INTERNATIONAL CHEMICAL SERIES
LOUIS P. HAMMETT, PH.D., *Consulting Editor*

INTRODUCTION TO CHEMICAL THERMODYNAMICS

A SELECTION OF TITLES FROM THE

INTERNATIONAL CHEMICAL SERIES

LOUIS P. HAMMETT, PH.D., *Consulting Editor*

Amsden—
Physical Chemistry for Premedical Students

Arthur—
Lecture Demonstrations in General Chemistry

Arthur and Smith—
Semimicro Qualitative Analysis

Booth and Damerell—
Quantitative Analysis

Briscoe—
Structure and Properties of Matter

Coghill and Sturtevant—
An Introduction to the Preparation and Identification of Organic Compounds

Crist—
A Laboratory Course in General Chemistry

Daniels—
Mathematical Preparation for Physical Chemistry

Daniels, Mathews, and Williams—
Experimental Physical Chemistry

Desha—
Organic Chemistry

Dole—
Experimental and Theoretical Electrochemistry

Eastman and Rollefson—
Physical Chemistry

Gibb—
Optical Methods of Chemical Analysis

Glasstone, Laidler, and Eyring—
The Theory of Rate Processes

Griffin—
Technical Methods of Analysis

Hamilton and Simpson—
Calculations of Analytical Chemistry

Hammett—
Physical Organic Chemistry
Solutions of Electrolytes

Henderson and Fernelius
Inorganic Preparations

Huntress—
Problems in Organic Chemistry

Leighou—
Chemistry of Engineering Materials

Long and Anderson—
Chemical Calculations

Mahin—
Introduction to Quantitative Analysis
Quantitative Analysis

Millard—
Physical Chemistry for Colleges

Moore—
History of Chemistry

Morton—
Laboratory Technique in Organic Chemistry
The Chemistry of Heterocyclic Compounds

Norris—
Experimental Organic Chemistry
The Principles of Organic Chemistry

Parr—
Analysis of Fuel, Gas, Water, and Lubricants

Reedy—
Elementary Qualitative Analysis
Theoretical Qualitative Analysis

Rieman, Neuss, and Naiman—
Quantitative Analysis

Robinson and Gilliland—
The Elements of Fractional Distillation

Schoch, Felsing, and Watt—
General Chemistry

Snell and Biffen—
Commercial Methods of Analysis

Steiner—
Introduction to Chemical Thermodynamics

Stillwell—
Crystal Chemistry

Stone, Dunn, and McCullough—
Experiments in General Chemistry

Thomas—
Colloid Chemistry

Timm—
General Chemistry
An Introduction to Chemistry

Watt—
Laboratory Experiments in General Chemistry and Qualitative Analysis

Williams and Homerberg—
Principles of Metallography

Woodman—
Food Analysis

INTRODUCTION TO
Chemical Thermodynamics

By LUKE E. STEINER
PROFESSOR OF CHEMISTRY, OBERLIN COLLEGE

SECOND EDITION

NEW YORK TORONTO LONDON
McGRAW-HILL BOOK COMPANY, INC.
1948

INTRODUCTION TO CHEMICAL THERMODYNAMICS

PRINTED IN THE UNITED STATES OF AMERICA

THE MAPLE PRESS COMPANY, YORK, PA.

PREFACE TO THE SECOND EDITION

In this edition, new material has been added and old material rearranged and rewritten. Two old chapters have been combined and an old chapter divided, the total number remaining unchanged. Discussion of the second law of thermodynamics, formerly extending over two chapters, has been rewritten and now appears as a single chapter. The section on calculations from thermodynamic functions derived by statistical methods has been expanded to form a new chapter. A full enough treatment is given to enable the student to use the published tables of values for the thermodynamic functions, detailed calculation of the values being left for more extended courses in thermodynamics. Because of the growing importance of equilibriums in the gaseous phase, the chapter on gases has been expanded to cover real gases more completely. Tables have been revised, and new tables and new problems, based on recent data, have been added. The parts of the first edition found through teaching experience to lack clarity or logic have been rewritten. A minor change, but one that should be useful to the reader, is the renumbering of equations, figures, and tables by chapter and the indication of the chapter number on each page. With the new numbering system, equations, figures, and tables in other chapters may be found more readily.

Recently the National Bureau of Standards through Research Project 44 of the American Petroleum Institute published a set of self-consistent constants and conversion factors. Although these values differ by less than the stated uncertainties from the self-consistent constants used in the first edition, the newer set has been adopted for this edition because the author felt that the advantages of a general uniformity in use of constants outweigh the labor required to make changes. In the future thermochemists, physical chemists, physicists, and engineers will doubtless agree on "best values" for constants, for it would seem that individual sets of constants are as obsolete as individual tables of atomic weights.

The author wishes to thank Dr. Clara L. Deasy for careful and detailed criticism of the first edition and Dr. J. A. Campbell for criticism of some of the new material; he himself takes the responsibility for any errors that remain.

LUKE E. STEINER

OBERLIN, OHIO
January, 1947

PREFACE TO THE FIRST EDITION

The laws of thermodynamics are the foundations of chemical thermodynamics, laid by the masters who enunciated and developed these laws. The thermodynamic functions of Gibbs form the framework for its superstructure. Different names and symbols have been applied to the Gibbs functions at various times and places but the functions themselves remain scarcely altered by the changing architectural styles. However, different exteriors have been built on this framework, some emphasizing one pattern or angle or detail, and some another. Among the structures is that constructed by Lewis and his school, who developed methods for evaluating the thermodynamic functions of chemical systems, particularly those of solutions. This structure has been especially important because it has been so useful.

Chemistry is a healthy growing science which embraces new theories, methods, techniques, and tools whenever they are useful, but which shuns theories and speculations not susceptible to verification by experiment. Thus, when certain thermodynamic methods and functions were shown to give quantitative answers to the chemical problems of equilibrium and stability, they were adopted by chemists as "chemical thermodynamics." This chemical thermodynamics stimulated the collection of more and better data both through the extension of older methods and through the development of newer methods for evaluating the thermodynamic functions. The new data in turn increased the practical usefulness of chemical thermodynamics to a remarkable degree. In consequence, thermodynamics has taken its place among the basic courses in chemistry. It is no longer reserved for the specialist alone; it is now deemed an essential part of the equipment of the modern chemist. Such a change in the status of thermodynamics has necessarily caused some modification in the character of the courses in chemical thermodynamics.

This book was developed for a short course in thermodynamics for seniors, some of whom are preparing for graduate work in chemistry and some of whom are not, and for graduate students without previous training in thermodynamics. In the earlier chemistry courses students develop facility in various thermodynamic calculations, but they are usually deficient in an understanding of the basic concepts of thermodynamics and of the relations between the thermodynamic functions. The first objective of this book is therefore to acquaint the student with this fundamental theory. A second objective is to prepare the student to utilize the various tables of thermodynamic data and the data found in the current chemical literature. A third objective is to give the student a sound background for more extended work in thermodynamics. There have been some important omissions under this plan. In particular, the methods of evaluating the thermodynamic functions from spectroscopic data are not included. These, and other omitted material, may quite properly follow in a second-semester course.

To further the above objectives, primary attention is given to the thermodynamic functions which are most useful for chemical systems and consequently to those for which numerical data are most generally available. At the same time the symbols and nomenclature selected are those most frequently met in the American chemical literature. Various other features of the book are designed to augment its usefulness in the classroom. The lists of problems and exercises at the ends of the chapters vary in difficulty and importance but all are selected to illustrate some principle or application. Derivations of formulas are given somewhat fully to free the class time for more important discussions. Numerical computations are indicated so as to show the relative importance of various terms in the formulas. An attempt is made to report good modern values for numerical data both in the text and in the problems, though older data are occasionally used for special reasons. The sources of the data are cited. These references to the chemical literature serve to identify the data; at the same time they may be used to set up further problems or as reading assignments.

In systematic calculations on data from many sources, self-consistent conversion factors are highly desirable. The "International Critical Tables" contained such a set of accepted values, but some of these have been revised since the publication of the "Tables." A revised set of conversion factors and defined values based on the values accepted by specialists is therefore used in this book. Because most undergraduates are unfamiliar with the sources of these constants and factors, a brief discussion of the accepted constants is included.

The author wishes to acknowledge the aid of his former students and in particular the help of those in his class of 1940 who read and criticized the final manuscript.

LUKE E. STEINER

OBERLIN, OHIO
October, 1941

CONTENTS

TABLE OF SYMBOLS

The Lewis and Randall notation, E, H, S, A, and F, is used for the thermodynamic functions. The values of the extensive properties of substances for 1 mole of the substances are printed in small capitals, for example, E, H, S, A, F, V, and C_P. The corresponding partial molal quantities are printed as barred small capitals, for example, $\bar{\mathrm{E}}$, $\bar{\mathrm{H}}$, $\bar{\mathrm{S}}$, $\bar{\mathrm{A}}$, $\bar{\mathrm{F}}$, $\bar{\mathrm{V}}$, and $\bar{\mathrm{C}}_P$. The superscript ° denotes a function for substances in their standard states, for example, E°, H°, S°.

The symbol (g), (liq), (c), or (aq) following a chemical formula indicates the phase, gas, liquid, crystalline solid, or aqueous solution of indefinite composition, respectively, represented by the formula.

A	a constant
A	a molecular species
A	a particular system or body
A	a state
A	surface area
A	first virial coefficient
A'	first virial coefficient
A	work content, Helmholtz free energy
A	work content per mole
a	activity
a	atomic diameter (Debye-Hückel)
a	a constant
a	number of moles of the Ath kind
B	a constant
B	a molecular species
B	a particular system
B	a state
B	second virial coefficient
B'	second virial coefficient
b	a constant
b	number of moles of the Bth kind
C	concentration, moles per liter, molarity
c	centigrade
C	a constant
C	heat capacity
C_m	mean heat capacity
C_P	heat capacity at constant pressure
C_P	molar heat capacity at constant pressure
C_V	heat capacity at constant volume
C_V	molar heat capacity at constant volume
C	a molecular species

C	number of chemical constituents (phase rule)
C	a state
c	a constant
c	heat capacity per gram
c	number of components (phase rule)
$\boldsymbol{c}$	velocity of light
D	a constant
D	dielectric constant
D	a molecular species
D	a state
d	density
d	number of moles of the Dth kind
E	a constant
$\boldsymbol{E}$	electromotive force
$\boldsymbol{E}$	(with subscript) single electrode potential, arbitrary
$\boldsymbol{E}'$	counter electromotive force
E	energy of a system, internal or intrinsic energy
E	internal energy per mole
E	a molecular species
e	base of the natural logarithms
e^-	the electron
$\boldsymbol{e}$	electronic charge (charge equal and opposite to that of the electron)
e	number of moles of the Eth kind
$\boldsymbol{F}$	faraday constant
F	free energy, Lewis or Gibbs
F	free energy per mole
$\boldsymbol{f}$	activity coefficient in terms of molarities
f	fugacity
G	generalized extensive thermodynamic function
G_i	generalized thermodynamic function per mole of solution
$\boldsymbol{g}$	acceleration due to gravity (standard)
g	statistical or quantum weight
H	heat content of a system, enthalpy
H	heat content per mole
h	gravitational potential
$\boldsymbol{h}$	Planck's constant
I	an integration constant
j	freezing point lowering function
K	a constant
K	equilibrium constant
K_a	equilibrium constant in terms of activities
K_f	equilibrium constant in terms of fugacities
K_m	equilibrium constant in terms of molalities
K_C	equilibrium constant in terms of molarities
K_N	equilibrium constant in terms of mole fractions
K_P	equilibrium constant in terms of partial pressures
K	Kelvin
k	a constant
k_f	molality freezing point constant
$\boldsymbol{k}$	molecular (Boltzmann) gas constant

l	length
M	molar (gram-molecular) weight
M	molar concentration (moles per liter of solution)
m	mass
m	molal concentration (moles of solute per 1,000 grams of solvent)
m	molality
$\boldsymbol{N}$	Avogadro's number
N	mole fraction
N	number of molecules
n	number of gram-equivalents or faradays (emf equations)
n_i	number of ions
n_i	number of moles of *i*th substance
n	number of molecules
n	number of moles
P	pressure
P	thermometric property
P'	opposing pressure
p	number of phases (phase rule)
$\boldsymbol{Q}$	heat of solution
$\mathbf{Q}_i$	integral heat of solution per mole of solution
Q	concentration ratio in the emf equations
Q	partition function
q	heat (positive when entering system)
q_P	heat absorbed at constant pressure
q_V	heat absorbed at constant volume
q_r	heat for a reversible change
q_s	heat for a spontaneous change
$\boldsymbol{R}$	molar gas constant
R	resistance
r	number of reversible reactions (phase rule)
r	radius
S	entropy of a system
S	entropy per mole
s	solubility
T	temperature on the Kelvin scale
t	temperature in degrees centigrade
u	molecular velocity
$\overline{u^2}$	mean square molecular velocity
V	volume of a system
V	volume per mole
V_i	molar volume of ideal gas
v	variance, number of degrees of freedom (phase rule)
W	probability function
w	weight
w	work (positive when done by system)
w_n	net or useful work
w'	net reversible work
w_e	electrical work
w_P	work of expansion against pressure
w_r	work for a reversible change

X	number of types of energy absorption in a molecule
z	charge of an ion
α	activity coefficient in mole fraction units
α	coefficient of thermal expansion
α	a constant
α	molar volume defect of a real gas
β	compressibility
β	a constant
γ	activity coefficient in molality units
γ	a constant
γ	ratio of heat capacities, C_P/C_V
γ	surface tension
ϵ	energy per molecule
ϵ'_1	energy per molecule in first energy level
ϵ_0	energy per molecule in ground state
ϵ_1	excess energy of molecule in first energy level
θ	characteristic temperature (Debye)
θ	observed freezing point lowering
θ	temperature on real gas scale
θ	temperature of a substance
κ	factor in the Debye-Hückel equation
μ	chemical potential
μ	ionic strength
μ	Joule-Thomson coefficient
ν	frequency
ν	number of ions per molecule
ϕ	apparent molar volume
ψ	potential of an ion in solution (Debye-Hückel)

MATHEMATICAL SYMBOLS

D	the inexact differential operator
d	the total differential operator
f	function
∂	the partial differential operator
Δ	increment. ΔG for a thermodynamic property for a chemical reaction refers to the increase in G as the result of the chemical reaction that proceeds as indicated in the chemical equation. $\Delta G = G_2 - G_1$
Σ	sum
ϕ	function
lim	limit
log	logarithm to the base 10
ln	natural logarithm
$\doteq$	approximately equal to, or approaches as a limit
$\neq$	does not equal
$\equiv$	defined as

CHAPTER 1

INTRODUCTION

The science of thermodynamics is based on empirical energy relations. These relations may be summarized verbally in two important general statements and a third supplementary statement known as the "laws of thermodynamics."

Laws of Thermodynamics.—The first law of thermodynamics states the principle of the conservation of energy: *Energy may be converted to other forms of energy but is neither created nor destroyed.* Although experimental work was carried out by Rumford and Davy, it remained for Joule, in 1840 and thereafter, to put the first law on a firm experimental foundation. Independently, in the same decade, Mayer, Helmholtz, and others assisted in establishing the principle.

The second law of thermodynamics states the principle of *a general tendency toward equilibrium.* Various aspects of this tendency may be emphasized. The engineer or physicist who is interested in utilizing this tendency in engines to do useful work develops those expressions of the second law most directly applicable to "heat engines." The chemist, on the other hand, is especially interested in chemical equilibrium and in statements of the energy laws that may be related directly to substances and to their transformations. The second law of thermodynamics is older than the first. In 1824, Carnot made the first study of what is now known as the second law but in terms of an obsolete heat theory. After the first law was formulated, Kelvin showed that Carnot's conclusions were correct, and he and Clausius developed what we consider the classical formulation of the second law. In 1875–1878, Gibbs published his papers "On the Equilibrium of Heterogeneous Substances" which laid the groundwork for chemical thermodynamics.

A third principle called the "third law of thermodynamics" has a somewhat different status than the first and the second. According to this principle, the *entropy of substances at the absolute zero of temperature is zero or a small finite number.* The principle was formulated by Nernst in 1906 in his attempt to make calculations of chemical equilibrium from thermal data alone.

Because the laws of thermodynamics can be expressed in the form of mathematical equations, they are subject to the various treatments of the mathematician. However, thermodynamics is more than an exercise in mathematics. Though all of a countless array of possible equations may be equally valid, they are not equally useful. The actual number of fundamental equations used in thermodynamics is not great. Because the chemist restricts his primary consideration to those equations in which he can substitute experimentally measured values, the relationships that he must consider are limited in number.

Validity of the Laws and Methods of Thermodynamics.—Today no competent person seriously questions the validity of the laws of thermodynamics when applied to large-scale phenomena. However, the general laws do not become useful until they are applied to specific systems; and, in this application, chances for inexactness of statement and analysis arise. For example, we concern ourselves in practice not with energy as an abstract concept but with the energy of real substances having specific properties. Frequently, we express the relationship between the properties of substances in terms of equations, known as "equations of state," that represent the observed behavior of the substances only to a limited degree of exactness. Equations of state that do not represent the exact behavior of any single substance are often used because they represent the idealized behavior of a whole class of substances. It is obvious that the combinations of such approximate equations with the exact equations of thermodynamics yield formulas whose exactness is limited by the approximations.

The well-known ideal gas law $P\text{v} = RT$ furnishes an example. Every chemist knows that all gases deviate to a greater or lesser degree from this "ideal" equation, which assumes the validity of Boyle's and Charles's laws. Because R is not strictly constant for actual gases, equations containing this gas constant do not represent accurately the relations between P, v, and T unless corrections have been made for deviation of $P\text{v}$ from the ideal. Consequently, when the equation $P\text{v} = RT$ is introduced into any exact thermodynamic equation, an implicit assumption is made that restricts the applicability of the derived equation.

On the other hand, the properties of substances are frequently expressed by empirical equations which represent the data well enough over the experimental range but which grossly misrepresent the known behavior outside this range. For example, the heat capacity of substances is often expressed in terms of a quadratic or cubic equation fitting the data between certain limits, such as 0 to 100°c. It is known, however, that, over the entire temperature range from absolute zero upward, an elongated ʃ-shaped (sigmoidal) curve with its origin at zero represents the relation between heat capacity and temperature for simple substances. Such a curve cannot be represented by a quadratic (or cubic) equation even though the quadratic equation may fit restricted portions of the curve. When, therefore, such equations of limited applicability are introduced into heat content or free-energy equations by the methods given in subsequent chapters, the resulting heat content and free-energy equations cannot be valid beyond the temperature range in which the heat capacity equation is valid.

In addition to these limitations resulting from the representation of the properties of real substances by equations that do not conform strictly to the behavior of these substances, there may be further limitations resulting from convenient mathematical approximations. For example, the familiar laws for the boiling point rise and the freezing point depression of solutions are derived from the thermodynamic equation on the basis that, where the mole fraction N of the solvent is nearly unity, a change in $\ln N$ is approximately equal to a change in N. Although this assumption is justifiable when the concentration of solvent is high, ($N \doteq 1$), and the concentration of solute is correspondingly low, the assumption becomes unjustifiable in solutions with higher concentrations of solute.

Physical or mathematical approximations made in deriving an equation may be extremely advantageous because they facilitate the mathematical treatment. The explicit assumptions are not readily misunderstood. But implicit assumptions, made whenever approximate equations or equations valid only under restricted conditions are combined with the exact thermodynamic statements, may be so subtle as to be overlooked and disregarded. For this reason, we shall emphasize wherever possible the extent and nature of the various assumptions and approximations as we introduce them into exact equations.

Thermodynamics and the Atomic Theory.—Traditional thermodynamics is independent of the atomic hypothesis. It is based on the observed energy relations of weighable amounts of material and applies to chemical reactions as well as to other processes. Its laws are generalizations of our experience on the earth, hence any extension of the laws to the universe as a whole or to submicroscopic quantities are plausible but not proved. However, none of our observations on the universe or on small-scale phenomena are inconsistent with or contradictory to the laws of thermodynamics when proper allowance is made for mass-energy interconversions. Thermodynamics is older than our modern atomic theory, and it is not based on any particular theory of matter. Because thermodynamics is independent of the atomic theory, its general statements do not need revision whenever new details of atomic structure are established. On the other hand, because of this independence we are not able to establish the structure of atoms and molecules from the laws of thermodynamics. Thermodynamics sets up rules that any atomic or molecular system must obey, but it cannot go further than this.

For example, the heat capacity of a substance is an experimentally derivable quantity related in a very definite way to the other thermodynamic functions. On the basis of the atomic theory, one can attempt to calculate the heat capacity of the substance after assuming that the laws of motion apply to the molecules themselves. But the number of molecules in any finite sample of material is so large and the size of the molecules is so minute that the motions of individual molecules cannot be followed. The behavior of the system of molecules must, therefore, be explained in terms of statistical concepts. It is one of the triumphs of the quantum mechanics that, when it is applied to atomic and molecular systems, it yields calculated values for the thermodynamic functions, including heat capacities, in excellent agreement with the experimental values. Thus, the thermodynamics furnishes us with an excellent criterion for judging the various theories applied to atoms and molecules.

For submicroscopic systems containing few atoms or molecules, statistical studies show that the various thermodynamic functions would have fluctuating values. This conclusion does not trouble us, however, for the fluctuations for any finite system are too small to be detected experimentally. According to the kinetic theory, the pressure of a gas results from the bombardment of the walls of the container by the molecules. Only on the average will the exact number of molecules bombarding an equal area in unit time be identical, but any fluctuations about the average are too small to be measured. Similarly the "temperature" of any particular molecule varies as the molecule exchanges energy with its neighbors. The volume of a container for a substance will also show fluctuations, for the container walls consist of molecules that have a limited motion of their own. In all thermodynamic functions, however, the relative importance of the fluctuations decreases as the number of atoms in a system increases. Similarly, the laws of thermodynamics hold fully when applied not to individual submicroscopic systems but to ensembles of such systems.[1]

TEMPERATURE

Observations on energy relations cannot be dissociated from the concept of temperature. All bodies have temperatures detectable by our senses if the values occur within the proper range. Relative, qualitative temperatures are obtained readily; we can decide without much difficulty whether a body is colder than, or warmer than, some other body. However, it is more difficult to place a temperature precisely on an objective

---

[1] KEMBLE, E. C., *Phys. Rev.*, **56**, 1003 (1939).

scale. We may start with the observation that substances, in general, change properties when their temperature is changed, some properties showing greater variation with changing temperature than others. Any property that changes with temperature in a continuous, relatively uniform manner can be used as a thermometric property, especially if the property can be measured easily and accurately.

When the temperature of a body A is to be measured, another body,[1] the thermometer, whose thermometric property is to be measured, is placed in thermal contact with it. The value of the thermometric property so obtained can then be compared with the value of the same property when the thermometer is in thermal contact with a substance at some reference temperature. It becomes evident at once that the reading of the thermometric property can represent the temperature of A only when the thermometer has the same temperature as that of A. If the thermometer initially is colder or warmer than A, it must exchange energy with it until the temperatures of the two are identical. When the two bodies have thus reached the same temperature, they are in *thermal equilibrium*. The attainment of thermal equilibrium is an indispensable requirement for the measurement of temperature with a thermometer.

Centigrade Temperature Scale.—Some of the problems of thermometry become evident when one studies the method of setting up the centigrade scale. Two temperatures on this scale are fixed by international agreement: The temperature of an equilibrium mixture of water and ice in contact with air at one normal or standard atmosphere pressure is fixed at exactly 0°, and that of water vapor in equilibrium with water at this same pressure is fixed at exactly 100°. The difference in temperature between these two points is, therefore, 100°C. Suppose that a thermometer in thermal equilibrium with melting ice (0°C) under the specified standard condition has an observed value of the thermometric property P equal to P_0. When the same thermometer is in thermal equilibrium with condensing steam under the standard conditions (100°C), the value of P becomes equal to P_{100}. With this thermometer, 100° corresponds to $(P_{100} - P_0)$, and the value of 1°C is defined as

$$1^\circ = \frac{P_{100} - P_0}{100} \tag{1.1}$$

---

[1] Sometimes a property of the body whose temperature is to be measured is used as the thermometric property. In optical pyrometry the brightness of the glowing object is usually compared with that of a filament of a lamp. At low temperatures the vapor pressure of the liquid under observation (hydrogen or helium) may be used as a measure of its temperature. In the production of temperatures below 1°K by the method of adiabatic demagnetization, the magnetic susceptibility of the substance is used to measure its temperature.

The value of any temperature t, at which the thermometer has the value of P equal to P_t, is then given on this scale by

$$t^\circ = \frac{P_t - P_0}{P_{100} - P_0} \times 100 \tag{1.2}$$

Thus, if P_t is exactly intermediate between P_0 and P_{100},

$$P_t - P_0 = \tfrac{1}{2}(P_{100} - P_0) \tag{1.3}$$

and $t^\circ = 50^\circ\text{c}$.

Unfortunately, this procedure serves to define 50°c only in terms of the one thermometer. When a different thermometric substance is used, its value of P_t may not be exactly intermediate between P_0 and P_{100}.

TABLE 1.1.—READING* OF LIQUID-IN-GLASS THERMOMETERS AT VARIOUS TEMPERATURES

(The calibration points of each thermometer are listed in **bold-faced** type)

Fixed points	Solid carbon dioxide with vapor pressure at 760 mm		Melting ice			Condensing steam at 760 mm
Thermodynamic temperature......	−78.51°c	−40°c	0°c	30°c	50°c	100°c
Mercury in *verre dur*...	....	......	**0**	30.102	50.103	**100**
Mercury in Kew glass..	....	......	**0**	29.955	49.99	**100**
Mercury in Jena 16^{III}..	....	......	**0**	30.11	50.12	**100**
Pentane in Jena 16^{III}..	**−78.51**	−43	**0**	37.6		
Toluene in *verre dur*....	**−78.51**	−41.2	**0**	......	......	124
Alcohol in *verre dur*....	**−78.51**	−40.9	**0**	33.6		

* Values derived from the data in the "International Critical Tables," Vol. 1, pp. 55, 56, McGraw-Hill Book Company, Inc., New York, 1926.

The two thermometers need not give the same scale between 0 and 100° or beyond these defined temperatures. This problem, therefore, needs further consideration.

Reproducing the Centigrade Scale.—In a mercury thermometer the volume change of the mercury with temperature is measured (more precisely, the difference in the expansion of the mercury and that of the glass enclosing the mercury). If the bulb is full and the expansion occurs in a capillary tube of uniform bore, the volume change can be read directly in terms of the length of the mercury column in the capillary. The length of the mercury column then becomes the thermometric property actually observed.

As a matter of fact, as may be seen in Table 1.1, the temperature at which a mercury column reaches a point halfway between the 0 and the

100° marks depends on the kind of glass enclosing the mercury. Thus, mercury in French hard glass reads 50.10° when mercury in Kew glass reads 49.99°. When liquids other than mercury are used, the discrepancies become even greater. A thermometer of pentane in Jena 16^{III} glass, when calibrated at −78.51° (vapor pressure of solid carbon dioxide equals 1 atmosphere) and at 0°, reads 3° lower than a helium gas thermometer at −40° and 7.6° higher than the helium thermometer at 30°.

The various thermometric substances commonly used up to the freezing point of gold at 1063°C and the measured properties are indicated in Table 1.2. Of these thermometers, gas thermometers show the greatest agreement among themselves, especially those containing the more ideal gases helium and hydrogen. Gas thermometers, when filled with other gases, yield a temperature scale corresponding to that of the hydrogen or helium thermometers when corrections are made for deviations of these gases from ideality. All gases can, therefore, be made to give the same temperature scale. As we shall see later, the laws of thermodynamics give a temperature scale that is independent of the properties of any particular substance whether gas, liquid, or solid—the scale called the *thermodynamic scale*. This is the scale given by all gases as they approach ideal behavior. Thermodynamic temperatures are proportional to the pressures of an ideal gas in a constant-volume thermometer and to the volumes of an ideal gas in a constant-pressure thermometer. They can also be obtained from any other substance if the necessary data are available.

TABLE 1.2.—COMMON THERMOMETRIC SUBSTANCES

Type of thermometer	Thermometric substance	Property measured
Primary:		
Gas		
Constant volume	Helium, hydrogen, nitrogen, air	Pressure
Constant pressure	Helium, hydrogen, nitrogen, air	Volume
Secondary:		
Liquid-in-glass	Mercury, ethanol, toluene, pentane	Length of column
Resistance	Platinum, copper	Electrical resistance
Thermocouple	Platinum, platinum-rhodium; copper, constantan; iron, constantan; Chromel X, Copel	Emf developed between two junctions of dissimilar metals at different temperatures
Optical pyrometer	....	Brightness of glowing object

Working Temperature Scales.—The pressure (or volume) of an ideal gas thermometer is a desirable thermometric property to measure because it varies linearly with the temperature. However, gas thermometers are not convenient to use, partly because of their bulk, for they must be large enough to enclose sufficient gas for precise measurement. Because they are bulky, the essential thermometric requirement—that the thermometer be in thermal equilibrium with the body whose temperature is to be measured—cannot easily be met. This requirement is fundamental; yet lack of thermal equilibrium within the body itself or between body and thermometer is undoubtedly the greatest source of error in thermometry. Thus, a mercury thermometer, calibrated for no emergent stem, may be used with a partly emergent stem so that part of the mercury is at a different temperature from that of the bulb; a resistance thermometer may be incompletely immersed so that part of the resistance wire is at a different temperature from the rest; a thermocouple junction may be at a different temperature from that of the body it is to measure because the metallic wires, which necessarily have a high thermal conductivity, carry heat to or from the junction. Likewise, an optical pyrometer may give the wrong temperature of a body because it reads surface temperatures that may differ materially from interior temperatures whenever radiation losses are permitted.

As was indicated earlier, gas thermometers are not suitable for routine use. They reproduce the thermodynamic temperature scale within the accuracy of the measurement over a wide temperature range, but the precision of any single reading is not high enough. For this reason, the national standards laboratories of the United States, Great Britain, and Germany and other laboratories established, as accurately as possible, the temperatures of reproducible, isothermal equilibriums such as freezing points, boiling points, and other phase transition points, on the thermodynamic centigrade scale.[1] These temperatures, on recommendation of the respective national laboratories, the Bureau of Standards, the National Physical Laboratory, and the Physikalisch-technische Reichsanstalt, were accepted in 1927 by the Seventh General Conference of Weights and Measures[2] as defining the *international temperature scale.* The temperatures, called *basic fixed points*, are printed in Table 1.3 in **bold-faced** type; they are the temperatures used to calibrate other thermometers, such as the platinum resistance thermometer, which can be read accurately.

---

[1] The thermometric substances must, of course, be chemically pure.

[2] For more information on the international temperature scale, read the report of the scale adopted by the Seventh General Conference on Weights and Measures representing 31 nations: G. K. Burgess, *Bur. Standards J. Research*, **1**, 635 (1928).

For example, in the range 0 to 660°c the resistance R of the platinum resistance thermometer reproduces very well the temperature of the thermodynamic temperature scale as expressed in the equation

$$R = R_0(1 + At + Bt^2) \tag{1.4}$$

The values of the constants R_0, A, and B (with t in degrees centigrade)

TABLE 1.3.—FIXED POINTS ON THE INTERNATIONAL TEMPERATURE SCALE*
(Basic fixed points are in **bold-faced**, secondary fixed points in ordinary roman type)
[All temperatures are for equilibrium processes under a pressure of 1 standard atmosphere (= 1,013,250 dynes/cm²)]

Substance	Phenomenon	Temperature, °C
Liquid O_2	**Vapor pressure**	**−182.97**
Solid CO_2	Vapor pressure	− 78.5
Mercury	Freezing	− 38.87
Ice	**Melting**	**0.000**
Na_2SO_4	Transition	32.38
Steam	**Condensing**	**100.000**
Naphthalene	Condensing	217.96
Tin	Freezing	231.85
Benzophenone	Condensing	305.9
Cadmium	Freezing	320.9
Lead	Freezing	327.3
Zinc	Freezing	419.45
Sulfur	**Condensing**	**444.60**
Antimony	Freezing	630.5
Silver	**Freezing**	**960.5**
Gold	**Freezing**	**1063**
Copper	Freezing (in reducing atmosphere)	1083
Palladium	Freezing	1555
Tungsten	Melting	3400

* BURGESS, G. K., *Bur. Standards J. Research*, **1**, 635 (1928).

are evaluated from the measured values of R at the basic fixed points, freezing water 0.000°, condensing steam 100.000°, and condensing sulfur 444.60°. When the constants are evaluated, the temperature corresponding to any other resistance within the stated range can be obtained from the equation. (The equation is sometimes transformed into other forms to facilitate computations.) If the thermometer is to be used in the range −190 to 0°c, the measured value of R at a fourth basic fixed point, the oxygen point at −182.97°c, is used to evaluate an additional constant C. In this range, temperatures are then related to values of R by the equation

$$R = R_0[1 + At + Bt^2 + C(t - 100)t^3] \tag{1.5}$$

where R_0, A, and B have their previously determined values.

The standard platinum *vs.* platinum-rhodium thermocouple is used from 660°c to the gold point, 1063°c, the electromotive force (emf) E being represented by the equation

$$E = a + bt + ct^2 \tag{1.6}$$

The constants a, b, and c are evaluated by calibration[1] at the freezing point of antimony, as measured with the resistance thermometer (approximately 630.5°), and the basic fixed points, freezing silver 960.5° and freezing gold 1063°. For convenience in calibrating working thermometers, other fixed points called *secondary points* are established on the same scale as accurately as possible with thermometers calibrated at the basic fixed points. The secondary points are also listed in Table 1.3.

