Calculate $\bar{S}^\circ$ at that temperature by the Sackur-Tetrode equation, Eq. (10-97*a*), and compare with the experimental value.

10-5. (*a*) For Zn(c) at 298.16°K,

$$\bar{S}^\circ = 9.95 \text{ eu/mole} \qquad \text{and} \qquad \frac{\bar{H}^\circ - \bar{H}_0^\circ}{T} = 4.52 \text{ cal/mole deg}$$

from low-temperature heat-capacity data. Above 298.16°K, the heat capacities of the solid and the liquid are given by the empirical equations [K. K. Kelley, *U.S. Bur. Mines Bull.* 371 (1934)]:

$$\text{Zn(c)}: \bar{C}_p^\circ = 5.25 + 2.70 \times 10^{-3}T \qquad (273\text{–}692.6^\circ\text{K})$$
$$\text{Zn(l)}: \bar{C}_p^\circ = 7.59 + 0.55 \times 10^{-3}T \qquad (692.6\text{–}1122^\circ\text{K})$$

the latent heat of fusion at the normal melting point, 692.6°K, being 1595 cal/mole. Calculate the values of $(\bar{H}^\circ - \bar{H}_0^\circ)$ and $(\bar{F}^\circ - \bar{H}_0^\circ)/T$ for the condensed phase, Zn(l), at the normal boiling point, 1180°K, where $\bar{H}_0^\circ$ still refers to Zn(c).

(*b*) Zn(g) has a single ground state, the lowest excited electronic term lying more than 30,000 cm^{-1} above the ground level. Calculate the values of $(\bar{H}^\circ - \bar{H}_0^\circ)$ and $(\bar{F}^\circ - \bar{H}_0^\circ)/T$ for Zn(g) at 1180°K.

(*c*) Assuming Zn(g) to satisfy the ideal-gas law, calculate ΔH_0° for the process

$$\text{Zn(c)} = \text{Zn(g)}$$

and also the latent heat of vaporization of Zn(l) at 1180°K, where $\bar{F}^\circ_{\text{Zn(l)}} = \bar{F}^\circ_{\text{Zn(g)}}$.

(*d*) From the preceding data, calculate $(\bar{F}^\circ - \bar{H}_0^\circ)/T$ for Zn(g) at 298.16°K, and the standard free energy of formation of Zn(g) at that temperature.

10-6. The vapor pressure of beryllium has been measured between 1171 and 1552°K by R. B. Holden, R. Speiser, and H. L. Johnston [*J. Am. Chem. Soc.*, **70**, 3897–3899 (1948)], using both the rate of evaporation into a vacuum and the rate of effusion of the saturated metal vapor through an orifice. The following table presents several typical results selected from their data, together with the values of $(\bar{F}^\circ - \bar{H}^\circ_0)/T$ for Be(c) calculated by them from heat-capacity data by means of Eqs. (10-68) and (10-69):

T, °K	$-(\bar{F}^\circ - \bar{H}^\circ_0)/T$ (solid), cal/mole deg	$-\log p$, atm
1172	5.26	8.0726
1209	5.40	7.4528
1265	5.58	6.8692
1320	5.77	6.2673
1419	6.03	5.2859
1457	6.23	5.0254
1552	6.52	4.3471

The ground state of Be(g) atoms is nondegenerate, and the lowest excited electronic state (21,980 cm^{-1}) lies so far above the ground state that its contribution to the thermodynamic functions is negligible at the temperatures under consideration. Calculate $(\bar{F}^\circ - \bar{H}^\circ_0)/T$ for Be(g) at each of the above temperatures by means of Eq. (10-101) (with $\zeta_{\text{int}} = 1$), and making use of the thermodynamic relationship $\Delta F^\circ/T = -R \ln p$, calculate ΔH°_0 at each temperature for the process Be(c) = Be(g). Using the mean value of ΔH°_0 so obtained, calculate ΔH° and ΔF° at 298.16°K, using for Be(c) the following data: $\bar{S}^\circ_{298.16} = 2.28$ eu/mole, and $(\bar{H}_{298.16} - \bar{H}^\circ_0) = 0.47$ kcal/mole.

10-7. The following spectroscopically determined constants have been obtained for the Na_2(g) molecule (Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement IIIc, p. 2349, 1936): $I = 181.3 \times 10^{-40}$ g cm²; $\nu_0 = 158.5\ \text{cm}^{-1}$. The dissociation energy, also spectroscopically determined, is 17,800 cal/mole (A. G. Gaydon, "Dissociation Energies of Diatomic Molecules," John Wiley & Sons, Inc., New York, 1947). Calculate the equilibrium constant, K°_p, for the reaction

$$Na_2(g) = 2Na(g)$$

at the normal boiling point of sodium, 1165°K, and assuming the ideal-gas law, calculate the fraction of the sodium vapor at 1 atm in the form of Na_2(g) molecules. [From the data for Na(g) given in Prob. 10-3, electronic excitation is negligible at the given temperature, but $\zeta_{\text{int}} = 2$ for Na(g) on account of the spin of the odd electron.]

10-8. Using for H_2(g), $I = 0.4719 \times 10^{-40}$ g cm² and $\nu_0 = 4283\ \text{cm}^{-1}$, together with molecular constants for Cl_2(g) and HCl(g) and the value of ΔH°_0 for the reaction $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) = HCl(g)$ given in the text, calculate $\Delta F^\circ/T$ for the reaction and the per cent dissociation of HCl at 1810°K and 1 atm. [Compare with the value given in the "International Critical Tables," Vol. VII, p. 233, McGraw-Hill Book Company, Inc., New York, 1930; compare also W. F. Giauque and R. Overstreet, *J. Am. Chem. Soc.*, **54**, 1731–1744 (1932).]

10-9. (*a*) For I_2(g), $I = 750.2 \times 10^{-40}$ g cm² and $\nu_0 = 214\ \text{cm}^{-1}$. Calculate the values of $(\bar{H}^\circ - \bar{H}^\circ_0)$, $\bar{C}^\circ_p$, $\bar{S}^\circ$, and $(\bar{F}^\circ - \bar{H}^\circ_0)/T$ at 0°C, 25°C, 50°C and 1000°K.

(*b*) At 50°C, the vapor pressure of I_2(c) is 2.154 mm Hg [G. P. Baxter, C. H. Hickey, and W. C. Holmes, *J. Am. Chem. Soc.*, **29**, 127–136 (1907); G. P. Baxter and M. R. Grose, *ibid.*, **37**, 1061–1072 (1915)]. Calculate $(\bar{H}^\circ - \bar{H}^\circ_0)$ and $(\bar{F}^\circ - \bar{H}^\circ_0)/T$ for I_2(c) at 50°C, using the following data for I_2(c) at 25°C: $(\bar{H}^\circ - \bar{H}^\circ_0) = 3182$ cal/mole; $\bar{S}^\circ = 27.9$ eu/mole; $\bar{C}^\circ_p = 13.14$ cal/mole deg. Calculate therefrom ΔH°_0 for the sublimation of iodine: $I_2(c) = I_2(g)$.

(*c*) From the foregoing results, calculate the standard enthalpy and free energy of formation of $I_2(g)$ at 25°C, and the vapor pressure of iodine at that temperature. [Compare W. F. Giauque, *J. Am. Chem. Soc.*, **53**, 507–514 (1931), for a general treatment of this problem.]

10-10. (*a*) The ground level of I(g) is a fourfold degenerate state, $^2P_{3/2}$, and the lowest excited electronic state is a twofold degenerate state, $^2P_{1/2}$, with term value of 7598 cm^{-1}. Calculate the thermodynamic functions $(\bar{H}^\circ - \bar{H}_0^\circ)$ and $(\bar{F}^\circ - \bar{H}_0^\circ)/T$ for I(g) at 298.16 and at 1000°K.

(*b*) The vibrational terms of the $I_2(g)$ molecule are given accurately by the equation

$$\epsilon_n(\text{cm}^{-1}) = 214.26(n + \tfrac{1}{2}) - 0.592(n + \tfrac{1}{2})^2$$

and it is believed that in the limit, the molecule dissociates into one normal $^2P_{3/2}$ atom and one electronically excited $^2P_{1/2}$ atom. Estimate the dissociation energy ΔH_0° for the process $I_2(g) = 2I(g)$. A more accurate measure may be obtained from the convergence limit: 20,037 cm^{-1} of the visible absorption spectrum, corresponding also to dissociation into $^2P_{3/2} + {}^2P_{1/2}$. Calculate ΔH_0° from this experimental source. (Compare A. G. Gaydon, "Dissociation Energies of Diatomic Molecules," pp. 65–66, John Wiley & Sons, Inc., New York, 1947.)

(*c*) Using the results of Prob. 10-9*a*, calculate $\Delta F^\circ/T$ for the dissociation reaction $I_2(g) = 2I(g)$ at 298.16 and at 1000°K, and compute the per cent dissociation at 1000°K and 1 atm (assuming ideal-gas behavior). (Compare your $\Delta F^\circ/T$ value at 1000°K with that computed from the empirical formula based on experimental equilibrium measurements given in the "International Critical Tables," Vol. VII, p. 235, McGraw-Hill Book Company, Inc., New York, 1930.)

10-11. The HCN(g) molecule is linear, and the following molecular constants have been established by spectroscopy (G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., New York, 1945):

$I = 18.816 \times 10^{-40}$ g cm^2
$\nu_1 = 2089.0$ cm^{-1} (HC—N stretching)
$\nu_2 = 712.1$ cm^{-1} (H—C—N bending; twofold degenerate)
$\nu_3 = 3312.0$ cm^{-1} (H—C stretching)

Calculate $\bar{S}_{298.16}^\circ$. [Compare W. F. Giauque and R. A. Ruehrwein, *J. Am. Chem. Soc.*, **61**, 2626–2633 (1939), who also measured the heat capacity of HCN(c) and HCN(l) at low temperatures; the third-law data are complicated by the presence of approximately 10 per cent dimer and smaller percentages of higher polymers in the vapor phase at the normal boiling point, 298.80°K.]

10-12. The $BF_3(g)$ molecule is planar and symmetric, with $s = 6$. The B-F distance, according to electron diffraction measurements, is $(1.30 \pm 0.02) \times 10^{-8}$ cm [H. A. Lévy and L. O. Brockway, *J. Am. Chem. Soc.*, **59**, 2085–2092 (1937)]. Calculate the principal moments of inertia. (For this molecule, one principal axis passes through the central B atom, normal to the plane of the molecule, and $I_1 = 3m_F r_{B-F}^2$; the other two principal axes pass through the B atom in mutually perpendicular directions in the plane of the molecule, and it is easy to show that $I_2 = I_3 = \tfrac{1}{2}I_1$.)

The fundamental vibration frequencies, weighted in accordance with the normal isotopic abundance of B^{10} and B^{11}, have the values: $\nu_1 = 888$, $\nu_2 = 697$, $\nu_3(2) = 1456$, $\nu_4(2) = 480.7$ cm^{-1}, the numbers in parentheses denoting degeneracies (for the significance of these fundamental frequencies, see G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," p. 179, D. Van Nostrand Company, Inc., New

York, 1945). Calculate the values of the thermodynamic functions $(\bar{H}^\circ - \bar{H}_0^\circ)$, $\bar{C}_p^\circ$, $\bar{S}^\circ$, and $(\bar{F}^\circ - \bar{H}_0^\circ)/T$ at 298.16 and at 1000°K. [Compare H. M. Spencer, *J. Chem. Phys.*, **14**, 729–732 (1946).]

10-13. In CO(g), the internuclear distance is 1.13×10^{-8} cm, and the fundamental vibration frequency is 2155 cm^{-1}. Calculate $(\bar{H}^\circ - \bar{H}_0^\circ)$ and $(\bar{F}^\circ - \bar{H}_0^\circ)/T$ at 298.16, 800, 1000, and 1500°K.

Using for C(c, graphite), $(\bar{H}^\circ - \bar{H}_0^\circ) = 251.6$ cal/mole ("Selected Values of Chemical Thermodynamic Properties," Series III, National Bureau of Standards, Washington, D.C., Mar. 31, 1949), and for CO_2(g) the value of $(\bar{H}^\circ - \bar{H}_0^\circ)$ given in Table 10-6, at 298.16°K, together with standard thermochemical data (Appendix 2), calculate ΔH_0° for the producer gas reaction

$$\text{C(c, graphite)} + \text{CO}_2\text{(g)} = 2\text{CO(g)}$$

Using the molecular constants for CO_2(g) given in the text, and the following values of $(\bar{F}^\circ - \bar{H}_0^\circ)/T$ for graphite, derived by means of Eqs. (10-68) and (10-69) from heat-capacity data ("Selected Values of Chemical Thermodynamic Properties"),

T, °K	$(\bar{F}^\circ - \bar{H}_0^\circ)/T$ for C(c, graphite), cal/mole deg
800	−2.138
1000	−2.771
1500	−4.181

calculate the equilibrium ratio of p_{CO} to p_{CO_2} when CO_2 is passed over carbon (graphite) at 800, 1000, and 1500°K, at 1 atm total pressure. [Compare J. O. Clayton and W. F. Giauque, *J. Am. Chem. Soc.*, **54**, 2610–2626 (1932).]

10-14. (*a*) For the CH_4(g) molecule, a spherical top, with $I = 5.330 \times 10^{-40}$ g cm², and $s = 12$, the following fundamental vibration frequencies have been assigned (G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., New York, 1945):

ν, cm^{-1}	Number of Vibrations
1306.2	3 (H—C—H bending)
1526.	2 (H—C—H bending)
2914.2	1 (C—H stretching)
3020.3	3 (C—H stretching)

Calculate $\bar{S}^\circ$ at the normal boiling point, 111°K. [A. Frank and K. Clusius, *Z. physik. Chem.*, (B)**36**, 291–300 (1937), obtained 36.53 ± 0.10 eu/mole according to the third law from low-temperature heat-capacity data.] Calculate also $\bar{S}^\circ$ at 298.16°K.

(*b*) Using for C(c, graphite), $(\bar{H}^\circ - \bar{H}_0^\circ) = 251.6$ cal/mole and for H_2(g), 2023.8 cal/mole at 298.16°K ("Selected Values of Chemical Thermodynamic Properties," Series III, National Bureau of Standards, Washington, D.C., March 31, 1949), and F. D. Rossini's value of 212,790 cal/mole for the heat of combustion of CH_4(g) [to CO_2(g) and H_2O(l) at 298.16°K], together with standard enthalpy data for CO_2(g) and H_2O(l) given in Appendix 2, calculate ΔH_0° for the formation of CH_4(g),

$$\text{C(c, graphite)} + 2\text{H}_2\text{(g)} = \text{CH}_4\text{(g)}$$

and calculate the standard free energy of formation of CH_4(g), at 298.16°K.

(*c*) Calculate $\Delta F^\circ/T$ for the decomposition of methane into its elements at 800°K; the necessary data for graphite are given in Prob. 10-13, and for hydrogen in Prob.

10-8. Calculate the equilibrium percentage of decomposition, and the ratio of p_{H_2} to p_{CH_4} at that temperature and 1 atm total pressure.