Though knowledge of the proper methods for establishing temperatures of experimental substances on the thermodynamic temperature scale is not necessary for an understanding of the theories of thermodynamics, this knowledge is required for proper evaluation of many thermodynamic data. Detailed procedures for precision thermometry are given elsewhere.[2]

MATHEMATICAL REVIEW

Thermodynamics deals quantitatively with the relations between the energy and other properties of systems. These properties are all interrelated mathematically, and the treatment of these relationships is subject to the principles and rules of mathematics. A certain minimum of mathematical skill is therefore necessary. For the guidance of students who have studied elementary calculus, we shall present here a review of some of the mathematical principles that are used later.

Consider a system with definite values for its pressure, temperature, volume, energy, etc. If one of these properties, such as the energy or volume, is related in some definite way to several of the other properties, such as the pressure and temperature, the relationship being expressible in the form of some mathematical equation, the property (energy or volume) is called a *function* of the pressure and temperature.

---

[1] In practice the calibration values for a thermocouple are generally compared with the emf values for its particular pair of metals as listed in a "standard" table. A deviation curve is then prepared which enables the experimenter to read temperatures directly from the standard table.

[2] A comprehensive treatment of temperature and thermometry is the published report of a symposium conducted by the American Institute of Physics: "Temperature, Its Measurement and Control in Science and Industry," Reinhold Publishing Corporation, New York, 1941.

Where the energy is represented by E, the pressure by P, and the temperature by T, such relationship can be expressed in the language of mathematics as

$$E = \mathrm{f}(P, T) \tag{1.7}$$

A relationship between E, P, and T may exist even though we do not know the exact form of the equation that expresses it quantitatively. In the above equation, P and T, which may vary independently of each other, are called the *independent variables;* and E, whose value is fixed for each pair of values of P and T, is called the *dependent variable.* P and T are commonly expressed as independent variables because the resulting equations are simpler and more readily derived from the experimental data, but there is no theoretical reason why P or T should not be expressed as the dependent variable and the other properties as the independent variables. Thus, if E and T vary independently, the value of P becomes fixed for each pair of values of E and T. This relation may be expressed as

$$P = \mathrm{f}_1(E, T) \tag{1.8}$$

Whenever a property of a system depends on more than one other property, it is common experimental practice to secure data by permitting only one of the independent variables to change at a time, all the others being kept constant. In the above example, we might study the rate of change of energy with pressure, keeping the temperature constant, expressing the result for infinitesimal changes in the language of the calculus as $(\partial E/\partial P)_T$. This is called a *partial derivative,* the symbol ∂ being used to show that we are studying not the total change of energy but only the part of the energy change resulting from the change in pressure at a definite temperature T. The subscript T, which indicates that the temperature is kept constant during the differentiation, may be omitted; but the student should retain it until he is familiar enough with partial derivatives not to need the emphasis it gives. The same partial derivative may be written as $(\mathrm{d}E/\mathrm{d}P)_T$, with the symbol, d, as used for complete differentiation, but here the subscript T must be retained to show that the temperature remains constant at the value T during the differentiation. Similarly, the rate of change of energy with temperature may be studied at constant pressure, the corresponding partial derivative being written as $(\partial E/\partial T)_P$ or $\partial E/\partial T$ or $(\mathrm{d}E/\mathrm{d}T)_P$.

If the energy of a system is a function of pressure and temperature, an infinitesimal increase in energy, represented by the differential $\mathrm{d}E$, may often be expressed as the sum of the energy increase accompanying the change in pressure while the temperature remains unchanged and the energy increase accompanying the change in temperature while the pressure remains constant. Written with mathematical symbols, this statement is expressed by the differential equation

$$\mathrm{d}E = \left(\frac{\partial E}{\partial P}\right)_T \mathrm{d}P + \left(\frac{\partial E}{\partial T}\right)_P \mathrm{d}T \tag{1.9}$$

In a system in which the energy is a function of the volume as well as of the pressure and temperature, the partial derivative of energy with respect to pressure becomes $(\partial E/\partial P)_{T,V}$, the subscripts T and V indicating that both temperature and volume remain constant during the process. The differential equation for the total change in energy then becomes

$$\mathrm{d}E = \left(\frac{\partial E}{\partial P}\right)_{T,V} \mathrm{d}P + \left(\frac{\partial E}{\partial T}\right)_{P,V} \mathrm{d}T + \left(\frac{\partial E}{\partial V}\right)_{P,T} \mathrm{d}V \tag{1.10}$$

Under various restrictions, differential equations, such as (1.9), take on simplified forms. Thus, if the energy of the process remains constant, dE is 0 and equation (1.9) becomes

$$\left(\frac{\partial E}{\partial P}\right)_T \mathrm{d}P + \left(\frac{\partial E}{\partial T}\right)_P \mathrm{d}T = 0 \tag{1.11}$$

Dividing by dT and rearranging algebraically, we have (still under the restriction of constant energy)

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_E = \left(\frac{\partial P}{\partial T}\right)_E = -\frac{(\partial E/\partial T)_P}{(\partial E/\partial P)_T} = -\left(\frac{\partial E}{\partial T}\right)_P\left(\frac{\partial P}{\partial E}\right)_T \tag{1.12}$$

Other relations may be obtained from equation (1.9). If (1.9) is divided by dT, we have

$$\frac{\mathrm{d}E}{\mathrm{d}T} = \left(\frac{\partial E}{\partial P}\right)_T \frac{\mathrm{d}P}{\mathrm{d}T} + \left(\frac{\partial E}{\partial T}\right)_P \tag{1.13}$$

If we choose, we may place a restriction of constant volume on this equation; under these conditions the total derivatives dE/dT and dP/dT become partial derivatives, and equation (1.13) becomes

$$\left(\frac{\partial E}{\partial T}\right)_V = \left(\frac{\partial E}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial E}{\partial T}\right)_P \tag{1.14}$$

Calculations in Thermodynamics.—The precision with which one makes calculations depends on the precision [illegible] data used in the calculation and on the purpose for which the calculations are made. The beginning student who uses calculations primarily [illegible] familiarize himself with the laws of chemical combination needs to use fewer significant figures than the student in quantitative analysis who is trying to develop his analytical accuracy. In a study of thermodynamics, some problems are primarily to test the student's understanding of principles and methods; other problems, however, require a more rigorous treatment, for thermodynamics is studied in part because it can give more exact answers to many problems than are obtainable without it. Because of their training in physical chemistry, students in thermodynamics are informed about the various experimental methods and may, therefore, be expected to make realistic computations that take into account the probable accuracy of the experimental data. The theory of errors, as applied to experimental work, is discussed elsewhere.[1]

We are here concerned with the following problem: Given experimental data of a given accuracy (or precision), how accurate (or precise) are the conclusions drawn from these data by mathematical methods? In physical chemistry, the term "accuracy" relates to the degree of correspondence of data with the "absolute" value presumed to exist for the physical quantity. In general, we are confident of a high accuracy only if the same value is obtained by more than one independent experimental method. The term "precision" is used to denote the degree of agreement among the various values in a given experimental series. If these values agree closely, the indeterminate errors are small and the precision is high. If, however, the experimental method contains some constant source of error, such as an error in an instrument, the *accuracy* of a value may be low even though the *precision* of the measurement was high.

Good judgment in deciding whether a given datum is accurate or merely precise depends on one's knowledge of the experimental method used in obtaining the datum and sometimes on one's knowledge of the experimenter himself. This judgment can be developed only by experience but it will not be developed at all until the student becomes aware that the problem exists. Because it is just as foolish to carry on calculations with greater precision than the data warrant as to neglect precise data where available and necessary, the student should form the habit of

---

[1] JASPER, J. J., "Laboratory Manual of Physical Chemistry," Chap. I, Houghton Mifflin Company, Boston, 1938.

DANIELS, F., "Mathematical Preparation for Physical Chemistry," McGraw-Hill Book Company, Inc., New York, 1928.

MELLOR, J. W., "Higher Mathematics for Students of Chemistry and Physics," Longmans, Green & Company, New York, 1922.

LIVINGSTON, ROBERT, "Physico Chemical Experiments," The Macmillan Company, New York, 1939.

CRUMPLER, T. B., and J. H. YOE, "Chemical Computations and Errors," John Wiley & Sons, Inc., New York, 1940.

adapting his calculation method to the requirements of his problem. Some rules for computation are given below.

Computation Rules.—Contrary to the opinion of many students, the position of the decimal point is no criterion of the precision or accuracy of a number; it depends entirely on the size of units expressed. Thus, a volume of 21.3 ml is identical with a volume of 0.0213 liter. Where no limits of error are indicated, it is often possible to deduce them from the number itself. In the above example, one may assume that the true value of the measurement lies nearer 21.3 ml than to either 21.2 or 21.4, that is, that it lies between 21.25 and 21.35. The digits 2, 1, and 3 are called *significant figures*, whether they appear in the number 21.3 or 0.0213. If the measured value is actually 21.3 ml to the nearest hundredth milliliter, it is expressed by the number 21.30 ml (or 0.02130 liter). Here the terminal zero is also a significant figure, though a zero used to show the position of the decimal point is not. Terminal zeros in a number should be retained whenever they are significant digits. The number 1.000 gram implies one gram to the nearest milligram, and the number 1.00 gram implies one gram to the nearest centigram. Uncertain digits are sometimes indicated as in the $_6$ in 2.1_6.

In a computation, the number of digits retained in the result is properly the number that is significant.[1] If we multiply 21.3 by 1.47, both numbers having three significant figures, we obtain the number 31.311, but not all the five digits are significant. If the true value of the first number lies between 21.25 and 21.35 and that of the second between 1.465 and 1.475, the true value of the product must lie between the minimum $21.25 \times 1.465 = 31.13125$ and the maximum

$$21.35 \times 1.475 = 31.49125.$$

Because only the first two digits in these products agree exactly, it is meaningless to report more than three digits in the result which becomes 31.3, for the true value lies between 31.13 and 31.49. If the multiplier 1.47 is known to four significant figures, it is properly written as 1.470, and the true value lies between 1.4695 and 1.4705. The maximum and minimum products are $21.25 \times 1.4695 = 31.226875$ and

$$21.35 \times 1.4705 = 31.395175,$$

respectively. Here the true value lies between 31.23 and 31.40. The precision has not been helped greatly by the greater number of significant figures in only one of the factors.

---

[1] There are exceptions to this rule. When known differences are to be derived from numbers, additional digits beyond those "significant" are sometimes recorded so that the correct difference is reproduced when one number is subtracted from the other.

Thus, it becomes evident that in multiplication or division the percentage precision of a product or quotient cannot be greater than the percentage precision of the least precise factor in the computation. All superfluous digits are, therefore, rejected, the last retained digit being increased by 1 if the following rejected digit is 5 or over. Thus, in rounding off, 47.55 becomes 47.6. Where four-place logarithms are used, four significant figures are automatically retained; with five-place logarithms, five significant figures are retained.

In additions or subtractions, the position of the decimal point is important. If the last significant figures of two numbers occur in the same decimal place, the final significant figure of the sum or difference lies in that place. Otherwise, the last significant figure of the sum or difference agrees with respect to the decimal place with that of the number having its last significant figure farther to the left with respect to the decimal point (for example, fewer figures after the decimal place). When the student is in doubt about the number of significant figures in his result, he should compute the maximum and the minimum values of the result. In this way, he learns to judge the relation between his final values and the data on which they rest.

UNITS AND ACCEPTED CONSTANTS

The relationships of thermodynamics are especially useful because they permit correlation of the results of many different types of measurement with each other. In the thermodynamic equations as in other equations, the value of any one term can be found if the values of the other terms are known. These data, however, may come from many different sources. For example, the experimental data for one of the terms in the thermodynamic equation may be obtained with a calorimeter at room temperature, those for a second term may come from a chemically determined equilibrium constant or from the emf of an electrolytic cell, and those of a third term may come from heat capacity measurements at temperatures ranging from room temperature to temperatures approaching absolute zero, or from the combination of statistical theory with band spectrum data. When values assembled from such a variety of data are combined in a single equation, they must be stated in terms of some common unit, the data being converted with the aid of proper conversion factors. It is obvious that, if the values obtained by entirely different methods are to be compared, the conversion factors utilized must be accurate enough to permit the comparison.

The question of conversion factors frequently arises when older data are compared with newer data. For example, if the data are tabulated on a molar basis, their numerical values depend on the assumed value for the molecular weight, for the practical experimental unit of mass is the gram and not the mole. Whenever the degree of accuracy of the data is comparable with that of the molecular weights, any subsequent revision of the pertinent molecular weights necessitates a corresponding revision of the molar values.[1]

The calorie is a traditional unit of energy, originally defined as the heat required to raise the temperature of one gram of water one degree centigrade. Unfortunately, the heat capacity[2] of water is not independent of the temperature of the water so that the calorie is not an invariable unit. Therefore, one should note the particular calorie utilized when examining energy data expressed in calories. Similarly, it is the duty of the author or compiler of data to give the necessary information. If an experimenter does not indicate the conversion factors he selects, one may safely infer that his attention to the other niceties of experimentation is not sufficiently careful for the securing of precise data.

Some of the fundamental units and constants are given below. A more complete list of self-consistent constants and conversion factors is given in Tables I, II, and III of the Appendix.

Fundamental Units.—The fundamental units of length and mass are the platinum-iridium standards prepared in 1875 and deposited at the Bureau International des Poids et Mesures at Sèvres, France. Copies of these standards are held by the National Bureau of Standards at Washington.

The fundamental unit of *length* is the *meter* (m), which is the distance at 0°c between the axis of two lines ruled on the prototype in France. The other metric units of length are multiples or submultiples of this unit. (In the United States the yard is defined as 3,600/3,937 meter.)

The fundamental unit of *mass* is the *kilogram* (kg), which is the mass of the prototype in France. The gram (g), which is 10^{-3} kg, is frequently treated as a primary unit. (In the United States the avoirdupois pound is defined as 453.5924277 grams.)

The fundamental unit of *capacity* is the liter, which is the volume of one kilogram of pure water at the temperature of its maximum density under a pressure of one normal atmosphere. Modern density determinations have shown that the maximum density of water (in grams per cubic centimeter) is slightly less than unity; hence, one liter is slightly greater than 1,000 cm^3. The best values for the maximum density of water indicate that

---

[1] For apparent exceptions to this rule, see F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of Chemical Substances," p. 10, Reinhold Publishing Corporation, New York, 1936.

[2] See Table 3.1.

$$1 \text{ liter} = 1{,}000.028 \text{ cm}^3$$

The fundamental unit of *time* is the *second* (sec), which is defined as 1/86,400 of a mean solar day.

Conventional Constants.—Among the constants defined arbitrarily is the *standard gravity* (g). It is defined, not as the gravity at any particular place, but as exactly 980.665 cm/sec^2.

The *normal atmosphere* (atm), also called the *standard atmosphere,* adopted by the Seventh General Conference of Weights and Measures[1] in 1927, is defined as the pressure due to a column of mercury 760 mm high, having a mass of 13.5951 grams per cm^3, subject to a gravitational acceleration of 980.665 cm/sec^2, and is equal to 1,013,250 dynes per square centimeter.

Another unit of pressure, the *millimeter of mercury* (mm), is defined as 1/760 of the standard atmosphere.

Mole.—Although the kilogram (or the gram) is the fundamental unit of mass, it is not the most convenient unit for expressing the unit mass of substances undergoing chemical reactions. Here the convenient unit is the molecule or the gram molecule consisting of N molecules, where N is Avogadro's number. The unit of mass which consists of the N molecules, a molecular weight in grams of a pure substance, is called the *mole.* The term "molecular" can then be reserved for the individual molecule. In this terminology, the molecular energy is the energy of a single molecule, and the molar (or molal) energy that of the mole of substance. Thus, the terms "molar energy" and "molar volume" refer to 32.0000 grams of oxygen, 16.042 grams of methane, or 18.016 grams of water.

The convenience of the molar unit of mass is so great that nearly all the data for pure substances are recorded in molar units. Physicists have not followed this practice so widely as have chemists, in part because the experimental unit of mass is the gram, and in part because molar values need revision whenever the atomic weights on which they are based are revised. However, the advantages of the molar units are great enough to overcome these handicaps.

We write chemical formulas for many substances whose precise molecular weights we do not know. The formulas O_2 and CH_4 represent very well the molecular and, therefore, the molar composition of oxygen and methane, but the formula H_2O is not so satisfactory for water. It represents the molecular weight of the vapor but not that of liquid water. The term "formula weight" has been proposed to represent the weight in grams of the sum of the atoms indicated by the formula. We shall attempt no such discrimination. The term "mole" will be used to

---

[1] BURGESS, *op. cit.*

represent the molar, formula, or atomic weight in grams of the substance, as indicated by the formula as written. Thus, we take the molar volume of NaCl as the volume of 58.454 grams of the salt without thereby implying that the formula NaCl represents a real "molecule" of the salt either in the crystal or in an aqueous solution. Whenever the molar weight is not well established by experiment or usage, we shall always indicate with a chemical formula the quantity of substance to which we apply the term "mole" or "molar."

Concentration Units.—Many of the thermodynamic properties of a substance are functions of the concentration of the substance. For this reason, we shall review briefly the various methods of expressing concentration in common use. The concentration of a pure solid or liquid does not change rapidly with either pressure or temperature; hence, expressions for the change in concentration of these condensed phases do not enter the usual thermodynamic equations applied to chemistry. But the concentration of pure gases changes so rapidly with pressure and temperature that this change cannot be disregarded as negligible. For n moles of an ideal gas, the pressure, volume, and temperature being equal to P, V, and T, respectively, the ideal gas law gives the relation,

$$PV = nRT \tag{1.15}$$

When V is measured in liters and P in atmospheres, R is the gas constant in liter-atmospheres per degree and the concentration in moles per liter is given by

$$C = \frac{n}{V} = \frac{P}{RT} \tag{1.16}$$

At constant temperature the pressure may be used as a measure of the concentration of the gas, for

$$P = CRT \tag{1.17}$$

However, it is in dealing with solutions that we find most need for expressing the concentration of the various constituents of the solution. If a solute is to be emphasized, the concentration is frequently expressed in terms of number of moles of solute in unit volume of solution. Thus, a solution containing one mole of solute per liter is called a *molar* solution. In many problems, however, the functions take on their most instructive form if concentrations are expressed in mole fractions. If the solution is composed of n_A moles of the substance A, n_B moles of the substance B, and n_C moles of the substance C, the *mole fraction* N_A of A in the solution is

$$N_A = \frac{n_A}{n_A + n_B + n_C} \tag{1.18}$$

Similarly, the mole fraction of B, N_B, and that of C, N_C, are given by

$$N_B = \frac{n_B}{n_A + n_B + n_C}; \qquad N_C = \frac{n_C}{n_A + n_B + n_C} \tag{1.19}$$

The sum of all the mole fractions in a solution is unity, for, from the defining equations (1.18) and (1.19), we have

$$N_A + N_B + N_C = \frac{n_A + n_B + n_C}{n_A + n_B + n_C} = 1 \tag{1.20}$$

Sometimes, *moles per cent* are used in place of mole fractions, the numerical values of the former being 100 times those of the latter.

Mole ratios are also used as concentration units. Thus, in a binary solution of A and B, we have

$$\frac{n_A}{n_B} = \frac{N_A}{N_B} \tag{1.21}$$

where n_A/n_B is the *mole ratio* of the two substances.

For liquid solutions, especially aqueous solutions, another method of expressing concentrations is employed, which is equivalent to the mole ratio. Thus, a solution containing 1 mole of a constituent (called the "solute") in 1,000 grams of a second constituent (called the "solvent") is defined as a *molal* solution. In general, even for aqueous solutions, a liter of the solution does not contain exactly 1,000 grams of solvent. *Molalities* designated by m, therefore, differ from *molarities*, designated by C. Because 1,000 grams of water contains 55.506 moles, the mole ratio of a molal aqueous solution is 1/55.506.

Electrical Units.—The electrical units in common use, called "practical units," are defined in terms of the fundamental units. Thus, the volt is 10^8 cgsm units of emf, the ampere (amp) is $\frac{1}{10}$ cgsm unit of current (the coulomb being the corresponding unit of quantity of electricity), and the ohm is 10^9 cgsm units of resistance. The practical unit of energy, the joule, equal to the volt-ampere-second or the volt-coulomb, is equal to

$$10^8 \times \tfrac{1}{10} = 10^7 \text{ ergs (dyne-cm)}$$

In experimental work, however, electric measurements are made not in terms of the above absolute units but in terms of standards selected by international agreement. Units expressed in terms of these standards are called "international" units. Thus, the emf of the Weston normal cell at 20°c is defined as exactly 1.0183 international volts; 1 international volt therefore becomes 1/1.0183 of this value. The international ampere is defined as the unvarying electric current that, under specified conditions, deposits silver at the rate of 0.00111800 gram per sec. The international ohm is the resistance at 0°c of a column of mercury of constant cross section, having a mass of 14.4521 grams and a length of 106.300 cm at this temperature. Although the international units at the time they were established (1908) agreed with the absolute units within the precision of the measurements, the two sets of units do not agree within the limits of present-day accuracy.

The "best values" for the relations between the international units and the corresponding absolute units, selected by the National Bureau of Standards are

1 international ohm = 1.000494 ± 0.000015 absolute ohm
1 international volt = 1.000332 ± 0.000029 absolute volt
1 international coulomb = 0.999838 ± 0.000025 absolute coulomb

From these values, we have

1 international joule = 1.000170 ± 0.000052 absolute joule

Calorie.—Historically, the *calorie* (cal) sometimes called the *gram calorie,* was defined in terms of the specific heat capacity of water, that is, as the quantity of heat required to raise the temperature of 1 gram of water 1°c. The *kilocalorie* (kcal), also called the *kilogram calorie,* is defined as 1,000 calories.

When more careful measurements showed that the heat capacity of water is not constant but changes with temperature, three different calories came into common use. The 15° *calorie* was defined as the quantity of heat required to raise 1 gram of water from 14.5 to 15.5°c and the 20° *calorie* as that required from 19.5 to 20.5°c. The *mean calorie* was defined as 1/100 the quantity of heat required to raise 1 gram of water through the 100° interval from 0 to 100°c. The heat capacity values corresponding to each of these calories may also be measured in terms of the joule. The ratio between the specific heat capacity of water in joules and in calories is called the "mechanical equivalent of heat" or the "electrical equivalent of heat," there being as many ratios as kinds of calories. These ratios, being dependent on experimental measurements, changed as the heat capacities of water became more and more accurately known. As long as experimental calorimetric results did not have a high degree of accuracy, such changes were not particularly important, but with the rise of modern calorimetry the experimental heats of reaction became more precise than the conversion ratios.

In modern calorimetry[1] heats are not measured in terms of the specific heat capacity of water, that is, in terms of one of the "calories." Instead,

---

[1] For an excellent review, read the paper of F. D. Rossini, "Modern Calorimetry," *Chem. Rev.*, **18**, 233 (1936).

they are compared directly or indirectly with the electrical energy required to produce a similar temperature rise in a system as nearly identical with the reacting system as possible. By this method heats are measured directly in terms of the electrical unit of energy, the international joule. The experimental heats in joules are then converted to calories with the aid of the appropriate conversion factor. But such data, expressed in calories, would be subject to revision whenever more accurate heat capacities of water became known. For these reasons Rossini[1] introduced a *defined calorie,* now called the *thermochemical calorie*, based on the following relations:

TABLE 1.4.—VALUES OF THE VARIOUS CALORIES IN JOULES*

	International joules	Absolute joules†
15° calorie	4.1850*	4.1857
20° calorie	4.1811*	4.1818
Mean calorie	....	4.1900*
Thermochemical calorie	4.1833‡	4.1840

* From the data of N. S. Osborne, H. F. Stimson, and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 197 (1939).

† Calculated with the relation, 1 int joule = 1.00017 abs joule.

‡ Defined value.

$$1 \text{ calorie (defined)} = 4.185 \text{ absolute joules} \qquad (1.22)$$

$$1 \text{ calorie (defined)} = 4.1833 \text{ international joules} \qquad (1.23)$$

Equations (1.22) and (1.23) agreed with the then accepted relation between the absolute joule and the international joule. When new determinations at the National Bureau of Standards resulted in a revised ratio between the international joule and the absolute joule, both of the defining equations (1.22) and (1.23) could not be maintained. Because the experimental data are obtained directly in international joules, Rossini[2] elected to retain equation (1.23) as the definition of the thermochemical calorie. This defined calorie, not directly related to the heat capacity of water, has been accepted generally by thermochemists. We shall use it exclusively except where a definite statement is made to the contrary. Similarly, the kilocalorie will represent 1,000 defined thermochemical calories.

---

[1] See BICHOWSKY, F. R., and F. D. ROSSINI, "Thermochemistry of Chemical Substances," Reinhold Publishing Corporation, New York, 1936.

[2] ROSSINI, F. D., *J. Research Natl. Bur. Standards*, **22**, 407 (1939).

The relative values of the different kinds of calories may be obtained from the data of Osborne, Stimson, and Ginnings on the heat capacity of water listed in Table 3.1. These workers used the relation, 1 international joule = 1.00019 absolute joule, and not the more recent value. When we use the relation, 1 international joule = 1.00017 absolute joule, we obtain the values in Table 1.4. The data in Table 3.1 indicate that the thermochemical calorie corresponds to the specific heat capacity of water at about 17°c. Observe, however, that the present calorie is connected only historically with the heat capacity of water.

Volt-faraday, or Volt-equivalent.—For most purposes of chemistry, the convenient units of quantity of electricity are the electronic charge, equal but opposite in sign to that of an electron, and the *faraday*, the charge per oxidation-equivalent of an element or compound. The faraday is frequently called an "equivalent." The corresponding energy units are the *volt-electron* and the *volt-faraday*, or *volt-equivalent*.

The best value[1] for the electronic charge is

$$\begin{aligned} 1 \text{ electronic charge} &= 4.8024 \times 10^{-10} \text{ esu} \\ &= 1.6020 \times 10^{-19} \text{ absolute coulomb} \end{aligned}$$

When this value is multiplied by the Avogadro number, we obtain for the faraday

$$1 \text{ faraday} = 96{,}486 \text{ absolute coulombs}$$

From the values for the electrical units previously given, we obtain for the energy units, the volt-electron and the volt-faraday:

$$\begin{aligned} 1 \text{ absolute volt-electron} &= 1.6020 \times 10^{-19} \text{ absolute joules} \\ 1 \text{ absolute volt-faraday} &= 96{,}486 \text{ absolute joules} \\ &= 23{,}061 \text{ calories} \\ 1 \text{ international volt-faraday} &= 96{,}501 \text{ international joules} \\ &= 23{,}068 \text{ calories} \end{aligned}$$

From these relations, we obtain the faraday constant F which is used to convert volt-faradays to calories or joules. Values for the more commonly used constants and conversion factors are given in the Appendix.

Problems

The use of handbooks as a source of data for calculations in thermodynamics is deprecated primarily because most handbooks do not indicate the original sources of their data. In general, their data in different tables are not based on a self-consistent set of conversion factors. Problems in thermodynamics frequently require data from different sources. Whenever a student looks up a datum in the chemical literature, he should record its source. In this way, he learns to relate the result of a calculation with the data on which it rests.

---

[1] The values in this section are those selected by the American Petroleum Institute Research Project 44 at the National Bureau of Standards. Selected Properties of Hydrocarbons. Table α, Values of Constants, Mar. 15, 1945.

1.1. What is the mole fraction of the solute in a molal aqueous solution? What additional data are required to determine the molarity of the solution?

1.2. At 20°c the density of an aqueous solution of 25 per cent sulfuric acid is 1.1783. Calculate (*a*) the molality of the sulfuric acid, (*b*) its molarity, and (*c*) its mole fraction.

1.3. The linear expansion of aluminum is given by the equation

$$l_t = l_0(1 + at + bt^2)$$

where $a = 22.65 \times 10^{-6}$, $b = 9.5 \times 10^{-9}$, t is the temperature in degrees centigrade as indicated by a gas thermometer, l_0 is the length at $t = 0$, and l_t is the length at the temperature t.

If temperatures are measured with an aluminum thermometer on the basis that equal increases in length of an aluminum rod represent equal intervals of temperature and if the thermometer is calibrated at the fixed points of melting and boiling water, what temperature will the aluminum thermometer indicate when the gas scale reads 50°c?

1.4. (*a*) When 1 cc of nitrogen at 0°c and a pressure of 1 m Hg is cooled to −100°c at constant pressure, its volume decreases 0.3686 cc; if the volume is kept constant, its pressure decreases 0.3673 m. Calculate the apparent absolute zero of temperature (1) for the constant-pressure and (2) for the constant-volume nitrogen thermometer. Give reasons for the difference.

(*b*) When 1 cc of nitrogen at 0°c and a pressure of 1 m Hg is heated to 100°c at constant pressure, its volume increases 0.36745 cc; if the volume is kept constant, its pressure increases 0.36742 m. Calculate the apparent absolute zero of temperature from these data. Compare with the results in (*a*). Explain any differences.

1.5. A benzene-toluene solution contains 50 per cent of benzene by weight. What is the mole fraction of the benzene? What is the mole ratio of benzene and toluene?

1.6. A benzene-toluene solution contains 50 per cent of benzene by volume at 20°c. What is the mole fraction of benzene? The weight fraction of benzene?

1.7. A given energy has a value of 1,000 defined thermochemical calories. What will be the value in 15° calories and in 20° calories? Calculate the percentage deviations of the 15 and the 20° calories from the thermochemical calorie.

1.8. From the values of the constants in the Appendix calculate the value of 1 electron-volt per molecule in calories per mole.

CHAPTER 2

THE FIRST LAW OF THERMODYNAMICS

Thermodynamics deals with the science of energy and with its exchange between bodies. It establishes the limitations on the possible types of exchange and furnishes the basis for calculation of the quantity of energy exchanged, but it does not concern itself with the mechanism of the process. A typical thermodynamic problem is of the following kind: Given a system in an initial thermodynamic state. Is the system at equilibrium or will it change to another state at which it will be at equilibrium? If it does change, what energy quantities are involved? The answer can be stated in terms of certain properties of the system in the initial state and in the final state. These properties, of special utility in thermodynamics, are called "thermodynamic properties." It appears that a science of this kind has particular applications to chemistry for it offers an answer to the chemical problem: Can a desired chemical process take place and, if so, what are the optimum conditions for the process? Thus, since thermodynamics can give quantitative answers to equilibrium problems, it is almost indispensable to the chemist who wishes a fundamental understanding of chemical equilibrium.

The terms energy, system, and state appeared in the preceding outline of the scope of thermodynamics. Since these terms are basic in the logic of thermodynamics, they deserve more detailed study.

Energy and Its Forms.—Energy is often given descriptive names in connection with certain processes, substances, or configurations. Thus, it has been classified as potential, kinetic, thermal, mechanical, electrical, radiant, chemical, surface, or atomic energy. However, such classification is not particularly helpful in thermodynamics, which is concerned more with states and changes in states than in mechanisms. The laws of thermodynamics are general laws, not limited by these or other classifications. Accordingly, although we may use some of the terms for descriptive purposes, they are to be regarded only as terms of convenience.

Chemists usually deal with substances at rest and in the absence of electrical and magnetic fields. Furthermore, chemical energies are relatively large and tend to overshadow gravitational and minor mechanical effects. Except for substances of colloidal dimensions, surface energies are relatively small and may usually be disregarded. Of course, when any of these forms of energy, usually disregarded, become large enough to contribute to the total energy effects, they must be included in the calculations.

The energy effects of atomic transmutations are relatively enormous, but they must be considered only for processes in which the transmutations occur. In the ordinary chemical processes, the atoms remain stable and their states can be represented accurately by the proper thermodynamic functions. The energy produced through atomic fission or other transmutation is subject to the same restrictions as other "types" of energy.

In the preceding classification, heat and work did not appear. In thermodynamics, heat and work are not considered forms of energy.[1] A system has energy but not heat and work. When the system loses energy, some of the energy may be measured as "heat" and the remainder as "work." But, when the heat enters a second system and the work is done on this second system, the second system increases in energy; it is not said to have more heat or more work. It has more energy, equal according to the first law of thermodynamics to the decrease in energy of the first system. Thus, heat and work are to be regarded as energy in transit.

System.—Energy is an extensive property of a substance; its quantity depends on the amount of material under consideration. If we wish to specify definite values for the energy and the other extensive thermodynamic functions, we must therefore consider definite bodies or substances. For this reason, the concept of the thermodynamic system is utilized. A *system* is any space or any material that we wish to consider separately from all other space or material, the system being separated from the rest of the universe, called the *surroundings*, by real or imaginary boundaries. The system may be a calorimeter and its contents, a single crystal of a solid, a polycrystalline mass, a definite mass of gas that may change volume and shape, or a mixture of solid and liquid. It may be large or small, and it may contain inert parts. It may change in volume, provided that boundaries remain between it and its surroundings. The essential requirement is that it be so separated from its surroundings that exchanges of energy between the system and the surroundings can be observed and controlled. In general, we shall discuss systems containing a definite mass of material, but we may also discuss systems representing a definite space into which definite masses of materials are introduced or from which definite masses are extracted. In thermo-

---

[1] The above classification is that of classical thermodynamics. J. N. Brønsted, in his system of energetics, uses the two terms in somewhat different senses. Accordingly, the energy equations that he derives, though correct, differ somewhat from those of the classical thermodynamics. *J. Phys. Chem.*, **44**, 699 (1940); *Phil. Mag.*, (7) **29**, 449 (1940); *Kgl. Danske Videnskab. Selskab., Mat.-fys. Medd.* **XIX**, 8 (1941).

dynamic discussions, it is common practice to select systems that permit a simple and clear analysis of a problem.

A system that does not exchange energy with its surroundings is said to be an *isolated* system. Within such a system, there may be exchange of energy as long as all these changes take place in the system itself. An *adiabatic* system is one that does not exchange heat with the surroundings; it may still exchange work. For the purposes of thermodynamics, it is more important that energy exchanges between system and surroundings be of known kind and amount than that they be nonexistent.

State.—A system is said to be in a given *state* when its various properties have definite values. Thus, when its values of the volume, temperature, pressure, composition, energy, etc., are fixed, the system is in a definite state. Some of these properties are *extensive properties*, that is, properties dependent on the amount of substance. Examples are energy, volume, and mass. Other properties, such as temperature and pressure, do not depend on the amount of substance; they are called *intensive properties*. The molar[1] or specific properties such as density, concentration, or the related molar or specific volume, and the molar, or specific, energy play the role of intensive properties in describing the state of a system. In general, all molar quantities that describe the state of a system may be classed as properties of the system.[2]

Additional thermodynamic functions may be used to describe the state of a system. However, not all these functions are independent. Thus, if the molar volume and the pressure are known for a perfect gas, the temperature has the value indicated by the gas equation $P\mathrm{v} = RT$. The energy and the other thermodynamic functions will also have definite values determined by the independent variables P and v. The number of variables or properties necessary to define the state of a system increases with the complexity of the system. However, the question as to which of the variables shall be chosen as the independent variables is one of taste and convenience.

When a system is left to itself, some of the properties of the system tend to become uniform throughout the system. Pressure and temperature tend to become equalized in this way. If pressure differences (or differences in partial pressures) exist in a system, the parts of the system at the higher partial pressures tend to move to regions of lower partial pressures until the partial pressures are uniform in all parts. If pressure

---

[1] A specific property is the property referred to unit mass of the substance which is traditionally one gram of the substance. As stated earlier, in chemistry the convenient unit of mass of a substance is the mole. Molar properties are therefore specific properties based on the mole as a unit of mass.

[2] In general, molar values of extensive properties will be printed as small capitals. Thus, where V is volume in general, v is the volume per mole.

is used to indicate the state of a system or the states of different parts of it, it must obviously refer to a uniform pressure throughout the system or to a specified pressure in each part of it. Similarly, a specified pressure for any part of a system has meaning only if it refers to a uniform pressure within that part. The temperature must also be uniform if it is to describe the state of the system. If temperature differences do exist in an isolated system and the system is allowed to stand, energy will flow among the various parts of the system until thermal equilibrium has been established and the temperature is uniform. The concept of the *state* of a system, therefore, can be applied only to systems at equilibrium in these important respects.

Under special conditions, the attainment of uniform values of pressure and temperature in a system may be impossible. A flow of material or of heat through the system may produce pressure or temperature gradients that become stabilized so that the pressure or the temperature of any part of the system reaches a constant value which differs, however, from that of other parts of the system. Such a system is in a *steady state*, but it is not in equilibrium. Unless other conditions are expressed specifically, we shall use the term "state" to represent an equilibrium state.

Equilibrium.—If a system is to be in complete equilibrium, it is necessary that there be *mechanical equilibrium*, that is, (1) that there be no unbalanced forces in the system, tending to displace the parts of the system with respect to each other; and (2) that there be no unbalanced forces between the system and its surroundings, tending to displace the system with respect to its surroundings. A system in which diffusion is occurring obviously is not in mechanical equilibrium. However, in most of the systems that we shall discuss, the requirement of mechanical equilibrium is fully met. In such systems, there are no unopposed pressure differences.

A second requirement of a system at equilibrium is that there be *thermal equilibrium*, that is, that there be no temperature differences in the system. If there are temperature differences in a system, our common experience is that energy flows from the hotter parts of the system to the colder parts until a uniform temperature is established.

A third requirement for complete equilibrium is that there be *chemical equilibrium*, that is, that the substances represent the possible combinations of the constituent elements in their most stable proportions at the experimental conditions. This equilibrium requirement is the hardest to secure in many chemical systems. As chemists, we know that many substances can be kept for long periods of time even though they represent combinations of the elements less stable than other possible combinations. Thus, a mixture of hydrogen and oxygen gases at room temperature may be maintained for long periods of time even though water is much more stable than the mixture of the two constituent substances. Under these circumstances, one can treat the mixture of hydrogen and oxygen gases as a system at a definite state for the state of the system can be expressed in terms of definite, characteristic properties. Hence, the various thermodynamic functions can be used to characterize the system. However, a system that remains unchanged when not in chemical equilibrium should be called *inert* rather than stable.

As we have stated, a system may be in mechanical and thermal equilibrium without being in chemical equilibrium. As chemists, we know also that a system may be in chemical equilibrium without being in thermal or mechanical equilibrium. For *thermodynamic equilibrium,* however, the system must be in equilibrium in *all three respects.* When a system is in thermodynamic equilibrium, all its properties have definite values, representative of its equilibrium state. These properties, therefore, characterize and define the state of thermodynamic equilibrium of the system.

Phase.—The concept of state, as used by the thermodynamicist, should not be confused with the restricted meaning of state sometimes used in elementary chemistry and physics to denote the physical form in which a substance occurs. In physical chemistry and in thermodynamics, the different homogeneous physical forms of a substance are called *phases.* Thus a pure substance may be a gas, a liquid, or a solid; the different phases being the gaseous phase, the liquid phase, or a solid phase. As we know, for a pure substance there is only one gaseous phase, all parts of the gas at equilibrium having properties like all other parts of the gas. The gas phase is homogeneous, with uniform properties throughout the phase at equilibrium. The primary requirement of a phase is that it shall be homogeneous, and a system composed of only one phase is called a *homogeneous system.* A mixture of gases at equilibrium is also homogeneous, and it therefore consists of only one phase.

For a pure liquid, there is, in general, only one liquid phase, the liquid being homogeneous. An apparent exception will exist for those liquids which form "liquid crystals." When two liquids, such as alcohol and water, that are miscible in all proportions are mixed to form a homogeneous solution, there is only one phase, the solution phase. When two slightly miscible liquids such as water and benzene are mixed, two separate liquid layers form, a water-rich layer and a benzene-rich layer, each of which is homogeneous but different in composition from the other. There are, therefore, two phases, and the system containing the two phases is a *heterogeneous system.* A heterogeneous system is one containing more than one homogeneous phase, each separable from the other by definite physical boundaries.

Most pure substances can crystallize in more than one crystalline form, each with its own lattice dimensions and with its own properties such as solubility, thermal conductivity, and heat capacity. Each of the crystalline forms is homogeneous and represents a separate phase. Under special conditions, several of these solid phases may coexist, and the system containing the pure substance becomes a heterogeneous system. When more than one pure substance is present, the number of solid or other phases that may coexist increases, but the number that can coexist at equilibrium is limited by the rules of thermodynamics. This question is discussed in more detail under the *phase rule* of Gibbs (Chap. 17).

In the application of thermodynamics to specific systems, the question may arise as to whether a system is homogeneous or heterogeneous. A solution that is a homogeneous dispersion of not too large molecules of one substance among the molecules of another is commonly classified as a homogeneous system. However, when the dispersed molecules are macromolecules of high molecular weight or when the dispersed particles are of so-called "colloidal" dimensions, the classification of the system as homogeneous or heterogeneous is not obvious. In such cases, it is evident that special formulas of thermodynamics derived for strictly homogeneous systems cannot be applied without qualification. Because chemistry is an experimental science, the correct procedure must be to see if the formulas do apply and then to classify the systems on the basis of their behavior. One cannot, by defining a given system in a given formal way, change its behavior and make it conform to any preconceived or "theoretical" formula.

First Law of Thermodynamics.—Before the law of the conservation of energy could be established, proof was required that heat and work represent equal changes in energy. Just before 1800, Count Rumford had observed the large amounts of heat produced when cannon were bored and had estimated the amount produced per hour by the power of one live horse. Subsequently, Sir Humphry Davy observed the increase in the rapidity of the melting of ice when two pieces are rubbed together. The implications of these experiments were neglected whereas the *caloric* theory of heat, which considered heat as a substance, persisted. It remained for Joule in a series of experiments, beginning in 1840, to show the interconvertibility of electrical, mechanical, chemical, and thermal energies. In his experiments, he obtained the relation between the energy measured in the "heat" unit and that measured in the "work" unit, the ratio known as the "mechanical equivalent of heat." These experiments laid the experimental basis for the first law of thermodynamics.

In the meantime, others were investigating energy relations. Seguin, the French engineer (1839), had worked on the problem of the "equivalence of heat and work"; Mayer, the German physician, had independently stated the principle of their equivalence in 1842. In 1848, Helmholtz, at that time a Prussian surgeon, published his paper, "Über die Erhaltung der Kraft," which brought widespread acceptance of the new principle.

The results of Joule and the other experimenters may be summarized as follows: When heat and work are expressed in the same energy units, equivalent amounts of either added to a system produce equal changes in the energy of the system. Similarly, when a system loses energy, some of it being transmitted as heat and some as work, the quantity is the same (if heat and work are expressed in a common unit) as when the system loses the same quantity of energy, all as heat, or all as work. These facts are the basis for the first law of thermodynamics. They are represented by the statement: *Energy may be exchanged as heat, work, or both, but the total quantity remains constant; energy is neither created nor destroyed.*

Consider a system with an initial quantity of energy, E_1. After it has exchanged energy, it has energy represented by E_2. The *increase* in energy is expressed as ΔE and defined by the equation

$$\Delta E \equiv E_2 - E_1 \tag{2.1}$$

According to this definition, ΔE is positive in value if E_2 is greater than E_1 and negative if E_1 is the greater.

But, if the system exchanges energy with its surroundings, which initially had the energy E'_1 and finally the energy E'_2, the increase in energy of the surroundings may be represented by $\Delta E'$. If ΔE, the increase in energy of the system, is positive, the increase in energy of the surroundings $\Delta E'$ must be negative by an equal amount in accordance with the principle of the conservation of energy. Hence,

$$\Delta E = -\Delta E'$$

and

$$\Delta E + \Delta E' = 0 \tag{2.2}$$

Equation (2.2) is a mathematical expression of the first law; the total energy change is zero.

The first law equation may be expressed in another form, more generally useful because it focuses attention on the system itself. Let the *heat absorbed by the system* during its energy change be designated by q

and the *work done by the system* be designated by w; q and w being expressed in the same energy units. Then the equivalence principle enables us to write

$$\Delta E = q - w \tag{2.3}$$

This relation is the usual algebraic statement of the first law of thermodynamics.

Validity of the First Law.—When a system in the state 1 is transformed to some other state 2 and then brought back to the state 1, the system is said to have undergone a *cyclic process*. We have stated as an experimental fact that the precise value of the energy gained on going from 1 to 2 is regained on the conversion from 2 to 1. The changes in energy are numerically equal but opposite in sign so that the net change in energy for the whole process is zero. If this were not true and if the system required less energy on going from 1 to 2 than it evolved in the reverse process, useful energy would have been created in the cycle. The excess energy could then be used to drive a machine doing useful work continuously—a perpetual-motion machine operating in violation of the first law. Such violation is called *perpetual motion of the first kind*. This socially useful prospect has long challenged men to construct a machine embodying an energy-creating cycle that would create enough energy to overcome frictional resistance in the machine. Every failure of such an attempt must be accepted as additional experimental evidence for the law of the conservation of energy. We should point out, however, that man has collected direct experimental evidence for the validity of the first law of thermodynamics only on the earth; the generalization of terrestrial experience to include the universe, although reasonable, rests on a less rigorous foundation.

Another generalization extended from ordinary chemical reactions to the universe is the law of the conservation of mass. For many years, however, evidence from the high temperature reactions in the stars and from terrestial experiments on atomic disintegrations has cast doubt on both conservation laws. In 1905, Einstein proposed his equation for transformations between energy and mass, $E = mc^2$, in which E is energy, m is mass, and c is the velocity of light. This equation has for some years facilitated the interpretation of the mass and energy relations in atomic disintegration reactions and has had powerful confirmation in the recent large-scale operation of atomic fission reactions. Consequently, neither the law of the conservation of energy nor the law of the conservation of mass is entirely valid. For the strictest accuracy the two conservation laws should be combined in the general law of the conservation of mass-energy. However, since we perform our ordinary chemical experiments under conditions unfavorable to these mass-energy transformations, we find the separate laws valid within the limits of our experimental error. With these qualifications, we can accept the first law of thermodynamics as a working principle.

Energy of a System.—In assigning a definite energy E_1 to a system in the state 1, we assumed implicitly that the system in that state has energy fixed in amount. In chemical thermodynamics we deal primarily with systems without independent motion as a whole. If the system itself has no kinetic energy, and it does not move in the earth's gravitational field or in other potential fields, all energy changes of the system occur within the system itself. Under these conditions, the energy of the system is a characteristic function or property. It is fixed by the state of the system, which in turn is determined by the mass, volume, composition, temperature, etc., of the system. We know, for example, that a gram of water at a temperature of 1°c and atmospheric pressure has more energy than it has at 0°c and that this difference in energy is a definite quantity; for the amount of energy required to raise the temperature of the water from 0 to 1° is identical with that obtained from the water when it is cooled from 1 to 0° under the same conditions. Furthermore, the amount of energy is entirely independent of the way in which the energy is added to, or subtracted from, the water: the energy may be added as heat, as electrical work, as mechanical work used to warm the water by frictional devices, or as radiant energy. The same statements apply to different samples of water of equal mass under the same conditions. Furthermore, 2 grams require twice the energy required by 1 gram. At every temperature, a sample of water has more energy than it has at some lower temperature; hence, at all finite temperatures, it has more energy than it has at the lowest attainable temperature. At all temperatures, the water, therefore, contains energy. This characteristic energy has been called the *internal* or *intrinsic energy*, or *energy content.* Since we shall, in general, consider only the energy of the system itself, we shall usually employ the brief term, energy.

The energy in a heterogeneous system is also a property of the system. At 0°c and at 1 atmosphere pressure, a gram of water can be converted to a gram of ice at the same temperature and pressure. Here again, the energy required to melt the ice is identical with that released when the water is frozen to ice. This quantity of energy is unchanged whether the energy is added as mechanical energy used to rub two pieces of ice together, as electrical energy, as heat, or in any combination of these. In this instance, also, when $\frac{1}{2}$ gram of the ice is melted to form $\frac{1}{2}$ gram of water, the energy required is one-half that required to melt a whole gram. For each state of the water-ice system, a definite amount of energy exists: a system $\frac{1}{2}$ water + $\frac{1}{2}$ ice has a characteristic energy value, as representative of the system as its volume or any other property characterizing the state of the system. As the student knows well, the term *latent heat* is used to indicate that the water is richer in energy than the ice even though its temperature is unchanged. The term *latent energy* would be more satisfactory; it is less dogmatic about the nature of the energy that the water possesses in excess of that possessed by an equal quantity of ice at the same temperature.

The same principles apply to chemical systems containing more than one substance. Two different equal samples of sucrose in the same state have equal internal energies. When these two samples are burned under similar conditions in a bomb calorimeter, they yield equivalent amounts of water and carbon dioxide, in accordance with the laws of chemical combination. They also deliver equal quantities of heat to the calorimeter. These heats of chemical reaction, called, more simply, *heats of reaction*, represent the difference in internal energy between the system sucrose plus oxygen and the system carbon dioxide plus water. In terms of the atomic theory, they represent a type of latent energy called *chemical energy* associated with the arrangements of the atoms in the different molecules of substances participating in the chemical reaction.

The first law of thermodynamics has nothing to say concerning the nature of the internal energy of a system whether "thermal," "latent," or "chemical." In terms of the atomic theory and the kinetic theory of matter, part of the internal energy of a system is interpreted as being in the form of the kinetic energy of the individual molecules and atoms in the system. Other parts of the energy appear to have the character of energy of configuration. These questions, though interesting and important for a study of chemical processes and inherent in the application of statistical mechanics, are not among the primary problems of classical thermodynamics. Thermodynamics concerns itself chiefly with experimental quantities and not with kinetic interpretations.

Heat.—The term "heat" has been widely used both in popular and in scientific language and has come to have a variety of meanings, some of which are vague. If it is to be used in thermodynamic formulas, however, it must be more exactly defined. Consider a system surrounded by a calorimeter in such a way that no work is done by (or on) the system on (or by) the calorimeter or any other part of the surroundings. If the system absorbs energy from the calorimeter, we know from the first law that the calorimeter has lost an equivalent amount of energy. Since w equals zero in this experiment, we have for the system, from equation (2.3),

$$\Delta E = q \tag{2.4}$$

But all of the energy absorbed by the system was evolved by the calorimeter. This energy increase, detectable and measurable by the calorimeter, is represented by a positive energy quantity called *heat*. But one does not say that the calorimeter now has less "heat"; it has less energy, the amount being $\Delta E'$, where $\Delta E = -\Delta E'$.

As we shall see, the heat q is not a property either of the system or of the calorimeter or other surroundings. It is merely a measure of the energy change of the system (or of the calorimeter). Observe that we write ΔE to represent the energy change $E_2 - E_1$ but we do not write Δq for there is no "change" in heat. The system does not have an increased value of heat though it has absorbed a definite *quantity* of heat q. This quantity q may be large or small depending on the value of ΔE. When ΔE becomes small enough to be represented by the differential $\mathrm{d}E$, q becomes a very small quantity which will be represented as $\mathrm{D}q$. Since q is not a property, $\mathrm{D}q$ is not an exact differential. $\mathrm{D}q$ should be read as "a small value of q" and not "an increase in the function q."

Now consider that the system absorbs energy from the calorimeter as before but that the rest of the surroundings does work in some way on the system. Let the increase in energy due to energy absorbed from the calorimeter be $\Delta E_h = q$. Since work was defined as positive when done *by* the system, the work done *on* the system becomes $-w$, and the increase in energy of the system due to the work done on it is $\Delta E_w = (-w)$. The total increase in energy of the system is

$$\Delta E = \Delta E_h + \Delta E_w = q + (-w) = q - w$$

which is the first law equation (2.3).

In each of these examples, the heat q is that part of the energy increase derived from the calorimeter and, therefore, measured by it. For this reason q has been defined as *calorimetric heat.*

Equation (2.3) may be expressed in a form that emphasizes q. Thus,

$$q = \Delta E + w \tag{2.5}$$

When a system has an energy increase ΔE but does the work w during the process, the energy q required from the calorimeter is the sum of the increase in energy of the system and the work done by the system. Consequently, when work is done in a process, equation (2.5) shows that the heat absorbed, q, no longer measures the change in energy of the system. Indeed, in some process ΔE may be zero; if so, q is a measure of w.

Another aspect of the thermodynamic concept of heat is important. In the exchange of energy between system and calorimeter, no material substance was transported. Only energy unaccompanied by matter passed between system and the calorimeter. As we shall see, the doing of work is always associated with the transport of matter as well as of energy. This difference helps to differentiate between heat and work. We find also that energy passes from the calorimeter to the system only if the calorimeter is at a higher temperature. There must be a temperature difference, however slight, if "heat" is to flow. This aspect of heat will be discussed more fully in connection with the the second law of thermodynamics.

In thermodynamics, the student who has used the term "heat" in other senses must learn the narrower but more exactly defined concept. He may be forgiven occasional lapses from correct usage for all of us tend through carelessness, if not ignorance, to continue usages that contradict thermodynamic definitions of heat.

Heat Capacity.—Historically, water was used as the calorimetric substance whose rise in temperature was a measure of the energy absorbed by the calorimeter. Its specific capacity for heat, as measured by the quantity of energy required to raise the temperature of one gram of water one degree centigrade became the heat unit, the caloric. In general, all substances have more energy at higher than at lower temperatures, absorbing heat as their temperatures increase. And for each substance the heat capacity C depends directly on the amount of substance. The heat capacity per gram[1] is called *the specific heat capacity c* and that per mole is called the *molar heat capacity* c. It appears from equation (2.5) that the quantity of heat absorbed by a substance depends on the amount of work done during the rise in temperature as well as on the increase in energy of the substance. Hence, the heat capacity of the substance may vary with the conditions under which its temperature is raised. Heat capacity may also vary with temperature.

In the experimental determination of heat capacity what is ordinarily measured is not the heat required for a rise of one degree but the quantity of heat q absorbed during a rise in temperature from T_1 to T_2 or the corresponding heat evolved during the temperature fall between the same limits. Because heat capacity varies with temperature, its values at the temperatures T_1 and T_2 are usually different. Then the measured heat capacity over the interval $T_2 - T_1 = \Delta T$ is not the heat capacity at either T_1 or T_2 but is the *mean heat capacity* C_m. It is defined by the relation

$$C_m = \frac{q}{T_2 - T_1} = \frac{q}{\Delta T} \tag{2.6}$$

If the temperature interval ΔT becomes smaller and smaller, in the language of the calculus we may write, $T_1 = T$ and $T_2 = T + \mathrm{d}T$ so

---

[1] The traditional term "specific heat" is a misnomer. What is measured is the capacity of one gram of the substance to absorb heat when its temperature is *raised one degree* in temperature and not the amount of "heat" present in one gram of the substance.

that ΔT becomes $\mathrm{d}T$. The value of q also becomes smaller and smaller and may be represented as $\mathrm{D}q$. The true heat capacity C at the temperature T is then

$$C = \frac{\mathrm{D}q}{\mathrm{d}T} \tag{2.7}$$

The differential $\mathrm{d}T$ represents an increment in temperature that is unambiguous because temperature is a property of a system and is, therefore, uniquely defined by the state of the system. The temperature interval $T_2 - T_1$ has a single value. The temperature at any stage does not depend at all on the previous history of the system or on the path or process by which the system was brought to that state. In the language of mathematics, $\mathrm{d}T$ is an exact, or perfect, differential.[1] We shall reserve the symbol d for exact differentials.

The first law of thermodynamics, equation (2.3), indicates that the heat absorbed is not a complete measure of the internal energy of a system unless the work done is zero. As we shall see later, the work and, therefore, also the heat absorbed when a system is changed from one state to another are not determined by the initial and final states but are dependent on the path by which the system is changed between the two states. The infinitesimal value of q is, therefore, not an exact differential. We shall use the symbol D for inexact differentials and shall indicate the infinitesimal value of q by $\mathrm{D}q$ as in equation (2.7).

Heat of Reaction.—Heat is absorbed or evolved by many substances even though the temperature is maintained essentially constant during the process. Examples of such isothermal heat effects are the *latent heats* and *heats of reaction* that accompany transitions from one phase to another and changes in chemical composition. In terms of the kinetic theory, some of the "heat capacity" energy absorbed by a substance results in increased kinetic energy of the molecules of the substance and hence in increased temperature. On the other hand, latent heat and the heat of reaction must be related to changes in potential energies resulting from rearrangements of atoms or molecules without an increase in the average kinetic energy.

For most of the purposes of chemical thermodynamics, latent heats may be treated as a simple form of heat of reaction. We shall write chemical equations for the phase transitions in the same manner as for "chemical" reactions. The two types of equation can then be combined by the usual methods of combining chemical equations. The heat absorbed when 1 mole of liquid water evaporates at 25° to form the

---

[1] See EPSTEIN, P. S., "Textbook of Thermodynamics," pp. 22–24, John Wiley & Sons, Inc., New York, 1937, for criteria for determining whether or not a linear differential expression is an exact differential.

saturated vapor is 10,514 calories. This information is summarized in the thermochemical equation

$$H_2O(\text{liq}) = H_2O(\text{g, } 0.03122 \text{ atm}); \qquad q = 10{,}514 \text{ cal} \qquad (2.8)$$

where H_2O(liq) represents 1 mole of liquid water at the specified conditions of temperature and pressure and H_2O(g, 0.03122 atm) represents 1 mole of water in the gaseous form under the stated conditions. According to the usual conventions, the substance disappearing in the process is written on the left and the substance produced in the process is written on the right side of the equation.

If the above process is reversed, one mole of the vapor condensing to liquid water, the 10,514 calories of heat are *evolved.* The chemical equation for this process is the reverse of equation (2.8), and the sign of the heat q is also reversed as in

$$H_2O(\text{g, } 0.03122 \text{ atm}) = H_2O(\text{liq}); \qquad q = -10{,}514 \text{ cal} \qquad (2.9)$$

When 1 mole of gaseous water at 25°c and at the saturated vapor pressure is formed from the elements, 57,803 calories of heat are evolved. The thermochemical equation for this reaction is

$$H_2(\text{g, } 1 \text{ atm}) + \tfrac{1}{2}O_2(\text{g, } 1 \text{ atm}) = H_2O(\text{g, } 0.03122 \text{ atm}); \qquad q = -57{,}803 \text{ cal} \qquad (2.10)$$

According to equation (2.9), when this water is condensed to liquid, 10,514 calories more of heat are evolved. The heat of formation of liquid water from the elements can, therefore, be found by adding equations (2.9) and (2.10) to give equation (2.11). Thus,

$$\begin{array}{rll}
H_2(\text{g, } 1 \text{ atm}) + \tfrac{1}{2}O_2(\text{g, } 1 \text{ atm}) = H_2O(\text{g, } 0.03122 \text{ atm}); & & \\
 & q = -57{,}803 \text{ cal} & (2.10) \\
H_2O(\text{g, } 0.03122 \text{ atm}) = H_2O(\text{liq}); & q = -10{,}514 \text{ cal} & (2.9) \\
\hline
H_2(\text{g, } 1 \text{ atm}) + \tfrac{1}{2}O_2(\text{g, } 1 \text{ atm}) = H_2O(\text{liq}); & q = -68{,}317 \text{ cal} & (2.11)
\end{array}$$

If the pressure of the water vapor is 1 atmosphere instead of 0.03122 atmosphere (23.73 mm), the heat of the reaction for equations (2.8) to (2.10) is changed by the energy difference between a mole of water vapor at 25° and 0.03122 atmosphere and a mole at 1 atmosphere pressure. This energy difference is slightly more than 5 calories.

Work.—As was indicated earlier, work is always associated with the displacement of matter. This means that, when there are no frictional losses, one displacement may be used to produce another equivalent displacement. Under these conditions, one kind of work can be converted to another kind of work. Thus, mechanical work can be converted to electrical work and electrical work to mechanical work. Work may compress a gas, raise a weight, transfer a substance from one solution to another, or expand a surface against surface tension, thereby increasing the energy of systems without a rise in temperature. When a system does work w on another system and there are frictional losses, the second system receives work less than w, the remainder of the work energy appearing as heat, which can be detected in the usual way by a calorimeter. The first law applies to all these energy exchanges.

Work of Expansion.—The types of work that must be considered in chemical systems are limited in number. One type commonly found is work of expansion. Consider a system that expands slightly, the increase in volume being represented by the differential dV. The system will do work in the expansion only if the increase in volume is against an opposing pressure P'. Where the infinitesimal amount of work accompanying the expansion dV is represented by Dw, we have

$$Dw = P' \, dV \tag{2.12}$$

As the symbol D indicates, Dw is not an exact differential. In general, the pressure P' of the surroundings is not a function of the volume V of the system and we cannot integrate equation (2.12) unless P' is a function of V. Thus, the work w done, when a system expands from the initial state with volume V_1 to the final state with volume V_2, depends on the value of P' during the expansion. For the special case in which P' remains constant, we can integrate and write

$$w = P' \, \Delta V = P'(V_2 - V_1) \tag{2.13}$$

Equation (2.13) applies to the expansion of a system against the atmosphere that remains at constant pressure during the expansion.

When pressure is measured in dynes per square centimeter and volume in cubic centimeters, the work is expressed in ergs, for

$$\frac{\text{dynes}}{\text{cm}} \times \text{cm}^3 = \text{dyne-cm} = \text{ergs}$$

The more common unit of pressure is the *normal* or *standard atmosphere* (atm) defined as equal to 1,013,250 dynes/cm^2. Another common pressure unit is the *millimeter of mercury* (mm) defined as $\frac{1}{760}$ atmosphere. The work done in an expansion of one cubic centimeter against one standard atmosphere is

$$1 \text{ cm}^3\text{-atm} = 1{,}013{,}250 \text{ ergs} = 0.101325 \text{ joule} = 24.217 \text{ cal}$$

since

$$1 \text{ abs joule} = 10^7 \text{ ergs} = 4.1840 \text{ cal}$$

In chemistry, the liter is a more common volume unit than the cubic centimeter. From the relation between these two volume units, we have

$$1 \text{ liter-atm} = 1{,}000.028 \times 0.101325 \text{ joule} = 101.328 \text{ joules} = 24.218 \text{ cal}$$

Electrical Work.—Electrochemical work is usually recorded in terms of the transport of the charge in faradays against an electrical potential E' measured in volts. Where dn represents the number of faradays, the element of work (electrical) is

$$\mathrm{D}w = E'\,\mathrm{d}n \tag{2.14}$$

In general, E' is not a function of n, and the work for a given value of n will vary. However, if the opposing potential remains constant, we can integrate and obtain

$$w = nE' \tag{2.15}$$

When n equals 1 faraday and E' 1 volt, the electrical work is equal to 1 volt-faraday.

In practical work E' is measured in international volts and w in international joules. From the relations between the faraday and the coulomb, and the international joule and the calorie, we have

$$\begin{aligned} 1 \text{ int volt-faraday} &= 96{,}501 \text{ int volt-coulombs} \\ &= 96{,}501 \text{ int joules} = 23{,}068 \text{ cal} \end{aligned}$$

In chemical problems, the value for electrical work is usually desired in joules or calories. It has, therefore, become the custom to introduce a conversion factor, the *faraday constant* F into equations such as (2.14) and (2.15). Thus,

$$\mathrm{D}w = FE'\,\mathrm{d}n \tag{2.16}$$

$$w = nFE' \tag{2.17}$$

When $F = 96{,}501$ int joules/int volt-faraday, equation (2.17) gives the value for the work in international joules. When $F = 23{,}068$ cal/int volt-faraday, the work is in calories.

Surface Work.—Surface work rarely is important in chemical problems. It is usually expressed in ergs, the surface tension being expressed in dynes per centimeter and the change of surface in square centimeters. When γ is the surface tension and dA the increase in area, we have for surface work

$$\mathrm{D}w = \gamma\,\mathrm{d}A \tag{2.18}$$

Again, if surface tension remains constant,

$$w = \gamma\,\Delta A \tag{2.19}$$

Chemical Work.—The equations for the various kinds of work called "chemical work" will be developed as the need for them arises. Chemical work, like other work, can be expressed in terms of a "potential" such as P or E, and a "quantity" such as dV or dn. The energy units used to express chemical work are often determined by the methods used to measure the work. Osmotic work, the work of transferring substances from one solution to another, is sometimes calculated from vapor-pressure measurements. The results may then be expressed in liter-atmospheres.

In most thermochemical tables, the values for internal energies and heats are expressed in calories or joules. When values for work are to be combined with these values in thermochemical calculations, they must be converted to the same units. For this reason, we shall usually express values for work in calories. The more common relations between energy units are listed in Table II of the Appendix. This list facilitates conversion from one unit to another.

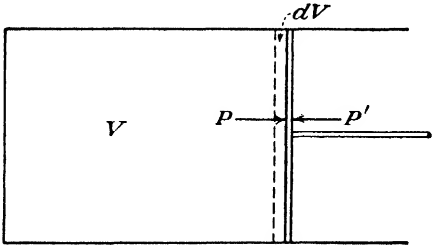


FIG. 2.1.—Expansion against an opposing pressure.

Reversible Work along a Path.—In the previous section we indicated that the value for the work Dw depends on the value of the opposing potential. Thus, for a given expansion dV, the work of expansion depends directly on the value of the opposing pressure P'. When P' is zero, no work is done during the expansion; when P' has a maximum value, the work done will be a maximum. It is instructive to consider what this maximum value can be.

Consider the system in Fig. 2.1 with volume V and pressure P increasing dV in volume against an opposing pressure P'. The work done during the expansion becomes larger and larger as P' increases in value. There is, however, an upper limit to the value for P' if expansion is to occur. The system can expand only if P' is less than P, the pressure of the system itself. When $P' = P$, no movement of the piston takes place and no work is done. The system is then in equilibrium with the surroundings. When P' becomes greater than P, the movement of the piston is reversed and the system is compressed. Thus, we see that the maximum work of expansion is the work done as the system approaches equilibrium with its surroundings during the expansion. When $P' \doteq P$, the direction of movement of the piston is determined by infinitesimal pressure differences so that, with a frictionless piston, the work of expansion and the work of compression approach the same value. This value represents the *reversible work*. It is determined by the properties of the system, in this case the pressure and volume of the system. Consequently, the reversible work, w_r or $\mathrm{D}w_r$, may be represented by the equations

$$\mathrm{D}w_r = P\,\mathrm{d}V \tag{2.20}$$

$$w_r = \int P\,\mathrm{d}V \tag{2.21}$$

Equation (2.20) can be integrated since the property P is a function of V. The value of w_r will evidently depend on the path, which determines how P varies with V during the change.

By similar reasoning, we find that the electrochemical work is also greatest when the emf E of the cell is very nearly balanced by the opposing potential E'. When $E \doteq E'$, infinitesimal differences in potential will permit a reversible cell to do work or will result in an equal amount of work being done on the cell. For the balanced reversible cell, the reversible work is, therefore,

$$\mathrm{D}w_r = EF\,\mathrm{d}n \tag{2.22}$$

$$w_r = F\int E\,\mathrm{d}n \tag{2.23}$$

where the emf E is a property of the cell and a function of dn. Here, also the value of w_r depends on the path, which determines how E varies with n.

Similarly, for the other kinds of work we find that only when work is carried out reversibly can it be calculated from the change in properties of the system. Whenever we express work in terms of properties of a system, we are implying that it represents the work for a reversible process.