10-15. The following molecular constants have been determined for the symmetric-top $CH_3Cl(g)$ molecule:

$$I_1 = 5.49 \times 10^{-40}\text{ g cm}^2; \qquad I_2 = I_3 = 57.1 \times 10^{-40}\text{ g cm}^2$$

$$\begin{aligned} \nu_3 &= 732.1\text{ cm}^{-1} & \nu_6(2) &= 1015.0\text{ cm}^{-1} \\ \nu_2 &= 1354.9\text{ cm}^{-1} & \nu_5(2) &= 1454.6\text{ cm}^{-1} \\ \nu_1 &= 2966.2\text{ cm}^{-1} & \nu_4(2) &= 3041.8\text{ cm}^{-1} \end{aligned}$$

(for the significance of these frequencies, see G. Herzberg, "Infrared and Raman Spectra for Polyatomic Molecules," p. 314, D. Van Nostrand Company, Inc., New York, 1945). Calculate $\bar{S}^\circ_{298.16}$. [Compare G. H. Messerly and J. G. Aston, *J. Am. Chem. Soc.*, **62,** 886–890 (1940), who derived 55.94 eu/mole by the third law from low-temperature calorimetry.]

10-16. For the $NH_3(g)$ molecule, the following molecular constants have been determined by spectroscopic means:

$$I_1 = 4.44 \times 10^{-40}\text{ g cm}^2; \qquad I_2 = I_3 = 2.816 \times 10^{-40}\text{ g cm}^2$$

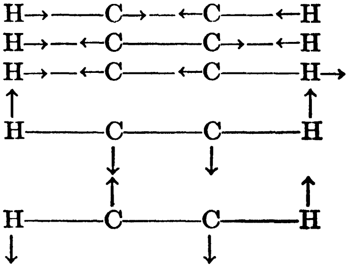
$$\begin{aligned} \nu_1 &= 3335\text{ cm}^{-1} & \nu_3(2) &= 3450\text{ cm}^{-1} \\ \nu_2 &= 948\text{ cm}^{-1} & \nu_4(2) &= 1628\text{ cm}^{-1} \end{aligned}$$

(*a*) Calculate $\bar{S}^\circ$ at the normal boiling point, 239.68°K. From low-temperature thermal data, R. Overstreet and W. F. Giauque [*J. Am. Chem. Soc.*, **59,** 254–259 (1937)] obtained for the liquid, at the normal boiling point, $\bar{S}^\circ = 20.78$ eu/mole; they measured the latent heat of vaporization, and obtained 5581 cal/mole at that temperature (compare Prob. 3-24). Calculate $\bar{S}^\circ$ for $NH_3(g)$ from the thermal data, correcting from 1 atm to the ideal-gas state by means of Berthelot's equation of state (Prob. 6-10), and compare with the spectroscopic value.

(*b*) Calculate $\bar{S}^\circ_{298.16}$ for $NH_3(g)$, and using for $H_2(g)$ the value $\bar{S}^\circ_{298.16} = 31.211$ eu/mole and for $N_2(g)$ the value $\bar{S}^\circ_{298.16} = 45.767$ eu/mole (spectroscopically determined, from "Selected Values of Chemical Thermodynamic Properties"), calculate $\Delta S^\circ_{298.16}$ for the formation of $NH_3(g)$ from its elements. Using the thermochemically determined value of $\Delta H^\circ_{298.16} = -11.04$ kcal, calculate $\Delta F^\circ_{298.16}$, and compare with the value derived from high-temperature equilibrium measurements in Sec. 8-1*c*. [Compare C. C. Stephenson and H. D. McMahon, *J. Am. Chem. Soc.*, **61,** 437–440 (1939).]

10-17. The acetylene molecule is linear; the C≡C distance is 1.203×10^{-8} cm, and the C—H distance is 1.060×10^{-8} cm, the symmetry number *s* being 2. Following are the fundamental vibration frequencies:

$\nu_2(s) = 1975\text{ cm}^{-1}$
$\nu_1(s) = 3370\text{ cm}^{-1}$
$\nu(a) = 3277\text{ cm}^{-1}$
$\delta(a) = 729(2)\text{ cm}^{-1}$
$\delta(s) = 600(2)\text{ cm}^{-1}$



(δ stands for a bending frequency, while *s* and *a* denote respectively, symmetric and antisymmetric modes of vibration). Calculate the values of $(\bar{H}^\circ - \bar{H}^\circ_0)$, $\bar{C}^\circ_p$, $\bar{S}^\circ$, and

$(\bar{F}^\circ - \bar{H}_0^\circ)/T$ at 298.16°K. [Compare, D. D. Wagman, J. E. Kilpatrick, K. S. Pitzer, and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 467–496 (1946).]

From the standard heat of combustion at 25°C, 310,615 cal/mole, together with appropriate thermochemical data from Appendix 2, and the values of $(\bar{H}^\circ - \bar{H}_0^\circ)$ at 298.16°K for C(c, graphite) and H_2(g) given in Prob. 10-14, calculate ΔF° for the formation of C_2H_2(g) from its elements at 298.16°K.

10-18. B. L. Crawford and R. G. Parr [*J. Chem. Phys.*, **16**, 233–236 (1948)] have worked out a table based on the Einstein function, by means of which the contributions of any vibrational frequency to the "best" (least squares) values of the constants in the empirical equation

$$(\bar{C}_p^\circ)_{\text{vibr}} = a_0 + a_1T + a_2T^2$$

for the vibrational heat capacity over the range 250 to 1500°K may be determined. These contributions to a_0, a_1, and a_2 are to be added for each fundamental vibration frequency, account being taken of repeated contributions from degenerate frequencies. There is finally to be added a constant term, $\frac{7}{2}R = 6.954$ cal/mole deg for linear molecules, or $4R = 7.948$ cal/mole deg for nonlinear molecules, to give the corresponding empirical equation for the total heat capacity, $\bar{C}_p^\circ$, including translational and rotational terms. By consulting their table in the reference cited, construct a heat-capacity equation of the form $\bar{C}_p^\circ = a + bT + cT^2$ [Eq. (3-58)] for SO_2(g), using the fundamental vibration frequencies 525, 1152, 1361 cm^{-1} for this nonlinear molecule. Test the equation at 1000°K, where $\bar{C}_p^\circ = 12.90$ cal/mole deg, by direct spectroscopic computation (D. M. Yost and H. Russell, "Systematic Inorganic Chemistry," p. 319, Prentice-Hall, Inc., New York, 1944).

Carry out a similar construction for CO_2(g), using the fundamental vibration frequencies given in the text.

10-19. Equations (10-100) and (10-101) may be applied to free electrons in the solar and stellar atmospheres, as shown originally by M. N. Saha [*Phil. Mag.*, (6) **40**, 472–488, 809–824 (1920); *Proc. Roy. Soc.* (*London*), (A)**99**, 135–152 (1921)]. One substitutes for $\bar{M}$ the electron mass on the atomic-weight scale, 5.485×10^{-4} g/mole, and lets $\zeta_{\text{int}} = 2$ to take account of electron spin (two different spin states, with opposite spin orientations, for each translational state). Boltzmann's statistics apparently apply at the high temperatures and relatively low electron densities involved. Calculate ΔF° for the ionization reaction

$$\text{Ca(g)} = \text{Ca}^+\text{(g)} + e\text{(g)}$$

at 6500°K (the approximate temperature of the sun's chromosphere); the value of ΔH_0° may be computed from the ionization potential, 6.111 volts. Note that the neutral Ca(g) atom has no net electron spin (therefore $\zeta_{\text{int}} = 1$), but that the Ca^+(g) ion has the same spin as the electron itself (therefore $\zeta_{\text{int}} = 2$). Note also that the terms contributed to $\Delta(\bar{F}^\circ - \bar{H}_0^\circ)/T$ by Ca(g) and by Ca^+(g) cancel, except for the term $-R \ln 2$ contributed by Ca^+(g) through spin degeneracy.

From the value of $\Delta F^\circ/T = -R \ln K_p^\circ$, calculate the percentage of ionization of Ca(g) at the given temperature, at pressures of 1 atm, 0.01 atm, and 0.0001 atm, assuming that all the electron gas results from this process (this is not actually the case, of course, in actual stellar atmospheres, but since the ratio of Ca to Ca^+ can be directly observed by means of the relative intensities of the corresponding spectral lines, these calculations are of considerable value in the establishment of stellar conditions; see M. N. Saha and N. K. Saha, "A Treatise on Modern Physics," pp. 628–656, The Indian Press, Ltd., Allahabad, 1934).

Carry out similar computations for the reaction

$$\mathrm{Na(g)} = \mathrm{Na^+(g)} + e\mathrm{(g)}$$

at 6500°K. The ionization potential of Na(g) is 5.138 volts. Note that $\zeta_{\text{int}} = 2$ for Na(g) atoms, because of the spin of the odd electron, but $\zeta_{\text{int}} = 1$ for $\mathrm{Na^+(g)}$ ions.

10-20. (*a*) The following molecular constants have been determined for the spectroscopically observed OH(g) molecule:

$$I = 1.512 \times 10^{-40}\ \mathrm{g\ cm^2}; \qquad \nu_0 = 3649\ \mathrm{cm^{-1}}$$

The ground state $(^2\Pi_{3/2})$ is an electronic doublet (because of the odd electron), and there is another low-lying electronic term $(^2\Pi_{1/2})$, also a doublet, whose term value is 140.3 $\mathrm{cm^{-1}}$. These electronic contributions to the thermodynamic functions may be treated as approximately independent of the rotational and vibrational contributions, and may be simply added. Calculate accordingly the values of $(\bar{H}^\circ - \bar{H}_0^\circ)$ and $(\bar{F}^\circ - \bar{H}_0^\circ)/T$ at 298.16, 1000, and 2000°K. Because of the relatively small moment of inertia, and the correspondingly low degree of rotational excitation at 298.16°K, the rotational contributions calculated according to Eqs. (10-111) will be slightly too high in magnitude, as compared with calculations based on the actual rotational-vibrational energy levels. [Compare H. L. Johnston and D. H. Dawson, *J. Am. Chem. Soc.*, **55**, 2744–2753 (1933).]

(*b*) Calculate at 298.16, 1000, and 2000°K, the enthalpies and the equilibrium constants of the following reactions:

$$\begin{aligned}
\tfrac{1}{2}\mathrm{O_2(g)} + \tfrac{1}{2}\mathrm{H_2(g)} &= \mathrm{OH(g)} \\
\mathrm{H_2(g)} + \mathrm{OH(g)} &= \mathrm{H_2O(g)} + \mathrm{H(g)} \\
\mathrm{O_2(g)} + \mathrm{H(g)} &= \mathrm{OH(g)} + \mathrm{O(g)} \\
\mathrm{H_2O(g)} &= \mathrm{OH(g)} + \tfrac{1}{2}\mathrm{H_2(g)}
\end{aligned}$$

using the following supplementary information ("Selected Values of Chemical Thermodynamic Properties," Series III, National Bureau of Standards, Washington, D.C., March 31,1949):

Substance	298.16°K		1000°K		2000°K	
	$(\bar{H}^\circ - \bar{H}_0^\circ)$, kcal	$(\bar{F}^\circ - \bar{H}_0^\circ)/T$, kcal/deg	$(\bar{H}^\circ - \bar{H}_0^\circ)$, kcal	$(\bar{F}^\circ - \bar{H}_0^\circ)/T$, kcal/deg	$(\bar{H}^\circ - \bar{H}_0^\circ)$, kcal	$(\bar{F}^\circ - \bar{H}_0^\circ)/T$, kcal/deg
$\mathrm{O_2(g)}$	2069.8	−42.061	7497.0	−50.697	16,218	−56.104
O(g)	1607.4	−33.078	5158.8	−39.460	10,143	−43.003
$\mathrm{H_2(g)}$	2023.8	−24.423	6965.8	−32.738	14,672	−37.669
H(g)	1481.2	−22.425	4968.0	−28.436	9,936	−31.880
$\mathrm{H_2O(g)}$	2367.7	−37.165	8608.0	−47.010	19,630	−53.322

The zero-point dissociation energy of $\mathrm{O_2(g)}$, from spectroscopic data, is 117.172 kcal/mole; that of OH(g) is 100.2 kcal/mole; that of $\mathrm{H_2(g)}$ is given in the text. The standard enthalpy of formation of $\mathrm{H_2O(g)}$ is given at 298.16°K in Appendix 2.

10-21. (*a*) Using the data for formaldehyde in Table 10-7 and the standard entropy values given in Appendix 2, calculate ΔS° at 298.16°K for the hypothetical reaction

$$\mathrm{CO_2(g)} + \mathrm{H_2O(l)} = \mathrm{H_2CO(g)} + \mathrm{O_2(g)}$$

From the heat of combustion of $H_2CO(g)$ at 25°C, 134,700 cal/mole, together with appropriate thermochemical data from Appendix 2, calculate ΔH° and ΔF° for this reaction at 298.16°K.

(*b*) Formaldehyde in dilute aqueous solution apparently satisfies Henry's law, at least up to $x_2 = 0.04$, and the partial vapor pressure of H_2CO from a 1*m* solution is 0.000248 atm at 25°C (G. S. Parks and H. M. Huffman, "Free Energies of Some Organic Compounds," p. 158, Reinhold Publishing Corporation, New York, 1932). Calculate the standard free-energy change for the process $H_2CO(g) = H_2CO(aq)$, and using the result of part (*a*), calculate $\Delta F^\circ_{298.16}$ for the reaction

$$CO_2(g) + H_2O(l) = H_2CO(aq) + O_2(g)$$

(*c*) Calculate the value of ΔF for the above reaction when $p_{CO_2} = 0.0003$ atm, $p_{O_2} = 0.20$ atm, and $m_{H_2CO} = 0.001$ mole/kg. If the nonthermal energy required to effect the transformation were in the form of radiation of wavelength 6750 Å (the absorption peak for chlorophyll), at least how many light quanta of energy $N_0h\bar{\nu}$ per mole would theoretically be required per mole of H_2CO?

10-22. Investigate the thermodynamic feasibility of the reaction

$$H_2(g) + CO(g) = H_2CO(g)$$

at 298.16, 500, and 1000°K, using information given in this chapter and in preceding problems.

10-23. The following data have been established for the five isomeric hexanes. The enthalpies of isomerization given in the second column were determined by a relative heat-of-combustion method [E. J. R. Prosen and F. D. Rossini, *J. Research Natl. Bur. Standards*, **27**, 289–310 (1941)], while the thermodynamic data for the pure isomers given in the last four columns were obtained by a combination of spectroscopic information with third-law entropy data (to establish the potential barriers hindering free rotation), summarized in *Natl. Bur. Standards Circ.* C461, pp. 194, 230 (1947).

Isomer (ideal gas)	$\Delta H^\circ_{298.16}$ for n-C_6H_{14} = i-C_6H_{14}, cal/mole	298.16°K		500°K	
		$\bar{H}^\circ - \bar{H}^\circ_0$, cal/mole	$(\bar{F}^\circ - \bar{H}^\circ_0)/T$, cal/mole deg	$\bar{H}^\circ - \bar{H}^\circ_0$, cal/mole	$(\bar{F}^\circ - \bar{H}^\circ_0)/T$, cal/mole deg
n-Hexane	0	6691	−70.01	15,550	−83.65
2-Methylpentane	−1680	6097	−70.20	14,950	−83.0
3-Methylpentane	−1090	6148	−70.15	15,100	−83.1
2,2-Dimethylbutane	−4440	5936	−65.81	14,800	−78.4
2,3-Dimethylbutane	−2580	6070	−66.97	14,950	−79.8

Calculate the theoretical equilibrium composition of "hexane" in the ideal-gas state at 298.16°K and at 500°K. Which is the most stable isomer at each of these temperatures? Compare F. D. Rossini, E. J. R. Prosen, and K. S. Pitzer, *J. Research Natl. Bur. Standards*, **27**, 529–541 (1941); compare also the experimental study by B. L. Evering and E. L. d'Ouville, *J. Am. Chem. Soc.*, **71**, 440–445 (1949)].

APPENDIX 1

MATHEMATICAL TECHNIQUE

The state of a homogeneous chemical substance ordinarily depends on at least two independent variables, for example, temperature and pressure, and in special cases may depend on additional variables, such as magnetic field strength, altitude, etc. The state of a homogeneous substance of continuously variable composition (a solution) depends on one or more additional independent variables required to define the composition. Since the fundamental laws of thermodynamics are general statements concerning changes that may take place in the state of a thermodynamic system, these laws applied to material systems are therefore expressible in the form of differential equations in two or more independent variables. The discrete structure of matter, which might conceivably interfere with the continuity of our functional relationships, does not concern us in purely thermodynamic investigation, which is confined to observations on macroscopic systems containing enormous numbers of molecules.

When we are dealing with a continuous function $f(x)$ of a single independent variable x, then changes in this function with changes in the variable x may be represented in terms of the derivative function $f'(x)$, which if it exists, is defined by the relationship

$$f'(x) \equiv \frac{df}{dx} \equiv \lim_{\Delta x \to 0} \frac{f(x + \Delta x) - f(x)}{\Delta x} \tag{1}$$

For a sufficiently small increment Δx in the variable x, at say the value x_0, the corresponding change in $f(x)$ is given to a first order of approximation by the formula

$$\Delta f = f'(x_0)\Delta x \tag{2}$$

so that if the value of $f'(x_0)$ were known, the value of Δf could be computed accordingly. Since $f'(x)$ itself varies in general with x, this approximation breaks down as Δx increases in magnitude, but we may then invoke the methods of the integral calculus, in the symbolic form

$$f(x) - f(x_0) = \int_{x_0}^{x} f'(x)dx \tag{3}$$

Provided that $f'(x)$ is continuous and finite over the range x_0 to x, this integral always exists, and it defines the function $f(x)$, though this function is not necessarily expressible in terms of familiar algebraic or trigonometric forms. One may always evaluate the integral function $f(x)$ between two specific values x_0 and x of the independent variable, given $f'(x)$, by graphical or numerical integration, *e.g.*, by means of a series expansion of $f'(x)$ integrated term by term. The Debye function $D(\theta/T)$ presented in Appendix 4 is an example of such a function of the variable θ/T, whose value has been worked out by series expansion and integration, but the integral function may be established in principle even for a quite arbitrary function $f'(x)$, provided that it is continuous and finite over the range of integration.

Now, for a function $f(x, y)$ of *two* independent variables, x and y, the value of f may vary with either variable independently of the other. We thus have two first derivatives

$$\left.\begin{aligned} \left(\frac{df}{dx}\right)_y &= \lim_{\Delta x \to 0} \frac{f(x + \Delta x, y) - f(x, y)}{\Delta x} \\ \left(\frac{df}{dy}\right)_x &= \lim_{\Delta y \to 0} \frac{f(x, y + \Delta y) - f(x, y)}{\Delta y} \end{aligned}\right\} \tag{4}$$

both of which in general are functions of both variables, x and y. The change of f with small changes dx and dy in both variables may therefore be expressed formally, to a first order of approximation, by

$$df = \left(\frac{df}{dx}\right)_y dx + \left(\frac{df}{dy}\right)_x dy \tag{5}$$

on the supposition that changes in the functions $(df/dx)_y$ and $(df/dy)_x$ themselves become infinitesimals of order higher than that of dx and dy, when dx and dy become sufficiently small.

Let $f'_y(x, y)$ and $f'_x(x, y)$ denote, respectively, the two first derivatives defined by Eqs. (4), the subscript denoting the variable held constant as each of these functions is derived from $f(x, y)$. Then for a finite change of the independent variables from x_0, y_0, to x, y, we may represent the change of $f(x, y)$ in either of the equivalent forms

$$f(x, y) - f(x_0, y_0) = \int_{x_0}^{x} f'_y(x, y_0)dx + \int_{y_0}^{y} f'_x(x, y)dy \tag{6a}$$

where the first integral is to be evaluated at constant $y = y_0$ and the second at constant x, or

$$f(x, y) - f(x_0, y_0) = \int_{x_0}^{x} f'_y(x, y)dx + \int_{y_0}^{y} f'_x(x_0, y)dy \tag{6b}$$

where the first integral is to be evaluated at constant y and the second at constant $x = x_0$. For that matter, since the value of f depends only on the values of x and y and not on how one gets from (x_0, y_0) to (x, y), one may evaluate $f(x, y) - f(x_0, y_0)$ by integrating (5) along any convenient path connecting (x_0, y_0) with (x, y) in the X-Y plane, but the particular paths corresponding to Eqs. (6*a*) and (6*b*) reduce the general integral to a sum of two integrals each involving one of the two variables separately. This procedure was followed, for example, when we set up $\bar{U}$ and $\bar{H}$ as functions of T and p in Eqs. (3-33) and (3-47) for a homogeneous chemical substance of fixed composition.

Given, however, the general form

$$dF = L(x, y)dx + M(x, y)dy \tag{7}$$

where $L(x, y)$ and $M(x, y)$ are arbitrary finite continuous functions of x and y, it does *not* necessarily follow that a function $F(x, y)$ exists, satisfying the relationship (5), where $L(x, y)$ may be identified with $(dF/dx)_y$ and $M(x, y)$ with $(dF/dy)_x$. A pair of simple illustrations will make this clear. Thus, consider first the differential equation

$$df = y\,dx + x\,dy \tag{8}$$

where by definition, $(df/dx)_y = y$ and $(df/dy)_x = x$. It is obvious by inspection in this case that

$$df = d(xy)$$

Therefore f must have the form

$$f = xy + \text{const}$$

i.e., it is a function of x and y, completely defined by Eq. (8) except for a constant of integration independent of x and y. Consider on the other hand the differential equation

$$d'F = y\,dx - x\,dy \tag{9}$$

This equation, unlike (8), cannot be integrated unless one specifies how y is to vary with x; in other words, the value of $F(x, y) - F(x_0, y_0)$ is not determined solely by the values of x and y for given x_0, y_0, but depends on the particular curve $y(x)$ in the X-Y plane by which one goes from (x_0, y_0) to (x, y). [Compare for example its value along the curve $y = x^2$ with its value along the straight line $y = x$, in going from the origin (0, 0) to the point (1, 1), or compare its value between the same pair of points along the path $x = 0$, $y = 0$ to 1, followed by $y = 1$, $x = 0$ to 1, with that along the path $y = 0$, $x = 0$ to 1, followed by $x = 1$, $y = 0$ to 1.]

The differential of a quantity such as f in Eq. (8) is called a *perfect* or *complete differential,* corresponding to a definite function $f(x, y)$ completely defined (except for an integration constant) by the values of the independent variables; according to the first law of thermodynamics, dU and dH are such perfect differentials for changes in the state of a thermodynamic system. A differential quantity $d'F$ such as in Eq. (9), on the other hand, is not a perfect differential, and the corresponding integral quantity F is not determined solely by the initial and final values of the independent variables; we have used the notation d' instead of d to indicate this condition, and $d'Q$ and $d'W$ are examples drawn from thermodynamics of such quantities. In inducing a change of state in a thermodynamic system, we have experimentally a certain degree of choice whether to introduce or remove energy in thermal or in nonthermal form, but we have no such choice concerning the net quantity of energy, which is fixed by nature for a given change of state.

The general condition for a differential expression of the form of Eq (7) to be integrable, independently of any imposed connection between the variables x and y, is that

$$\left(\frac{dL}{dy}\right)_x = \left(\frac{dM}{dx}\right)_y \tag{10}$$

In view of Eq. (5), this condition, attributed to L. Euler, is equivalent to

$$\frac{\partial^2 F}{\partial x\,\partial y} = \frac{\partial^2 F}{\partial y\,\partial x} \tag{11}$$

which merely expresses the fact that if the value of F is determined completely by the values of x and y (except for a constant independent of x and y), then the order of differentiation with respect to the two variables is immaterial. In other words, if there exists a function $F(x, y)$ satisfying Eq. (7), then by supposition this function satisfies in particular Eq. (6a), which we may rewrite in the form

$$F(x, y) - F(x_0, y_0) = \int_{x_0}^{x} L(x, y_0)dx + \int_{y_0}^{y} M(x, y)dy$$

Therefore

$$\frac{\partial F}{\partial x} = L(x, y_0) + \int_{y_0}^{y} \left(\frac{dM}{dx}\right)_y dy$$
$$\frac{\partial}{\partial y}\left(\frac{\partial F}{\partial x}\right) = \left(\frac{dM}{dx}\right)_y$$

Since, however, according to Eq. (7) [compare also Eq. (5)], $M(x, y) = (\partial F/\partial y)$, therefore Eq. (11) and its equivalent Eq. (10) follow. Thus, given a differential equation in the form of Eq. (7), and knowing that F is a function completely defined by the values of the independent variables x and y (except possibly for an arbitrary additive integration constant), we may immediately infer the relationship, Eq. (10). On the other hand, a quantity F defined by a differential equation of the form, Eq. (7), where $L(x, y)$ and $M(x, y)$ satisfy the relationship, Eq. (10), can be shown to be a function of the variables x and y, independent of the manner in which x and y are interconnected during a particular change, (x_0, y_0) to (x, y).

When we have a differential quantity dF in the form of Eq. (7) *not* satisfying Eq. (10), it may be possible for us to find an *integrating factor*, which when multiplied into dF transforms this quantity into a perfect differential. Thus, it is obvious that if we multiply $d'F$ defined by Eq. (9) by the factor $(1/xy)$, then the resulting expression

$$\frac{d'F}{xy} = d \ln x - d \ln y$$

is a perfect differential of the function $\ln (x/y) +$ constant. Let $\xi(x, y)$ represent an integrating factor for the general differential expression (7); then, according to (10),

$$\left[\frac{d(\xi L)}{dy}\right]_x = \left[\frac{d(\xi M)}{dx}\right]_y$$
$$\xi \frac{\partial L}{\partial y} + L \frac{\partial \xi}{\partial y} = \xi \frac{\partial M}{\partial x} + M \frac{\partial \xi}{\partial x}$$
$$L \frac{\partial \xi}{\partial y} - M \frac{\partial \xi}{\partial x} = \xi \left(\frac{\partial M}{\partial x} - \frac{\partial L}{\partial y}\right) \tag{12}$$

The integrating factor $\xi(x, y)$, if one exists, must satisfy the differential equation (12). It is in such a sense that $(1/T)$ is an integrating factor for $d'Q_r$ the differential element of heat absorbed by a thermodynamic system during any reversible change of state; this condition is implied by the second law of thermodynamics.

We may readily extend the treatment to functions of more than two independent variables. Thus, let $f(x_1, x_2, \ldots, x_c)$ represent a continuous function of the independent variables $x_1, x_2, \ldots, x_c$. Then to a first order of approximation for sufficiently small changes $dx_1, dx_2, \ldots, dx_c$ in the independent variables, provided that all the first derivatives with respect to the different variables exist, the change in f will be represented by the equation

$$df = \left(\frac{df}{dx_1}\right)_{x_2, \ldots, x_c} dx_1 + \left(\frac{df}{dx_2}\right)_{x_1, x_3, \ldots, x_c} dx_2 + \cdots + \left(\frac{df}{dx_c}\right)_{x_1, x_2, \ldots, x_{c-1}} dx_c \tag{13}$$

where

$$\frac{\partial}{\partial x_i}\left(\frac{\partial f}{\partial x_j}\right) = \frac{\partial}{\partial x_j}\left(\frac{\partial f}{\partial x_i}\right) \tag{14}$$

for each pair of variables, x_i, x_j. On the other hand, given the differential form

$$dF = X_1\,dx_1 + X_2\,dx_2 + \cdots + X_c\,dx_c \tag{15}$$

where $X_1, X_2, \ldots, X_c$ are functions of all c independent variables $x_1, x_2, \ldots, x_c$, then the condition that F represents some completely defined function $F(x_1, x_2, \ldots, x_c)$ of the independent variables $x_1, x_2, \ldots, x_c$ (except for an arbitrary additive integration constant independent of $x_1, x_2, \ldots, x_c$) is that for each pair of variables x_i, x_j:

$$\left(\frac{dX_j}{dx_i}\right)_{x_1,x_2,\ldots,x_{i-1},x_{i+1},\ldots,x_c} = \left(\frac{dX_i}{dx_j}\right)_{x_1,x_2,\ldots,x_{j-1},x_{j+1},\ldots,x_c} \tag{16}$$

APPENDIX 2

SELECTED VALUES OF CHEMICAL THERMODYNAMIC PROPERTIES

The following table presents the standard enthalpy *of formation* $\bar{H}^\circ$ and free energy *of formation* $\bar{F}^\circ$, the standard entropy $\bar{S}^\circ$ *relative to the Third Law convention,* and the standard heat capacity at constant pressure $\bar{C}_p^\circ$, for a number of chemical substances at 25°C. The $\bar{H}^\circ$ and $\bar{F}^\circ$ values refer to the chemical elements in the particular allotropic forms stable at 25°C and 1 atm. The data have been taken from the definitive National Bureau of Standards compilation, "Selected Values of Chemical Thermodynamic Properties," as of March 31, 1950. These tables have been compiled by F. D. Rossini, project director, assisted by D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe. References to the original sources will be found in the tables when they are ultimately published in bound form. The data here presented include but a small fraction of the work contained in the original compilation, to which the reader is referred for further information. The data are listed in the same order as in the original compilation, where to eliminate duplication, the elements are taken up in a standard order by families, in general from right to left through the periodic table. One should note that entropy values for ions in aqueous solutions have significance by convention only in relation to balanced equations for complete ionic reactions, such as, for example: $\mathrm{Na(c)} + \mathrm{H^+(aq)} = \mathrm{Na^+(aq)} + \frac{1}{2}\mathrm{H_2(g)}$; while in this illustration the standard entropy of $\mathrm{H^+(aq)}$ is taken conventionally to be zero, the entropy of $\mathrm{H_2(g)}$ [as well as that of Na(c)] is *not* zero.

Following the table, there is presented a list of accepted values of certain natural constants and conversion factors adopted for the project by the National Bureau of Standards, Dec. 31, 1947.