There is another aspect to the securing of work through a reversible process. A system will expand fastest when there is no opposing pressure and it is doing no work. An electrochemical cell will discharge fastest when it is short-circuited and does no work. The greater the opposing potential, the slower the rate of doing the work. The more nearly the work done approaches the reversible work, the slower the rate at which the work is done. Thus, the reversible work could be obtained only at an infinitely slow rate, requiring infinite time. In thermodynamics, however, we are not troubled by this limitation for we can perform our calculations for the reversible process in terms of the properties of the system and need not actually carry out the reversible process.

Heat from a Reversible Process along a Path.—If the energy of a system depends only on the state of the system, the change in energy when the system changes from one state to another has a definite value. We have seen that, when the change is carried out reversibly along a path, the work done also has a characteristic value. Therefore, from the first law, the heat absorbed in the reversible process for that path must have a definite value. This value we shall indicate by the symbol q_r. Thus, from equation (2.5), we have for the reversible process

$$q = \Delta E + w_r = q_r$$

whence

$$\Delta E = q_r - w_r \tag{2.24}$$

Equation (2.24) indicates that, if w_r has a definite value when the change of the system from one state to another is carried out reversibly along a path, q_r must also have a definite value for this path.

Conventions.—There have been widespread differences in the use of signs and symbols in thermodynamics. The differences, especially those in sign, have been troublesome and have led to misunderstandings and mistakes. In recent years greatly increased uniformity has been attained. In the United States the signs and symbols of Lewis and Randall[1] have been rather generally adopted. In 1932, the Deutschen Bunsengesellschaft[2] and in 1937 a joint committee of the Chemical Society, Faraday Society, and the Physical Society (Great Britain)[3] adopted similar conventions with respect to sign and adopted also the majority of the symbols used by Lewis and Randall. We shall follow these conventions. The symbols will be introduced as the need for them arises.

In these conventions, the *system* is the center of attention. Thus,
q is positive when heat is *absorbed* by the system.
ΔE is positive when the internal energy of the system *increases.*
w is positive when work is done *by* the system.

The rule on the sign of w may seem unique; it is justified in part on the basis that if the work done equals $\int P\,dV$, dV will be positive when the volume increases, that is, when work is done *by* the system.

The convention concerning the sign of the heat absorbed, q, is contrary to the usage of some chemists. Chemists formerly considered the heat of an exothermic reaction positive and the heat of an endothermic reaction negative. This custom focuses the attention on the surrounding (that is, the calorimeter) rather than on the system undergoing change. According to our conventions, these signs are reversed, the heat being

---

[1] LEWIS, G. N., and M. RANDALL, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York, 1923.

[2] EUCKEN, A., and K. FAJANS, *Z. physik. Chem.*, **A161**, 233 (1932).

[3] RIDEAL, E. K., Chairman, *Chemistry & Industry*, **56**, 860 (1937).

positive when the system *gains* heat (endothermic reaction). Instead of the older thermochemical equation, such as

$$H_2 + \tfrac{1}{2}O_2 = H_2O(\text{g, 0.03122 atm}) + 57{,}803 \text{ cal}$$

we shall use exclusively the form in equation (2.10). Because of the existence of the two conventions with respect to sign, however, it is necessary to inspect each table of thermal data consulted for reference, to determine the convention followed by the compiler of the table. Heat of formation tables frequently list heats evolved as positive; in such tables a different symbol for the heat of reaction is sometimes used.[1]

Equation (2.10) states specifically that at some temperature (25°c) 57,803 calories of heat are evolved when 1 mole of water vapor is formed from 1 mole of gaseous hydrogen and $\frac{1}{2}$ mole of gaseous oxygen. When no qualifying symbol (g = gas, liq = liquid, and c = crystalline solid) is enclosed parenthetically, it is understood that the substances are in their stable form under the experimental conditions. A pressure of 1 atmosphere is assumed unless another pressure is indicated. It will be noted that the sign of the heat is that for the reaction as it proceeds from *left* to *right*. If the equation is reversed, the sign of q must also be reversed as was done for equation (2.9). Also, for the formation of 2 moles of water the heat of reaction is double that for the formation of 1 mole. Thus,

$$2H_2 + O_2 = 2H_2O(\text{g, 0.03122 atm}); \qquad q = -2 \times 57{,}803 \text{ cal} \tag{2.25}$$

Here it is not necessary to indicate the phase for the hydrogen and oxygen; they are both gases at 25°c and 1 atmosphere pressure.

The Differential First Law Equation.—The statement of the first law of thermodynamics previously made applies to finite energy changes. We have pointed out that the internal energy of a system is a property of the system; finite changes in energy can therefore be represented by ΔE, and infinitesimal changes can be represented by the exact differential, dE. From equation 2.3 it appears that, since ΔE can be expressed in terms of properties of a system, the difference $(q - w)$ can be also, even though q and w, taken separately, may vary from process to process. Furthermore, if ΔE is small, $(q - w)$ must also be small even though q and w, taken separately, may be relatively large. All that is required here is that their difference be small. As one differential expression of equation (2.3), we have, therefore,

$$dE = D(q - w) \tag{2.26}$$

---

[1] F. R. Bichowsky and F. D. Rossini in their "Thermochemistry of Chemical Substances," Reinhold Publishing Corporation, New York, 1936, use Q_f for the heat *evolved* on formation of a compound at constant pressure. For heat *absorbed* the corresponding symbol is ΔH.

When q and w have small values, we may use the symbols previously defined and obtain, as the differential expression of the first law equation,

$$dE = Dq - Dw \qquad (2.27)$$

Dependence of Heat and Work on the Path.—Consider a system containing metallic copper and zinc and large quantities of aqueous solutions of copper sulfate and zinc sulfate at unit activity and at room temperature (state 1). Let us now allow these substances to react, so that 1 mole each of zinc and copper sulfate are consumed and 1 mole each of copper and zinc sulfate are produced, there being enough of the solutions so that their concentration remains unchanged. This new state of the system is designated state 2. The difference in energy of the system found for this change is

$$\Delta E = E_2 - E_1 = -51{,}400 \text{ cal}$$

the minus sign indicating that the system has less energy in state 2 than in state 1. These facts are summarized in the equation

$$Zn + CuSO_4(a = 1) = ZnSO_4(a = 1) + Cu; \quad \Delta E = -51{,}400 \text{ cal} \qquad (2.28)$$

The notation ($a = 1$) indicates that the substance is at unit activity. The actual reaction may be carried out in a variety of ways. It may occur (*a*) in a calorimeter in which the materials are merely mixed together, (*b*) in an electrochemical cell in which the electrical energy produced does the reversible work w_r, or (*c*) in a Daniell cell in which less than the maximum work is produced. In all the processes, the same final state is reached from the initial state, for the properties of the final products do not depend on the method of manufacture.[1] Each process leading from a definite initial state to a definite final state is called a *path*.

Along path (*a*) no work is done, so that from equation (2.3)

$$\Delta E = q - 0 = q = -51{,}400 \text{ cal}$$

Here the heat evolved in the process is 51,400 calories.

Along path (*b*) the maximum work w_r is obtained, the emf of the cell being constant at $E°$ the maximum, equilibrium value for the cell. From equation (2.23), n being 2 and $E°$ being constant at 1.107 volts,

$$w_r = FE° \int dn = nFE° = 2 \times 23{,}068 \times 1.107 = 51{,}070 \text{ cal}$$

---

[1] The tendency of the displaced copper to form brass with the metallic zinc is here neglected. See VAN STRATEN, F. W., and W. F. EHRET, *J. Am. Chem. Soc.*, **61,** 1798 (1939).

Hence, from equations (2.24) and (2.28),

$$\Delta E = q_r - 51{,}070 = -51{,}400 \text{ cal}$$
$$q_r = -51{,}400 + 51{,}070 = -330 \text{ cal}$$

Here only 330 calories are evolved instead of the 51,400 calories as in the irreversible path (*a*) in which no work is done.

For (*c*) there are an infinite number of paths. The actual work may vary from 0 as in path (*a*) (short-circuited cell) to 51,070 calories as in path (*b*) (reversible cell). The corresponding values of q range from $-51{,}400$ to -330 calories. These calculations show that q and w depend on the path followed in going from one state to another and are, therefore, not properties of the system. The results are summarized in Table 2.1 which also includes values for a path in which half the reversible work is obtained.

TABLE 2.1.—HEAT AND WORK FROM THE REACTION BETWEEN ZINC AND COPPER SULFATE ALONG SEVERAL PATHS
(Values in calories per mole)

Path (*b*) Reversible $w = w_r$	Path (*c*) Partly irreversible $w = \frac{1}{2}w_r$	Path (*a*) Completely irreversible $w = 0$
$\Delta E = -51{,}400$ $w = w_r = 51{,}070$ $q = q_r = -330$	$\Delta E = -51{,}400$ $w = \frac{1}{2}w_r = 25{,}535$ $q = -25{,}865$	$\Delta E = -51{,}400$ $w = 0$ $q = -51{,}400$

Heat of Reaction at Constant Volume.—The data in Table 2.1 indicate that the heat of a chemical reaction varies according to the amount of work done during the course of the reaction. When no useful work is done by a reacting system, as in the usual calorimetric process, the path followed is an irreversible one, but it yields a value for the heat of reaction characteristic of the path. Consider a chemical reaction carried out in a closed vessel such as the bomb of a bomb calorimeter. During the reaction, the system does not change volume; hence there is no work of expansion. Since there is also no other kind of work, $w = 0$ for the reaction. Hence, from the first law,

$$q_V = \Delta E_V \tag{2.29}$$

The subscript $_V$ is used to emphasize the experimental condition under which equation (2.29) is valid, namely, constant volume. *For a reaction at constant volume, the calorimetric heat of reaction measures the increase in internal energy.*

The relation in equation (2.29) is simple and important but it cannot be applied directly to many chemical reactions since the usual experimental condition under which chemical reactions occur is that of constant pressure. For any reaction in an open vessel, the external pressure is that of the atmosphere, which remains essentially constant during the course of the reaction. None of the equations (2.8) to (2.11) represent constant-volume reactions; hence the q values listed for these reactions cannot be identified with the change in internal energy. On the other hand, equation (2.28) represents a reaction which, although taking place in an open vessel, is essentially at constant volume. All the reacting substances are solid or in solution, and the volume change resulting from the reaction is so small that the work of expansion is negligible in value compared with the other energy changes. In identifying all the reversible work for this reaction with the electrical work, we assumed implicitly that the work of expansion and other possible types of work were negligible.

Heat of Reaction at Constant Pressure.—When a chemical reaction is carried out in a vessel open to the atmosphere, there will be work of expansion if the reacting system increases in volume. Where the increase in volume is ΔV and the atmospheric pressure is P', the work of expansion is $P' \Delta V$. If, however, the initial and the final pressures of the system equal atmospheric pressure, the work can be expressed in terms of the pressure P of the system itself. Then, there being no other kinds of work, we have

$$w = w_P = P \Delta V_P$$

and, from the first law,

$$q_P = \Delta E_P + P \Delta V_P \tag{2.30}$$

The subscript P indicates the condition of constant pressure. Equation (2.30) shows that the heat of reaction in an open vessel does not equal the change in internal energy whenever there is a change in volume of the system. *For a reaction at constant pressure, the calorimetric heat of reaction equals the sum of the increase in internal energy and the work of expansion.*

However, it must not be assumed that the increase in internal energy at constant volume is identical with that at constant pressure. Consider an isothermal gaseous reaction in which the final number of moles of gas is double the initial number, the initial pressure being 1 atmosphere. In a closed calorimeter (constant volume) of 1 liter capacity, the values of P and V at the final state will be $P = 2$, $V = 1$. In an open calorimeter (constant pressure) with the same initial state, $P = 1$, $V = 1$, the final state will differ from that in the closed calorimeter, being $P = 1$, $V = 2$. Thus, since the final states in the two processes are different,

$$\Delta E_V \neq \Delta E_P$$

The general relation between q_P and q_V may be derived from equations (2.29) and (2.30). From equation (2.30),

$$q_P = (\Delta E_P - \Delta E_V) + \Delta E_V + P\,\Delta V_P$$

Hence, from equation (2.29),

$$q_P = q_V + P\,\Delta V_P + (\Delta E_P - \Delta E_V) \tag{2.31}$$

In most chemical reactions, however, the values of ΔE resulting from chemical changes are so great compared with the change in E resulting from isothermal changes in volume (and pressure) of the system that we may write

$$\Delta E_V \doteq \Delta E_P$$

When the difference between ΔE_V and ΔE_P becomes negligible, equation (2.31) becomes

$$q_P = q_V + P\,\Delta V_P \tag{2.32}$$

In precise calorimetry,[1] however, the differences between ΔE_V and ΔE_P cannot always be neglected. Similarly, for processes without large heat effects, small energy differences become relatively important and equation (2.32) cannot be used.

As was indicated, the $P\,\Delta V$ work term is relatively important only when there is an appreciable change in volume. For solids or liquids, the volume changes are not great but when gases are evolved or consumed the work of expansion becomes significant. Whenever deviation of these gases from the ideal gas laws produces errors of a minor order only, we may calculate the value of the $P\,\Delta V$ term with the aid of the ideal gas equation (1.15). At constant pressure P and constant temperature T, we have, for n_1 moles of gas before the reaction, $PV_1 = n_1RT$ and, for the n_2 moles of gas after the reaction, $PV_2 = n_2RT$. Therefore,

$$P(V_2 - V_1) = (n_2 - n_1)RT = \Delta nRT$$

Accordingly, from equation (2.32),

$$q_P = q_V + \Delta nRT$$

Heat Content.—In thermodynamic calculations on chemical reactions at constant pressure, the sum $(\Delta E_P + P\,\Delta V_P)$ appears so often that it is convenient to represent it by a symbol. Since E, P, and V are properties of a system, the sum may be represented by the change in some quantity H which is a function of E, P, and V. Let the change in H for the constant-pressure process be represented by ΔH_P, so that

$$\Delta H_P = \Delta E_P + P\,\Delta V_P \tag{2.33}$$

[1] For the kinds of calculations required when heats of reaction at 1 atmosphere pressure are derived from the data secured with bomb calorimeters, see the series of papers by Rossini and his coworkers at the National Bureau of Standards published in the *Journal of Research of the National Bureau of Standards.*

Then, for the conditions under which equation (2.30) was derived

$$\Delta H_P = q_P \tag{2.34}$$

The function[1] H has been variously named *heat content*, *enthalpy*, and *total heat*. None of these names is entirely satisfactory. A system does not contain "heat." On the other hand, the term "enthalpy" is as forbidding to the student mind as entropy. Since the change in H for a process at constant pressure may be measured by the calorimetric heat for the process, no work except work of expansion being done, H can by analogy with "heat capacity" be called "heat content."

Equation (2.33) serves to define only the change in heat content for a constant-pressure process. The *general definition of heat content* is the following equation which reduces to equation (2.33) under the special condition of constant pressure

$$H \equiv E + PV \tag{2.35}$$

Since E, P, and V are properties of a system, H is also a property of the system. In a given state a system has definite values of E, P, and V and, therefore, a definite value of H. In a new state, with new values of E, P, and V, there will be a corresponding new value of H. The increase in heat content, $\Delta H \equiv H_2 - H_1$, on going from state 1 to state 2, may be derived from equation (2.35) as follows:

At state 1,

$$H_1 = E_1 + P_1V_1$$

At state 2,

$$H_2 = E_2 + P_2V_2$$

The increase in heat content is, therefore,

$$\begin{aligned} \Delta H &= H_2 - H_1 = (E_2 + P_2V_2) - (E_1 + P_1V_1) \\ &= (E_2 - E_1) + (P_2V_2 - P_1V_1) \\ &= \Delta E + \Delta(PV) \end{aligned} \tag{2.36}$$

However, it is the increase in heat content under the restriction of constant pressure, equation (2.33), that is generally referred to as representing the ΔH value for a chemical reaction and not the more general relation shown in equation (2.36). From the relations in equations (2.33) and (2.34), we may state: *For a reaction at constant pressure, the increase in heat content is equal to the heat of reaction.* Hence, ΔH_P may be expected to be particularly useful at constant pressure, the usual experimental condition.

It is evident from equation (2.36) that there is also a change in heat

---

[1] Gibbs represented the H function by the symbol χ and called it the *heat function for constant pressure.*

content for a reaction taking place under the experimental condition of constant volume. Thus,

$$\Delta H_V = \Delta E_V + V\,\Delta P \tag{2.37}$$

However, this change in heat content is seldom used, for it represents no value that is measured directly. Therefore, whenever ΔH is written without the qualifying subscript, it refers to ΔH_P and not to ΔH_V. Furthermore, we should remind ourselves that the heat of reaction under consideration is that measured in a calorimeter *when no work is done* except work of expansion. When there is electrical, or surface, or chemical work during the process, equation (2.33) is valid but does not represent the heat of reaction.

Differential Expressions for H.—From the defining equation for the heat content, [equation (2.35)], we obtain the differential forms

$$\mathrm{d}H = \mathrm{d}E + \mathrm{d}(PV) \tag{2.38}$$

$$= \mathrm{d}E + V\,\mathrm{d}P + P\,\mathrm{d}V \tag{2.39}$$

At constant pressure, equation (2.39) becomes

$$\mathrm{d}H_P = \mathrm{d}E_P + P\,\mathrm{d}V_P \tag{2.40}$$

If the reversible work of expansion in a process is equal to $P\,\mathrm{d}V$ as in equation (2.20), there being no other kinds of work such as electrical work, the differential first law equation (2.27) becomes

$$\mathrm{d}E = \mathrm{D}q - P\,\mathrm{d}V \tag{2.41}$$

A comparison with (2.40) shows that, under these conditions,

$$\mathrm{d}H_P = \mathrm{D}q_P \tag{2.42}$$

Absolute Values of E.—We have seen that energy is a function that depends only on the state of the system and not on its previous history. Thus, the gram of water at 1° at a definite pressure has a definite energy regardless of whether it has just been obtained from warmer water, from ice, or from the combustion of hydrogen. In all our calorimeter measurements, however, we obtain only the changes in energy which accompany changes in the state of a system and not the values of the energies themselves. If we know the absolute value of the energy of a system in the state 1, we can determine the energy of the system in any other state 2 by measuring the increment of energy E on going from 1 to 2. However, we have no direct method of measuring the absolute energy at any state.

Since we now have methods for calculating the energies associated with the motions of molecules, and of the atoms and electrons within the molecules, we might expect to secure absolute energy values. The energy levels for the different types of motion and of electron excitation in relatively simple molecules can be secured from spectroscopic data. The quantum mechanics and the methods of statistical mechanics then enable us to calculate the energies of gaseous systems of molecules. Thus, all the molecules have translational energy, which contributes the energy E_t to the system. Molecules, other than monatomic molecules, may rotate about their axes and contribute the rotational energy E_r to the system. The atoms may vibrate about their equilibrium positions in the molecules and contribute the vibrational energy E_v to the system. Furthermore, electrons may be raised to higher energy levels, contributing the electronic energy E_e to the system. All these energies depend on the temperature, for the number of molecules at quantum states with higher energies increases with increasing temperature. None of them take into account any possible energies at the absolute zero of temperature.

But molecules, according to the quantum mechanics, have energy at zero temperature. This energy is called *zero point energy;* it may be represented by the symbol E_0. Furthermore, the energies, which vary with temperature, are calculated by summation of the energies of the individual molecules and do not take into account the energy associated with interaction between the molecules. For real gases, this energy, attributed to gas "imperfections" because of the resulting deviation from the perfect gas law, may be represented by E_i. Then, the absolute energy E of the gas under the specified conditions may be represented by the sum of all the energies and

$$E = E_0 + E_t + E_r + E_v + E_e + E_i \tag{2.43}$$

However, E_0 is not evaluated and hence what is tabulated is the excess of the absolute energy over the zero point energy, $E - E_0$. Furthermore, in the tabulations the gas imperfections are not taken into account, the energies being given for the real gas at unit fugacity[1] which corresponds to the state of an ideal gas at unit pressure. If the standard energy of the gas at unit fugacity is represented as E° and the zero point energy as E_0°, the reported energy then becomes

$$E^\circ - E_0^\circ = E_t + E_r + E_v + E_e \tag{2.44}$$

Thus, it appears that here also we deal with relative energies and not absolute energies.

Absolute Values of ***H*****.**—Values of P and V are expressed as absolute values. However, it appears from the definition of heat content that, if we do not have absolute values for E, we also do not have them for H. From the perfect gas law, we find that, since PV is proportional to T,

---

[1] Fugacity is defined in Chap. 12.

its value at zero temperature is zero. From equation (2.35), therefore, $H_0 = E_0$. Hence, for the gas in the ideal gas state,

$$H^\circ - H_0^\circ = H^\circ - E_0^\circ = (E^\circ - E_0^\circ) + (PV)^\circ \tag{2.45}$$

Thus tables of heat content give the values of H referred to some suitable standard reference state at which H is arbitrarily assigned zero value. The reference standard state is often chosen within the experimental range, so that changes from it can be measured accurately. In this way, accurate tables of *relative values* are prepared in which positive values of H are given for the states with more energy than the standard state and negative values of H for the states with less energy than the standard state.

From the following relations, we can see that the particular reference state chosen does not alter the value of the difference in heat content between two states:

If the absolute value of the heat content of a system at some selected standard state is H_s, the absolute value at the state 1 is H_1, and that at the state 2 is H_2, the difference in heat content between states 1 and 2 is $H_2 - H_1 = (H_2 - H_s) - (H_1 - H_s)$. But the differences $(H_2 - H_s)$ and $(H_1 - H_s)$ are the *relative* values which we may designate as H_2^* and H_1^*; hence,

$$\Delta H = H_2 - H_1 = H_2^* - H_1^* \tag{2.46}$$

The difference between the relative values is therefore equal to the difference between the absolute values. In standard heat of formation tables, the heat contents of compounds have values relative to those of the elements. The heat contents of the elements in their standard state are arbitrarily placed at zero.

Problems

2.1. For the combustion of diamond at 25°C, E. J. Prosen, R. S. Jessup, and F. D. Rossini [*J. Research Natl. Bur. Standards*, **33**, 447 (1944)] report a value of

$$\Delta H = -395{,}343 \pm 96 \text{ int joules/mole}$$

For the combustion of graphite at the same temperature, they report

$$\Delta H = -393{,}447 \pm 45 \text{ int joules/mole}$$

Calculate the values (including the uncertainties) for the heats of combustion at constant pressure in calories per mole.

2.2. Calculate the minimum work in calories required to change 1 cm^3 of water at 20° to a spray in which the average diameter of the water droplets is 100 millimicrons.

2.3. The capacity of a lead storage battery is 100 amp-hr. At 2 volts, what is the amount of heat in calories developed by this current? What weight of lead is consumed at the positive electrode during this process?

2.4. The heat of evaporation of water at 1 atmosphere pressure and 100°C is $q_P = \Delta H = 9{,}717$ cal. At this temperature and pressure the molar volume of the vapor is 30.14 liters and that of the liquid is approximately 0.02 liter. What is the value of $P\ \Delta V$ for this reaction (in calories)? What is the change in internal energy, ΔE?

2.5. The difference between the heat content of water vapor as an ideal gas at 25°C and at the saturation pressure of 0.031222 atmosphere is given by

$$H^\circ - H^{P=0.031222} = 5 \text{ cal}$$

The molar volume of water vapor at the saturation pressure is 781.9 liters. Calculate Pv for water vapor at 25°. From the ideal gas law, calculate Pv for the ideal gas. What part of the 5 calories above must be attributed to a change in Pv as the gas is brought to the ideal state? What part to a change in internal energy of the gas?

2.6. Calculate the difference, in calories, between ΔH and ΔE for the following combustions, assuming that $\Delta E_P = \Delta E_V$,

(*a*) Ethylene at 18°C.
(*b*) Benzene at 25°C.
(*c*) Benzene at 100°C.
(*d*) Hydrogen at 500°C.
(*e*) Carbon monoxide at 300°C.

2.7. Benzoic acid is used as a standard substance in calibrating bomb calorimeters. R. S. Jessup [*J. Research Natl. Bur. Standards*, **33**, 439 (1944)] reports a heat of combustion of a standard sample of benzoic acid as 26,428.4 ± 2.6 int joules per gram mass (weight corrected for buoyancy of air at 25°C). For a mole of benzoic acid, calculate ΔE_V.

CHAPTER 3

HEAT CAPACITY

In this chapter we shall consider only simple systems, that is, nonreacting systems in which the only work is work of reversible expansion. The heat effects considered in our discussion of heat capacity will, therefore, be only those associated with changes in internal energy and in $P\,\mathrm{d}V$ work.

Heat Capacity.—In Chap. 2, we defined the heat capacity in terms of the heat absorbed q per degree rise in temperature. We also observed that the value of heat absorbed between two states depends on the conditions under which it is absorbed, that is, on the path followed during the heating. In practice, measurements of heat capacity are made almost exclusively under either of two experimental conditions: *constant pressure* or *constant volume.* However, since systems tend to expand (with few exceptions) when the temperature increases, two systems identical at the first state will not be at the same final state when one is heated at constant pressure and the other at constant volume. The specific heat capacities at constant pressure and constant volume are represented by c_P and c_V, respectively, the molar heat capacities by c_P and c_V, respectively, and the heat capacities of an indefinite number of moles by C_P and C_V, respectively. We shall use the molar heat capacities or multiples of these molar values almost exclusively for the same reasons that we use molar heats of reaction instead of the corresponding heats per gram.

Where $\mathrm{D}q$ is the infinitesimal quantity of heat absorbed by a mole of pure substance heated over an infinitesimal temperature interval $\mathrm{d}T$, we have for the constant-volume process, from equation (2.29)

$$\mathrm{d}E_V = \mathrm{D}q_V \tag{3.1}$$

From our definition of heat capacity [compare equation (2.7)]

$$C_V = \frac{\mathrm{D}q_V}{\mathrm{d}T} = \frac{\mathrm{d}E_V}{\mathrm{d}T} = \left(\frac{\partial E}{\partial T}\right)_V \tag{3.2}$$

and, therefore,

$$\mathrm{d}E_V = C_V\,\mathrm{d}T \tag{3.3}$$

For the constant-pressure process, we have, from equation (2.34) or (2.42), the equations corresponding to the above, namely,

$$\mathrm{d}H_P = \mathrm{D}q_P \tag{3.4}$$

$$C_P = \frac{\mathrm{D}q_P}{\mathrm{d}T} = \frac{\mathrm{d}H_P}{\mathrm{d}T} = \left(\frac{\partial H}{\partial T}\right)_P \tag{3.5}$$

$$\mathrm{d}H_P = C_P\,\mathrm{d}T \tag{3.6}$$

Between any two temperatures T_1 and T_2 the heat absorbed by a substance at constant pressure equals the increase in heat content, $H_2 - H_1$; it is represented by the integral

$$H_2 - H_1 = \int_{T_1}^{T_2} C_P\,\mathrm{d}T \tag{3.7}$$

This equation can be integrated if the relation between C_P and T is known, that is, if C_P is a known function of T. If the heat capacity does not vary with temperature, that is, if C_P is constant, equation (3.7) becomes

$$H_2 - H_1 = C_P \int_{T_1}^{T_2} \mathrm{d}T = C_P(T_2 - T_1) \tag{3.8}$$

This is the form of the equation used with mean heat capacity data, because the mean heat capacity C_m is by definition constant for the stated temperature range.

Measurement of Heat Capacity.—Heat capacity at constant volume is important theoretically because it is related directly to the internal energy. It is rarely measured, however, because of experimental difficulties. If a system is not to expand during heating, the retaining vessel must be strong and rigid enough to withstand the pressures that are built up. Such a vessel has a relatively high heat capacity. Furthermore, the heat capacity of the substance is observed as the difference between the total heat capacity of the system and the heat capacity of the vessel. If this difference is small compared with the two heat capacities that are measured experimentally, even a small error in either of the measured values will lead to a relatively large uncertainty in the value of C_V for the substance. For this reason, heat capacities are measured almost entirely under the condition of constant pressure. Heat capacities at constant volume are then obtained from these data with the aid of other data and calculations by methods some of which will be indicated later.

In ordinary heat capacity determinations, what is measured is the finite rise in temperature produced by a finite quantity of heat, or the finite quantity of heat released when the substance is cooled over a finite temperature interval, the pressure remaining constant. The observed ratio $\Delta H/\Delta T$ measures the mean heat capacity over the temperature interval and not necessarily the true heat capacity at any specified temperature. Some of the relations between the observed values of ΔH and the heat capacities are indicated in Fig. 3.1.

When the substance is heated from the reference temperature T_0 to the temperature T_1 at constant pressure, the heat absorbed is equal to $H_1 - H_0$; when it is heated from T_0 to the temperature T_2, the total heat absorbed is equal to $H_2 - H_0$. These values may be plotted as in Fig. 3.1 where the ordinates represent the various values of relative heat content and the abscissas the corresponding values of the temperature. The experimental values $(H - H_0)$ at the various temperatures are indicated by the circles.

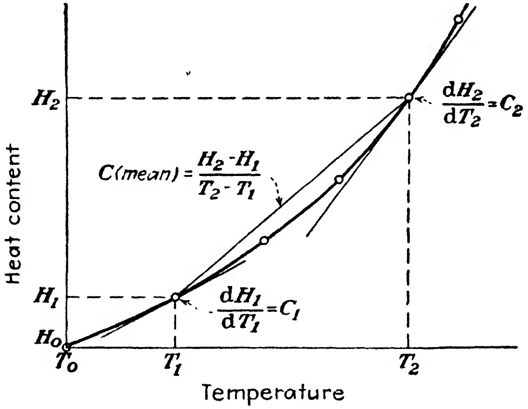


FIG. 3.1.—Some relations between relative heat content, true heat capacity at various temperatures, and mean heat capacity.

The heat capacity at the temperature T_1 is represented by the slope of the H-T curve at T_1, namely, dH_1/dT_1, that at the temperature T_2 is given by dH_2/dT_2. The mean heat capacity between the temperatures T_1 and T_2 is represented by the slope

$$\frac{(H_2 - H_1)}{(T_2 - T_1)}$$

of the straight line between the points H_1, T_1 and H_2, T_2. [Compare equation (3.8).] The various heat capacities can, therefore, be obtained directly from the graph as illustrated; they can be obtained more precisely from the algebraic equation that relates H to T. In the more accurate work, heat capacities are obtained from the empirical equations that represent the experimental data as well as possible.

Observe that C_m is, in general, not equal to $(C_2 + C_1)/2$. From the definition of mean heat capacity, we have from equation (3.8) for the heat absorbed between two states

$$H_2 - H_1 = C_m(T_2 - T_1) \tag{3.9}$$

When equation (3.9) is combined with equation (3.7), we have

$$C_m(T_2 - T_1) = \int_{T_1}^{T_2} C_P \, dT$$

whence,

$$C_m = \frac{\int_{T_1}^{T_2} C_P \, dT}{T_2 - T_1} \tag{3.10}$$

Only when C_P is a linear function of temperature as in equation (3.18) will C_m be equal to the average of the heat capacities over the temperature range from T_1 to T_2.

Some Relations between C_V and C_P.—Some thermodynamic relations between the heat capacity at constant volume and that at constant pressure may be derived for a simple system in the following way: From equations (3.5) and (2.35), we obtain for the heat capacity of a system at constant pressure.

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial(E + PV)}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \tag{3.11}$$

Here the term $(\partial E/\partial T)_P$ does not represent the heat capacity at constant volume, for $C_V = (\partial E/\partial T)_V$. In order to substitute C_V in equation (3.11), we must find the relation between $(\partial E/\partial T)_P$ and $(\partial E/\partial T)_V$. The equation of state for a simple one-phase system can be represented as a function of P, V, and T, only two of which are independent variables. The energy E of such a system can be expressed as a function of P and T as in equation (1.9) or as a function of V and T. In terms of the latter independent variables, the change in E may be expressed

$$dE = \left(\frac{\partial E}{\partial V}\right)_T dV + \left(\frac{\partial E}{\partial T}\right)_V dT \tag{3.12}$$

On dividing by dT, we have

$$\frac{dE}{dT} = \left(\frac{\partial E}{\partial V}\right)_T \frac{dV}{dT} + \left(\frac{\partial E}{\partial T}\right)_V \tag{3.13}$$

At a definite pressure P, the derivative (dE/dT) takes on a definite value $(\partial E/\partial T)_P$ which can be substituted directly in equation (3.11). We have the right to impose this condition on equation (3.13), for it is a general equation valid under any condition and consequently valid under the special condition of a definite pressure. We may also substitute C_V for $(\partial E/\partial T)_V$. At the pressure P, (dV/dT) takes the value $(\partial V/\partial T)_P$ and equation (3.13) becomes

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + C_V \tag{3.14}$$

When this value for the change of the internal energy with temperature at the pressure P is substituted in equation (3.11), we obtain

$$\begin{aligned} C_P &= C_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \\ &= C_V + \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P \end{aligned} \tag{3.15}$$

which may also be written

$$C_P - C_V = \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P \tag{3.16}$$

Equation (3.16) is useful because it contains only quantities that can be evaluated experimentally. The isothermal change of internal energy with volume, the pressure, and the change of volume with temperature at constant pressure (thermal expansion), all at a definite pressure P, can be measured. The difference $C_P - C_V$ can then be calculated; and if C_P is known, C_V is obtained. Most of the mathematical operations we shall perform are made for this purpose—to derive equations that enable us to use experimental data in the calculation of relations not readily observed in the laboratory. A number of expressions of the function $C_P - C_V$ may be set up, but these various possibilities are more interesting to the mathematician than to the chemist. Thus, by a method similar to that used in deriving (3.16) the following equation is obtained:

$$C_P = C_V + \left[V - \left(\frac{\partial H}{\partial P}\right)_T\right]\left(\frac{\partial P}{\partial T}\right)_V \tag{3.17}$$

In the derivation of equation (3.15), we assumed that E can be expressed as a function of V and T alone, that is, that the energy of the system is uniquely defined by its volume and temperature. If the energy depends also on other variables, as it does when chemical reactions or phase transitions occur, this derivation is not valid. We must, therefore, restrict our application of these equations to pure substances or to those mixtures of substances whose molar energies depend only on temperature and pressure or volume and not on the composition of the mixture.