Thermodynamic Properties at 298.16°K

Substance	$\bar{H}^\circ$, kcal/mole	$\bar{F}^\circ$, kcal/mole	$\bar{S}^\circ$, cu/mole	$\bar{C}_p^\circ$, cal/mole deg
Oxygen:				
$O(g)$	59.159	54.994	38.469	5.236
$O_2(g)$	0.000	0.000	49.003	7.017
Hydrogen:				
$H(g)$	52.089	48.575	27.393	4.968
$H^+(aq)$	0.000	0.000	0.000	0.000
$H_2(g)$	0.000	0.000	31.211	6.892
$OH(g)$	10.06	8.93	43.888	7.141
$OH^-(aq)$	−54.957	−37.595	−2.519	−32.0
$H_2O(g)$	−57.7979	−54.6351	45.106	8.025
$H_2O(l)$	−68.3174	−56.6899	16.716	17.996
Fluorine:				
$F(g)$	32.25	28.19	37.917	5.436
$F^-(aq)$	−78.66	−66.08	−2.3	−29.5
$F_2(g)$	0.000	0.000	48.6	7.52
$HF(g)$	64.2	−64.7	41.47	6.95
Chlorine:				
$Cl(g)$	29.012	25.192	39.4569	5.2203
$Cl^-(aq)$	−40.023	−31.350	13.17	−30.0
$Cl_2(g)$	0.0000	0.0000	53.286	8.11
$ClO_3^-(aq)$	−23.50	−0.62	39.0	−18
$ClO_4^-(aq)$	−31.41	−2.47	43.2	
$HCl(g)$	−22.063	−22.769	44.617	6.96
Bromine:				
$Br(g)$	26.71	19.69	41.8052	4.9680
$Br^-(aq)$	−28.90	−24.574	19.29	−30.7
$Br_2(g)$	7.34	0.751	58.639	8.60
$Br_2(l)$	0.000	0.000	36.4	
$Br_2(aq)$	−1.1			
$HBr(g)$	−8.66	−12.72	47.437	6.96
Iodine:				
$I(g)$	25.482	16.766	43.1841	4.9680
$I^-(aq)$	−13.37	−12.35	26.14	−31.0
$I_2(g)$	14.876	4.63	62.280	8.81
$I_2(c)$	0.000	0.000	27.9	13.14
$I_2(aq)$	5.0			
$I_3^-(aq)$	−12.4	−12.31	41.5	
$HI(g)$	6.20	0.31	49.314	6.97
Sulfur:				
$S(g)$	53.25	43.57	40.085	5.66
$S(c,rhombic)$	0.000	0.000	7.62	5.40
$S^{=}(aq)$	10.0	20.0	5.3	
$SO_2(g)$	−70.96	−71.79	59.40	9.51
$SO_3(g)$	−94.45	−88.52	61.24	12.10
$SO_3^{=}(aq)$	−149.2	−118.8	10.4	
$SO_4^{=}(aq)$	−216.90	−177.34	4.1	4.0

THERMODYNAMIC PROPERTIES AT 298.16°K.—(*Continued*)

Substance	$\bar{H}^\circ$, kcal/mole	$\bar{F}^\circ$, kcal/mole	$\bar{S}^\circ$, eu/mole	$\bar{C}_p^\circ$, cal/mole deg
HS^-(aq)	−4.22	3.01	14.6	
H_2S(g)	−4.815	−7.892	49.15	8.12
H_2S(aq)	−9.4	−6.54	29.2	
HSO_3^-(aq)	−150.09	−126.03	31.64	
HSO_4^-(aq)	−211.70	−179.94	30.32	
H_2SO_4(l)	−193.91			32.88
Nitrogen:				
N(g)	85.566	81.476	36.6145	4.968
N_2(g)	0.000	0.000	45.767	6.960
NO(g)	21.600	20.719	50.339	7.137
NO_2(g)	8.091	12.390	57.47	9.06
NO_2^-(aq)	−25.4			
NO_3^-(aq)	−49.372			
N_2O(g)	19.49	24.76	52.58	9.251
N_2O_4(g)	2.309	23.491	72.73	18.90
NH_3(g)	−11.04	−3.976	46.01	8.523
NH_4^+(aq)	−31.74	−19.00	26.97	
HNO_3(l)	−41.404	−19.100	37.19	26.26
NH_4Cl(c,II)	−75.38	−48.73	22.6	20.1
$(NH_4)_2SO_4$(c)	−281.86	−215.19	52.65	44.81
Carbon:				
C(g)	171.698	160.845	37.7611	4.9803
C(c,diamond)	0.4532	0.6850	0.5829	1.449
C(c,graphite)	0.0000	0.0000	1.3609	2.066
CO(g)	−26.4157	−32.8079	47.301	6.965
CO_2(g)	−94.0518	−94.2598	51.061	8.874
CO_2(aq)	−98.69	−92.31	29.0	
CH_4(g)	−17.889	−12.140	44.50	8.536
H_2CO(g)	−27.7	−26.2	52.26	8.45
HCOOH(l)	−97.8	−82.7	30.82	23.67
HCOOH(aq)	−98.0	−85.1	39.1	
CH_3OH(g)	−48.10	−38.70	56.8	
CH_3OH(l)	−57.036	−39.75	30.3	19.5
CH_3OH(aq)	−58.79	−41.90	31.63	
CCl_4(l)	−33.34	−16.43	51.25	31.49
CS_2(l)	21.0	15.2	36.10	18.1
HCN(g)	31.2	28.7	48.23	8.58
HCN(aq)	25.2	26.8	30.8	
C_2H_2(g)	54.194	50.000	47.997	10.499
C_2H_4(g)	12.496	16.282	52.45	10.41
C_2H_6(g)	−20.236	−7.860	54.85	12.585
CH_3COOH(l)	−116.4	−93.8	38.2	29.5
C_2H_5OH(l)	−66.356	−41.77	38.4	26.64
C_3H_8(g)(propane)*	−24.820	−5.614	64.51	17.57
C_6H_6(g)(benzene)*	19.820	30.989	64.34	19.52

* From Selected Values of Properties of Hydrocarbons, *Natl. Bur. Standards Circ.* C461, (1947).

THERMODYNAMIC PROPERTIES AT 298.16°K.—(*Continued*)

Substance	$\bar{H}°$, kcal/mole	$F°$, kcal/mole	$\bar{S}°$, eu/mole	$\bar{C}_p°$, cal/mole deg
Tin:				
Sn(g)	72	64	40.245	5.081
Sn(c,white)	0.000	0.000	12.3	6.30
SnO(c)	−68.4	−61.5	13.5	10.6
SnO_2(c)	−138.8	−124.2	12.5	12.57
Lead:				
Pb(g)	46.34	38.47	41.890	4.968
Pb(c)	0.000	0.000	15.51	6.41
Pb^{++}(aq)	0.39	−5.81	5.1	
PbO(c,I,yellow)	−52.07	−45.05	16.6	11.60
PbO_2(c)	−66.12	−52.34	18.3	15.4
Pb_3O_4(c)	−175.6	−147.6	50.5	35.14
$Pb(OH)_2$(c)	−123.0	−100.6	21	
$PbCl_2$(c)	−85.85	−75.04	32.6	18.4
PbS(c)	−22.54	−22.15	21.8	11.83
$PbSO_4$(c,II)	−219.50	−193.89	35.2	24.9
Zinc:				
Zn(g)	31.19	22.69	38.45	4.968
Zn(c)	0.000	0.000	9.95	5.99
Zn^{++}(aq)	−36.43	−35.184	−25.45	
ZnO(c)	−83.17	−76.05	10.5	13.7
$ZnCl_2$(c)	−99.40	−88.255	25.9	18.3
ZnS(c,II,sphalerite)	−48.5	−47.4	13.8	10.8
$ZnSO_4$(c)	−233.88	−208.31	29.8	28
Cadmium:				
Cd(g)	26.97	18.69	40.067	4.968
Cd(c,α)	0.000	0.000	12.3	6.19
Cd^{++}(aq)	−17.30	−18.58	−14.6	
CdO(c)	−60.86	−53.79	13.1	10.38
$Cd(OH)_2$(c)	−133.26	−112.46	22.8	
$CdSO_4 \cdot 8/3 H_2O$(c)	−411.82	−349.63	57.9	
Mercury:				
Hg(g)	14.54	7.59	41.80	4.968
Hg(l)	0.000	0.000	18.5	6.65
Hg^{++}(aq)		39.38		
Hg_2^{++}(aq)		36.79		
HgO(c,red)	−21.68	−13.990	17.2	10.93
Hg_2Cl_2(c)	−63.32	−50.350	46.8	24.3
Hg_2Br_2(c)	−49.42	−42.714	50.9	
Hg_2I_2(c)	−28.91	−26.60	57.2	25.3
Hg_2SO_4(c)	−177.34	−149.12	47.98	31.55
Copper:				
Cu(g)	81.52	72.04	39.744	4.968
Cu(c)	0.000	0.000	7.96	5.848
Cu^{+}(aq)	12.4	12.0	−6.3	
Cu^{++}(aq)	15.39	15.53	−23.6	
CuO(c)	−37.1	−30.4	10.4	10.6

THERMODYNAMIC PROPERTIES AT 298.16°K.—(*Continued*)

Substance	$\bar{H}°$, kcal/mole	$\bar{F}°$, kcal/mole	$\bar{S}°$, eu/mole	$\bar{C}_p°$, cal/mole deg
Cu_2O(c)	−39.84	−34.98	24.1	16.7
CuCl(c)	−32.5	−28.2	20.2	
$CuSO_4$(c)	−184.00	−158.2	27.1	24.1
$CuSO_4 \cdot H_2O$(c)	−259.00	−219.2	35.8	31.3
$CuSO_4 \cdot 3H_2O$(c)	−402.27	−334.6	53.8	49.0
$CuSO_4 \cdot 5H_2O$(c)	−544.45	−449.3	73.0	67.2
Silver:				
Ag(g)	69.12	59.84	41.3221	4.9680
Ag(c)	0.000	0.000	10.206	6.092
Ag^+(aq)	25.31	18.430	17.67	9
Ag_2O(c)	−7.306	−2.586	29.09	15.67
AgF(c)	−48.5	−44.2	20	
AgCl(c)	−30.362	−26.224	22.97	12.14
AgBr(c,II)	−23.78	−22.390	25.60	12.52
AgI(c,II)	−14.91	−15.85	27.3	13.01
$AgNO_3$(c,II)	−29.43	−7.69	33.68	22.24
Nickel:				
Ni(g)	101.61	90.77	43.592	5.5986
Ni(c,III)	0.000	0.000	7.20	6.21
Ni^{++}(aq)	−15.3	−11.1	− 38.1	
NiO(c)	−58.4	−51.7	9.22	10.60
Iron:				
Fe(g)	96.68	85.76	43.11	6.13
Fe(c)	0.000	0.000	6.49	6.03
Fe^{++}(aq)	−21.0	−20.30	−27.1	
Fe^{+++}(aq)	−11.4	−2.52	−70.1	
Fe_2O_3(c)	−196.5	−177.1	21.5	25.0
Fe_3O_4(c)	−267.0	−242.4	35.0	
Manganese:				
Mn(g)	68.34	58.23	41.493	4.9680
Mn(c,α)	0.000	0.000	7.59	6.29
Mn^{++}(aq)	−52.3	−53.4	−20	
MnO(c,I)	−92.0	−86.8	14.4	10.27
MnO_2(c,I)	−124.5	−111.4	12.7	12.91
MnO_4^-(aq)	−123.9	−101.6	45.4	
MnS(c,I)	−48.8	−49.9	18.7	11.94
Aluminum:				
Al(g)	75.0	65.3	39.303	5.112
Al(c)[1]	0.000	0.000	6.769	5.817
Al^{+++}(aq)	−125.4	−115.0	−74.9	
Al_2O_3(c,corundum)	−399.09	−376.77	12.186	18.88
$Al(NO_3)_3 \cdot 9H_2O$(c)	−897.34	−700.2	136	
Magnesium:				
Mg(g)	35.9	27.6	35.504	4.9680
Mg(c)	0.000	0.000	7.77	5.71

THERMODYNAMIC PROPERTIES AT 298.16°K.—(*Continued*)

Substance	$\bar{H}°$, kcal/mole	$\bar{F}°$, kcal/mole	$\bar{S}°$, eu/mole	$\bar{C}_p°$, cal/mole deg
Mg^{++}(aq)	−110.41	−108.99	−28.2	
MgO(c)	−143.84	−136.13	6.4	8.94
$Mg(OH)_2$(c)	−221.00	−199.27	15.09	18.41
MgF_2(c)	−263.5	−250.8	13.68	14.72
$MgCl_2$(c)	−153.40	−141.57	21.4	17.04
$MgCl_2 \cdot 6H_2O$(c)	−597.42	−505.65	87.5	75.46
$MgSO_4$(c)	−305.5	−280.5	21.9	23.01
$Mg(NO_3)_2$(c)	−188.72	−140.63	39.2	33.94
$MgCO_3$(c)	−266	−246	15.7	18.05
$MgSiO_3$(c)	−357.9	−337.2	16.2	19.56
Calcium:				
Ca(g)	46.04	37.98	36.993	4.968
Ca(c,II)	0.000	0.000	9.95	6.28
Ca^{++}(aq)	−129.77	−132.18	−13.2	
CaO(c)	−151.9	−144.4	9.5	10.23
$Ca(OH)_2$(c)	−235.80	−214.33	18.2	20.2
$CaSO_4$(c,anhydrite)	−342.42	−315.56	25.5	23.8
$CaSO_4 \cdot \frac{1}{2}H_2O$(c,α)	−376.47	−343.02	31.2	28.6
$CaSO_4 \cdot \frac{1}{2}H_2O$(c,β)	−375.97	−342.78	32.1	29.6
$CaSO_4 \cdot 2H_2O$(c)	−483.06	−429.19	46.36	44.5
$Ca(NO_3)_2$(c)	−224.00	−177.34	46.2	35.69
$Ca_3(PO_4)_2$(c,β)	−988.9	−932.0	56.4	54.45
CaC_2(c)	−15.0	−16.2	16.8	14.90
$CaCO_3$(c,calcite)	−288.45	−269.78	22.2	19.57
$CaCO_3$(c,aragonite)	−288.49	−269.53	21.2	19.42
$CaSiO_3$(c,β,wollastonite)	−378.6	−358.2	19.6	20.38
Strontium:				
Sr(g)	39.2	26.3	39.325	4.9680
Sr(c)	0.000	0.000	13.0	6.0
Sr^{++}(aq)	−130.38	−133.2	−9.4	
SrO(c)	−141.1	−133.8	13.0	10.76
$SrCl_2$(c)	−198.0	−186.7	28	18.9
$SrSO_4$(c)	−345.3	−318.9	29.1	
$SrCO_3$(c,II)	−291.2	−271.9	23.2	19.46
Barium:				
Ba(g)	41.96	34.60	40.699	4.9680
Ba(c,II)	0.000	0.000	16	6.30
Ba^{++}(aq)	−128.67	−134.0	3	
BaO(c)	−133.4	−126.3	16.8	11.34
$BaCl_2$(c)	−205.56	−193.8	30	18.0
$BaCl_2 \cdot 2H_2O$(c)	−349.35	−309.7	48.5	37.10
$BaSO_4$(c)	−350.2	−323.4	31.6	24.32
$Ba(NO_3)_2$(c)	−237.06	−190.0	51.1	36.1
$BaCO_3$(c,II)	−291.3	−272.2	26.8	20.40

THERMODYNAMIC PROPERTIES AT 298.16°K.—(*Continued*)

Substance	$\bar{H}^\circ$, kcal/mole	$\bar{F}^\circ$, kcal/mole	$\bar{S}^\circ$, eu/mole	$\bar{C}_p^\circ$, cal/mole deg
Lithium:				
Li(g)	37.07	29.19	33.143	4.9680
Li(c)	0.000	0.000	6.70	5.65
Li^+(aq)	−66.554	−70.22	3.4	
Sodium:				
Na(g)	25.98	18.67	36.715	4.9680
Na(c)	0.000	0.000	12.2	6.79
Na^+(aq)	−57.279	−62.589	14.4	
Na_2(g)	33.97	24.85	55.02	
Na_2O(c)	−99.4	−90.0	17.4	16.3
NaOH(c,II)	−101.99			19.2
$NaOH{\cdot}H_2O$(c)	−175.17	−149.00	20.2	
NaF(c)	−136.0	−129.3	14.0	11.0
NaCl(c)	−98.232	−91.785	17.30	11.88
Na_2SO_3(c)	−260.6	−239.5	34.9	28.7
Na_2SO_4(c,II)	−330.90	−302.78	35.73	30.50
$Na_2SO_4{\cdot}10H_2O$(c)	−1033.48	−870.93	141.7	140.4
$NaNO_3$(c,II)	−101.54	−87.45	27.8	22.24
Na_2CO_3(c)	−270.3	−250.4	32.5	26.41
$NaHCO_3$(c)	−226.5	−203.6	24.4	20.94
Na_2SiO_3(c)	−363	−341	27.2	26.72
$NaBH_4$(c,I)	−43.82	−28.57	25.02	20.7
Potassium:				
K(g)	21.51	14.62	38.296	4.9680
K(c)	0.000	0.000	15.2	6.97
K^+(aq)	−60.04	−67.466	24.5	
KF(c)	−134.46	−127.42	15.91	11.73
KHF_2(c)	−219.98	−203.73	24.92	18.37
KCl(c)	−104.175	−97.592	19.76	12.31
$KClO_3$(c)	−93.50	−69.29	34.17	23.96
$KClO_4$(c)	−103.6	−72.7	36.1	26.33
KBr(c)	−93.73	−90.63	23.05	12.82
$KBrO_3$(c)	−79.4	−58.2	35.65	25.07
KI(c)	−78.31	−77.03	24.94	13.16
KIO_3(c)	−121.5	−101.7	36.20	25.42
K_2SO_4(c,II)	−342.66	−314.62	42.0	31.1
KNO_3(c)	−117.76	−93.96	31.77	23.01
$KMnO_4$(c)	−194.4	−170.6	41.04	28.5
Rubidium:				
Rb(g)	20.51	13.35	40.628	4.9680
Rb(c,I)	0.000	0.000	16.6	7.27
Rb^+(aq)	−58.9	−67.45	29.7	
Cesium:				
Cs(g)	18.83	12.24	41.944	4.9680
Cs(c)	0.000	0.000	19.8	7.42
Cs^+(aq)	−59.2	−67.41	31.8	

NATURAL CONSTANTS AND CONVERSION FACTORS

Standard gravity: $g_0 \equiv 980.665$ cm/sec^2
International liter: 1 liter $= 1000.028 \pm 0.004$ cm^3
Standard atmosphere: 1 atm $\equiv$ 1,013,250 dynes/cm^2
$= 1.033227$ kg/cm^2
1 mm Hg $\equiv \frac{1}{760}$ atm
International volt: 1 volt $= 0.999670 \pm 0.000029$ int volt
International joule: 1 joule $= 0.999835 \pm 0.000052$ int joule
Thermochemical calorie: 1 cal $\equiv 4.1840$ joules
$= 4.1833$ int joules
$= 0.0412917 \pm 0.0000020$ liter atm
Absolute ice point: $T_0 = 273.160 \pm 0.010°$K
$p\tilde{V}$ for ideal gas at 0°C: $(p\tilde{V})_0 = 22.4140 \pm 0.0004$ liter atm/mole
Ideal-gas constant: $R = 8.31439 \pm 0.00034$ joules/deg mole
$= 1.98719 \pm 0.00013$ cal/deg mole
$= 0.0820544 \pm 0.0000034$ liter atm/deg mole
Avogadros number: $N_0 = (6.02283 \pm 0.0022) \times 10^{23}$/mole
Faraday constant: $\mathfrak{F} = 96485.3 \pm 10.0$ coulombs/g-eq
$= 23060.5 \pm 2.4$ cal/volt g-eq
$= 23068.1 \pm 2.4$ cal/int volt g-eq
Electron charge: $e = (1.60199 \pm 0.00060) \times 10^{-19}$ coulomb
$= (4.80239 \pm 0.00180) \times 10^{-10}$ esu
Planck constant: $h = (6.6242 \pm 0.0044) \times 10^{-27}$ erg sec
Speed of light: $c = (2.99776 \pm 0.00008) \times 10^{10}$ cm/sec
Boltzmann constant: $k = (1.38048 \pm 0.00050) \times 10^{-16}$ erg/deg
Relationship between energy and wave number (Bohr's law): $N_0hc = 11.9600 \pm 0.0036$ joule cm/mole
$= 2.85851 \pm 0.0009$ cal cm/mole
Natural to common log: $\ln(\ ) = 2.302585 \log(\ )$
$R \ln(\ ) = (4.57567 \pm 0.00030) \log(\ )$ cal/deg mole
$RT_{298.160} \ln(\ ) = (1364.282 \pm 0.089) \log(\ )$ cal/mole
$\frac{RT_{298.160}}{\mathfrak{F}} \ln(\ ) = (0.0591610 \pm 0.0000061) \log(\ )$ volt g-eq/mole

APPENDIX 3

EMPIRICAL HEAT-CAPACITY EQUATIONS*

Substance	Equation, cal/deg mole	Error, %	Range, °K
CaO(c)	$\bar{C}_p^\circ = 10.00 + 0.00484T - 108{,}000/T^2$	2	273–1173
$CaCO_3$(c)	$\bar{C}_p^\circ = 19.68 + 0.01189T - 307{,}600/T^2$	3	273–1033
C(c, graphite)	$\bar{C}_p^\circ = 2.673 + 0.002617T - 116{,}900/T^2$	2	273–1373
CO(g)	$\bar{C}_p^\circ = 6.60 + 0.00120T$	2	273–2500
CO_2(g)	$\bar{C}_p^\circ = 10.34 + 0.00274T - 195{,}500/T^2$	1.5	273–1200
H_2(g)	$\bar{C}_p^\circ = 6.62 + 0.00081T$	2	273–2500
H_2O(l)	$\bar{C}_p^\circ = 18.03$	0.5	273–373
H_2O(g)	$\bar{C}_p^\circ = 8.22 + 0.00015T + 1.34 \times 10^{-6}T^2$	?	300–2500
N_2(g)	$\bar{C}_p^\circ = 6.50 + 0.00100T$	3	300–3000
NH_3(g)	$\bar{C}_p^\circ = 6.70 + 0.00630T$	1.5	300–800
O_2(g)	$\bar{C}_p^\circ = 8.27 + 0.000258T - 187{,}700/T^2$	1.5	300–5000
SO_2(g)	$\bar{C}_p^\circ = 7.70 + 0.00530T - 0.83 \times 10^{-6}T^2$	2.5	300–2500

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* Selected from K. K. Kelley, Contributions to the Data on Theoretical Metallurgy. II. High-temperature Specific-heat Equations for Inorganic Substances, *U.S. Bur. Mines Bull.* 371 (1934).

APPENDIX 4

DEBYE FUNCTION $D(\theta/T)$*

(Based on $R = 1.9872$ cal/deg mole)

θ/T	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	5.962	5.958	5.949	5.934	5.913	5.887	5.855	5.817	5.774	5.726
1	5.673	5.615	5.553	5.486	5.416	5.341	5.263	5.182	5.098	5.011
2	4.922	4.831	4.741	4.641	4.546	4.447	4.348	4.249	4.150	4.050
3	3.950	3.852	3.753	3.656	3.559	3.462	3.367	3.272	3.180	3.088
4	2.998	2.911	2.824	2.739	2.655	2.575	2.499	2.418	2.345	2.272
5	2.199	2.129	2.061	1.993	1.929	1.868	1.808	1.748	1.691	1.635
6	1.583	1.533	1.482	1.434	1.369	1.342	1.298	1.256	1.215	1.176
7	1.138	1.101	1.066	1.032	0.9992	0.9671	0.9361	0.9069	0.8782	0.8501
8	0.8239	0.7983	0.7741	0.7507	0.7271	0.7047	0.6832	0.6624	0.6427	0.6236
9	0.6046	0.5880	0.5699	0.5527	0.5372	0.5217	0.5068	0.4925	0.4784	0.4650
10	0.4521	0.4395	0.4271	0.4156	0.4044	0.3945	0.3830	0.3728	0.3629	0.3535
11	0.3449	0.3354	0.3266	0.3190	0.3102	0.3024	0.2948	0.2875	0.2804	0.2735
12	0.2669	0.2606	0.2542	0.2482	0.2414	0.2368	0.2313	0.2259	0.2207	0.2157
13	0.2111	0.2063	0.2017	0.1970	0.1927	0.1884	0.1843	0.1803	0.1763	0.1726
14	0.1689	0.1653	0.1620	0.1586	0.1553	0.1521	0.1490	0.1459	0.1431	0.1402
15†	0.1374	0.1347	0.1321	0.1296	0.1271	0.1247	0.1223	0.1200	0.1178	0.1156

* From Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Supplement I, p. 705, 1927. but corrected to the currently accepted value of R.

† For $\theta/T \geqq 16$, $D(\theta/T) = \dfrac{464.57}{(\theta/T)^3}$ within 0.0001 cal/deg mole.

APPENDIX 5

EINSTEIN FUNCTIONS

The following table was obtained by E. B. Wilson by interpolation from unpublished calculations of H. L. Johnston, and has been corrected to the basis of current values of the natural constants (essentially those of Appendix 2) by S. C. Schumann and M. L. Schwartz.[1] In these tables,

$$
\begin{aligned}
x &= 1.4385\,\frac{\nu_0}{T}\\
E_1(x) &= \frac{Rx^2e^x}{(e^x-1)^2}\\
E_2(x) &= \frac{Rx}{(e^x-1)}\\
E_3(x) &= -R\ln\left(1-e^{-x}\right)
\end{aligned}
$$

The contributions (in cal/deg mole) of a fundamental vibration frequency ν_0 (wave number in cm^{-1}) to the heat capacity, enthalpy, free energy, and entropy, assuming the simple harmonic law, are given by

$$
\begin{aligned}
\bar{C}_{\nu_0} &= E_1(x)\\
\left(\frac{\bar{H}-\bar{H}_0^\circ}{T}\right)_{\nu_0} &= E_2(x)\\
\left(\frac{\bar{F}-\bar{H}_0^\circ}{T}\right)_{\nu_0} &= -E_3(x)\\
\bar{S}_{\nu_0} &= E_2(x)+E_3(x)
\end{aligned}
$$

A more elaborate table has recently been published by H. L. Johnston, L. Savedoff, and J. Belzer, Contributions to the Thermodynamic Functions by a Planck-Einstein Oscillator in One Degree of Freedom, *Office of Naval Research Pub.* P-646 (1949), in which the contributions to the thermodynamic functions are given at intervals of 0.001 in x between 0 and 3, and at intervals of 0.01 between 3 and 15; a companion table in the same publication lists the contributions in terms of ν_0/T instead of x itself as variable, as in the table immediately following.

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[1] Reproduced with permission of the publisher from "A Treatise on Physical Chemistry," H. S. Taylor and S. Glasstone, editors, 3d ed., Vol. I, pp. 655–658, D. Van Nostrand Company, Inc., New York, 1942.

ν_0/T	$E_1(x)$	$E_2(x)$	$E_3(x)$	ν_0/T	$E_1(x)$	$E_2(x)$	$E_3(x)$
0.10	1.9834	1.8473	3.9942	0.50	1.9033	1.3573	1.3267
0.11	1.9827	1.8338	3.8186	0.51	1.9001	1.3464	1.3001
0.12	1.9819	1.8203	3.6596	0.52	1.8966	1.3354	1.2741
0.13	1.9810	1.8068	3.5143	0.53	1.8933	1.3248	1.2488
0.14	1.9801	1.7935	3.3807	0.54	1.8898	1.3140	1.2242
0.15	1.9791	1.7801	3.2572	0.55	1.8863	1.3034	1.2001
0.16	1.9780	1.7670	3.1428	0.56	1.8827	1.2929	1.1766
0.17	1.9768	1.7538	3.0361	0.57	1.8791	1.2823	1.1539
0.18	1.9756	1.7407	2.9362	0.58	1.8754	1.2719	1.1316
0.19	1.9744	1.7276	2.8424	0.59	1.8718	1.2616	1.1099
0.20	1.9731	1.7147	2.7542	0.60	1.8680	1.2513	1.0887
0.21	1.9717	1.7018	2.6710	0.61	1.8641	1.2411	1.0681
0.22	1.9703	1.6890	2.5920	0.62	1.8602	1.2308	1.0481
0.23	1.9687	1.6763	2.5142	0.63	1.8562	1.2207	1.0284
0.24	1.9671	1.6636	2.4662	0.64	1.8522	1.2107	1.0093
0.25	1.9655	1.6510	2.3786	0.65	1.8481	1.2007	0.9905
0.26	1.9638	1.6384	2.3140	0.66	1.8441	1.1908	0.9722
0.27	1.9620	1.6260	2.2525	0.67	1.8398	1.1810	0.9545
0.28	1.9601	1.6135	2.1935	0.68	1.8357	1.1711	0.9370
0.29	1.9583	1.6012	2.1372	0.69	1.8315	1.1614	0.9200
0.30	1.9563	1.5889	2.0831	0.70	1.8272	1.1517	0.9033
0.31	1.9542	1.5767	2.0311	0.71	1.8227	1.1420	0.8870
0.32	1.9521	1.5645	1.9813	0.72	1.8184	1.1325	0.8713
0.33	1.9500	1.5525	1.9333	0.73	1.8140	1.1230	0.8557
0.34	1.9478	1.5404	1.8872	0.74	1.8093	1.1135	0.8405
0.35	1.9454	1.5285	1.8427	0.75	1.8047	1.1041	0.8256
0.36	1.9430	1.5167	1.7998	0.76	1.8002	1.0948	0.8110
0.37	1.9406	1.5048	1.7584	0.77	1.7955	1.0856	0.7968
0.38	1.9381	1.4931	1.7185	0.78	1.7908	1.0764	0.7828
0.39	1.9356	1.4814	1.6799	0.79	1.7863	1.0674	0.7692
0.40	1.9330	1.4698	1.6425	0.80	1.7813	1.0582	0.7558
0.41	1.9303	1.4583	1.6063	0.81	1.7765	1.0492	0.7437
0.42	1.9275	1.4468	1.5713	0.82	1.7716	1.0403	0.7299
0.43	1.9247	1.4354	1.5374	0.83	1.7667	1.0314	0.7174
0.44	1.9218	1.4240	1.5045	0.84	1.7618	1.0226	0.7052
0.45	1.9188	1.4128	1.4726	0.85	1.7568	1.0138	0.6931
0.46	1.9159	1.4016	1.4416	0.86	1.7517	1.0050	0.6812
0.47	1.9128	1.3904	1.4117	0.87	1.7466	0.9964	0.6697
0.48	1.9097	1.3793	1.3826	0.88	1.7415	0.9878	0.6583
0.49	1.9066	1.3682	1.3543	0.89	1.7364	0.9793	0.6473