Heat Capacity Equations.—For small temperature intervals, the heat capacity of a substance may frequently be considered constant over the temperature interval. If this constant heat capacity is plotted on coordinate paper as ordinate against the temperature as abscissa, the resulting curve will be a straight line parallel to the t-axis, as in Fig. 3.2. Data that are not precise may be given in this form over considerable temperature intervals. Quite generally, heat capacities increase with increasing temperature. To a close approximation, the heat capacity frequently increases directly with temperature over temperature ranges that are not too extreme. If so, the heat-capacity curve becomes a straight line not parallel to the t-axis. Such a curve is represented by an equation of the type

$$C_P = a + bt \tag{3.18}$$

where t represents temperature. At $t = 0$, C_P equals the constant a, which is frequently designated C_0. The change in heat capacity with temperature is measured by the slope which for the straight-line equation (3.18) is

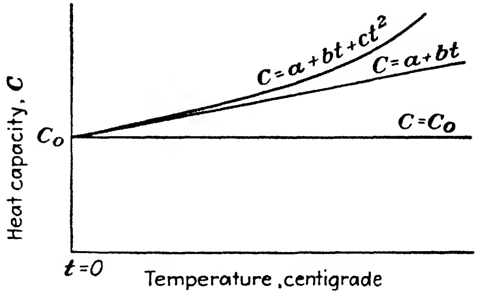


FIG. 3.2.—Curves representing several common types of heat capacity equations.

$$\frac{C_2 - C_1}{t_2 - t_1} = b \tag{3.19}$$

In the notation of the calculus, the slope is

$$\frac{dC_P}{dt} = b \tag{3.20}$$

In general, precise heat capacity data are still more closely fitted by an equation using higher powers of t, such as

$$C_P = a + bt + ct^2 + \cdots \tag{3.21}$$

Here again, the heat capacity at $t = 0$ is a and may be designated as C_0. The change of heat capacity with temperature may, for this curved line, be derived by differentiation of equation (3.21). Accordingly,

$$\frac{dC_P}{dt} = b + 2ct + \cdots$$

Heat capacity equations are expressed either in terms of t as degrees centigrade or of T as degrees Kelvin. In terms of absolute temperatures, equation (3.21) would be transformed to

$$C_P = \alpha + \beta T + \gamma T^2 + \cdots \tag{3.22}$$

The values of the parameters α, β, and γ may be calculated from a, b, and c by the rules of analytical geometry. To represent heat capacities up to high temperatures, Maier and Kelley[1] proposed an equation of the form

$$C_P = a + bT + c'\,T^{-2} \tag{3.23}$$

in which the coefficient c' in the T^{-2} term has a negative value.

Equations of the above types may be used only within definite temperature limits, for heat capacity curves may have points of inflection not representable by such simple equations.[2] Hence, it is unwise to extrapolate the equations beyond the experimental limits. Thus, if equation (3.21) is derived for the limits $t_1 = 0°\text{C}$ and $t_2 = 100°\text{C}$, it may be used with exactness within those limits, the heat capacity at 0° being a and that at 100° being $(a + 100b + 100^2c)$. It does not follow, however, that when equation (3.21) is transformed to equation (3.22) where T represents the temperature in degrees Kelvin, the new equation is valid over a wider range. Equation (3.22) would still hold between the former temperature limits 273.16 and 373.16°K, but it would not necessarily hold down to zero absolute. All that could be deduced is that, *if* equation (3.22) were valid at $T = 0°\text{K}$, the heat capacity at zero, C_0, would equal α. In a particular equation, α might have a negative value, but it would be absurd to assume from this that heat is evolved when the substance is made to increase in temperature in the neighborhood of 0°K. The proper interpretation is that the equation has been extended beyond its limits of validity. We find, as a matter of fact, that heat capacity at absolute zero approaches zero as a limit; hence, no equation of the type of equation (3.22) can be expected to hold at low temperatures. This question is discussed in more detail under the third law of thermodynamics.

Heat Capacity of Solids.—In 1819, Dulong and Petit announced the empirical rule that the gram-atomic heat capacity of all solid elements is the same, the value being slightly larger than 6 calories per degree. The elements of the smaller atomic weights furnish exceptions to this rule. On the basis of the classical kinetic theory, Boltzmann calculated that the value of the constant should be $c_V = 3R$, which equals 5.96 calories per degree. Lewis[3] found that the heat capacities of the solid elements agree better for c_V than for c_P, for the work of expansion varies with the different elements. The value $3R$ appears to be an upper limit for c_V. It is reached for the heavier elements at temperatures below room tem-

[1] MAIER, C. G., and K. K. KELLEY, *J. Am. Chem. Soc.*, **54,** 3243 (1932).

[2] *Ibid.*

[3] LEWIS, G. N., *J. Am. Chem. Soc.*, **29,** 1165, 1516 (1907); LEWIS, G. N., and G. E. GIBSON, *ibid.*, **39,** 2554 (1917).

perature; hence, the law of Dulong and Petit holds for these heavier elements.

As we shall see in Chap. 14, the heat capacity varies as T^3 near the absolute zero. As temperature approaches 0°K, the heat capacity and its temperature coefficient both approach zero. Figure 3.3, in which c_V is plotted against T, shows that the lower limits of c_V and of dC_V/dT approach zero (as $T \rightarrow 0$) and that the upper limit of c_V (at room temperature and above) is 6 calories per degree. At the upper limit, dC_V/dT approaches zero again.[1] Because of these limits, the heat capacity of solids must have a point of inflection and hence cannot be represented by a simple equation such as (3.21) or (3.22). In Fig. 3.3, curve *a* represents those elements which have reached the value $c_V = 6$ at 273°K, and *b* and *c* represent the lighter elements which do not reach the maximum until a higher temperature is reached. (Compare with the c_P values for carbon in Table 3.2.)

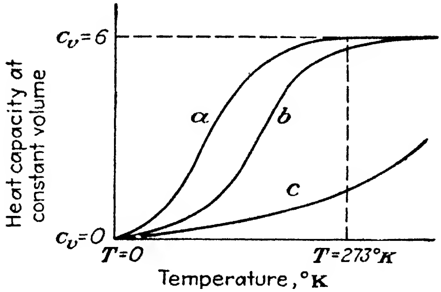


FIG. 3.3.—Different forms of heat capacity curves found for solid elements between zero absolute and room temperature.

As was stated earlier, values of c_V are difficult to measure accurately. They might be calculated from the heat capacity measurements at constant pressure by the use of equation (3.16), but values of $(\partial E/\partial V)_T$ for solids are difficult to measure. By methods that involve the second law of thermodynamics, Lewis derived the relation

$$c_P - c_V = \frac{\alpha^2 vT}{\beta} \tag{3.24}$$

where α is the coefficient of thermal expansion, β is the compressibility, and v the molal volume. This equation is obtained from equation (8.48).

Kelley[2] has compiled heat capacity equations for many inorganic substances, indicating at the same time the probable average error of the

---

[1] These statements imply that no new forms of heat absorption, such as ionization, electron excitation, or phase or other transitions, develop at either the higher or the lower temperatures.

[2] KELLEY, K. K., "High-temperature Specific-heat Equations for Inorganic Substances," *U. S. Bur. Mines, Bull.* 371 (1934).

equations. For solid compounds including those containing the lighter elements, Kopp found that the molecular heat capacity equals the sum of the atomic heat capacities. For the heavier elements, he used $c_p = 6.4$; for the lighter elements, he assigned values, such as S, 5.4; O, 4.0; H, 2.3; and C, 1.8. The rule is useful as a rough approximation when direct experimental data are lacking.

Heat Capacity of Liquids.—Just as our general knowledge of the behavior of molecules in the liquid state is not on an adequate theoretical basis, so our knowledge of the heat capacity of liquids is limited to empirical results. The empirical heat capacity equation for a liquid in the neighborhood of its melting temperature, together with the corresponding equation of the solid, is used in the usual determination of the latent heat of melting. In general, the heat capacity of the liquid is greater than that of the solid although of the same order of magnitude; for a few organic compounds, however, the liquid appears to have a slightly smaller heat capacity than the solid. For an undercooled liquid, the heat capacity curve is continuous with that of the liquid above the freezing point. There is, in general, a rather abrupt change in heat capacity, however, when the liquid is undercooled so far as to form a glass.

TABLE 3.1.—HEAT CAPACITY OF AIR-FREE WATER AT A PRESSURE OF 1 ATM

°C	c_p		°C	c_p	
	Absolute joules/gram*	Defined thermochemical cal/gram†		Absolute joules/gram*	Defined thermochemical cal/gram†
0	4.2177	1.0080	50	4.1807	0.9992
5	4.2022	1.0043	55	4.1824	0.9996
10	4.1922	1.0019	60	4.1844	1.0001
15	4.1858	1.0004	65	4.1868	1.0006
20	4.1819	0.9995	70	4.1896	1.0013
25	4.1796	0.9989	75	4.1928	1.0021
30	4.1785	0.9987	80	4.1964	1.0029
35	4.1782	0.9986	85	4.2005	1.0039
40	4.1786	0.9987	90	4.2051	1.0050
45	4.1795	0.9989	95	4.2102	1.0063
			100	4.2130	1.0076

* Data of N. S. Osborne, H. F. Stimson, and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 238 (1939).

† Corresponding values in terms of the defined calorie. Since the original measurements were made in terms of the international joule and the reported values were calculated to absolute joules with the factor, 1 int joule = 1.00019 abs joules, this same factor was used to calculate the values in defined calories. Hence, in this table, 1 cal = 4.1841 abs joules.

The heat capacities of pure liquids and of liquid solutions are ordinarily measured over limited temperature ranges. They are used to calculate the heats of reaction at a temperature different from the experimental temperature. The heat capacity of water is of special interest because it has served historically to define the unit of heat, the calorie.

TABLE 3.2.—MOLAR HEAT CAPACITIES* FOR SOME SUBSTANCES AT CONSTANT PRESSURE

(Heat capacities in calories per degree at 1 atmosphere pressure)

Temperature, °K	Carbon (graphite)	Carbon monoxide	Carbon dioxide	Hydrogen	Nitrogen	Oxygen	Water	Methane
298.16	2.066	6.965	8.874	6.892	6.960	7.017	8.025	8.536
300	2.083	6.965	8.894	6.895	6.961	7.019	8.026	8.552
400	2.851	7.013	9.871	6.974	6.991	7.194	8.185	9.736
500	3.496	7.120	10.662	6.993	7.070	7.429	8.415	11.133
600	4.03	7.276	11.311	7.008	7.197	7.670	8.677	12.546
700	4.43	7.451	11.849	7.035	7.351	7.885	8.959	13.88
800	4.75	7.624	12.300	7.078	7.512	8.064	9.254	15.10
900	4.98	7.787	12.678	7.139	7.671	8.212	9.559	16.21
1000	5.14	7.932	12.995	7.217	7.816	8.335	9.869	17.21
1100	5.27	8.058	13.26	7.308	7.947	8.440	10.172	18.09
1200	5.42	8.167	13.49	7.404	8.063	8.530	10.467	18.88
1300	5.57	8.265	13.68	7.505	8.165	8.608	10.749	19.57
1400	5.67	8.349	13.85	7.610	8.253	8.676	11.015	20.18
1500	5.76	8.419	13.99	7.713	8.330	8.739	11.263	20.71
2000	.....	8.665	14.5	8.175	8.602	9.024	12.24	
3000	.....	8.899	15.0	8.791	8.862	9.518	13.3	
4000	.....	9.015	......	9.151	8.989	9.879		
5000	.....	9.099	......	9.389	9.076	10.105		

* WAGMAN, D. D., J. E. KILPATRICK, W. J. TAYLOR, K. S. PITZER, and F. D. ROSSINI, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

Table 3.1 gives values for the heat capacity of water at 1 atmosphere pressure. The data indicate that the heat capacity of water is at a minimum at about 35°C. According to these data, the defined calorie represents the heat capacity of a gram of water at about 17°C. These data indicate also that the 15° calorie (4.1858 abs joules) is slightly larger than the value previously assigned to it ("International Critical Tables," 4.1850 abs joules; Birge,[1] 4.1852 abs joules).

Heat Capacity of Gases.—The heat capacities of gases are difficult to measure accurately because of their low values. However, c_P can be

---

[1] BIRGE, R. T., *Rev. Modern Phys.*, **1**, 1 (1929).

measured, and the ratio c_P/c_V can be measured still more accurately. From these data or from equation (3.16), c_V can then be calculated. The heat capacity of an ideal monatomic gas has particular theoretical importance both because the "noble" gases closely approximate this ideal behavior and because it represents that part of the heat capacity of other gases attributable to the increase in translational energy of the gas molecules. Heat capacity in excess of the translational heat capacity can then be attributed to the energy absorbed in the increased rotation of the gas molecule and in the increased vibration of the atoms in the molecule. For simple gases, the heat capacities and other thermodynamic

TABLE 3.3.—MOLAR HEAT CAPACITY EQUATIONS* FOR SOME GASES AT CONSTANT PRESSURE

(Temperature in degrees Kelvin, heat capacities in calories per degree per mole for the gas in its standard state)

The values listed in the columns are those for the corresponding constants in one of the following equations:

$$c_P^\circ = a + bT + cT^2$$

$$c_P^\circ = a + bT + \frac{c'}{T^2}$$

Substance	a	$b \times 10^3$	$c \times 10^7$	$c' \times 10^{-5}$	Per cent deviation		Range, °K
					Maximum	Average	
Br_2	8.911	0.140	....	−0.0298	0.09	0.02	300–1500
CH_4	3.381	18.044	−43.00	....	1.80	0.52	298.16–1500
C_2H_4	2.706	29.160	−90.59	....	1.46	0.92	291.16–1500
C_2H_6	2.195	38.282	−110.01	....	0.91	0.43	298.16–1500
C_2H_5OH	3.578	49.847	−169.91	....	0.28	0.15	300–1000
Cl_2	8.764	0.271	....	−0.656	0.24	−0.11	300–1500
CO	6.420	1.665	−1.96	....	1.17	0.55	298.16–1500
CO_2	6.214	10.396	−35.45	....	1.41	0.77	298.16–1500
HBr	6.5776	0.9549	1.581	....	1.23	0.54	300–1500
HCl	6.7319	0.4325	3.697	....	0.98	0.49	300–1500
H_2	6.9469	−0.1999	4.808	....	0.49	0.19	300–1500
H_2O	7.256	2.298	2.83	....	0.74	0.45	298.16–1500
H_2S	6.385	5.704	−12.10	....	2.00	0.50	298.1–1800
N_2	6.524	1.250	−0.01	....	1.15	0.60	298.16–1500
NH_3	6.189	7.887	−7.28	....	0.65	0.23	291.16–1000
N_2O	6.529	10.515	−35.71	....	1.26	0.68	298.1–1500
O_2	6.148	3.102	−9.23	....	0.65	0.24	298.16–1500
SO_2	11.895	1.089	....	−2.642	3.18	1.31	298.1–1800

* Equations of H. M. Spencer and J. L. Justice, *J. Am. Chem. Soc.*, **56**, 2311 (1934); H. M. Spencer and G. N. Flannagan, *ibid.*, **64**, 2511 (1942); H. M. Spencer, *ibid.*, **67**, 1859 (1945).

functions can be calculated from the observed energy levels in the band spectra of the molecules and the distribution of the molecules among those energy levels as calculated by the methods of statistical mechanics. These calculated heat capacities are more precise and appear to be more accurate than the values obtained experimentally. In recent years, a number of heat capacities of gases have been calculated. The difference in heat capacity of *ortho*- and *para*-hydrogen, predicted on theoretical grounds, was used to demonstrate the existence of these two forms of hydrogen.

The molar heat capacities of the monatomic gases remain constant over large temperature ranges. Thus, for argon, helium, krypton, neon, radon, xenon, cesium, lithium, mercury, potassium, and sodium, the molar heat capacities at constant volume and constant pressure are, respectively, very near 3 and 5 calories per degree. As we shall see in Chap. 4, these values correspond, respectively, to $\frac{3}{2}R$ and $\frac{5}{2}R$ so that we may write for these gases, $c_V = 2.98$ cal/deg and $c_P = 4.97$ cal/deg. The heat capacities of diatomic and polyatomic gases are greater. The values of c_P for some gases and for carbon (graphite) are listed in Table 3.2.

Some heat capacity equations for gases are given in Table 3.3. Equations of this type do not represent the observed heat capacities at low temperatures. They appear to indicate a positive heat capacity at zero absolute where $T = 0$; but before this temperature is reached, the gases will have condensed to liquids or solids and the gas heat capacity equations no longer apply. Even within this temperature range, equations of the type of (3.22) and (3.23) do not give perfect agreement with the best data. The indicated deviations of the equations listed in the table show the type of agreement that may be expected. Within these limits the equations are useful in thermodynamic calculations. The temperature range of each equation is stated.

Additivity of Heat Capacities.—In dealing with heat capacities, we shall have occasion to obtain the heat capacity of a reaction system by adding the heat capacities of the constituents of the system. This procedure is justifiable for pure substances and mixtures of pure substances when the various substances do not interact. It fails in solutions where there are energy changes on assemblage of the system. The question of solutions that behave in this way is reserved for later discussion. We shall here restrict our attention to systems in which the properties of the various constituents of the system correspond to the proportional properties of these constituents when separate in a pure state. Systems showing energy changes when the constituents are mixed will be considered in later chapters.

Gaseous mixtures do not depart greatly from the laws of ideal solutions in the range of moderate temperatures and pressures. The internal energy of such systems is, therefore, very nearly equal to the sum of the internal energies of the pure constituent gases under corresponding conditions. This is also true of the heat content function H, for gases have PV values of the same order of magnitude at the same temperatures. Accordingly, the heat capacities of the mixture can be calculated from the heat capacities of the pure constituents. Thus, the heat capacity of a system containing 1 mole of hydrogen and $\frac{1}{2}$ mole of oxygen is obtained from the equations in Table 3.3 as follows:

$$\begin{array}{lrl}
\text{For 1 mole of } H_2;\ c_P = & 6.9469 & - 0.1999 \times 10^{-3}T + 4.808 \times 10^{-7}T^2 \\
\text{For } \tfrac{1}{2} \text{ mole of } O_2;\ \tfrac{1}{2}c_P = & 3.074 & + 1.551 \times 10^{-3}T - 4.615 \times 10^{-7}T^2 \\
\hline
\text{Total heat capacity} = & 10.021 & + 1.351 \times 10^{-3}T + 0.193 \times 10^{-7}T^2 \\
 & & \text{cal/deg}
\end{array}$$

Heat Content Equations for Homogeneous Systems.—We observed in Chap. 2 that ordinary thermal measurements do not yield absolute values of E and H. However, we can set up expressions for the relative heat content of systems in terms of temperature if we know the relation between heat capacity and temperature. We observe for the constant-pressure process that, if C_P can be expressed as a function of T, equation (3.6) can be integrated. Thus, if

$$C_P = \alpha + \beta T + \gamma T^2$$

we have

$$\int dH = \int (\alpha + \beta T + \gamma T^2)\, dT \tag{3.25}$$

For the indefinite integral of equation (3.25), we have

$$H = \alpha T + \tfrac{1}{2}\beta T^2 + \tfrac{1}{3}\gamma T^3 + I \tag{3.26}$$

where I is an integration constant. I can be evaluated from the value of H at absolute zero. If the value of H at $T = 0$ is H_0, we have

$$H_0 = I \tag{3.27}$$

The integration constant, therefore, represents the extrapolated value of the heat content at zero absolute. I will, of course, actually equal H_0 only if the original heat capacity equation is valid down to zero absolute.

If we integrate equation (3.25) between the temperature limits $T = 0$, where H has the value H_0, and $T = T_1$, where H has the value H_1, we have

$$\int_{H_0}^{H_1} dH = \int_0^{T_1} (\alpha + \beta T + \gamma T^2)\, dT$$

whence, we obtain

$$H_1 - H_0 = \alpha T_1 + \tfrac{1}{2}\beta T_1^2 + \tfrac{1}{3}\gamma T_1^3 \tag{3.28}$$

Similarly, between the limits T_2 and 0 where H has the respective values H_2 and H_0, we obtain the corresponding equation

$$H_2 - H_0 = \alpha T_2 + \tfrac{1}{2}\beta T_2^2 + \tfrac{1}{3}\gamma T_2^3 \tag{3.29}$$

Thus, between the limits H_1, T_1 and H_2, T_2

$$\int_{H_1}^{H_2} dH = \int_{T_1}^{T_2} (\alpha + \beta T + \gamma T^2)\, dT \tag{3.30}$$

$$H_2 - H_1 = \alpha(T_2 - T_1) + \tfrac{1}{2}\beta(T_2^2 - T_1^2) + \tfrac{1}{3}\gamma(T_2^3 - T_1^3) \tag{3.31}$$

This is, of course, the equation obtained by subtracting (3.28) from (3.29). It represents the change in heat content of a system between any two temperatures for which the heat capacity equation is valid. The corresponding equation for the indefinite integral obtained from (3.26) and (3.27) is

$$H = H_0 + \alpha T + \tfrac{1}{2}\beta T^2 + \tfrac{1}{3}\gamma T^3 \tag{3.32}$$

Again we call attention to the fact that all these equations based on the heat capacity equation cannot be used beyond the temperature range for which the equation is valid.

Problems

For gases, use the heat capacity equations in Table 3.3.

3.1. Find in the "International Critical Tables" (Vol. 5, page 92) the equation for the heat capacity of aluminum over the range 0 to 100°c. With this equation, calculate the value of c_P (in joules) for the temperatures −273, 0, 100, and 300°c. The heat capacity at 0°K is zero. Calculate with the equation, valid over the range 200 to 300°c, the value for c_P at 300°. Compare with the value obtained with the 0 to 100° equation. Explain any discrepancies.

3.2. (*a*) Calculate the heat required to raise 100 grams of nitrogen from 27 to 127°c at constant pressure.

(*b*) Calculate, for 1 mole of nitrogen, (1) the heat capacity at 27°c, (2) that at 127°c, and (3) the mean heat capacity between these temperatures. Could the mean heat capacity have been used in (*a*)? Explain.

3.3. One cubic foot of gas at 740 mm pressure and 20°c with the composition hydrogen, 48 per cent; carbon monoxide, 44 per cent; carbon dioxide, 6 per cent; and water vapor 2 per cent by volume is heated at constant pressure from 20 to 100°c. Calculate the heat absorbed by the gas.

3.4. What is the sign of $(C_P - C_V)$

(*a*) For a gas at 100°c, assuming that $(\partial E/\partial V)_T$ is zero?

(*b*) For water in the temperature range 0 to 10°c, assuming that $(\partial E/\partial V)_T$ is positive?

3.5. Derive equation (3.17)

$$C_P = C_V + \left[V - \left(\frac{\partial H}{\partial P}\right)_T\right]\left(\frac{\partial P}{\partial T}\right)_V$$

3.6. The molar heat capacity of a substance is represented by the equation $c_P = a + bt + ct^2$ where t is the temperature in degrees centigrade. Calculate the value of the parameters α, β, and γ in the equation

$$c_P = \alpha + \beta T + \gamma T^2$$

that represents the heat capacity of the same substance, T being the temperature in degrees Kelvin.

3.7. From the data in Prob. 3.1, calculate the rate of change of heat capacity of aluminum with temperature at 0, 100, 200, and 300°C.

3.8. From the data in Table 3.1, calculate the value of the mean calorie in joules and in defined calories.

3.9. K. J. Frederick and J. H. Hildebrand [*J. Am. Chem. Soc.*, **60,** 1436 (1938)] find that the molar heat capacity of solid iodine is represented by the empirical equation

$$c_P = 13.07 + 3.21 \times 10^{-4}(t - 25)^2$$

between 25°C and the melting point 113.6°C, t being the temperature in degrees centigrade. Calculate the heat required to raise 1 mole of iodine from 25°C to the melting point.

3.10. Derive the heat content equations corresponding to equations (3.26) and (3.31) for a substance whose heat capacity is represented by the equation

$$c_P = a + bT + c'T^{-2}$$

3.11. Plot the heat capacity values in calories per gram, given for water in Table 3.1, against temperature. Calculate the difference in heat content per gram for water at 0° and at 50°; at 50° and at 100°; at 0° and at 100°. Calculate values for the mean heat capacity of water over the temperature ranges, 0 to 50°; 50 to 100°; 0 to 100°. What is the value of the mean calorie in terms of the thermochemical calorie? Compare with the value for the mean calorie obtained in Prob. 3.8.

3.12. (*a*) For the gases listed in Table 3.2, calculate the heat capacities at 1000 and 1500°K, using the heat capacity equations in Table 3.3. Compare the calculated values with the heat capacities given in Table 3.2. Calculate the percentage deviations and compare them with the maximum and average deviations listed in Table 3.3.

(*b*) For these gases (except methane) calculate the heat capacities at 2000 and 3000°K. and compare with the listed heat capacities. Note the stated temperature ranges of the heat capacity equations. This problem illustrates the danger of extrapolating equations expressed as a power series beyond the range for which the equations were derived.

3.13. The difference between the molar heat content of manganese dioxide at the temperatures T and 298.16°K as determined experimentally by G. E. Moore [*J. Am. Chem. Soc.*, **65,** 1398 (1943)] is represented in the range 298 to 780°K by the equation

$$H_T - H_{298.16} = 16.60T + 1.22 \times 10^{-3}T^2 + \frac{388{,}000}{T} - 6{,}359 \text{ cal}$$

From this equation,

(*a*) Calculate the value of the mean heat capacity of manganese dioxide between 300 and 700°K.

(*b*) Derive the heat capacity equation

$$c_P = 16.60 + 2.44 \times 10^{-3}T - \frac{388{,}000}{T^2}$$

CHAPTER 4

APPLICATION OF THE FIRST LAW TO GASES

The pressure, volume, and temperature relations of gases are represented more or less accurately by Boyle's and Charles's laws, so that all gases conform in a general way to a single equation, the ideal gas law equation.

Ideal Gas Law Equation.—The states of all gases that obey Boyle's and Charles's laws may be represented by the equation

$$\frac{P\text{v}}{T} = \frac{P_0\text{v}_0}{T_0} = R \tag{4.1}$$

where v is the molar volume[1] of the gas at the pressure P and the temperature T, and v_0, P_0, and T_0 are the corresponding values under any other conditions including "standard conditions." Since the ratio $P\text{v}/T$ remains constant as P, v, and T vary and has the same value for all gases obeying the above gas laws, it may be represented by a *universal gas constant* ***R***. Real gases conform only approximately to equation (4.1) but follow the equation more and more closely the farther their temperatures rise above the liquefaction temperatures of the gases and the larger their molar volumes. Under these conditions, the interactions of the molecules of the gases become less important. At 0°c, for example, the $P\text{v}$ values for the more permanent gases change slightly as the pressure decreases, the changes being linear at pressures below 2 atmospheres, but they change in such a way that, as the pressure approaches zero, the $P\text{v}$ values for all the gases approach the same value, $(P\text{v})_i$, characteristic of the ideal gas. Thus, at the ice point, 0°c, the limiting value[2] is

$$(P\text{v})_{i,0} = \lim_{P=0} (P\text{v})_0 = 22.4140 \text{ liter-atm} \tag{4.2}$$

A similar limit to $P\text{v}$ is found at the steam point, 100°c. This limiting value, which is 1.36609 times greater than the limiting value at 0°c, enables us through the relations between $P\text{v}$ and T in equation (4.1) to

---

[1] General values of the extensive functions such as energy, volume, heat content, and heat capacity, are printed as large capitals and the corresponding molar values as small capitals.

[2] CRAGOE, CARL S., "Slopes of PV Isotherms of He, Ne, A, H_2, N_2, and O_2 at 0°c," *J. Research Natl. Bur. Standards*, **26**, 495 (1941).

calculate the value for T_0, the temperature of the ice point on the ideal gas temperature scale. The ratio T_{100}/T_0 being 1.36609 and $T_{100} - T_0$ being 100°, we obtain for the temperature of the ice point on the ideal gas scale

$$T_0 = 273.16°\text{K} \tag{4.3}$$

The values from equations (4.2) and (4.3) substituted in equation (4.1) give for the value of the universal gas constant

$$R = 0.082054 \text{ liter-atm/deg mole}$$

In terms of calories, the value is

$$R = 1.9872 \text{ cal/deg mole}$$

From equation (4.1) the *ideal gas equation* for 1 mole of gas may be expressed as

$$(P\text{v})_i = P\text{v} = RT \tag{4.4}$$

For n moles of gas with volume $V = n\text{v}$

$$PV = nRT \tag{4.5}$$

Equations (4.4) and (4.5) are extremely useful for indicating the limiting relations of gases and as simple approximations to the actual relations of real gases. It is to be expected that gases about to condense as solids or liquids are far from ideal in behavior; hence, equation (4.5) cannot be applied without qualification to gases in equilibrium with liquid or solid phases. Any equation representing a solid or liquid that includes the gas constant R must, therefore, be only approximately valid unless other terms have been introduced to represent the deviation from ideal behavior of gases under these experimental conditions.

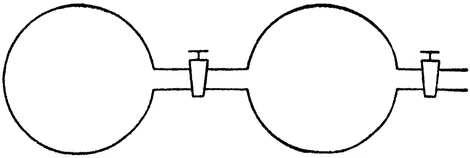


FIG. 4.1.—Apparatus for the free expansion of gases according to the experiments of Gay-Lussac and Joule.

Ideal Gases.—As a first defining equation for an ideal gas we may select either equation (4.4) or (4.5). Whenever we refer to the ideal gas equation without further qualification, we shall mean one of these equations. However, additional relations are important for correlating the thermodynamic behavior of gases with the kinetic theory of gases.

Early experiments by Gay-Lussac (1807) and Joule (1845) indicated that, when gases are expanded without doing work or absorbing heat, as in Fig. 4.1, they do not change in temperature. Under these conditions, the gases evidently did not change in energy to a measurable degree. The energy of the gases, therefore, did not depend on the volume at constant temperature, so that

$$\left(\frac{\partial E}{\partial V}\right)_T = 0 \tag{4.6}$$

Equation (4.6) implies that there are no interactions between the gas molecules which would produce energy changes with changing volume, that is, with the changing distance between the molecules. Later, more careful work showed that actual gases do show a slight change in temperature on expansion under the above conditions. We may consider equation (4.6), as a *second defining equation* for an ideal gas. As we shall see in Chap. 8, equation (4.6) is a consequence of equation (4.5) and the second law of thermodynamics.

If $(\partial E/\partial V)_T = 0$, it follows that $(\partial E/\partial P)_T$ must also equal zero. From equation (4.5), we see that, at constant temperature, P varies inversely with V. If E does not change with changing V, it also does not change with changing P. For the ideal gas $(\partial H/\partial P)_T$, and consequently $(\partial H/\partial V)_T$, also equal zero as may be seen from the following:

On differentiating the general relation

$$H = E + PV$$

with respect to pressure, the temperature being constant, we obtain

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial E}{\partial P}\right)_T + \left[\frac{\partial(PV)}{\partial P}\right]_T \tag{4.7}$$

But, for the ideal gas,

$$\left(\frac{\partial E}{\partial P}\right)_T = 0 \quad \text{and} \quad \left[\frac{\partial(PV)}{\partial P}\right]_T = 0$$

for, at constant temperature, $PV = nRT = \text{const.}$ Hence,

$$\left(\frac{\partial H}{\partial P}\right)_T = 0 \tag{4.8}$$

Real Gases.—Real gases deviate somewhat from the ideal gas equation but to varying degrees at different pressures and temperatures. Figure 4.2 shows how $\frac{P\mathrm{v}}{RT} = \frac{P\mathrm{v}}{(P\mathrm{v})_i}$ for nitrogen changes with pressure at different temperatures. Observe that the deviation of the ratio from unity is greatest for the lowest temperature (−50°c) and that the 50° isotherm is practically ideal at pressures below 50 atmospheres. The figure shows also that, if one is satisfied with deviations of less than 10 per cent, he can use the ideal gas equation for nitrogen for pressures up to 200 atmospheres within the indicated temperature limits. Other gases show deviations of similar types. Gases below their critical temperatures show the greatest deviations. In view of these facts, it is not at all surprising that no single equation has been developed to represent this complex behavior of gases. A great number of different equations of state for gases have been proposed, one of the earliest being the van der Waals equation, which fails at high pressures and in the neighborhood of the critical point, its "constants," a and b, not remaining constant under all conditions. Other equations with more empirical constants may represent the actual data better, but even these may not be extrapolated safely beyond the range for which the constants were derived.