ν_0/T	$E_1(x)$	$E_2(x)$	$E_3(x)$	ν_0/T	$E_1(x)$	$E_2(x)$	$E_3(x)$
0.90	1.7312	0.9708	0.6363	1.30	1.4966	0.6771	0.3326
0.91	1.7259	0.9620	0.6256	1.31	1.4902	0.6708	0.3275
0.92	1.7206	0.9541	0.6151	1.32	1.4839	0.6646	0.3225
0.93	1.7154	0.9458	0.6049	1.33	1.4774	0.6585	0.3175
0.94	1.7099	0.9377	0.5948	1.34	1.4710	0.6523	0.3126
0.95	1.7045	0.9295	0.5848	1.35	1.4646	0.6462	0.3078
0.96	1.6991	0.9212	0.5751	1.36	1.4583	0.6402	0.3030
0.97	1.6935	0.9132	0.5657	1.37	1.4520	0.6342	0.2983
0.98	1.6882	0.9051	0.5563	1.38	1.4455	0.6283	0.2937
0.99	1.6826	0.8971	0.5471	1.39	1.4390	0.6223	0.2893
1.00	1.6770	0.8893	0.5382	1.40	1.4324	0.6164	0.2848
1.01	1.6714	0.8815	0.5294	1.41	1.4259	0.6107	0.2804
1.02	1.6658	0.8737	0.5208	1.42	1.4194	0.6049	0.2761
1.03	1.6601	0.8659	0.5123	1.43	1.4129	0.5998	0.2719
1.04	1.6544	0.8582	0.5040	1.44	1.4065	0.5935	0.2677
1.05	1.6487	0.8507	0.4959	1.45	1.3999	0.5879	0.2636
1.06	1.6429	0.8430	0.4877	1.46	1.3934	0.5823	0.2595
1.07	1.6371	0.8355	0.4800	1.47	1.3868	0.5768	0.2556
1.08	1.6312	0.8281	0.4722	1.48	1.3802	0.5713	0.2518
1.09	1.6254	0.8207	0.4647	1.49	1.3736	0.5658	0.2471
1.10	1.6196	0.8133	0.4572	1.50	1.3671	0.5604	0.2441
1.11	1.6137	0.8060	0.4499	1.51	1.3605	0.5550	0.2404
1.12	1.6077	0.7988	0.4426	1.52	1.3538	0.5493	0.2367
1.13	1.6017	0.7916	0.4357	1.53	1.3473	0.5445	0.2332
1.14	1.5957	0.7845	0.4287	1.54	1.3406	0.5392	0.2297
1.15	1.5897	0.7774	0.4218	1.55	1.3340	0.5340	0.2262
1.16	1.5837	0.7703	0.4151	1.56	1.3274	0.5288	0.2227
1.17	1.5776	0.7634	0.4086	1.57	1.3208	0.5238	0.2193
1.18	1.5715	0.7564	0.4021	1.58	1.3143	0.5187	0.2161
1.19	1.5653	0.7495	0.3957	1.59	1.3077	0.5138	0.2129
1.20	1.5592	0.7427	0.3894	1.60	1.3010	0.5088	0.2097
1.21	1.5531	0.7359	0.3832	1.61	1.2943	0.5039	0.2065
1.22	1.5468	0.7292	0.3773	1.62	1.2878	0.4988	0.2034
1.23	1.5406	0.7225	0.3713	1.63	1.2812	0.4942	0.2004
1.24	1.5343	0.7159	0.3656	1.64	1.2746	0.4893	0.1974
1.25	1.5281	0.7093	0.3598	1.65	1.2680	0.4847	0.1944
1.26	1.5217	0.7027	0.3542	1.66	1.2613	0.4799	0.1914
1.27	1.5156	0.6963	0.3486	1.67	1.2547	0.4753	0.1885
1.28	1.5091	0.6898	0.3432	1.68	1.2481	0.4706	0.1858
1.29	1.5030	0.6834	0.3379	1.69	1.2415	0.4659	0.1830

ν_0/T	$E_1(x)$	$E_2(x)$	$E_3(x)$	ν_0/T	$E_1(x)$	$E_2(x)$	$E_3(x)$
1.70	1.2349	0.4613	0.1802	2.20	0.9161	0.2773	0.08576
1.71	1.2283	0.4568	0.1775	2.22	0.9041	0.2716	0.08326
1.72	1.2217	0.4523	0.1749	2.24	0.8921	0.2659	0.08084
1.73	1.2151	0.4478	0.1723	2.26	0.8799	0.2605	0.07850
1.74	1.2086	0.4435	0.1698	2.28	0.8682	0.2551	0.07622
1.75	1.2018	0.4391	0.1672	2.30	0.8570	0.2497	0.07402
1.76	1.1952	0.4348	0.1647	2.32	0.8455	0.2445	0.07189
1.77	1.1887	0.4304	0.1622	2.34	0.8339	0.2394	0.06982
1.78	1.1822	0.4262	0.1599	2.36	0.8225	0.2344	0.06780
1.79	1.1756	0.4219	0.1575	2.38	0.8112	0.2295	0.06585
1.80	1.1690	0.4177	0.1551	2.40	0.8000	0.2246	0.06395
1.81	1.1625	0.4135	0.1528	2.42	0.7885	0.2198	0.06213
1.82	1.1559	0.4096	0.1505	2.44	0.7778	0.2151	0.06032
1.83	1.1493	0.4053	0.1484	2.46	0.7669	0.2106	0.05859
1.84	1.1428	0.4011	0.1461	2.48	0.7560	0.2061	0.05690
1.85	1.1363	0.3972	0.1440	2.50	0.7453	0.2017	0.05526
1.86	1.1298	0.3932	0.1418	2.52	0.7346	0.1974	0.05370
1.87	1.1233	0.3893	0.1397	2.54	0.7240	0.1932	0.05217
1.88	1.1167	0.3855	0.1377	2.56	0.7135	0.1891	0.05065
1.89	1.1102	0.3816	0.1356	2.58	0.7031	0.1850	0.04919
1.90	1.1038	0.3777	0.1336	2.60	0.6928	0.1810	0.04778
1.91	1.0973	0.3739	0.1316	2.62	0.6826	0.1771	0.04640
1.92	1.0909	0.3701	0.1297	2.64	0.6725	0.1732	0.04507
1.93	1.0845	0.3665	0.1278	2.66	0.6625	0.1695	0.04379
1.94	1.0780	0.3627	0.1259	2.68	0.6527	0.1656	0.04253
1.95	1.0716	0.3591	0.1240	2.70	0.6429	0.1622	0.04131
1.96	1.0653	0.3554	0.1222	2.72	0.6332	0.1587	0.04014
1.97	1.0589	0.3518	0.1205	2.74	0.6236	0.1553	0.03901
1.98	1.0525	0.3482	0.1187	2.76	0.6140	0.1519	0.03788
1.99	1.0461	0.3446	0.1169	2.78	0.6046	0.1483	0.03679
2.00	1.0398	0.3412	0.1152	2.80	0.5953	0.1454	0.03572
2.02	1.0272	0.3342	0.1118	2.82	0.5862	0.1422	0.03471
2.04	1.0146	0.3275	0.1085	2.84	0.5771	0.1391	0.03371
2.06	1.0020	0.3208	0.1054	2.86	0.5680	0.1361	0.03275
2.08	0.9897	0.3142	0.1023	2.88	0.5591	0.1331	0.03181
2.10	0.9772	0.3077	0.0992	2.90	0.5502	0.1301	0.03089
2.12	0.9649	0.3014	0.09640	2.92	0.5417	0.1272	0.03003
2.14	0.9526	0.2952	0.09362	2.94	0.5331	0.1244	0.02917
2.16	0.9405	0.2891	0.09091	2.96	0.5246	0.1216	0.02834
2.18	0.9284	0.2832	0.08828	2.98	0.5163	0.1189	0.02752

ν_0/T	$E_1(x)$	$E_2(x)$	$E_3(x)$
3.00	0.5080	0.1162	0.02673
3.05	0.4876	0.1099	0.02486
3.10	0.4680	0.1038	0.02311
3.15	0.4489	0.0981	0.02150
3.20	0.4305	0.0927	0.02000
3.25	0.4127	0.0875	0.01861
3.30	0.3956	0.0826	0.01731
3.35	0.3787	0.0780	0.01608
3.40	0.3627	0.0736	0.01498
3.45	0.3471	0.0696	0.01393
3.50	0.3323	0.0656	0.01297
3.55	0.3177	0.0619	0.01207
3.60	0.3038	0.0584	0.01124
3.65	0.2903	0.0550	0.01045
3.70	0.2775	0.0519	0.00972
3.75	0.2651	0.0489	0.00904
3.80	0.2532	0.0461	0.00842
3.85	0.2417	0.0435	0.00783
3.90	0.2307	0.0410	0.00729
3.95	0.2201	0.0387	0.00678
4.00	0.2099	0.0364	0.00631
4.10	0.1907	0.0322	0.00547
4.20	0.1732	0.0286	0.00473
4.30	0.1571	0.0253	0.00409
4.40	0.1424	0.0225	0.00354
4.50	0.1286	0.0200	0.00306
4.60	0.1166	0.0176	0.00265
4.70	0.1054	0.0156	0.00230
4.80	0.0952	0.0138	0.00199
4.90	0.0859	0.0122	0.00173
5.00	0.0775	0.01074	0.00150
5.10	0.0697	0.00948	0.001290
5.20	0.0628	0.00836	0.001116
5.30	0.0563	0.00740	0.000965
5.40	0.0506	0.00652	0.000837
5.50	0.0454	0.00575	0.000727
5.60	0.0409	0.00507	0.000629
5.70	0.0367	0.00447	0.000545
5.80	0.0330	0.00393	0.000472
5.90	0.0295	0.00347	0.000409
6.00	0.0265	0.00305	0.000353
6.10	0.0236	0.00269	0.000306
6.20	0.0212	0.00236	0.000266
6.30	0.0189	0.00208	0.000231
6.40	0.0169	0.00183	0.000200
6.50	0.0151	0.00161	0.000173
6.60	0.0134	0.00142	0.000151
6.70	0.0120	0.00125	0.000131
6.80	0.0107	0.00110	0.000114
6.90	0.00960	0.000962	0.0000993
7.00	0.00852	0.000845	0.0000865
7.10	0.00758	0.000742	0.0000750
7.20	0.00674	0.000651	0.0000651
7.30	0.00600	0.000571	0.0000565
7.40	0.00534	0.000502	0.0000491
7.50	0.00474	0.000441	0.0000427
7.60	0.00423	0.0003868	0.0000369
7.70	0.00376	0.0003497	0.0000320
7.80	0.00332	0.0002979	0.0000278
7.90	0.00298	0.0002618	0.0000241
8.00	0.00265	0.0002292	0.0000209
8.10	0.00234	0.0002008	0.0000181
8.20	0.00208	0.0001759	0.0000156
8.30	0.00185	0.0001542	0.0000135
8.40	0.00164	0.0001352	0.0000117
8.50	0.00145	0.0001187	0.0000101
8.60	0.00129	0.0001038	0.0000088
8.70	0.00113	0.0000908	0.0000077
8.80	0.00101	0.0000795	0.0000067
8.90	0.00089	0.0000696	0.0000058
9.00	0.000792	0.0000610	0.0000050
9.10	0.000701	0.0000535	0.0000043
9.20	0.000620	0.0000466	0.0000037
9.30	0.000549	0.0000408	0.0000032
9.40	0.000486	0.0000357	0.0000028
9.50	0.000341	0.0000312	0.0000024
9.60	0.000380	0.0000273	0.0000021
9.70	0.000335	0.0000239	0.0000018
9.80	0.000297	0.0000209	0.0000016
9.90	0.000262	0.0000184	0.0000014
10.00	0.000232	0.0000161	0.0000012

APPENDIX 6

LIST OF SYMBOLS

In general, extensive properties are represented by italic capitals; the corresponding molal properties for chemical substances are represented by the same symbols with bar superscripts, *e.g.*, V for volume in general and $\bar{V}$ for molal volume. The corresponding differential or partial molal properties for the components of a homogeneous mixture are represented by small Greek letters, except for v representing partial molal volume. In the following table, the last column gives the equation or the page in which the symbol is first introduced in the given sense.

English Letter Symbols

Symbol	*Quantity to Which Symbol Refers*	*Equation or Page Number*
A	Number of degrees assigned between steam point and ice point on arbitrary temperature scale	(1-1)
A	Constant in Grüneisen law	(3-57)
A	Madelung constant	(4-18)
A	Empirical constant in Rossini heat-capacity equation for electrolytes	(4-46)
A	Helmholtz free energy or maximum work function	(5-49)
A	Universal constant in Debye-Hückel limiting law	(7-4-28)
A'	Modified Debye-Hückel constant for single electrolyte of given charge type	(7-5-61)
$\bar{A}$	Molal Curie constant	(6-99)
A_1, A_2	Van Laar constants for binary liquid solution	(7-3-54)
A, B	Constants in Young's vapor-pressure formula	(6-70*a*)
A', B', C	Constants in Kirchhoff-Rankine vapor-pressure equation	(6-73*a*)
A, B, C	Constants in general empirical E vs. t relationship for thermocouples	(1-16)
a	Constant in Debye T^3 heat-capacity law at low temperatures	(3-55)
a	Activity function, in general	(7-3-40)
a_1	Solvent activity, relative to pure solvent	(7-3-63)
a_2^0	Solute activity, based on ideal dilute solution behavior extrapolated to $x_2 = 1$	(7-3-63)
a_2'	Solute activity, based on ideal dilute solution behavior extrapolated to $m_2 = 1$ mole/kg solvent	(7-3-81)
a_2''	Solute activity, based on ideal dilute solution behavior extrapolated to $C_2 = 1$ mole/liter	(7-3-101)
a	Empirical constant in Morse equation	(10-120)
a, b	Empirical constants in total-radiation pyrometer formula	p. 35

English Letter Symbols

Symbol	*Quantity to Which Symbol Refers*	*Equation or Page Number*
a, b	Van der Waals' constants	(3-69)
a, b, c	Constants in empirical thermocouple equation	(1-17)
a', b', c'	Constants in empirical thermocouple equation, high-temperature range	p. 30
a, b, c	Empirical constants in equation for mean specific heat as function of t	p. 90
a, b, c	Constants in empirical heat-capacity equation	(3-58)
a', b', c'	Constants in Kelley's form of the empirical heat-capacity equation	(3-59)
B	Repulsive-energy constant in Born-Landé theory	(4-19)
B	Representing an extensive property, in general	(4-44)
B	Universal constant in Debye-Hückel limiting law	(7-4-32)
C	Number of components	p. 73
C	Heat capacity in general	(3-21)
C_v	Heat capacity at constant volume	(3-22)
C_p	Heat capacity at constant pressure	(3-38)
$\bar{C}_p^{\circ}$	Standard molal heat capacity at constant pressure (1 atm; gases corrected to ideal-gas state)	p. 85
C	Parameter in quantum statistical distribution law	(10-53)
C_2	Molar concentration (by volume)	(7-3-96)
C_0	Number of moles diffusing electrolyte, in discussion of Donnan equilibrium	(7-7-5)
c	Speed of light	(10-84)
c	Specific heat in general	(2-17)
c_p	Specific heat at constant pressure	(3-50)
c_1, c_2	First and second radiation constants	(1-19)
$c_1, c_2, c_3, \ldots$	First, second, third, . . . virial coefficients	(6-18)
$c_1, c_2, \ldots$	Coefficients in a linear combination of eigenfunctions	(10-90)
D	Dissociation-energy constant in the Morse equation	(10-120)
D_0	Dissociation energy, relative to zero-point vibrational energy	(10-126)
D	Dielectric constant	(6-104)
d	Differential sign	
d'	Sign representing incomplete differential (see Appendix 1)	(2-22)
d_i	Mean ionic diameter in Debye-Hückel limiting law	(7-4-32)
E	Electromotive force or potential difference	(1-16), (2-8)
E°	Standard emf of a galvanic cell reaction	(9-2-14)
E	Total energy of a Gibbs assembly	(10-2)
E_i	Energy of an individual system of an assembly	(10-2)
$\bar{E}_e$	Electrostatic potential energy per mole for an ionic crystal lattice	(4-18)
$\bar{E}_r$	Repulsive lattice energy per mole	(4-19)
e	Base of natural logarithms	

English Letter Symbols

Symbol	*Quantity to Which Symbol Refers*	*Equation or Page Number*
e	Electron charge	(4-18)
$\mathcal{E}$	Electric field strength	(6-104)
F	Force	(2-1)
F	Gibbs free-energy function	(5-57)
$\bar{F}^{\circ}_{T_s}$	Standard molal free energy of a chemical substance	(6-14)
ΔF°_{T}	Standard free energy of a reaction	p. 263, (8-1-6)
f	General function representing equation of state	(3-1)
f	Fugacity function	(6-22)
$\mathfrak{F}$	Faraday electrochemical constant	(9-1-1)
g	Gravity acceleration (g_0 = standard gravity)	p. 6
g	Number of molecule states of lowest energy	(10-37)
H	Enthalpy	(3-35)
$\bar{H}^{\circ}_{T_s}$	Standard molal enthalpy of a chemical substance	pp. 85, 139
ΔH°_{T}	Standard enthalpy of reaction	(4-12)
H	Hamiltonian operator	(10-91)
h	Height coordinate	p. 270
h	Planck's constant	(10-83)
$\mathcal{H}$	Magnetic field strength	(6-93)
I	Current	(2-8)
I	Integral in Joule-Thomson theory	(3-74)
I	Ionization energy	p. 154
I	Moment of inertia (I_1, I_2, I_3 represent moments of inertia about principal axes)	(10-104)
J	Thermal radiation flux, wavelength λ to $\lambda + d\lambda$	(1-19)
J_{15}	Joule equivalent of the 15° calorie	(2-18)
$\mathcal{J}$	Molal intensity of magnetization	(6-93)
j	Quantity of electricity accompanying electrochemical reaction	(5-6)
j	Freezing-point depression variable	(7-5-57)
K	Rotational quantum number	(10-104)
K'	Molal distribution "constant" (K'_0, ideal dilute-solution value)	(7-6-6)
K''	Molar concentration distribution "constant" (K''_0, ideal dilute-solution value)	(7-6-10)
K_s	Solubility product in terms of molar concentrations	(7-4-39)
K'_s	Thermodynamic molal solubility product constant	(7-4-36)
K''_s	Thermodynamic molar solubility product constant	(7-4-39)
K_p	Equilibrium "constant" in terms of partial pressures (K°_p, ideal-gas value)	(8-1-16)
K_ν	Fugacity coefficient factor	(8-1-19)
K_x	Mole-fraction equilibrium "constant"	(8-1-28)
K_m	Equilibrium "constant" in terms of molalities (K°_m, ideal dilute-solution value)	(8-1-44)
K_γ	Molal activity coefficient factor	(8-1-44)

English Letter Symbols

Symbol	*Quantity to Which Symbol Refers*	*Equation or Page Number*
K_c	Equilibrium "constant" in terms of molar concentrations (K_c°, ideal dilute-solution value)	(8-1-35)
k	Boltzmann's constant	(10-28)
k	Proportionality constant in dissipative force law	p. 48
k_2	Henry's law constant, in terms of mole fraction	(7-3-18)
k_B	Mole-fraction boiling-point elevation constant	(7-5-16)
k'_B	Molal boiling-point elevation constant	(7-5-17)
k_F	Mole-fraction freezing-point depression constant	(7-5-44)
k'_F	Molal freezing-point depression constant	(7-5-46)
L	Latent heat in general; $\bar{L}_p$, molal latent heat of pressure variation	(3-28)
$\bar{L}_{cl}$	Molal latent heat of fusion	p. 86
$\bar{L}_{lg}$	Molal latent heat of vaporization	p. 86
$\bar{L}_{cg}$	Molal latent heat of sublimation	p. 154
$\bar{L}_{12}$	General latent heat of phase transition, phase 1 to phase 2	(6-67)
M	Mass	(2-1)
$\bar{M}$	Molecular weight, or formula weight	p. 69
m	Molecule mass	(10-73)
m_2	Solute molality	(4-46), (7-3-77)
N	Number of molecules	(6-47), (10-40)
N	Number of systems in an assembly	(10-1)
N_0	Avogadro's number	(4-18)
n	Number of moles	p. 69
n	Born exponent	(4-19)
n	Vibrational quantum number	(10-113)
n_x, n_y, n_z	Translational quantum numbers	(10-93)
P	Applied pressure (as distinguished from equilibrium vapor pressure)	(7-5-21)
P	Number of phases	(7-6-1)
P	Number of assembly states corresponding to a particular macroscopic equilibrium state	(10-3)
P_j	Probability of a system's being in system state j	(10-35*a*)
$\bar{P}$	Molal polarizability	(6-104)
p	Pressure, in general	p. 9, (3-1)
p	Momentum	(10-73)
p_c	Critical pressure	pp. 122, 234
p_1°	Vapor pressure of pure component 1	(7-3-14)
Q	Quantity of heat	(2-14)
Q_r	Quantity of heat received during a reversible change of state	(5-14)
Q_T°	Standard heat of reaction	pp. 132, (4-12)
$\bar{Q}_s$	Heat of solution ($\bar{Q}_s^\circ$, limiting value per mole of solute in an infinitely large number of moles of the given solvent)	(4-26)
$\bar{Q}_d$	Heat of dilution	(4-32)
q	Quantity of electricity	(2-8)

English Letter Symbols

Symbol	*Quantity to Which Symbol Refers*	*Equation or Page Number*
$q_1, q_2, \ldots$	Generalized coordinates	(10-89)
R	Ideal-gas constant	(1-6)
R	Electric resistance	(2-9)
R_t	Thermometer resistance (R_0, A, B, C, constants in empirical equation relating R_t to t)	(1-10)
R	Tube radius in capillarity theory	p. 270
R_0	Number of moles of nondiffusing electrolyte in discussion of Donnan equilibrium	(7-7-5)
r	Reading of a thermometric property	(1-1)
r	Radius of curvature of a surface bounding two phases (r_1, r_2, principal radii of curvature for nonspherical surface)	(6-89)
r	Number of lowest system-energy levels	(10-36)
r	Equilibrium internuclear distance in a diatomic molecule	(10-105)
r_0	Equilibrium interionic distance in ionic crystal lattice	(4-18)
$\mathbf{r}$	Radius vector denoting position with respect to arbitrary origin	(2-1)
S	Entropy	(5-21)
s	Unit of phase space in classical statistics	(10-75)
s	Symmetry number	(10-109)
T	Absolute (thermodynamic) temperature (T_0, absolute ice point)	(1-3)
T_c	Critical temperature	pp. 112, 234
ΔT_B	Boiling-point elevation (T_B°, boiling point of pure solvent)	(7-5-13)
ΔT_F	Freezing-point depression (T_F°, freezing point of pure solvent)	(7-5-40)
t	Ordinary (thermodynamic) temperature	(1-2)
t_+, t_-	Transference numbers	(9-3-5)
U	Internal energy	(2-21)
u	Velocity	(2-3)
u	Sound velocity in a particular medium	(3-52)
V	Volume	(1-2)
$\bar{V}$	Molal volume	pp. 11, 69, (3-2)
V	Potential energy	(2-5)
v	Partial molal volume	(7-1-24)
v	Variance	(7-6-4); see also p. 70
W	Work	(2-4)
W'	Work exclusive of mechanical work of expansion	(3-17)
W_r	Work done by a system during a reversible change of state (or reversible cycle of changes)	(5-11)
$\bar{X}$	Molal magnetic susceptibility	(6-94)
x	Mole fraction	(4-43)
x	General variable, as in Debye function	(3-54)
x, y, z	Cartesian coordinates of a point mass	(2-2)

English Letter Symbols

Symbol	*Quantity to Which Symbol Refers*	*Equation or Page Number*
x_0	Anharmonicity coefficient	(10-124)
y	Mole fraction, particularly in gas phase	(7-2-1)
Z	Assembly partition function	(10-17)
z	Altitude coordinate	p. 46
z	Compressibility factor	(6-20)
z_+, z_-	Number of charge units on cation, anion	(4-18)

Greek Letter Symbols

Symbol	*Quantity to Which Symbol Refers*	*Equation or Page Number*
α	Coefficient of cubical expansion	(3-4)
α	Degree of ionization	(8-1-39)
β	Empirical constant in Van Dusen equation	(1-15)
β	Coefficient of compressibility	(3-5)
β_1, β_2	Representing partial molal properties in general	(4-44)
Γ	Mean specific heat	(2-14)
γ	Heat-capacity ratio ($\bar{C}_p/\bar{C}_v$)	(3-51)
γ	Surface or interfacial tension	(6-84)
γ	Mole-fraction activity coefficient relative to pure (liquid) component	(7-3-47)
γ_2°	Mole-fraction activity coefficient of solute relative to ideal dilute solution	(7-3-66)
γ_2'	Molal activity coefficient of solute relative to ideal dilute solution	(7-3-82)
γ_2''	Molar concentration activity coefficient of solute relative to ideal dilute solution	(7-3-102)
$\gamma_\pm$	Mean ionic activity coefficient (molal)	(7-4-22)
$\gamma_\pm''$	Mean ionic activity coefficient (molar concentration)	(7-4-31)
Δ	Fundamental interval of a particular thermometer	(1-1)
Δ	Change in general with change of state	(2-21)
δ	Constant in Callendar equation	(1-12)
δ	Correction term in Joule-Thomson coefficient method for absolute ice-point determination	(3-75)
δ	Freezing-point depression variable	(7-5-62)
ϵ	Total thermal-radiation flux	(1-18)
ϵ	Total energy	(2-7)
ϵ	Electron affinity	p. 154
ϵ	Molecule energy	(10-40)
ζ	Partial molal compressibility factor	(7-2-13)
ζ_+, ζ_-, ζ	Number of cations, number of anions, total number of ions, corresponding to electrolyte formula	(7-4-11)
ζ	Molecular partition function	(10-41)
η	Partial molal enthalpy	(4-33)
Θ	A thermodynamic temperature scale in general	(5-15)
θ	Angle, in general	p. 45

Greek Letter Symbols

Symbol	*Quantity to Which Symbol Refers*	*Equation or Page Number*
θ	Characteristic temperature in the Debye heat-capacity theory	(3-54)
θ	Representing a temperature scale generally defined	(5-14)
θ	Freezing-point depression variable	(7-5-48)
$\varkappa$	Force constant	(10-114)
λ	Wavelength	(1-19)
λ	Representing an arbitrary multiplier	p. 76, (7-1-19)
λ_1	Partial molal latent heat of vaporization	(7-5-10)
λ_{cl}	Partial molal latent heat of fusion	(7-5-47)
μ	Joule-Thomson coefficient	(3-64)
μ	Ionic strength	(7-4-28)
ν	Fugacity coefficient	(6-23)
$\tilde{\nu}$	Frequency of radiation	(10-83)
ν	Wave number	(10-84)
$\tilde{\nu}_0$	Fundamental vibration frequency	(10-113)
ν_0	Wave number corresponding to fundamental vibration frequency	(10-115)
Ξ	Kelvin's "first" temperature scale	(5-18)
π	Osmotic pressure	(7-5-22)
ρ	Density	(3-52)
ρ_1	Density of pure solvent	(7-3-98)
Σ	Summation sign	(10-1)
σ	Stefan-Boltzmann constant	(1-18)
σ	Surface or interfacial area	(6-84)
σ	Partial molal entropy	(7-1-23)
τ	Time	(2-1)
υ	Partial molal internal energy	(3-13)
Φ_h	Apparent molal enthalpy in solution ($\overset{\circ}{\Phi}_h$, limiting value in ideal dilute solution)	(4-27)
Φ_c	Apparent molal heat capacity in solution ($\overset{\circ}{\Phi}_c$, limiting value in ideal dilute solution)	(4-46)
Φ_v	Apparent molal volume in solution ($\overset{\circ}{\Phi}_v$, limiting value in ideal dilute solution)	(7-3-92)
ϕ	Thermodynamic potential, or partial molal free energy	(7-1-2)
$\overset{\circ}{\phi}_2$	Thermodynamic potential of solute in hypothetical ideal dilute solution extrapolated to $x_2 = 1$	(7-3-16)
ϕ_2'	Thermodynamic potential of solute in hypothetical ideal dilute solution at $m_2 = 1$ mole/kg solvent	(7-3-79)
ϕ_2''	Thermodynamic potential of solute in hypothetical ideal dilute solution at $C_2 = 1$ mole/liter	(7-3-99)
Ψ	General wave function, including time	(10-85)
ψ	Wave function (amplitude)	(10-86)

ANSWERS TO PROBLEMS

Chapter 1

1-1. 1945.4°F; 2405.1°R. **1-3.** +5.7 deg. **1-4.** 0.36602; 0.36618. **1-5.** +0.037°C.
1-6. $t' = 421.42$°C; $\delta = 1.5130$ deg; 203.17°C. **1-7.** 3.5577 ohm.
1-8. $\beta = 0.0571$ deg; −78.74°C. **1-10.** 0.0026 deg. **1-11.** 5760°K. **1-14.** 1958°K.
1-15. 1862°K.

Chapter 2

2-1. 49,000 joules. **2-2.** 0.447 joules/kg; 0.945 m/sec.
2-3. 1380×10^6 dynes/cm^2; 290 g. **2-5.** 500 joules/kg; 0.12 deg; 283,000 kw;
510,000 kw. **2-6.** 64.8 m. **2-7.** 2.45 deg. **2-8.** 269°C. **2-9.** 0.1001 cal/g deg.
2-10. 15.51°C. **2-11.** 0.58 kw; 116 kg/hr (including water diverted into boiler).
2-12. 60.5 joules/sec; 69.1 sec; 1.01 amp, 0.595 ohm. **2-14.** 40.52 cal/g; 499.25 cal.
2-15. 0.00098 cal/g; 75.00 cal/g. **2-16.** 262 m.
2-17. -8.196×10^{-12} erg, −117,980 cal/mole; 1.293, 1.456.