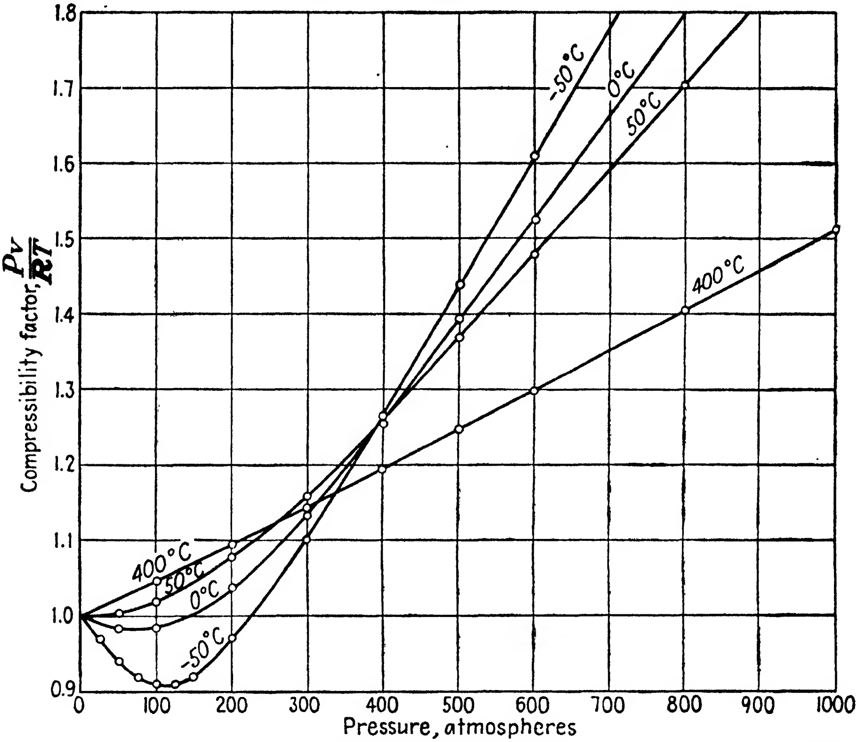


FIG. 4.2.—Deviation of nitrogen from ideal gas behavior. (*Data of E. P. Bartlett, H. L. Cupples, and T. H. Tremearne, J. Am. Chem. Soc.*, **50**, 1275 (1928); *E. P. Bartlett, H. C. Hetherington, H. M. Kvalnes, and T. H. Tremearne, ibid.*, **52**, 1363 (1930).)

Accurate pressure-volume data for gases, usually obtained under the experimental condition of constant temperature, can be represented very closely by equations of the types

$$Pv = A + BP + CP^2 + DP^3 \qquad (4.9)$$

and

$$Pv = A'\left(1 + \frac{B'}{v} + \frac{C'}{v^2} + \frac{D'}{v^3}\right) \tag{4.10}$$

In these equations A, B, C, and D, and A', B', C', and D', respectively, are known as the *first*, *second*, etc., *virial coefficients*, which are functions of temperature and, therefore, have different values for different isotherms. The terms containing coefficients of the higher powers of P (or $1/v$) become important only at high pressures, the values of the coefficients C and D (or C' and D') being small compared with that of B (or B'). As we shall see, the value of B is small compared with that of A. Thus, at low pressure the last terms on the right side of equations (4.9) and (4.10) become negligible.

That A and A' are identical may be seen from the following: As the pressure of a gas approaches zero, the molar volume of the gas becomes infinitely large. Then, the right sides of equations (4.9) and (4.10) reduce to A and A', respectively. At the same time, the Pv value for the gas approaches the limiting value $(Pv)_i$ characteristic of the ideal gas. Therefore,

$$\lim_{P=0} Pv = (Pv)_i = A = A'$$

and from equation (4.4)

$$A = A' = RT \tag{4.11}$$

That B and B' are nearly equal appears from the following: The second terms, BP and $A'B'/v$, respectively, are correction terms to the first term RT, and their value is not altered greatly if RT/P is substituted for v in accordance with the ideal gas relation. Then the second term on the right side of equation (4.10) becomes

$$\frac{A'B'}{v} = RT\frac{B'}{v} = RT\frac{B'P}{RT} = B'P$$

Comparison with equation (4.9) shows that, within the indicated approximation, B' is equal to B. As we have indicated, at low pressures the higher terms in P (or $1/v$) are unimportant and either equation (4.9) or (4.10) takes the form

$$Pv = RT + BP \tag{4.12}$$

This equation represents very well the isothermal expansion of gases at low pressures. It is a linear equation valid for the more permanent gases for pressures up to 2 atmospheres. However, B is a function of temperature so that its value must be determined for each isotherm. Equation (4.12) may be expressed in one of the following forms:

$$P(v - B) = RT \tag{4.13}$$

and

$$B = \mathrm{v} - \frac{RT}{P} = \mathrm{v} - \mathrm{v}_i \tag{4.14}$$

where v_i is the volume of the ideal gas at the pressure P and the temperature T.

Coefficient B.—Equation (4.14) indicates that the "second virial coefficient" B represents the difference between the molar volume of the gas and the volume of the ideal gas at the same pressure and temperature. B also represents the slope of the isotherm obtained when $P\mathrm{v}$ is plotted against P. Thus, on differentiating equation (4.12) with respect to pressure at constant temperature, we obtain

$$\left[\frac{\partial(P\mathrm{v})}{\partial P}\right]_T = B \tag{4.15}$$

Values of B in liters per mole for some gases at 0°C are listed in Table 4.1. Observe that for the gases listed the deviation of $P\mathrm{v}$ from

$$RT = (P\mathrm{v})_i = 22.4140 \text{ liter-atm}$$

is less than 0.1 per cent at $P = 1$. However, this correction must be made for certain purposes.

TABLE 4.1.—DEVIATIONS OF SOME GASES FROM THE IDEAL GAS LAW AT 0°C

$$B = \frac{P\mathrm{v} - (P\mathrm{v})_i}{P}; \qquad \alpha = \frac{B}{\mathrm{v}_0} \doteq \frac{B}{\mathrm{v}_i}$$

Gas	$10^5\alpha$* at 1 atm	B ($\alpha \times 22.41$), in liters/mole
Argon	-94 ± 1	-0.0211 ± 0.0002
Helium	53	0.0119
Hydrogen	61.9	0.0139
Neon	49 ± 1	0.0110 ± 0.0002
Nitrogen	-45.3 ± 0.3	-0.01015 ± 0.00007
Oxygen	-95.1 ± 0.9	-0.0213 ± 0.0002

* CRAGOE, CARL S., *J. Research Natl. Bur. Standards*, **26**, 495 (1941).

For example, from the data of Baxter and Starkweather[1] the density of oxygen is 1.428965 grams per liter at 0°C and 1 atmosphere ($g = 980.616$). Under these conditions, the molar volume of oxygen (molar weight exactly 32 grams by definition) is

$$\frac{32}{1.428965} = 22.3938 \text{ liters}$$

---

[1] BAXTER, G. P., and H. W. STARKWEATHER, *Proc. Natl. Acad. Sci.*, **12**, 703 (1926).

From Table 4.1 the value of B for oxygen is -0.0213 liters. Hence, from equations (4.4) and (4.13), P being 1 atmosphere,

$$(Pv)_i = RT = Pv - BP = 22.3938 - (-0.0213) = 22.4151 \text{ liter-atm}$$

When this value is corrected for the change to our present standard atmosphere ($g = 980.655$) it is decreased by 0.05 per cent to our present value,

$$(Pv)_i = RT = 22.4140 \text{ liter-atm}$$

at 0°C. This is the value previously used in the calculation of the value of the gas constant R.

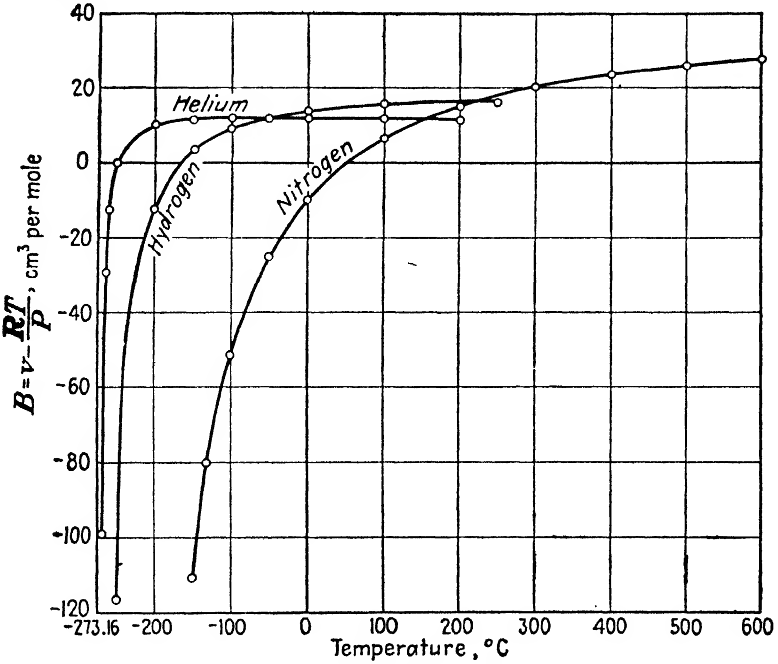


FIG. 4.3.—Variation of the second virial coefficient, B, with temperature.

The ideal molar volume being known it appears that one can, with the aid of the slope B for a gas, find the molar volume of the gas. If the density of the gas is then determined, one has all the data needed to calculate the molar weight of the gas. The method is used for the noble gases that form no compounds and for several other gases as well.

Knowledge of B is also useful in gas thermometry because it offers one method for deriving the temperature on the ideal gas scale from the readings made on the actual gas in a constant-volume or a constant-pressure thermometer. However, for this purpose the variation of B with temperature must be known. Figure 4.3 shows how the values of

B for helium, hydrogen, and nitrogen change with temperature. At low temperatures, B has negative values. As the temperature increases, the value of B increases through the value zero to a maximum positive value characteristic of each gas and then decreases again as the temperature increases indefinitely. The maximum value is shown only for helium, the maxima for hydrogen and nitrogen lying outside the temperature range of the figure. These values are listed in Table 4.2. Another characteristic temperature for each gas is that at which B equals zero. This temperature is called the *Boyle point*, the gas obeying the ideal gas equation over the range for which $\left[\frac{\partial(P\mathrm{v})}{\partial P}\right]_T$ remains zero. Table 4.2 lists the Boyle point of nitrogen as 51°C. As Fig. 4.2 shows, the 50° isotherm for nitrogen has a negligible slope for pressures below 50 atmospheres.

TABLE 4.2.—CHARACTERISTIC TEMPERATURES* OF SOME GASES
(In degrees centigrade)

	Boyle point $B = 0$	Maximum value of B
Helium	−249.1	−77.1
Hydrogen	−165.9	442.8
Nitrogen	51	1867

* KEYES, F. G., "Temperature, Its Measurement and Control in Science and Industry," p. 59, Reinhold Publishing Corporation, New York, 1941.

Some Relations of Real Gases.—For a perfect gas we found that $(\partial E/\partial V)_T$ and $(\partial E/\partial P)_T$ equal zero and that, in consequence, $(\partial H/\partial V)_T$ and $(\partial H/\partial P)_T$ also equal zero. The corresponding derivatives for a real gas represented by equation (4.12) are given below. When this equation is differentiated with respect to pressure at constant temperature, we obtain equation (4.15). On differentiating with respect to volume at constant temperature, we have

$$\left[\frac{\partial(P\mathrm{v})}{\partial \mathrm{v}}\right]_T = 0 + B\left(\frac{\partial P}{\partial \mathrm{v}}\right)_T \tag{4.16}$$

When the defining equation for heat content is differentiated with respect to volume at constant temperature, we obtain an equation corresponding to equation (4.7), namely,

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial E}{\partial V}\right)_T + \left(\frac{\partial(PV)}{\partial V}\right)_T \tag{4.17}$$

Similarly, equation (4.7) gives an equation for the isothermal change of heat content with pressure. But, since

$$\left(\frac{\partial E}{\partial P}\right)_T = \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T \tag{4.18}$$

equation (4.7) may be written

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T \tag{4.19}$$

This equation will be needed later. For the present, it will be instructive to apply it to the real gas obeying equation (4.12). For this gas, from equation (4.15), $\left[\frac{\partial (PV)}{\partial P}\right]_T = B$, and from equation (4.12),

$$\left(\frac{\partial V}{\partial P}\right)_T = \left[\frac{\partial \left(\frac{RT}{P} + B\right)}{\partial P}\right]_T = -\left(\frac{RT}{P^2}\right)_T \tag{4.20}$$

Hence,

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial E}{\partial V}\right)_T \left(-\frac{RT}{P^2}\right)_T + B \tag{4.21}$$

Thus, it appears that $(\partial E/\partial V)_T$ can be evaluated for the real gas if we can find a way to determine $(\partial H/\partial P)_T$.

In the next section we shall consider the variation of $P\text{v}$ with temperature for an ideal gas. For comparison, we find for the real gas obeying equation (4.12)

$$\begin{aligned}\frac{\partial (P\text{v})}{\partial T} &= \frac{\partial (RT)}{\partial T} + \frac{\partial (BP)}{\partial T} \\ &= R + P\left(\frac{\partial B}{\partial T}\right) + B\left(\frac{\partial P}{\partial T}\right)\end{aligned} \tag{4.22}$$

Figure 4.3 indicates how B may vary with temperature. At constant pressure, equation (4.22) becomes

$$P\left(\frac{\partial \text{v}}{\partial T}\right)_P = R + P\left(\frac{\partial B}{\partial T}\right)_P \tag{4.23}$$

At low pressures and high temperatures, the last term in equation (4.23) is small compared with R so that for many real gases equation (4.23) reduces to

$$P\left(\frac{\partial \text{v}}{\partial T}\right)_P = R \tag{4.24}$$

It will be instructive to calculate a value of $(\partial \text{E}/\partial \text{v})_T$ for a real gas. According to Rossini and Frandsen,[1] the value of $(\partial \text{E}/\partial P)_T$ for air and

---

[1] ROSSINI, F. D., and M. FRANDSEN, *Bur. Standards J. Research*, **9**, 733 (1932).

oxygen remained constant for pressures up to 40 atmospheres. For nitrogen at 28°C, they calculate a molar value of −5.97 int joules per atmosphere, the temperature coefficient being −0.4 per cent per degree. At 0°C, therefore, the value becomes −6.64 int joules or −1.59 calories per atmosphere. But, from equations (4.18) and (4.20),

$$\left(\frac{\partial E}{\partial P}\right)_T = -\left(\frac{\partial E}{\partial V}\right)_T \left(\frac{RT}{P^2}\right)_T$$

so that

$$\left(\frac{\partial E}{\partial V}\right)_T = -\frac{\left(\frac{\partial E}{\partial P}\right)_T P^2}{RT}$$

Where $RT = 22.41$ liter-atm, we have for 1 mole of nitrogen at 0°C and 1 atmosphere

$$\left(\frac{\partial E}{\partial V}\right)_{273.16} = \frac{1.59}{22.41} = 0.0710 \text{ cal/liter}$$

Relation between C_V and C_P for an Ideal Gas.—For substances in general, including gases, we derived equation (3.16) which, per mole of substance, is

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

For the special case of ideal gases, $(\partial E/\partial V)_T = 0$ and the equation reduces to

$$C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P \tag{4.25}$$

This equation can be applied to nonideal gases to a fair degree of approximation, for $(\partial E/\partial V)_T$ is small for gases compared with P. If the ideal gas law is differentiated with respect to temperature, the equation

$$\frac{d(PV)}{dT} = R$$

is obtained. Under the condition of constant pressure, this expression can be simplified to

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

which is equation (4.24). Hence, from equation (4.25),

$$C_P - C_V = R \tag{4.26}$$

for a perfect gas. Equation (4.26), though derived for the ideal gas, applies also to real gases, especially at high temperatures. Table 4.3

lists experimental values of $c_P - c_V$ for some gases at 15°c and Table 4.4 lists values up to 2000°c. Observe that, at the higher temperatures, the difference, $c_P - c_V$, approaches the value $R = 1.987$ cal/deg.

TABLE 4.3.—EXPERIMENTAL HEAT CAPACITY RATIOS AND DIFFERENCES IN MOLAR HEAT CAPACITY FOR SOME GASES*

(In calories per degree at 1 atmosphere pressure)

Gas	Temperature, °c	γ	$c_P - c_V$	Gas	Temperature, °c	γ	$c_P - c_V$
Monatomic gases:				Polyatomic gases:			
Argon	0–100	1.67	.....	Ammonia	15	1.310	2.108
Helium	−180	1.66_0	.....	Hydrogen sul-			
Neon	19	1.64	.....	fide	15	1.32	2.092
Mercury	360	1.67	.....	Acetylene	15	1.26	2.057
Sodium	750–920	1.68	.....	Ethylene	15	1.25_5	2.057
Diatomic gases:				Ethane	15	1.22	2.087
Chlorine	15	1.35_5	2.135	Propane	15	1.13	
Hydrogen	15	1.410	1.987	Ethanol	90	1.13	
Hydrogen chlo-				Ethyl ether	35	1.08	
ride	15	1.41	2.057	Benzene	90	1.10	
Nitric oxide	15	1.400	1.996	Cyclohexane	80	1.08	

* Data from the "International Critical Tables," Vol. 5, p. 80, McGraw-Hill Book Company, Inc., New York, 1926.

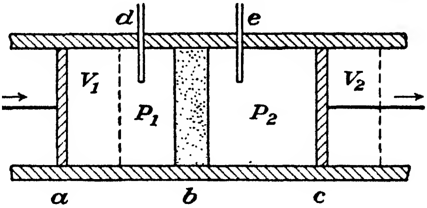
TABLE 4.4.—EXPERIMENTAL VALUES* OF $\frac{c_P}{c_V} = \gamma$ AND OF $c_P - c_V$ FOR SOME GASES AT 1 ATMOSPHERE PRESSURE

(Heat capacity in calories per degree per mole)

Temperature, °c	O_2, N_2, CO		CO_2		H_2O		CH_2	
	γ	$c_P - c_V$	γ	$c_P - c_V$	γ	$c_P - c_V$	γ	$c_P - c_V$
0	1.402	1.99_8	1.310	2.055	.....	.....	1.307	2.008
100	1.399	1.99_1	1.281	2.014	1.324	2.133	1.232	1.996
200	1.396	1.98_9	1.263	2.001	1.31_0	2.043	1.188	1.992
400	1.391	1.98_9	1.235	1.992	1.30_1	1.995	1.139	1.989
600	1.383	1.98_8	1.217	1.989	1.29_0	1.994	1.113	1.988
800	1.375	1.98_8	1.204	1.988	1.27_3	1.991		
1000	1.365	1.98_7	1.195	1.988	1.25_2	1.990		
1400	1.342	1.98_7	1.184	1.987	1.20_6	1.988		
2000	1.303	1.98_7	1.171	1.987	1.15_5	1.988		

* From data in the "International Critical Tables," Vol. 5, pp. 82–83, McGraw-Hill Book Company, Inc., New York, 1926.

Free Expansion of Real Gases.—The early experiments of Joule on the energy change during expansion of a gas not doing work (free expansion) were not suitable for detecting small changes in energy. In a new experiment, Joule and Thomson[1] (Lord Kelvin) observed the change in temperature of a gas when forced through a porous plug with a resulting drop in pressure. The method is indicated in Fig. 4.4 where b is a porous plug resistant enough to a flow of gas to permit a constant difference in pressure between the pressure P_1 of the entering gas and the constant lower pressure P_2 of the gas leaving the plug. If the apparatus is thermally insulated, the process is adiabatic, $q = 0$; hence, from the first law equation,



a,c = Pistons
b = Porous diaphragm
d,e = Thermometers

FIG. 4.4.—Apparatus for the Joule-Thomson expansion of a gas through a porous plug.

$$\Delta E = -w \tag{4.27}$$

Consider a mole of gas with volume v_1, temperature T_1, and energy E_1, forced into the porous plug at the pressure P_1, the pressure being maintained with the piston a. The work done on the gas is $P_1\text{v}_1$ and the work w_1 done by the gas is $P_1\,\Delta V_1 = -P_1\text{v}_1$ since $\Delta V_1 = -\text{v}_1$. When the mole of gas leaves the porous plug at the temperature T_2, energy E_2, and pressure P_2, it has a molar volume of v_2. It does work w_2 against the piston c equal to $P_2\,\Delta V_2 = P_2\text{v}_2$ since $\Delta V_2 = \text{v}_2$. For the pressure change $P_2 - P_1$, a temperature difference $T_2 - T_1$ is observed on thermometers d and e; and, from sufficient data, the limiting ratio $\partial T/\partial P$ is obtained from the experimental values of $\Delta T/\Delta P$ at different pressures.

Now, the energy change in the process is $\Delta\text{E} = \text{E}_2 - \text{E}_1$, and the work done by the gas is $w = w_2 + w_1 = P_2\text{v}_2 - P_1\text{v}_1$ so that from equation (4.27) we have

$$\text{E}_2 - \text{E}_1 = P_1\text{v}_1 - P_2\text{v}_2 \tag{4.28}$$

This may be rearranged to

$$\text{E}_2 + P_2\text{v}_2 = \text{E}_1 + P_1\text{v}_1$$

Comparison with the definition $\text{H} = \text{E} + P\text{v}$ shows that

$$\text{H}_2 = \text{H}_1 \tag{4.29}$$

There is no change in the heat content (enthalpy) during the process. The process is isenthalpic.

---

[1] JOULE, J. P., and W. THOMSON, *Proc. Roy. Soc. (London)*, **143**, 357 (1853).

The change of temperature with pressure at constant heat content is called the *Joule-Thomson coefficient* μ; it is represented by

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H \tag{4.30}$$

Let us now see how the Joule-Thomson coefficient may be used to calculate the change in energy with volume. Using the method of equation (1.9), we have for 1 mole

$$d\text{H} = \left(\frac{\partial \text{H}}{\partial P}\right)_T dP + \left(\frac{\partial \text{H}}{\partial T}\right)_P dT \tag{4.31}$$

But, because H is constant for this experiment, $d\text{H} = 0$. On rearranging (4.31) and dividing by dP, we have

$$\left(\frac{dT}{dP}\right)_H = -\frac{(\partial \text{H}/\partial P)_T}{(\partial \text{H}/\partial T)_P} \tag{4.32}$$

But $(\partial T/\partial P)_H = \mu$ and $(\partial \text{H}/\partial T)_P = c_P$; hence,

$$\left(\frac{\partial \text{H}}{\partial P}\right)_T = -\mu c_P \tag{4.33}$$

But equation (4.19), derived earlier, is applicable here so that for 1 mole

$$-\mu c_P = \left(\frac{\partial \text{E}}{\partial \text{v}}\right)_T \left(\frac{\partial \text{v}}{\partial P}\right)_T + \left[\frac{\partial (P\text{v})}{\partial P}\right]_T \tag{4.34}$$

These conclusions are not restricted to gases, for at no point have we made restrictive approximations applicable to gases alone. The equations and the methods are applicable to liquids and solutions also. Table 4.5 lists the values of μ for carbon dioxide at various temperatures and pressures. Values are given for liquid carbon dioxide as well as for the gas.

For a perfect gas, $(\partial \text{E}/\partial \text{v})_T$ and $[\partial(P\text{v})/\partial P]_T$ are zero; hence, μ must be zero. For hydrogen and helium at ordinary pressures and temperatures, μ is negative, that is, the gases become warmer on free expansion. All other gases cool when expanded. At low temperatures, hydrogen and helium become "normal"; the temperature at which μ changes sign, that is $\mu = 0$, is called the *inversion temperature.* As Table 4.5 indicates, the inversion temperature depends on the pressure.

We may again calculate the value of $(\partial \text{E}/\partial \text{v})_T$ for nitrogen, using Joule-Thomson data. When equation (4.34) is rearranged, it becomes

$$\left(\frac{\partial \text{E}}{\partial \text{v}}\right)_T = \frac{-\mu c_P - \left[\dfrac{\partial (P\text{v})}{\partial P}\right]_T}{\left(\dfrac{\partial \text{v}}{\partial P}\right)_T} \tag{4.35}$$

If nitrogen is represented by the relations in equations (4.15) and (4.20), it appears that equation (4.35) may be written

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{-\mu c_P - B}{-\left(\frac{RT}{P^2}\right)} = \frac{\mu c_P + B}{RT} P^2 \tag{4.36}$$

TABLE 4.5.—JOULE-THOMSON EFFECT FOR CARBON DIOXIDE*
(Values of $\mu = (dT/dP)_H$ in degrees per atmosphere at several temperatures and pressures)

Temperature, °C	Pressure, atmospheres					State
	1	20	60	100	200	
300	0.2650	0.2425	0.2080	0.1872	0.1505	Gas
200	0.3770	0.3575	0.3400	0.3150	0.2455	
100	0.6490	0.6375	0.6080	0.5405	0.2555	
50	0.8950	0.8950	0.8800	0.5570	0 0930	
0	1.2900	1.4020	0.0370	0.0215	0.0045	Liquid
−25	1.6500	0.0000	−0.0028	−0.0050	−0.0115	
−50	2.4130	−0.0140	−0.0150	−0.0160	−0.0248	
−75		−0.0200	−0.0200	−0.0228	−0.290	

* Values of J. R. Roebuck, T. A. Murrell, and E. E. Miller, *J. Am. Chem. Soc.*, **64**, 400 (1942).

The value for μ for nitrogen at 1 atmosphere and 0°C is given by Roebuck and Murrell[1] as 0.2655 degree per atmosphere. By extrapolating the heat capacity equation for nitrogen in Table 3.3 to 0°C, we have $c_P = 6.865$ calories or 0.2835 liter-atmosphere per degree. From Table 4.1 the value of B is -0.0105 liter. Consequently, at 1 atmosphere,

$$\left(\frac{\partial E}{\partial V}\right)_{273.16} = \frac{(0.2655)(0.2835) - 0.01015}{22.41}$$
$$= 2.906 \times 10^{-3} \text{ liter-atm/liter}$$
$$= 0.0704 \text{ cal/liter}$$

This value agrees well with that calculated in a previous section from different data.

Isothermal Expansion of an Ideal Gas.—For an ideal gas, we found that $(\partial E/\partial V)_T = 0$. This means that the energy of a definite amount of the ideal gas is a function of the temperature alone and does not change during an isothermal expansion. From the first law equation, therefore,

$$\Delta E = q - w = 0; \qquad q = w \tag{4.37}$$

In differential form, this becomes $Dq = Dw$.

---

[1] ROEBUCK, J. R., and T. A. MURRELL, "Temperature, Its Measurement and Control in Science and Industry," p. 70, Reinhold Publishing Corporation, New York, 1941.

Previously, we found that the work of expansion is given by the equation

$$\mathrm{D}w = P'\,\mathrm{d}V; \qquad w = \int P'\,\mathrm{d}V \tag{4.38}$$

where P' is the opposing pressure. In general, equation (4.38) can be evaluated only if we know how P' changes with V.

Irreversible Expansion.—The most completely irreversible expansion of the gas is the free expansion into a vacuum as in Fig. 4.1. Here $P' = 0$ and $\mathrm{D}w = 0$. Hence, q is also zero. Thus, the free expansion of an ideal gas is adiabatic as well as isothermal.

The maximum work of expansion will occur when P' has a value only slightly less than the pressure P of the gas. The expansion then approaches reversible expansion, and the work of expansion is the reversible work w_r. Thus, the work in an irreversible isothermal expansion may range from zero to w_r, and the heat absorbed, q, which equals w, will range between the same limits.

Reversible Expansion.—For the reversible expansion, $P' = P$ which, for the ideal gas, equals nRT/V. From equation (4.38), the reversible work w_r for the isothermal expansion between the limits $V = V_1$ and $V = V_2$ is, therefore,

$$w_r = \int_{V_1}^{V_2} P\,\mathrm{d}V = nRT \int_{V_1}^{V_2} \frac{\mathrm{d}V}{V} = nRT \ln \frac{V_2}{V_1} \tag{4.39}$$

The reversible heat absorbed in the expansion, from equation (4.37), is

$$q_r = w_r = nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{P_1}{P_2} \tag{4.40}$$

It is evident that the work in the isothermal reversible expansion depends only on the ratio of the initial and final volumes (or pressures) and not on their absolute values. It takes as much work to compress a sample of ideal gas from 10 to 1 ml, as from 10 to 1 liter or from 1,000 to 100 liters.

Adiabatic Expansion of an Ideal Gas.—In an adiabatic process, no heat is exchanged so that we have, from the first law equation,

$$\begin{aligned} \Delta E &= -w \\ \mathrm{d}\bar{E} &= -\mathrm{D}w \end{aligned} \tag{4.41}$$

Since the energy of a definite amount of an ideal gas is a function of the temperature only, we may write

$$\left(\frac{\partial E}{\partial T}\right)_V = \frac{\mathrm{d}E}{\mathrm{d}T}$$

But, if energy depends only on the temperature, the heat capacity at constant volume which measures the energy change with temperature must also depend only on the temperature and not on the volume at which the heat capacity is measured. Therefore, from equation (3.2) we have

$$dE = C_V\,dT \tag{4.42}$$

Thus, the change in energy of the ideal gas may be expressed as a function of the heat capacity at constant volume and the temperature. The work of expansion being $Dw = P'\,dV$, we have, from equation (4.41) for an adiabatic expansion,

$$-Dw = dE = C_V\,dT = -P'\,dV \tag{4.43}$$

Irreversible Expansion.—In the free expansion of an ideal gas, we found that dE, Dq, and Dw have zero values. Since dV and C_V have positive values, from equation (4.43) dT and P' must also be zero. In other words, the expansion is isothermal and at the same time adiabatic as we found earlier. For real gases, P' being still zero, a change of T in the expansion means a change in E with volume.

Reversible Expansion.—For the reversible, adiabatic expansion P' equals P, and for a mole of gas $P = RT/\mathrm{v}$ so that, from equation (4.43),

$$-Dw_r = c_V\,dT = -\frac{RT}{\mathrm{v}}\,d\mathrm{v} = -RT\,d\ln\mathrm{v} \tag{4.44}$$

Hence,

$$w_r = -\int_{T_1}^{T_2} c_V\,dT = -R\int_{V_1}^{V_2} T\,d\ln\mathrm{v} \tag{4.45}$$

The integrals in equation (4.45) can be evaluated if we know how c_V varies with T or how T varies with v. The gases most nearly ideal at ordinary conditions have heat capacities that vary only slightly with temperature. The monatomic gases in particular have nearly constant heat capacities. We shall, therefore, *define an ideal gas* further as one with a constant heat capacity. Hence, for the ideal gas,

$$w_r = -c_V\int_{T_1}^{T_2} dT = -c_V(T_2 - T_1) \tag{4.46}$$

We may obtain the reversible work for a real gas from the integral in equation (4.45) if we can express c_V as a function of T.

Equation (4.44) can be divided by T, so that

$$c_V\frac{dT}{T} = -R\,d\ln\mathrm{v}$$

But $dT/T = d\ln T$, hence

$$c_V\,d\ln T = -R\,d\ln\mathrm{v}$$

c_V for a perfect gas being constant, we may integrate this equation between the limits T_1, v_1 and T_2, v_2, and obtain the relation

$$c_V \ln \frac{T_2}{T_1} = -R \ln \frac{\mathrm{v}_2}{\mathrm{v}_1} = R \ln \frac{\mathrm{v}_1}{\mathrm{v}_2} \tag{4.47}$$

The negative sign indicates that T decreases as v increases, that is, that the gas cools on expansion.

Since $\mathrm{v} = RT/P$, equation (4.47) may be transformed to

$$c_V \ln \frac{T_2}{T_1} = R \ln \frac{RT_1/P_1}{RT_2/P_2} = R\left(\ln \frac{P_2}{P_1} + \ln \frac{T_1}{T_2}\right)$$

Therefore,

$$c_V \ln \frac{T_2}{T_1} + R \ln \frac{T_2}{T_1} = R \ln \frac{P_2}{P_1}$$

But, from equation (4.26), $c_V + R = c_P$; hence,

$$c_P \ln \frac{T_2}{T_1} = R \ln \frac{P_2}{P_1} \tag{4.48}$$

If we divide equation (4.48) by (4.47), we obtain

$$\frac{c_P}{c_V} = \gamma = \frac{\ln (P_2/P_1)}{\ln (\mathrm{v}_1/\mathrm{v}_2)} \tag{4.49}$$

This equation indicates a simple method for obtaining γ, the ratio c_P/c_V, from measurements on P_2/P_1 and $\mathrm{v}_1/\mathrm{v}_2$ during adiabatic expansion. From equation (4.49), we obtain

$$\gamma \ln \frac{\mathrm{v}_1}{\mathrm{v}_2} = \ln \frac{P_2}{P_1}$$

Therefore,

$$\left(\frac{\mathrm{v}_1}{\mathrm{v}_2}\right)^{\gamma} = \frac{P_2}{P_1}$$

$$P_1\mathrm{v}_1^{\gamma} = P_2\mathrm{v}_2^{\gamma} = \text{const} \tag{4.50}$$

Compare this equation with that for the isothermal expansion of a gas (Boyle's law).

Carnot Cycle for an Ideal Gas.—For future use, we shall consider here the reversible work obtained with an ideal gas in a Carnot cycle, which is discussed in more detail in Chap. 7. Consider an ideal gas in an initial state A. It is expanded reversibly and isothermally to state B and then expanded reversibly and adiabatically to state C. The gas is then compressed reversibly and isothermally to state D so chosen that, when the gas is now compressed reversibly and adiabatically, it returns to its initial state A. Such a series of changes resulting in a return to the initial state is called a *cycle*, this particular series of isothermal and adiabatic changes forming the Carnot cycle. It must not be assumed that the Carnot cycle is restricted to ideal gases or even to gases, but we have just derived the relations for ideal gases and shall apply them to this cycle.

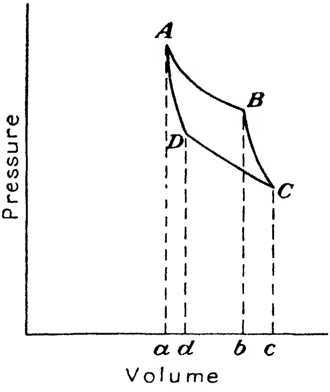


FIG. 4.5.—The Carnot cycle.

The various stages of the cycle are shown in Fig. 4.5, on a pressure-volume diagram. From the equations previously derived for reversible, isothermal expansion and reversible, adiabatic expansion of an ideal gas, we may summarize the quantities for the several stages.