Chapter 3

3-1. 36.26×10^{-6} deg^{-1} at −200°C. **3-2.** +2.47 liters; −0.90 liter; 23.7°C;
+148 cal/mole. **3-8.** 0.0177 cal; 1352 cal/mole. **3-9.** 149 cal; 661 cal/mole.
3-10. −0.0337 cal/mole atm; −3.33 cal; 0.185 deg. **3-11.** 0.202 cal/mole deg.
3-14. 4482 cal/mole.
3-15. 7161 cal/mole for O_2(g); 6764 cal/mole for CO(g); 10,690 cal/mole for CO_2(g).
3-17. $\bar{C}_p^\circ = 11.41 + 0.00144T - 1.825 \times 10^5 T^{-2}$ (cal/mole deg).
3-30. 92 atm; 76 atm; 40 atm; 4.7 atm. **3-31.** 285°C; 24.8.
3-32. 420 cal; 377 cal; 87°C.

Chapter 4

4-1. −22,060.6 cal/mole; +2.8 cal/mole correction to 25°C. **4-2.** −57,325 cal.
4-3. $\Delta H_c^\circ = -285.80$ kcal/mole at 298.16°K; $(\bar{H}^\circ_{298.16})_{WC(c)} = -3.92 \pm 0.9$ kcal/mole.
4-4. $(\bar{H}^\circ_{298.16})_{NaBH_4(c)} = -44.03 \pm 0.07$ kcal/mole (except for experimental error in the
H_3BO_3(aq) enthalpy of formation). **4-6.** 14.83 kcal/mole; 5.68 kcal.
4-7. −1766 cal. **4-8.** 2230 Btu; 302.5 Btu [both for H_2O(l) as product].
4-9. Standard enthalpies of formation: $3CaO{\cdot}B_2O_3$, −817.7 kcal/mole;
$2CaO{\cdot}B_2O_3$, −651.5 kcal/mole; $CaO{\cdot}B_2O_3$, −483.3 kcal/mole;
$CaO{\cdot}2B_2O_3$, −798.8 kcal/mole. **4-10.** −3992 cal; −4105 cal.
4-13. −26,415.7 ± 30.7 cal/mole; 9838 cal; 41,220 cal. **4-14.** 32,459 cal; 0.344:1.
4-15. −21,690 cal; −23,450 cal; −486 cal correction to 50 atm.
4-16. −754.48 ± 0.38 kcal; −754.64 ± 0.38 kcal; (17.88 ± 1.48) x kcal.
4-17. 2320°K (except for possible error in extrapolation of the CO_2(g) heat-capacity
equation). **4-20.** $\Delta H_c^\circ = -760.84$ kcal/mole; $(\bar{H}^\circ_{298.16})_{C_5H_8(g)} = +17.31$ kcal/mole.
4-25. At $m_2 = 0.01$ mole/kg, $\eta_1 - \bar{H}_1^\circ = -0.0043$ kcal/mole,
$\eta_2 - \bar{H}_2^\circ = -17.935$ kcal/mole; at 35% HCl, $\eta_1 - \bar{H}_1^\circ = -0.88$ kcal/mole,
$\eta_2 - \bar{H}_2^\circ = -11.10$ kcal/mole. **4-28.** −89.66 kcal; −95.14 kcal.
4-29. 10.83 kcal; 32 deg.

Chapter 5

5-1. −0.010 cal/sec. **5-2.** 26.1%; 82.9%. **5-3.** 52.7%; 20.1%. **5-4.** 57.0 kcal; 280.2 kcal; 4.92 vs. 5.53 **5-6.** 160 kcal.

5-7. $\Delta S = -5.094$ cal/mole deg; $Q/T = -5.190$ cal/mole deg.

5-12. −97.3 kcal; 7.4 eu for cell, 322 eu for water; 3.2% for energy withdrawn without lowering the water's temperature significantly; otherwise 1.3% net.

Chapter 6

6-1. 1250 cal. **6-2.** 497 cal; 1.55 eu; −0.218 cal/mole deg.

6-3. −7.55 cal/mole deg. **6-4.** 0.9919.

6-6. At 0°C, $\nu_{1\,\mathrm{atm}} = 0.9887$, $\nu_{10\,\mathrm{atm}} = 0.9034$.

6-7. 11,490 cal/mole to 5000 atm; 21,530 cal/mole to 10,000 atm. **6-9.** 0.9589.

6-13. 8.94 kcal/mole, 29.98 eu/mole; $\Delta S° = 26.48$ eu, $\Delta F° = 1.05$ kcal.

6-14. $\log p = -3284T^{-1} - 0.826 \log T + 7.495$.

6-15. $(\bar{L}_{cg})_{800°\mathrm{K}} = 51.15$ kcal/mole;
$\log p = -11.879(1000/T) + 2 \log (1000/T) + 8.125$.

6-18. 60 cal/g; 150% increase; 20% further increase; 3% "wet."

6-19. $(\bar{S}_{T,p} - \bar{S}^{\circ}_{T}) = -R \ln p - (cA/T^{c+1})p$.

Chapter 7

7-5. 254 cal/mole; $(\phi_{\mathrm{CH_3OH}} - \phi^{\circ}_{\mathrm{CH_3OH(aq)}}) = -1364$ cal/mole, $(\phi_{\mathrm{H_2O}} - \bar{F}^{\circ}_{\mathrm{H_2O(l)}}) = -62$ cal/mole. **7-6.** At $x_{\mathrm{CS_2}} = 0.20$, $\Delta F - (\Delta F)_{\mathrm{ideal}} = 177.1$ cal/mole. **7-7.** +2.71 deg. **7-9.** $A_1 = 0.52$, $A_2 = 1.10$.

7-11. $\phi''_{\mathrm{NH_3(aq)}} - \bar{F}^{\circ}_{\mathrm{NH_3(g)}} = -2411$ cal/mole [assuming NH_3(g) is ideal at 1 atm].

7-12. At 25°C, $\phi''_{\mathrm{H_2S(aq)}} - \bar{F}^{\circ}_{\mathrm{H_2S(g)}} = 1349$ cal/mole. **7-13.** $\phi'_{\mathrm{Br_2(aq)}} = 967$ cal/mole.

7-15. 457,140 cal/mole (*i.e.*, 3620 cal/mole $- 8\bar{F}^{\circ}_{\mathrm{H_2O(l)}}$). **7-16.** 508,510 cal/mole (*i.e.*, −1702 cal/mole $- 9\bar{F}^{\circ}_{\mathrm{H_2O(l)}}$).

7-17. 0.598; −1248 cal/mole. **7-21.** At $m_2 = 9.990$ mole/kg, $\phi_2 - \bar{F}^{\circ}_{\mathrm{HCl(g)}} = -3071$ cal/mole, $\gamma_{\pm} = 10.90$; at $m_2 = 0.1$ mole/kg, $p_{\mathrm{HCl}} = 2.31 \times 10^{-6}$ mm Hg. **7-22.** 0.9839 at 0.1*m*; 0.9743 at 0.2*m*; 0.9533 at 0.5*m*.

7-23. 0.633; 1994 cal/mole. **7-24.** 0.777; 3563 cal/mole.

Chapter 8

8-1. $\Delta F^{\circ}_{298.16} = 3930$ cal. **8-2.** 4710 cal; 0.0716 atm. **8-3.** At 420.9°C $\Delta H° = 22,450$ cal. **8-4.** $Cu_4SO_4 \cdot 5H_2O$(c) at $p_{\mathrm{H_2O}} \geqq 0.0105$ atm;
$CuSO_4 \cdot 3H_2O$(c) at 0.0105 atm $\geqq p_{\mathrm{H_2O}} \geqq 0.0058$ atm;
$CuSO_4 \cdot H_2O$(c) at 0.0058 atm $\geqq p_{\mathrm{H_2O}} \geqq 0.0000203$ atm;
$CuSO_4$(c) at $p_{\mathrm{H_2O}} \leqq 0.0000203$ atm. **8-5.** $\Delta F° = 5500$ cal; $\Delta H° = 27,600$ cal; $\Delta S° = 74.1$ eu. **8-6.** $\Delta F° = 7010$ cal; $\Delta H° = 30,580$ cal; $\Delta S° = 79.1$ eu; $p_{\mathrm{H_2O}} = 0.081$ atm. **8-7.** $\Delta H° = -1270$ cal; $\Delta F^{\circ}_{298.16} = -1790$; $\Delta S^{\circ}_{298.16} = 1.74$ eu.

8-9. At 900°K, $\Delta F° = 3360$ cal, $\Delta H° = 22,600$ cal; at 298.16°K, $\Delta H° = 23,490$ cal, $\Delta F° = 16,770$ cal, $\Delta S° = 22.53$ eu. **8-10.** (*a*) 5560 cal, 6040 cal; (*b*) 3510 cal, 5760 cal.

8-12. At 298.16°K, $\Delta H° = 12,890$ cal, $\Delta F° = 5980$ cal, $\Delta S° = 23.2$ eu. **8-13.** 0.1882; 4785 cal, −19,910 cal, −24.70 eu. **8-14.** For Sn(l,c),
$\bar{H}^{\circ}_{1000} - \bar{H}^{\circ}_{298.16} = 6430$ cal/mole, $\bar{S}^{\circ}_{1000} - \bar{S}^{\circ}_{298.16} = 11.57$ eu/mole;
for SnO(c), $\bar{H}^{\circ}_{1000} - \bar{H}^{\circ}_{298.16} = 8248$ cal/mole, $\bar{S}^{\circ}_{1000} - \bar{S}^{\circ}_{298.16} = 31.92$ eu/mole.

8-15. At 1000°K, $\Delta F° = -11,360$ cal, $\Delta H° = -11,900$ cal, $\Delta S° = -0.54$ eu.

8-16. $p_{\mathrm{CO}} = 578$ atm (ideal-gas value); $p_{\mathrm{H_2O}}/p_{\mathrm{H_2}} = 221$; $p_{\mathrm{O_2}} = 3.7 \times 10^{-16}$ atm.

8-19. At 250°C and 100 atm, $K_p = 0.00445\ \mathrm{atm}^{-2}$ (for $K_\nu = 0.521$); 79% conversion.

8-20. log $K_c^\circ = -4.374$; $\phi'_{Ca(HCO_3)_2(aq)} = -350{,}630$ cal/mole.

8-23. $\phi'_{SO_4^{=}(aq)} - \phi'_{HSO_4^{-}(aq)} = 2611$ cal/mole; $\eta^\circ_{SO_4^{=}(aq)} - \eta^\circ_{HSO_4^{-}(aq)} = -2229$ cal/mole [this quantity changes rapidly with T, indicating a relatively large difference between the ionic heat capacities of HSO_4^-(aq) and $SO_4^=$(aq)]. **8-24.** (*a*) -9320 cal/mole, -6510 cal/mole, 29.41 eu/mole; (*b*) -4140 cal/mole, 2960 cal/mole, 15.02 eu/mole.

8-26. $\bar{S} = 44.06$ eu/mole at 239.7°K and 1 atm; $\bar{S}^\circ_{298.16} = 45.94$ eu/mole.

8-27. (*a*) 41.41 eu/mole; (*b*) 64.42 eu/mole (correction for nonideality = +0.04 eu/mole).

8-28. $-79{,}634$ cal/mole; -109.056 eu/mole; $-47{,}118$ cal/mole.

Chapter 9

9-2. 146.7°C; 3.02 eu/mole; 1270 cal/mole. **9-3.** 0.3426 int volt; 0.408; $\phi'_{PbCl_2(aq)} - \bar{F}^\circ_{PbCl_2(c)} = 6536$ cal/mole. **9-4.** 1.467 int volts.

9-5. -1.230 int volts; $-55{,}140$ cal/mole; 17.1 eu/mole.

9-6. For Cs(c) = Cs^+(aq) + e, $E^\circ = 2.923$ int volts; for cell reaction, $\Delta H^\circ = -156{,}900$ cal (for $j = 2$ g-eq); for Cs(c) + H_2O(l) = CsOH(aq) + $\frac{1}{2}H_2$(g), $\Delta H^\circ = -55{,}130$ cal. **9-11.** -0.134 volt. **9-12.** -0.519 volt; $K'_s = 3.1 \times 10^{-7}$.

9-13. (*a*) 0.0353; (*b*) 153,770 cal/mole; (*c*) $-18{,}550$ cal/mole, $-349{,}660$ cal/mole.

9-16. (*a*) $-38{,}260$ cal [per mole of $ZnCl_2 \cdot 6NH_3$(c) formed]; (*b*) -2674 cal/mole; (*c*) $-142{,}680$ cal/mole; (*d*) $-126{,}050$ cal/mole. **9-17.** 0.5392 int volt.

9-18. 11,670 cal/mole. **9-21.** (*a*) 38.8 eu/mole; (*b*) $\phi'_{ClO_3^{-}(aq)} = -560$ cal/mole [see, however, A. R. Olson, *J. Am. Chem. Soc.*, **42**, 896–904 (1920), who reported -1374 cal/mole on the basis of equilibrium data for the reaction between Cl_2(aq) and H_2O(l) at 90°C; the temperature coefficient for the equilibrium constant of this reaction is rather large and uncertain in magnitude, but on the other hand, there is some doubt concerning the enthalpy of formation of $KClO_3$(c); see also G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," pp. 508–510, McGraw-Hill Book Company, Inc., New York, 1923].

Chapter 10

10-3. At 1500°K, 9.5×10^{-6} in $3p\ {}^2P_{1/2}$, 19.0×10^{-6} in $3p\ {}^2P_{3/2}$, 2×10^{-9} in $4s\ {}^2S_{1/2}$.

10-5. (*a*) 9489 cal/mole, -14.01 cal/mole deg; (*b*) 5862 cal/mole, -40.318 cal/mole deg; (*c*) $\Delta H_0^\circ = 31{,}050$ cal/mole, $\Delta H^\circ_{1180} = 27{,}420$ cal/mole; (*d*) $\bar{F}^\circ_{Zn(g)} = 22{,}680$ cal/mole. **10-6.** $\Delta H_0^\circ = 76{,}560$ cal/mole; $\Delta H^\circ_{298.16} = 77{,}570$ cal/mole, $\Delta F^\circ_{298.16} = 66{,}500$ cal/mole. **10-7.** $K_p^\circ = 5.55$ atm.

10-8. $\Delta F^\circ/T = -14.022$ cal/deg. **10-9.** (*a*) At 25°C, $(\bar{H}^\circ - \bar{H}_0^\circ) = 2412$ cal/mole, $(\bar{F}^\circ - \bar{H}_0^\circ)/T = -54.162$ cal/mole deg; at 50°C, $(\bar{H}^\circ - \bar{H}_0^\circ) = 2632$ cal/mole, $(\bar{F}^\circ - \bar{H}_0^\circ)/T = -54.815$ cal/mole deg; (*b*) $\Delta H_0^\circ = 15{,}620$ cal/mole. **10-10.** (*a*) At 298.16°K, 1481 cal/mole, -38.216 cal/mole deg; at 1000°K, 4968 cal/mole, -44.228 cal/mole deg; (*b*) $H_0^\circ = 35{,}550$ cal. **10-11.** 48.20 eu/mole. **10-19.** For Ca, $\Delta F^\circ = 31{,}830$ cal, 28.0% ionized at 1 atm [no account has been taken of equilibria with excited electronic states of Ca(g); this will tend to reduce the fraction of the total calcium in the ionized state]; for Na, $\Delta F^\circ = 27{,}370$ cal.

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