Stage AB. Isothermal Expansion. $T_A = T_B = T_2$

$$\Delta E = 0$$

$$q_{BA} = w_{BA} = nRT_2 \ln \frac{V_B}{V_A}$$

Stage BC. Adiabatic Expansion. $q = 0$

$$q_{CB} = 0$$

$$E_C - E_B = -w_{CB} = C_V(T_1 - T_2)$$

Stage CD. Isothermal Compression. $T_C = T_D = T_1$

$$\Delta E = 0$$

$$q_{DC} = w_{DC} = nRT_1 \ln \frac{V_D}{V_C}$$

Stage DA. Adiabatic Compression. $q = 0$

$$q_{AD} = 0$$

$$E_A - E_D = -w_{AD} = C_V(T_2 - T_1)$$

Before we summarize the results for the cycle, we shall show that $V_B/V_A = V_C/V_D$. We see from equation (4.47) that the ratio of the volumes of a definite amount of gas in an adiabatic expansion between two temperatures is determined by the ratios of the temperatures, C_V and R being constant. Consequently,

$$\frac{V_B}{V_C} = \frac{V_A}{V_D} \quad \text{and} \quad \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

Total Cycle.—The total change in energy for the cycle is zero, the gas having returned to its initial state. Since $E_A = E_B$ and $E_C = E_D$, we have for the four stages

$$\Delta E = 0 + E_C - E_B + 0 + E_A - E_D = 0$$

Let the total reversible work for the cycle be designated as w_r, the heat absorbed q_{BA} in the *reversible expansion* at the temperature T_2 be designated as q_2, and the heat absorbed q_{DC} in the *reversible compression* at the temperature T_1 be designated as q_1. Then the total reversible work done by the gas in the cycle is

$$\begin{aligned} w_r &= w_{BA} + w_{CB} + w_{DC} + w_{AD} \\ &= nRT_2 \ln \frac{V_B}{V_A} - C_V(T_1 - T_2) - nRT_1 \ln \frac{V_B}{V_A} - C_V(T_2 - T_1) \\ &= nR \ln \frac{V_B}{V_A} (T_2 - T_1) \qquad (4.51) \end{aligned}$$

The heat absorbed during the reversible expansion along the path ABC is

$$q_2 = q_{BA} = nRT_2 \ln \frac{V_B}{V_A} \qquad (4.52)$$

and that absorbed during the reversible compression along the path CDA is

$$q_1 = q_{DC} = -nRT_1 \ln \frac{V_B}{V_A} \qquad (4.53)$$

q_1 having a negative value because heat is evolved during the compression. The total heat absorbed is, consequently,

$$q_2 + q_1 = nR \ln \frac{V_B}{V_A} (T_2 - T_1) \qquad (4.54)$$

and, since $\Delta E = 0$, equation (4.54) equals equation (4.51). Thus, for the process we find that

$$q_2 + q_1 = w_r \qquad (4.55)$$

and, from equations (4.51) to (4.53),

$$\frac{q_2}{T_2} = \frac{-q_1}{T_1} = \frac{w_r}{T_2 - T_1} \qquad (4.56)$$

In this cycle for the ideal gas, the heat absorbed at T_2 and the heat evolved at T_1 are found to be proportional to the temperatures on the ideal gas scale, and the reversible work is proportional to the temperature difference. When there is no temperature difference, no total work is done in the cycle. These results based on the behavior of the ideal gas are discussed in more detail in connection with the second law of thermodynamics in Chap. 7.

We are reminded again, that the heat and work for a given change—for example, from state A to state C—depend on the path. Along the path ABC, the heat absorbed on expansion is

$$q_{CBA} = q_2 = nR \ln \frac{V_B}{V_A} T_2$$

and the work done is

$$w_{CBA} = nR \ln \frac{V_B}{V_A} T_2 + C_V(T_2 - T_1)$$

Along the path *ADC*, the heat absorbed on expansion (not compression) is

$$q_{CDA} = -q_1 = nR \ln \frac{V_B}{V_A} T_1$$

and the work done is

$$w_{CDA} = nR \ln \frac{V_B}{V_A} T_1 + C_V(T_2 - T_1)$$

Since

$$w_{CBA} - w_{CDA} = nR \ln \frac{V_B}{V_A} (T_2 - T_1)$$

and

$$q_{CBA} - q_{CDA} = q_2 + q_1 = nR \ln \frac{V_B}{V_A} (T_2 - T_1)$$

it appears that both the reversible heat and the reversible work depend on the path followed in the change.

Heat Capacity of Gases from the Kinetic Theory.—Although thermodynamics is not directly concerned with molecular theories, interesting and instructive conclusions may be drawn from a comparison of equations derived from the kinetic theory with the empirical equations obtained from the experimental data. Let us consider a mole of ideal gas composed of N molecules at the temperature T, and assume that the internal energy E is entirely an attribute of the kinetic energies of the individual molecules and their components. For an ideal monatomic gas, in which there is no rotational energy of the molecules or vibrational energy of the atoms within the molecules, the internal energy is the sum of the translational kinetic energies of the individual molecules. For a single molecule with mass m and velocity u_1, the kinetic energy ϵ_1 is given by

$$\epsilon_1 = \tfrac{1}{2} m u_1^2 \tag{4.57}$$

The velocity u_1 has components along the x-, y-, and z-axes. Not all the molecules have the same velocity, some moving much faster and some much slower than the average. Indeed, at different times any single molecule travels at different velocities, depending on the exchange of energy by collision with the other molecules. The average kinetic energy $\bar{\epsilon}$ of a single molecule is given by

$$\bar{\epsilon} = \frac{\epsilon_1 + \epsilon_2 + \epsilon_3 + \cdots \epsilon_N}{N} \tag{4.58}$$

From equation (4.57), which shows the relation between the ϵ's and the

u's for the individual molecules, we have, on substitution in equation (4.58),

$$\bar{\epsilon} = \frac{1}{2} m \frac{u_1^2 + u_2^2 + u_3^2 + \cdots u_N^2}{N} = \frac{1}{2} m\overline{u^2} \tag{4.59}$$

where $\overline{u^2}$ is the *mean square velocity*. The rms velocity $\sqrt{\overline{u^2}} = \sqrt{\Sigma u^2/N}$ is not the average velocity of the molecules which is $\Sigma u/N$. Since there are N molecules in the mole of gas, the total internal energy of the gas is

$$\text{E} = N\bar{\epsilon} = \tfrac{1}{2}Nm\overline{u^2} \tag{4.60}$$

Now, from a study of the pressure exerted by the molecules on the walls of the containing vessel, it can be shown that

$$P\text{v} = \tfrac{1}{3}Nm\overline{u^2} \tag{4.61}$$

When this equation is compared with the ideal gas equation $P\text{v} = RT$, it is evident that

$$P\text{v} = RT = \tfrac{1}{3}Nm\overline{u^2} = (\tfrac{2}{3})(\tfrac{1}{2}Nm\overline{u^2}) \tag{4.62}$$

whence, from equation (4.60)

$$RT = \tfrac{2}{3}\text{E} \tag{4.63}$$

This equation shows that the internal energy of the ideal monatomic gas varies directly with the absolute temperature.

The heat capacity at constant volume for such a gas is approximately 3 calories per degree, for we have, from equation (3.2),

$$\text{C}_V = \left(\frac{d\text{E}}{dT}\right)_V = \frac{3}{2} R = 2.981 \text{ cal/deg} \tag{4.64}$$

The heat capacity at constant pressure, obtained with the aid of equation (4.26), is R calories per degree greater (approximately 5 calories per degree).

$$\begin{aligned} \text{C}_P &= \left(\frac{\partial \text{H}}{\partial T}\right)_P = \text{C}_V + R \\ &= \tfrac{3}{2}R + R = \tfrac{5}{2}R = 4.968 \text{ cal/deg} \end{aligned} \tag{4.65}$$

These values are found experimentally for the monatomic gases and for hydrogen at temperatures below 40°K. Some C_V values for hydrogen are listed in Table 4.6.

For gases, the heat capacity ratio $\text{C}_P/\text{C}_V = \gamma$ can be measured more accurately than either C_P or C_V. As stated earlier, the experimental values of C_V are best obtained from the measured values of C_P and γ. Values of γ for some gases are given in Tables 4.3 and 4.4.

From equations (4.64) and (4.65) we see that the kinetic theory gives a simple ratio for c_P/c_V. For the monatomic gas,

$$\frac{c_P}{c_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.667 \tag{4.66}$$

The values of γ for all the monatomic gases are near this value. As we shall see, the ratio becomes smaller for more complicated molecules.

TABLE 4.6.—MOLAR HEAT CAPACITY OF ORDINARY HYDROGEN ($\frac{1}{4}$ *para* + $\frac{3}{4}$ *ortho*) CALCULATED FROM SPECTROSCOPIC DATA*
(In calories per degree)

Temperature, °K	c_V	Temperature, °K	c_V
0	2.980	150	4.087
20	2.980	175	4.341
30	2.980	200	4.536
40	2.982	225	4.602
50	2.990	250	4.785
75	3.116	273.1	4.854
100	3.411	298.1	4.905
125	3.815		

* GIAUQUE, W. F., *J. Am. Chem. Soc.*, **52**, 4816 (1930).

Heat Capacity of Diatomic Molecules.—According to the principle of the equipartition of energy in classical mechanics, the energy of a system is equally divided among the "degrees of freedom." If a gas has only translational energy, there are 3 degrees of freedom corresponding to the three rectangular coordinates x, y, and z. Associated with each degree of freedom is one-third the energy, and at constant volume the heat capacity for each degree of freedom is then $\frac{1}{2}R$. However, if the molecule of gas under consideration is diatomic, or linear if polyatomic, and, therefore, not a perfect sphere but dumbbell-shaped, collisions will produce rotational motion of the molecule in two planes, introducing 2 more degrees of freedom. Such a gas has 5 degrees of freedom, 3 translational and 2 rotational, and the molar heat capacity is

$$c_V = 5 \times \tfrac{1}{2}R = \tfrac{5}{2}R = 4.968 \text{ cal/deg} \tag{4.67}$$

$$c_P = \tfrac{5}{2}R + R = \tfrac{7}{2}R = 6.955 \text{ cal/deg} \tag{4.68}$$

Diatomic molecules, such as nitrogen and carbon monoxide, have these heat capacities at room temperature. Here, too, the heat capacity ratio c_P/c_V takes on a simple form

$$\frac{c_P}{c_V} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = \frac{7}{5} = 1.400 \tag{4.69}$$

This is the value of γ for many diatomic molecules at room temperatures. At low temperatures, the ratio tends to increase while c_P decreases. The reverse relation is found at high temperatures. Since 3 degrees of freedom may be assigned to each atom, the two atoms in a diatomic molecule have a maximum of 6 degrees of freedom and, therefore, the possibility of a vibrational degree of freedom in addition to translation and rotation. It appears, therefore, that, at low temperatures, diatomic molecules do not have complete rotation and that, at high temperatures, vibration of the atoms in the molecule arises. In this way, the heat capacity exceeds that predicted for 5 degrees of freedom.

The data for hydrogen in Table 4.6 illustrate this behavior. At 0°C = 273.1°K, the value of c_V lies slightly below the theoretical value for the diatomic gas. However, c_V decreases rapidly with decreasing temperature until its value approaches that of a monatomic gas with but 3 degrees of freedom. Here rotation ceases, and γ approaches the monatomic gas limit 1.67. In terms of the kinetic theory, we must assume that the molecule acquires rotational energy slowly, and in a way not accounted for by the classical prequantum theory. At higher temperatures the heat capacity increases above the classical diatomic gas value, as shown in Table 3.2, and the value of γ decreases, facts indicating that new types of energy absorption such as vibration of atoms or excitation of electrons have arisen in the hydrogen molecules.

Heat Capacity of Polyatomic Molecules.—A triatomic, nonlinear molecule may rotate in a third plane and have 3 rotational as well as 3 translational degrees of freedom. For such a gas in the absence of vibration of the atoms in the molecule,

$$c_V = 6 \times \tfrac{1}{2}R = 3R = 5.962 \text{ cal/deg} \tag{4.70}$$

$$c_P = 3R + R = 4R = 7.949 \text{ cal/deg} \tag{4.71}$$

Here the ratio c_P/c_V is

$$\frac{c_P}{c_V} = \frac{4R}{3R} = \frac{4}{3} = 1.333 \tag{4.72}$$

As Table 4.3 shows, this is the value at room temperature approached by the simple polyatomic gases. However, some polyatomic gases, such as CH_4, C_2H_6, C_2H_5OH, and $(C_2H_5)_2O$, show abnormally high heat capacities and low values of γ. Apparently, heat is absorbed, also, in the form of vibrational energy and of rotational energy within the molecules. If so, increased temperature should favor such vibrations and internal rotations and lead to increased heat capacities. We have seen that as c_P and c_V both increase, their ratio γ decreases. As Tables 3.2 and 4.4 show, these effects at higher temperatures are prominent in the organic gases such as methane, but they are evident also for the simpler gases N_2 and O_2.

At the higher temperatures, the difference $c_P - c_V$ approaches the value $R = 1.987$ cal/deg $= 8.314$ joules/deg. The rapid increase in c_P for gases is, therefore, paralleled by the increase in c_V. These increases in energy must result from new types of energy absorption. Let the number of new types of energy absorption in addition to the translational energy be represented by X. For each new type, the heat capacity will be increased by $\frac{1}{2}R$, and the total heat capacity of such a gas will be

$$c_P = \frac{3}{2}R + R + \frac{X}{2}R = \frac{5 + X}{2}R \tag{4.73}$$

With this equation, we may obtain the value of X from the experimental heat capacity.

Thus, for methane at 25°C, we have

$$\frac{5 + X}{2} \times 1.99 = 8.54$$

$$X = \frac{8.54 \times 2}{1.99} - 5 = 3.60$$

The 3 rotational degrees of freedom of the molecule are, therefore, not sufficient to account for the heat capacity of methane. At 1000°K, we have from Table 3.2, $c_P = 17.21$, so that $X = 12.3$. At these temperatures, vibrational energy becomes large enough to favor decomposition of the molecule. Observe, however, that even at this temperature the oxygen, nitrogen, and carbon dioxide have but a relatively small increase in heat capacity.

The variation of the heat capacity of hydrogen and of the other gases cannot be explained by the classical mechanics; the explanation is found in the quantum theory. Because of this and other facts, we believe that energy is not absorbed in a continuous manner but in small units of energy called *quanta*. Before a molecule can rotate, it must acquire a definite amount of energy; before it can change its velocity of rotation, it must acquire another quantum of energy. Vibrational energy is also acquired in quanta. The heat absorption of a single molecule therefore proceeds in a stepwise manner. However, if a sufficiently large number of molecules are dealt with, experimental results are obtained which are *averages;* such averages will vary in a continuous manner, for the quantum is very small compared with the total amount of energy considered in ordinary systems by the chemist. Even though the heat capacity of a single molecule would be represented by a steplike curve, the heat capacity of a macroscopic portion of the same substance can be accurately represented by a smooth empirical curve and fairly well by equations such as those in Table 3.3.

Problems

4.1. (*a*) The ratio of the PV product for an ideal gas at 0°c and 1 atmosphere pressure to the PV product of air at the same temperature and pressure is 1.00061. At this temperature and pressure, the molar volume of an ideal gas is 22.4140 liters. What is the molar volume of air under these conditions?

(*b*) Calculate the value of B for air at 0°c from the data in (*a*). Calculate the value of B from the data in Table 4.1, assuming that air is 78 per cent nitrogen, 21 per cent oxygen, and 1 per cent argon. Compare the two results.

4.2. Where the value of PV for a sample of air at 0°c and 1 atmosphere pressure is $PV = 1.0000$ liter-atm, the value of PV as a function of pressure up to 100 atmospheres is given by the equation

$$PV = 1.0006 - 0.0_3603P + 0.0_5302P^2$$

Calculate the value of $(\partial V/dP)_T$ and $[\partial(PV)/\partial P]_T$ at 1 atmosphere and at 100 atmospheres pressure. If v is the molar volume of air obtained from Prob. 4.1, what are the corresponding values of $(\partial \mathrm{v}/\partial P)_T$ and $[\partial(P\mathrm{v})/\partial P]_T$?

4.3. Rossini and Frandsen [*Bur. Standards J. Research,* **9,** 733 (1932)] report −6.08 joules per atmosphere as the value of $(\partial \mathrm{E}/\partial P)_T$ for 1 mole of air at 28°c between the pressures 0 to 40 atmospheres. The change in this value per degree rise in temperature is −0.4 per cent. Calculate the value of $(\partial \mathrm{E}/\partial P)_T$ in calories per atmosphere and in liter-atmospheres per atmosphere at 0°c. With the aid of the data in Prob. 4.2, calculate the values at 0°c of $(\partial \mathrm{E}/\partial \mathrm{v})_T$ and $(\partial \mathrm{H}/\partial P)_T$ for 1 mole of air at 1 atmosphere and at 40 atmospheres.

4.4. Show that for the adiabatic expansion of n moles of perfect gas,

$$\log \frac{P_2}{P_1} = \gamma \log \frac{V_1}{V_2} \tag{4.74}$$

4.5. Derive the equation

$$\left(\frac{\partial \mathrm{E}}{\partial P}\right)_T = -c_P\left(\frac{\partial T}{\partial P}\right)_H - \left(\frac{\partial (P\mathrm{v})}{\partial P}\right)_T \tag{4.75}$$

4.6. From the data on carbon dioxide in the "International Critical Tables," Vol. 3, pages 10–11, calculate the value for the change in PV with pressure at 100°c and 100 atmospheres. From this value and the Joule-Thomson coefficient, calculate the value of $(\partial \mathrm{E}/\partial P)_T$ per mole of carbon dioxide in calories per atmosphere and in liter-atmospheres per atmosphere.

4.7. A mole of nitrogen at 27°c and 1 atmosphere is expanded adiabatically to a final pressure of 0.1 atmosphere. Calculate the final temperature t in degrees centigrade. Assume that c_P for nitrogen is 29.0 joules per degree in this temperature range and that nitrogen obeys the ideal gas laws.

4.8. What is the final temperature of 1 gram of nitrogen expanded under the same conditions (27°c and 1 atmosphere adiabatically to 0.1 atmosphere and t°)? Of m grams?

4.9. Calculate the work done by the nitrogen during the expansions described in Probs. 4.7 and 4.8.

4.10. Calculate the work that is done by the mole of nitrogen in expanding reversibly and isothermally from 1 to 0.1 atmosphere, (*a*) at 27°c, (*b*) at the temperature t found in Prob. 4.7. Compare with the result of Prob. 4.9.

4.11. What work is done by a mole of nitrogen at 27°c in expanding from 1 atmosphere into a vacuum until the final pressure is 0.1 atmosphere? If no heat is exchanged with the surroundings, what is the final temperature of the gas? Assume that nitrogen here behaves as a perfect gas.

4.12. For a real gas obeying equation (4.12), show that at zero pressure

$$[\partial(P\text{v})/\partial P]_T = \text{const}$$

and that $[\partial(P\text{v})/\partial \text{v}]_T = 0$. For this gas show that at zero pressure, if $(\partial \text{E}/\partial \text{v})_T = 0$, $(\partial \text{H}/\partial \text{v})_T = 0$, and $(\partial \text{H}/\partial P)_T$ has a finite value.

4.13. Calculate the work required to compress 1,000 liters of a perfect gas at 1 atmosphere isothermally until the final volume is (*a*) 100 liters, (*b*) 10 liters, (*c*) 1 liter.

4.14. One mole of a perfect diatomic gas with a constant heat capacity has as its initial volume and temperature, 10 liters and 100°c, respectively. The gas is expanded and cooled reversibly until its final volume and temperature are 100 liters and 0°c, respectively, by one of the two following paths:

(*a*) The gas is first expanded adiabatically and reversibly until its temperature is 0°c and then expanded isothermally and reversibly until its final volume is 100 liters.

(*b*) The gas is first expanded isothermally and reversibly at 100°c until its volume has the proper value, and then expanded adiabatically and reversibly to its final state of 0°c and 100 liters. For each of the two indicated reversible paths, calculate the work done by the gas and the heat absorbed by it.

4.15. From the data in Table 4.5, calculate the change of heat content with pressure for carbon dioxide at 0°c and 1 atmosphere; 0°c and 100 atmospheres; 100°c and 1 atmosphere; 100°c and 100 atmospheres. Indicate the phases present at each point. The heat capacity of liquid carbon dioxide at 0°c and 100 atmospheres is 2.00 joules per gram.

4.16. With the aid of the data in Table 4.1, calculate values for the density of hydrogen and of argon in grams per liter at 1 atmosphere.

4.17. Calculate values of the molar volume of nitrogen at 1 atmosphere pressure for the temperatures −150, −100, −50, 0, 50, 100, 300, and 600°c, using values for B from Fig. 4.3. Compare with the molar volume of the ideal gas at these temperatures.

CHAPTER 5

HEAT OF REACTION

In simple homogeneous systems, the absorption of heat or energy in any form is usually accompanied by a rise in temperature. The systems studied in the previous chapters conform to this type. We saw, however, that the rise in temperature produced by a given amount of energy is different for the different pure substances and, indeed, for any one substance in the solid, liquid, or gas phases, or in any one phase at different temperatures. In a definite amount of perfect gas, the energy is a function of the temperature only, so that, if the temperature is kept constant and the gas does no work, there are no heat effects when the system is compressed or expanded. For all actual substances, however, energies do depend on the volume of the system, that is, on the distances between the atoms and molecules.

While a pure substance remains at constant temperature, it does not absorb large quantities of heat as it is expanded so long as the substance is not transformed into a new phase. Many mixtures of pure substances also behave in this way. However, it frequently happens that the mixture of pure substances reacts according to the law of chemistry, with the resultant formation of new substances. In terms of chemistry, the atoms of the different substances have so rearranged themselves that there are large changes in the potential energies known as "chemical energies." If the final mixture is at the same temperature as that of the initial mixture, none of this large amount of energy can be attributed to the heat capacity of the individual atoms in the system; all of it must be attributed to the change in energy resulting from the chemical rearrangement.

The isothermal energy changes of one-phase pure substances are relatively small; but the isothermal energy changes resulting from chemical reaction are, in general, relatively large, though a few reactions have an almost negligible energy change. However, when pure substances change from one physical form to another at constant temperature, energy changes called *latent heats* occur, which may also be relatively large. These latent energies are measures of the changes in potential energy resulting from the change in phase. The difference in energy between a liquid and a gas is usually large, and the latent heat of evaporation is, therefore, correspondingly large. The change from solid to liquid is a somewhat less drastic one, and the latent heats of melting are accordingly smaller than the heats of evaporation. For the change of a substance from one crystalline form to another, the heat of transition is likely to be relatively small. The above generalizations are only approximate; many exceptions to the rules may be found. Where exceptions exist, one must look for unusual conditions that result in abnormal differences in potential energies.

Latent Heat.—The latent heat effect was discovered by Joseph Black in 1761 while he was investigating the heat capacities of various substances. It is made evident by an abnormally high heat capacity within a restricted temperature range. Latent heat might be better named *latent energy*. It undoubtedly exists in substances in the form of potential energies and not in the form of kinetic energies.

When a gram of ice at 0°C is heated at atmospheric pressure, it melts to water. If the resulting water has a final temperature of 1°C, experiments show that 81 calories of energy have been absorbed. Of this energy, 80 calories are required to melt the ice to water at 0° and 1 calorie to heat the water from 0 to 1°. Where H_2 represents the heat content of the water at 1° and H_1 that of ice at 0°, the apparent heat capacity of the system over this temperature interval at constant pressure is $(H_2 - H_1)/(T_2 - T_1) = 81$ cal/deg. If the final temperature of the water is 0.5° instead of 1°, the apparent heat capacity over the half-degree interval is $(80 + 0.5)/0.5 = 161$ cal/deg; if the final temperature is 0.1° instead of 1°, the apparent heat capacity of the water is

$$(80 + 0.1)/0.1 = 801 \text{ cal/deg}$$

We see that, as the temperature range over which the latent heat is observed becomes smaller and smaller, the apparent heat capacity becomes greater approaching the limit, $(\mathrm{d}H/\mathrm{d}T)_{\mathrm{d}T\to 0} \to \infty$.

These facts are illustrated in Fig. 5.1 for finite temperature intervals. From the general relation $\mathrm{d}H_P = C_P\,\mathrm{d}T$, it follows that the increase in heat content between any two temperatures is given by the integral of $C_P\,\mathrm{d}T$ between those temperatures. The integration may be performed graphically. Thus, in Fig. 5.1 the value of $H_2 - H_1$ between T_1 and T_2 is the area under the curve between these temperatures. If the transition between solid and liquid takes place sharply at a definite temperature and the intervals over which the heat capacity is measured are very small, the heat capacity at the transition as indicated by the heavy line rises abruptly to a very large value. The heat of the transition is then the difference between the total area under the curve between T_3 and T_4 and that part which must be attributed to the true heat capacity in this temperature range. The heat capacity heat can be estimated from the heat capacity curves extrapolated to the transition temperature.

If the transition does not take place abruptly but extends over the temperature range T_2 and T_5, as shown by the dotted curve, the total change in heat content in the range is the area under the dotted curve, and the heat of transition is that remaining after the true heat capacity heat is deducted. For any given transition, the two heat of transition areas are identical in extent for $H_5 - H_1 = \int_{T_1}^{T_5} C_P \, dT$ is the same in either case.

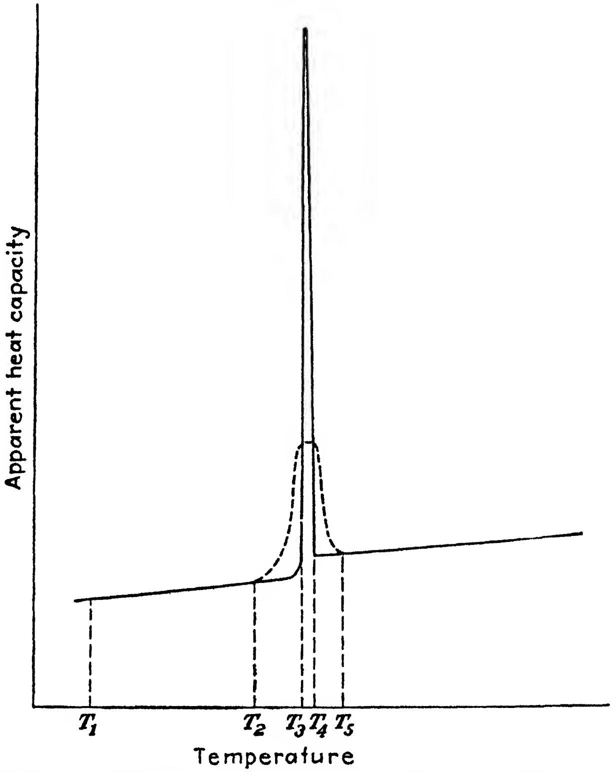


FIG. 5.1.—Influence of gradual or abrupt phase changes, or chemical reactions, on the apparent heat capacity curve.

Although the majority of phase transitions can be made to take place abruptly so that their influence on the measured heat capacity curves is restricted to very narrow limits, many transitions do not occur rapidly especially in systems that are being cooled; these transitions are detected by the abnormally high apparent heat capacities within the limits in which the transition occurs. Transitions in the solid state frequently behave in this way. This behavior becomes of increasing importance in the measured heat capacities at low temperatures where the low temperatures favor sluggish transitions. Although the errors in the heat content of a substance that result from the overlooking of small heats of transition at low temperatures may not be great, the errors in the function, entropy, as we shall see later, are as great for small neglected heat effects at low temperature as for large neglected heats at high temperatures. When mixtures of substances are heated or cooled and no phase transitions occur, abnormal heat capacities are taken as evidence for chemical reaction. The reactions or transitions, because of these abnormal heat capacity effects, are disclosed by "holds" in the time-temperature curves obtained when the systems are heated or cooled.

TABLE 5.1.—HEAT OF EVAPORATION OF WATER
(To form saturated vapor)

Temperature, °C	International joules/gram*	Defined cal/gram†	Defined cal/mole‡
0	2,500.17	597.66	10,767.4
5	2,488.46	594.86	10,716.9
10	2,476.74	592.05	10,666.4
15	2,464.99	589.25	10,615.8
20	2,453.21	586.43	10,565.1
25	2,411.40	583.61	10,514.3
30	2,429.57	580.78	10,463.3
35	2,417.68	577.94	10,412.1
40	2,405.76	575.09	10,360.8
45	2,393.77	572.22	10,309.1
50	2,381.73	569.34	10,257.3
55	2,369.63	566.45	10,205.2
60	2,357.45	563.54	10,152.7
65	2,345.19	560.61	10,099.9
70	2,332.84	557.66	10,046.7
75	2,320.39	554.68	9,993.1
80	2,307.83	551.68	9,939.0
85	2,295.16	548.65	9,884.4
90	2,282.35	545.59	9,829.3
95	2,269.41	542.49	9,773.6
100	2,256.30	539.36	9,717.1

* Data of N. S. Osborne, H. F. Stimson, and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 256 (1939).

† 1 cal = 4.1833 int joules.

‡ 1 mole = 18.016 grams.

Wherever possible, the problem of measuring heats of transition or reaction is simplified by having the processes occur at constant temperature so that the heats of transition or reaction may be kept distinctly separate from the true heat capacity effects. For this reason, we study as many of these processes as possible *at constant temperature.*

For reference, values of the latent heat of evaporation of liquid water to form the saturated vapor, calculated from the data of Osborne, Stimson, and Ginnings,[1] are given in Table 5.1.

Heat of Reaction.—Whenever a reaction takes place isothermally so that the final temperature of the reaction system is the same as the initial temperature, the entire heat of the reaction may be attributed to changes in the chemical energies and to the changes in potential energies that result from the volume changes or changes in surface or phase accompanying the reaction. Under these conditions, any thermal effects caused by the heat capacities of the atoms in the system are eliminated and the measured heats are representative of the changes in the chemical nature of the system. We have already indicated that the *heat at constant pressure* q_P, in the absence of work except work of expansion, equals the change in the $(E + PV)_P$ value, this change being designated by ΔH_P. Unless otherwise indicated, it is understood that the change in H refers to the constant-pressure process, there being also the ΔH_V function which is seldom used because it represents no directly measured physical quantity. Hereafter, we shall omit the subscript $_P$, which specifies constant pressure, because we shall frequently use that position to designate the constant temperature at which the reaction occurs. Thus the symbol $\Delta H_{298.16}$ refers to the isothermal heat of reaction at constant pressure at the temperature 298.16°K = 25°C.

We have also observed that the isothermal heat of reaction at constant volume q_V is represented by the change in the internal energy ΔE_V, there being here no work of any kind. Some heats, notably various heats of combustion, are measured directly in a bomb calorimeter, the corresponding heats at constant pressure being calculated from these values by the methods of equation (2.31).

Heat of Combustion.—Many elements and compounds combine quantitatively with oxygen to form oxides, releasing in the process relatively large quantities of energy. Thus, for the combustion of hydrogen[2]

---

[1] *J. Research Natl. Bur. Standards*, **23**, 256 (1939). It should be noted that the values for the heat of vaporization over the wider range, 0 to 374°C, by the same authors [*ibid.*, **23**, 261 (1939)] are smoothed values expressed in "International Steam Table" calories per gram. This unit is 6.5 parts per 10,000 smaller than our *defined calorie.*

[2] ROSSINI, F. D., *J. Research Natl. Bur. Standards*, **22**, 407 (1939). The value reported was later corrected for the change in the molecular weight of hydrogen. The value is given to more figures than are certain to permit energy differences to be calculated accurately. Thus, the heat of evaporation can be calculated by subtracting the value for the formation of water vapor from that for the formation of liquid water.

at 25°C and at constant pressure, we have

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(liq); \qquad \Delta H^\circ_{298.16} = -68{,}317.4 \pm 9.6 \text{ cal} \quad (5.1)$$

This corresponds to equation (2.11) previously given for the formation of water. As before, the subscript $_{298.16}$ represents the temperature of the reaction; the superscript ° indicates that the reactants and the products of the reaction are in their standard states. Similarly, for the combustion of methane[1] at 1 atmosphere and 25°C

$$\begin{aligned} CH_4(g) + 2O_2(g) &= CO_2(g) + 2H_2O(liq); \\ \Delta H^\circ_{298.16} &= -212{,}798 \text{ cal} \end{aligned} \qquad (5.2)$$

The heats of combustion are useful in the calculation of heats of formation of compounds that do not form directly from the elements.

Standard States.—In tables of heats of reactions, the number of different values that must be recorded is reduced drastically if the values are recorded for some definite constant pressure and a definite temperature. These equations can then be added or subtracted to yield the desired value at the standard conditions. The standard temperature selected depends almost entirely on experimental convenience, that temperature being selected which involves the fewest calculations in the correlation of the data. For many purposes, 25°C has been selected as the standard temperature. However, many of the older thermal data were measured at "room temperature," which at that time lay much nearer 18 than 20 or 25°C. For this reason, the tabulated data in Bichowsky and Rossini's "Thermochemistry of Chemical Substances" are reported for the standard reference temperature of 18°C.

The heat of a reaction depends also on the state of the reactants and the products. For a liquid or solid, the standard state is generally chosen as the form stable at the indicated temperature and at a pressure of 1 atmosphere. For a solid, if more than one crystalline form may exist at the standard pressure and temperature, it is necessary to specify the crystalline form explicitly. For gases, the standard pressure is usually 1 atmosphere. However, the pressure at which the *fugacity* of the gas is unity is frequently chosen as the standard state. The concept of fugacity is discussed later. We may point out here that, for a definite amount of ideal gas at constant temperature, its value of $H = E + PV$ is independent of the pressure, both E and PV remaining constant. For an ideal gas, the fugacity equals the pressure. However, for a definite quantity of a real gas, both E and PV vary with the volume and, therefore, with the pressure. The heat content of a gas in the ideal (hypothetical) standard state of unit fugacity of 1 atmosphere is equal to that

---

[1] PROSEN, E. J., and F. D. ROSSINI, *J. Research Natl. Bur. Standards*, **34**, 263 (1945).

of the gas behaving as an ideal gas at 1 atmosphere pressure and is identical with the heat content of the real gas at zero pressure. For a gas, the changes in E and the PV product with pressure depend on the attractive forces between the gas molecules; they are, therefore, a measure of the deviation of the gas from ideality. Table 5.2 shows the difference between the heat content of several gases at a fugacity of 1 atmosphere and a pressure of 1 atmosphere. Some of these values are used later. Observe the relatively large deviation of carbon dioxide from ideal behavior. For most known heats of reaction, though not all, the difference in heat content between the states of unit fugacity and unit pressure is within the experimental error of the measurement. The distinction between the two standard states is of practical importance only when accurate thermal data are available. The value of ΔH for the standard state is commonly designated by the superscript ° as in $\Delta H°$.

Table 5.2.—Deviation of the Heat Content of Some Real Gases* from That of the Ideal Gas at 25°c and 1 Atmosphere Pressure

Substance	$H_{\text{ideal}, f=1\,\text{atm}} - H_{\text{real}, P=1\,\text{atm}} = H_{\text{real}, P=0} - H_{\text{real}, P=1}$	
	In joules/mole	In cal/mole
$H_2(g)$	−0.48	−0.11
$O_2(g)$	+8.06	+1.93
$CO(g)$	7.20	1.72
$CO_2(g)$	41.4	9.90

* Data from F. D. Rossini, *J. Research Natl. Bur. Standards*, **22**, 407 (1939).

Heat of Formation.—Equation (5.1), which represents the combustion of hydrogen, also indicates the formation of 1 mole of liquid water from 1 mole of hydrogen gas and $\frac{1}{2}$ mole of oxygen gas. If the heat content of the mole of hydrogen under the standard condition is $\textsc{h}(H_2)$, that of the $\frac{1}{2}$ mole of oxygen is $\frac{1}{2}\textsc{h}(O_2)$, and that of the liquid water is $\textsc{h}(H_2O)$, we have

$$\Delta H = \textsc{h}(H_2O) - [\textsc{h}(H_2) + \tfrac{1}{2}\textsc{h}(O_2)] = -68{,}317 \text{ cal} \tag{5.3}$$

Because our heat content values are relative (see Chap. 2), we may arbitrarily set the value of the heat content of the elements in their standard states as zero, so that equation (5.3) becomes

$$\Delta H = \textsc{h}(H_2O) = -68{,}317 \text{ cal} \tag{5.4}$$

This relative molar heat content value of water is called its *heat of formation.*

The heat of reaction when carbon dioxide[1] is formed from graphite

---

[1] Prosen, E. J., R. S. Jessup, and F. D. Rossini, *J. Research Natl. Bur. Standards*. **33**, 447 (1944).

and oxygen is

$$\text{C(graphite)} + \text{O}_2(\text{g}, f = 1) = \text{CO}_2(\text{g}, f = 1); \quad \Delta H^\circ_{298.16} = -94{,}051.8 \pm 10.8 \text{ cal} \qquad (5.5)$$

If graphite is the form of crystalline carbon to which zero heat content is assigned, and unit fugacity is the standard pressure for carbon dioxide, the heat of formation of carbon dioxide is −94,051.8 ± 10.8 calories.

From Table 5.2, it appears that the relative value of $\text{H} = \text{E} + P\text{V}$ for carbon dioxide at unit fugacity exceeds that at unit pressure by 9.90 calories. There is also a difference of 1.93 calories for the oxygen. However, the estimated uncertainty of the calorimetric value is 10.8 calories this value being computed by Rossini[1] with a formula in which the "error" indicates the limits within which the "true" value has a 21 to 1 chance of being found. Using these data, we have

$$\begin{array}{rll}
\text{C(graphite)} + \text{O}_2(\text{g}, f = 1) = \text{CO}_2(\text{g}, f = 1); & \Delta H = -94{,}051.8 \pm 10.8 \text{ cal} \\
\text{O}_2(\text{g}, P = 1) = \text{O}_2(\text{g}, f = 1); & \Delta H = \quad 1.93 \text{ cal} \\
\text{CO}_2(\text{g}, f = 1) = \text{CO}_2(\text{g}, P = 1); & \Delta H = -\quad 9.90 \text{ cal} \\
\hline
\text{C(graphite)} + \text{O}_2(\text{g}, P = 1) = \text{CO}_2(\text{g}, P = 1); & \Delta H_{298.16} = -94{,}059.8 \pm 10.8 \text{ cal} & (5.6)
\end{array}$$

The difference between the heat of formation of carbon dioxide at unit pressure and at unit fugacity is found to be 8 calories.

For many compounds, the heat of formation cannot be measured directly because the direct combination of the elements takes place slowly or not at all at the temperatures at which calorimetric measurement is convenient. For such reactions, the heat of formation is obtained indirectly by the combination of reactions that are conveniently measured. The heat of formation of methane may be obtained by a combination of equations (5.1), (5.2), and (5.5). Thus,

$$\begin{array}{lrll}
2 \times \text{equation (5.1):} & 2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O(liq)}; & \Delta H^\circ = -136{,}635 \text{ cal} \\
+ \text{ equation (5.5):} & \text{C(graphite)} + \text{O}_2 = \text{CO}_2; & \Delta H^\circ = -\ 94{,}052 \text{ cal} \\
- \text{ equation (5.2):} & \text{CO}_2 + 2\text{H}_2\text{O(liq)} = \text{CH}_4 + 2\text{O}_2; & \Delta H^\circ = +212{,}798 \text{ cal} \\
\hline
 & \text{C(graphite)} + 2\text{H}_2 = \text{CH}_4; & \Delta H^\circ = -\ 17{,}889 \text{ cal} & (5.7)
\end{array}$$

---

[1] *Chem. Rev.*, **18**, 252 (1936).

TABLE 5.3.—HEAT OF COMBUSTION OF SOME CARBON COMPOUNDS* AT 25°C
(To form carbon dioxide gas and liquid water. Values in kilocalories per mole)

Compound	Formula	State of compound	
		Gas $-\Delta H^\circ_{298.16}$	Liquid $-\Delta H^\circ_{298.16}$
Methane	CH_4	212.798	
Ethane	C_2H_6	372.820	
Propane	C_3H_8	530.605	526.782†
n-Butane	C_4H_{10}	687.982	682.844†
2-Methylpropane (isobutane)	C_4H_{10}	686.342	681.625†
n-Pentane	C_5H_{12}	845.16	838.80
2-Methylbutane (isopentane)	C_5H_{12}	843.24	837.31
2,2-Dimethylpropane (neopentane)	C_5H_{12}	840.49	835.18†
n-Hexane	C_6H_{14}	1002.57	995.01
n-Heptane	C_7H_{16}	1160.01	1151.27
n-Octane	C_8H_{18}	1317.45	1307.53
Benzene	C_6H_6	789.08	780.98
Methylbenzene (toluene)	C_7H_8	943.58	934.50
Ethylbenzene	C_8H_{10}	1101.13	1091.03
1,2-Dimethylbenzene (*o*-xylene)	C_8H_{10}	1098.54	1088.16
1,3-Dimethylbenzene (*m*-xylene)	C_8H_{10}	1098.12	1087.92
1,4-Dimethylbenzene (*p*-xylene)	C_8H_{10}	1098.29	1088.16
Ethene (ethylene)	C_2H_4	337.234	
Propene (propylene)	C_3H_6	491.987	
1-Butene	C_4H_8	649.757	
cis-2-Butene	C_4H_8	648.115	
trans-2-Butene	C_4H_8	647.072	
2-Methylpropene (isobutene)	C_4H_8	646.134	
1-Pentene	C_5H_{10}	806.85	
1-Hexene	C_6H_{12}	964.26	
1-Heptene	C_7H_{14}	1121.69	
1-Octene	C_8H_{16}	1279.13	
Ethyne (acetylene)	C_2H_2	310.615	
Propyne (methylacetylene)	C_3H_4	463.109	
1-Butyne (ethylacetylene)	C_4H_6	620.86	
2-Butyne (dimethylacetylene)	C_4H_6	616.533	
1-Pentyne	C_5H_8	778.03	
2-Pentyne	C_5H_8	774.33	
3-Methyl-1-butyne	C_5H_8	776.13	
Alcohols:			
Methanol	CH_3OH	182.58	173.64
Ethanol	C_2H_5OH	336.78	326.66

---

* Values for the hydrocarbons are those of the American Petroleum Institute Research Project 44 at the National Bureau of Standards. Selected Values of Properties of Hydrocarbons. Table 1n, Heats of Combustion at 25°c., Mar. 31, 1944; April 30, 1945; Table 5n, *ibid.*, Mar. 31, 1945; Table 8n, *ibid.*, Oct. 31, 1945; Table 12n, *ibid.*, Mar. 31, 1945; Table 20n, *ibid.*, Dec. 31, 1945; Table 24n, *ibid.*, Dec. 31, 1945.

† For liquid at saturation pressure.

Because of these relationships, it follows that the heat of any reaction may be obtained if the heat of formation of every substance entering and leaving the reaction is known. If we wish to find the heat of reaction when Ba^{++} ions and SO_4^{--} ions from an infinitely dilute solution form 1 mole of crystalline $BaSO_4$, the heats of formation at 18° and 1 atmosphere pressure being respectively, −128,360, −215,800, and −349,400 calories, we calculate

$$\begin{aligned}\Delta H^\circ &= \text{H}[BaSO_4(c)] - [\text{H}(Ba^{++}, \infty) + \text{H}(SO_4^{--}, \infty)]\\ &= -349{,}400 - (-128{,}360 - 215{,}800) = -5{,}240 \text{ cal}\end{aligned}$$

Hence,

$$Ba^{++}(\infty) + SO_4^{--}(\infty) = BaSO_4(c). \qquad \Delta H^\circ = -5{,}240 \text{ cal} \tag{5.8}$$

The heat evolved in this reaction is, therefore, 5,240 calories per mole of $BaSO_4$ precipitated.

Heat of Combustion of Hydrocarbons.—For reactions of organic compounds, it is difficult to measure equilibrium directly because of the possibility of side reactions and the instability of many of the compounds. The equilibrium conditions must often be calculated indirectly, one of the necessary data being the heat of combustion or the heat of formation of the compounds. The earlier thermochemical data obtained by such able and industrious experimenters as Thomsen and Berthelot are not accurate enough for this purpose. For this reason, Rossini[1] and his coworkers at the National Bureau of Standards have investigated the heats of combustion of a large number of hydrocarbons with high accuracy. Their data are the basis for the values listed in Table 5.3. Observe that values in the table are for $-\Delta H$; in all the combustions, heat is evolved. As an example of the degree of error of some of the older data, we may call attention to the significant difference between Rossini's value for the heat of combustion of methane and the older value, $-\Delta H = 210.8$ kcal/mole selected for the "International Critical Tables," a difference of 2 kilocalories per mole.

Certain regularities in the data may be pointed out. In the normal paraffin series, methane, ethane, propane, *n*-butane, *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane, the increments in heat evolved on combustion of the gaseous hydrocarbons are, respectively, 160.02, 157.79, 157.38, 157.18, 157.41, 157.44, and 157.44 kilocalories. The increment seems to approach a constant value of 157.44 kilocalories. Hence, the heats of combustion of the higher members of the series can be calculated from experimental values for the lower members of the series. Thus, we

---

[1] For a review on the available data up to 1937, the student should read the review by F. D. Rossini, *Ind. Eng. Chem.*, **29**, 1424 (1937).

find for *n*-octadecane ($C_{18}H_{38} = C_8H_{18} + 10CH_2$) that $-\Delta H$ equals

$$1{,}317.45 + 1{,}574.4 = 2{,}891.9 \text{ kcal/mole}$$

Observe the minimum increment found between the four-carbon and the five-carbon paraffin. Similar minima are found for the corresponding hydrocarbons in the olefin and acetylene series. Thus, the increments per CH_2 in the ethylene series for the compounds ethene, propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, and 1-octene are, respectively, 154.75, 157.80, 157.06, 157.41, 157.44, 157.44. A minimum is found for the increment between 1-butene and 1-pentene, and the constant increment 157.44, is found for the higher members of the series.

Of special interest are the heats of combustion of the various isomers. Since isomers have the same empirical formulas and burn to yield identical amounts of carbon dioxide and water, their differences in heat of combustion reflect directly the differences in their heat contents. These differences may be relatively large, there being 4.67 kilocalories difference between *n*-pentane and neopentane; or small, there being only 0.17 kilocalorie between *m*-xylene and *p*-xylene. The table also lists values for the heats of combustion of the hydrocarbons from their liquid states. The difference in $-\Delta H$ for the combustion of the gaseous and the liquid hydrocarbon equals the heat of evaporation at 25°C of the liquid to form the gas at 1 atmosphere pressure (unit fugacity).

Heat of Formation of Hydrocarbons.—The method used in obtaining the heat of formation of methane from its heat of combustion may be extended to the other compounds in Table 5.3. For methane, the standard heat of formation $\Delta H°$ at 25°C was found in equation (5.7) to be $-17{,}889$ calories per mole. The heats of formation of the other hydrocarbons may be calculated in a similar manner. When they are obtained, they show definite trends related to the trends shown by their heats of combustion. In the previous section, we found that the heat evolved on combustion for each added CH_2 group had a value of about 157.44 kilocalories in the higher members of a series. An approximate value for the heat of formation of the CH_2 group in these compounds may, therefore, be calculated as follows:

$$\begin{array}{lll}
C + O_2 & = CO_2; & \Delta H = -\ 94.052 \text{ kcal} \\
H_2 + \frac{1}{2}O_2 & = H_2O \text{ (liq)}; & \Delta H = -\ 68.317 \text{ kcal} \\
CO_2 + H_2O \text{ (liq)} & = 1\frac{1}{2}O_2 + (CH_2 \text{ in compd}); & \Delta H = \ \ 157.44 \text{ kcal} \\
\hline
C + H_2 & = (CH_2 \text{ in compd}); & \Delta H = -\ \ 4.93 \text{ kcal}
\end{array}$$

Thus, because the increment in heat of combustion per CH_2 group is, in general, less than -162.4 kilocalories (which is the sum of -94.05 and -68.32), the heat of formation of hydrocarbons in each series becomes more negative with increasing molar weight. The values of the heats of formation of some hydrocarbons are listed in Table 5.4. Other values may be derived from the data in Table 5.3. For isomers, the heats of formation may be obtained directly from the heat of formation of the normal hydrocarbon and the difference in heats of combustion of the normal hydrocarbon and the isomer. Thus, normal butane has 1.64 kilocalories more energy than isobutane; normal pentane has 1.92 and 4.67 kilocalories more energy, respectively, than its isomers, isopentane and neopentane. With few exceptions, the most highly branched isomer has the lowest heat of formation and is the most stable.

TABLE 5.4.—HEAT OF FORMATION OF SOME HYDROCARBONS* AT 25°C
[From carbon (crystalline graphite) and hydrogen (gas) to form the hydrocarbon (gas). Values in kilocalories per mole]

Normal paraffins			Normal olefins			Normal acetylenes		
Compound	Formula	$\Delta H^\circ_{298.16}$	Compound	Formula	$\Delta H^\circ_{298.16}$	Compound	Formula	$\Delta H^\circ_{298.16}$
Methane	CH_4	−17.889						
Ethane	C_2H_6	−20.236	Ethene	C_2H_4	12.496	Ethyne	C_2H_2	54.194
Propane	C_3H_8	−24.820	Propene	C_3H_6	4.879	Propyne	C_3H_4	44.319
n-Butane	C_4H_{10}	−29.812	1-Butene	C_4H_8	0.280	1-Butyne	C_4H_6	39.70
n-Pentane	C_5H_{12}	−35.00	1-Pentene	C_5H_{10}	− 5.000	1-Pentyne	C_5H_8	34.50
n-Hexane	C_6H_{14}	−39.96	1-Hexene	C_6H_{12}	− 9.96	1-Hexyne	C_6H_{10}	29.55
n-Heptane	C_7H_{16}	−44.89	1-Heptene	C_7H_{14}	−14.89	1-Heptyne	C_7H_{12}	24.62
n-Octane	C_8H_{18}	−49.82	1-Octene	C_8H_{16}	−19.82	1-Octyne	C_8H_{14}	19.70

* American Petroleum Institute Research Project 44 at the National Bureau of Standards. Selected Values of Properties of Hydrocarbons. Table 20w, Heat of Formation, ΔH_f° at 0° to 1500°K, Nov. 30, 1945; Table 24w, *ibid.*, Nov. 30, 1945; April 30, 1946; Table 25w, *ibid.*, Feb. 28, 1946.

The heats of formation of the unsaturated hydrocarbons may be calculated from their heats of combustion by the method shown above. They may also be obtained from the known heats of hydrogenation of the olefins and the heats of combustion of the corresponding paraffins. Similarly, the heats of hydrogenation may be calculated from the heat of combustion data. From the experimental heats of combustion, we shall calculate the heats of hydrogenation of ethylene and propylene and shall then compare these calculated heats with the heats of hydrogenation determined directly. For the comparison, we shall use the original values of Rossini and his coworkers since the "best" values in Tables 5.3 and 5.4 are based on all the available data.

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O(\text{liq}); \qquad \Delta H^\circ = -337.28 \pm 0.07 \text{ kcal}$$

$$H_2 + \tfrac{1}{2}O_2 = H_2O(\text{liq}); \qquad \Delta H^\circ = -\ 68.318 \pm 0.010 \text{ kcal}$$

$$2CO_2 + 3H_2O(\text{liq}) = C_2H_6 + 3\tfrac{1}{2}O_2; \qquad \Delta H^\circ = +372.81 \pm 0.11 \text{ kcal}$$

$$\overline{C_2H_4 + H_2 = C_2H_6; \qquad \Delta H^\circ = -\ 32.79 \pm 0.13 \text{ kcal}} \tag{5.9}$$

The value for the hydrogenation of ethylene obtained by Kistiakowsky[1] and his coworkers from the direct calorimetric measurement of the catalytic hydrogenation is -32.575 ± 0.050 kcal. Because these two values differ by slightly more than their estimated uncertainty, the difference may be attributed to some minor systematic error such as the presence of ethane as impurity in the ethylene as suggested by Rossini.[2] Observe that, although the percentage accuracy of the heats of combustion is greater than that of the directly measured heat of hydrogenation, the estimated absolute error is greater. The small difference between two large numbers must assume the absolute error of the large numbers and not their percentage error.

TABLE 5.5.—HEAT OF HYDROGENATION* OF OLEFINS AT 82°C
(In calories per mole)

Substance	Formula	$\Delta H_{365.16}$
Ethylene	C_2H_4(g)	−32,824
Propylene	C_3H_6(g)	−30,115
1-Butene	C_4H_8(g)	−30,341
cis-2-Butene	C_4H_8(g)	−28,570
trans-2-Butene	C_4H_8(g)	−27,621
Isobutene	C_4H_8(g)	−28,389

* Data of G. B. Kistiakowsky, *et al.*, *J. Am. Chem. Soc.*, **57**, 65, 876 (1935).

The heat of hydrogenation of propylene can be calculated similarly.

$$C_3H_6 + 4\tfrac{1}{2}O_2 = 3CO_2 + 3H_2O(\text{liq}); \qquad \Delta H^\circ = -\ 491.82 \text{ kcal}$$

$$H_2 + \tfrac{1}{2}O_2 = H_2O(\text{liq}); \qquad \Delta H^\circ = -\ 68.318 \text{ kcal}$$

$$3CO_2 + 4H_2O(\text{liq}) = C_3H_8 + 5O_2; \qquad \Delta H^\circ = +\ 530.57 \text{ kcal}$$

$$C_3H_6 + H_2 = C_3H_8; \qquad \Delta H^\circ = -\ 29.57 \text{ kcal} \tag{5.10}$$

The value for equation (5.10) obtained from the catalytic hydrogenation[3] at 82°C is −30.115 kilocalories. When allowance is made for the variation of heat of reaction with temperature by the method explained later in this chapter, the value at 25°C becomes −29.79 kilocalories. The agreement between the two values obtained by two independent calorimetric methods is excellent. The differences in energy of formation of isomeric compounds are illustrated further by the hydrogenation data of the isomeric butenes at 82°C, given in Table 5.5. When 1-butene, *cis*-

[1] KISTIAKOWSKY, G. B., N. ROMEYN, JR., J. R. RUHOFF, H. A. SMITH, and W. C. VAUGHAN, *J. Am. Chem. Soc.*, **57**, 65 (1935).

[2] *J. Research Natl. Bur. Standards*, **17**, 629 (1936).

[3] KISTIAKOWSKY, G. B., J. R. RUHOFF, H. A. SMITH, and W. C. VAUGHAN, *J. Am. Chem. Soc.*, **57**, 876 (1935).

2-butene, and *trans*-2-butene are hydrogenated, the final product is the same, namely, normal butane. The differences in the heats of hydrogenation are, therefore, direct measures of the differences in the internal energy of these butenes at 82°. It is evident that the energy evolved when a mole of hydrogen is added to a double bond depends on the character of the groups held by the double bond. It appears that the *cis*-2-butene has 1 kilocalorie more energy than the *trans*-2-butene but 1.8 kilocalories less energy than the 1-butene. The symmetrical *trans*-2-butene, therefore, appears to be more stable than the less symmetrical *cis*-2-butene or the 1-butene.

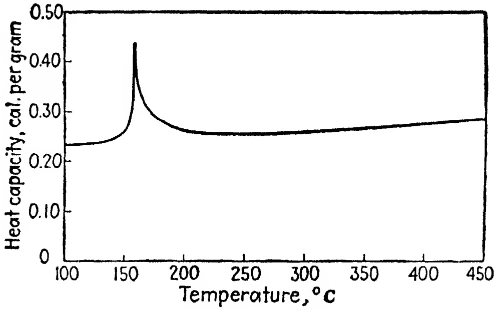


FIG. 5.2.—Heat capacity curve for liquid sulphur.

Heat of Transition.—As stated earlier, heats of transition may frequently be derived from observed abnormal heat capacities. The method is illustrated by the data of Lewis and Randall[1] on the heat capacity of liquid sulfur between 100 and 400°c. In this temperature range, there is also a transformation of S_λ to S_μ. The observed heat capacities are plotted in Fig. 5.2. There is evidently an abnormally high apparent heat capacity, especially in the neighborhood of 160°, because heat is being absorbed in the transition $S_\lambda = S_\mu$. The heat capacity per gram of S_λ is represented by the equation

$$c = 0.21 + 0.00016t$$

From the known percentage of S_μ at various temperatures, the heat of transition is calculated as

$$S_\lambda = S_\mu; \qquad q = 13 \text{ cal/gram}$$

Graphically, this represents the area under the curve not attributable to the heat capacity of the sulfur.

Heats of transition may also be obtained from observation of the heats of reaction when the two distinct phases of a substance are caused to undergo identical chemical reactions. For example, the heat of the

---

[1] LEWIS, G. N., and M. RANDALL, *J. Am. Chem. Soc.*, **33**, 476 (1911).

transition, diamond to graphite, may be obtained from a comparison of the heat of combustion of the two forms of carbon.[1] For the decomposition of carbon dioxide to form graphite and oxygen, we have

$$CO_2(g) = O_2(g) + C(\text{graphite}); \qquad \Delta H^\circ_{298.16} = +94{,}051.8 \pm 10.8 \text{ cal} \quad (5.11)$$

For the diamond, the heat of combustion is

$$C(\text{diamond}) + O_2(g) = CO_2(g); \qquad \Delta H^\circ_{298.16} = -94{,}505.1 \pm 22.9 \text{ cal} \quad (5.12)$$

For the transition, diamond to graphite, it follows that

$$C(\text{diamond}) = C(\text{graphite}); \qquad \Delta H^\circ_{298.16} = -453.2 \pm 20.3 \text{ cal} \quad (5.13)$$

The "accuracy error" defined by Rossini is given here to show how the precision suffers when a small energy value must be obtained from the difference between two large numbers. In equation (5.12) the accuracy error of the heat of combustion is about 2 parts in 10,000 of the "best value" given. The accuracy error of the heat of transition is relatively much greater, being about 450 parts in 10,000. Such indirect methods of obtaining heats of transition are necessary whenever the direct transition cannot be measured readily.

Heat of Solution.—When substances are mixed, the resulting heat may be a combination of the true solution effect due to the attractive forces between the molecules, the effect of the rearrangement of the elements composing the substances to form new substances, and the heat effect that results from changes of phase during the mixing. If we survey the different types of solution and the heat effects that may be expected even though there are no chemical reactions of the traditional type, we are in a position to differentiate between the "solution" and "chemical" effects of mixing. In any case, the final solution, if homogeneous, will correspond to one of the phases of matter previously mentioned; that is, it will be a gas phase, a liquid phase, or a solid phase. Several of these phases may coexist, but here we shall consider only homogeneous systems containing a single phase.

Gaseous Solutions.—When gases are mixed with gases, the thermal effects in the absence of chemical reaction are slight, being those associated with the gas imperfections. This is illustrated by the data in Table 5.2, which indicate the order of magnitude of the thermal effects when a mole of a pure gas is compressed isothermally from 0 to 1 atmosphere pressure. When liquids "dissolve" in gases, the final solution being gaseous, the thermal effect results almost entirely from the heat required

---

[1] PROSEN, E. J., R. S. JESSUP, and F. D. ROSSINI, *J. Research Natl. Bur. Standards*, **33**, 447 (1944).

to evaporate the liquid, the heat of evaporation being ordinarily large compared with the gaseous solution effect. Similarly, when solids dissolve in gases, the thermal effects are primarily those of the sublimation of the solid.

Liquid Solutions.—When liquids are mixed with liquids without specific chemical reaction, the heat effects are small, but larger than when gases are mixed because of the shorter distances between the molecules. Figure 5.3 indicates the magnitude of the heats of mixing of some liquids at room temperature. When methanol and ethanol are mixed, the maximum heat effect (curve A) is found near the composition, ethanol 60 per cent by weight, methanol 40 per cent, where 0.095 calorie is evolved per gram of solution. When 0.1 gram of ethanol is mixed with 0.9 gram of methanol, 0.024 calorie is evolved. When 0.4 gram of propanol is mixed with 0.6 gram of methanol, 0.56 calorie of heat is absorbed (curve B). When 0.7 gram of benzene is mixed with 0.3 gram of methanol, 2.43 calories of heat are absorbed (curve C). These heat effects for propanol and benzene in methanol are the maximum encountered in these systems.

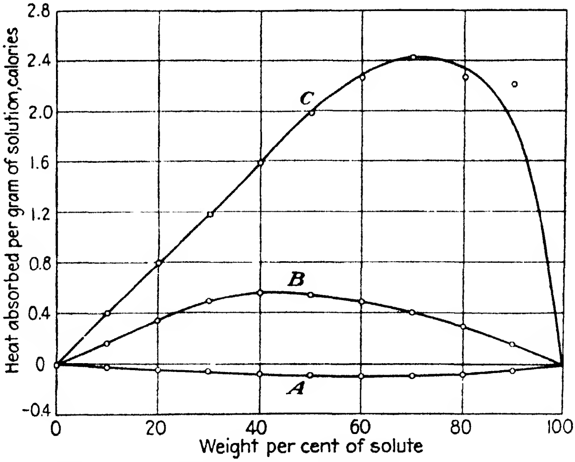


FIG. 5.3.—Heat of solution of methanol with the solutes A, ethanol; B, propanol; and C, benzene.

When gases dissolve in liquids, they enter the liquid phase and produce fairly large heat effects. In the absence of chemical reaction, the thermal effects are essentially those resulting from the liquefaction of the gas and the mixing of this liquid with the solvent liquid. Whenever the heat effect of mixing of liquids is relatively small, the heat of solution of gases is essentially that of liquefaction of the gas.

Similarly, when a solid is dissolved in a liquid, the solid "melts" into the liquid so that the normal heat effect is essentially the heat of melting of the solid. When the heat of solution of the solid differs markedly from the heat of melting the difference must be sought in the specific interaction of the dissolving molecules with the molecules of the solvent liquid. These abnormal heat effects are common in aqueous solution. They indicate, therefore, that an essential part of the process is the interaction of the solute with the water molecules. An example, the solution of KCl in water, is illustrated in Table 6.1.

Solid Solutions.—The same type of reasoning may be applied to solid solutions. Examples of solutions of gases, liquids, or solids in solids to form a solid phase are relatively limited. The thermal effects indicate whether the solution process is a normal one in which the primary effect is that accompanying a change in phase of the solute or whether there are specific chemical interactions accompanying the process.

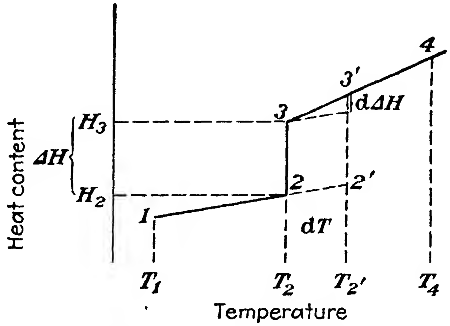


FIG. 5.4.—The change in heat content at constant pressure resulting from both a change in temperature and a heat of reaction. The change in heat of reaction with temperature at constant pressure.

Change of Heat of Reaction with Temperature.—In a reaction occurring at a definite temperature, the heat of the reaction of a definite amount of substance at constant pressure is a definite quantity represented by the change in the heat content ΔH. In general, the heat of reaction at some other temperature will be different. The relation between the heats of reaction at the different temperatures may be obtained by Kirchhoff's method. When a system in the state 1 is changed at constant pressure to the state 4, the change in heat content is $H_4 - H_1$, and the temperature change is $T_4 - T_1$. Because both H and T are properties of the system with values dependent only on the state of the system, both $H_4 - H_1$ and $T_4 - T_1$ are definite quantities that do not vary with the path over which the system travels in going from the state 1 to the state 4. The relation between H and T can, therefore, be plotted as in Fig. 5.4.

If the system is heated from the initial temperature T_1 to some intermediate temperature T_2 without undergoing reaction, it will nevertheless absorb heat because of its heat capacity, the quantity being $H_2 - H_1$. If now the system reacts isothermally at the temperature $T_2 = T_3$, the heat of the reaction will be given by $H_3 - H_2 = \Delta H$. If the temperature of the products of the reaction is raised to T_4 without further reaction, heat $H_4 - H_3$ will be absorbed because of the heat capacity of the products of the reaction.

A different path may be followed in going from H_1, T_1 to H_4, T_4. Consider the following path: The system is heated from T_1 to some temperature T_2' without reaction; the reaction then proceeds at the temperature $T_2' = T_3'$, the heat of the reaction being $\Delta H' = H_3' - H_2'$; finally, the products of the reaction are heated from T_3' to T_4. By the first path, the total heat absorbed is

$$H_4 - H_1 = (H_2 - H_1) + \Delta H + (H_4 - H_3) \tag{5.14}$$

and by the second path

$$H_4 - H_1 = (H_2' - H_1) + \Delta H' + (H_4 - H_3') \tag{5.15}$$

where $\Delta H = H_3 - H_2$ and $\Delta H' = H_3' - H_2'$.

By comparison with Fig. 3.1, we see that the mean heat capacity of the system before the reaction $C_{P,a}$ is presented by the slope of curve $\overline{12}$ in Fig. 5.4, for

$$C_{P,a} = \frac{H_2 - H_1}{T_2 - T_1} \tag{5.16}$$

The mean heat capacity of the system after the reaction $C_{P,b}$ is similarly represented by the slope of the curve $\overline{34}$, for

$$C_{P,b} = \frac{H_4 - H_3}{T_4 - T_3} \tag{5.17}$$

When $C_{P,a} = C_{P,b}$, the two curves are parallel and the heat of reaction ΔH, represented by the vertical distance between the two curves, remains constant even though the reaction temperature varies. Similarly, if $C_{P,b} > C_{P,a}$, as in Fig. 5.4, the two curves diverge with increasing temperature so that the heat of reaction ΔH must increase with increasing temperature. If $C_{P,b} < C_{P,a}$, the heat of reaction decreases with increasing temperature.

Now, from equation (5.16), the heat absorbed by the system between the states 1 and 2 is

$$H_2 - H_1 = C_{P,a}(T_2 - T_1) \tag{5.18}$$

and that absorbed between the states 3 and 4 is, from equation (5.17),

$$H_4 - H_3 = C_{P,b}(T_4 - T_3) \tag{5.19}$$

If the rise in reaction temperature is infinitesimal so that

$$T_2' = T_2 + \mathrm{d}T = T_3'$$

the change in heat of reaction is also infinitesimal so that

$$\Delta H' = \Delta H + \mathrm{d}\,\Delta H \tag{5.20}$$

For the second path, we have, therefore,

$$\left.\begin{aligned} H_2' - H_1 &= C_{P,a}(T_2' - T_1) = C_{P,a}(T_2 - T_1) + C_{P,a}\,\mathrm{d}T \\ H_4 - H_3' &= C_{P,b}(T_4 - T_3') = C_{P,b}(T_4 - T_3) - C_{P,b}\,\mathrm{d}T \end{aligned}\right\} \tag{5.21}$$

But, from equations (5.14) and (5.15),

$$(H_2 - H_1) + \Delta H + (H_4 - H_3) = (H_2' - H_1) + \Delta H' + (H_4 - H_3') \tag{5.22}$$

On substituting the above values in this equation, we find that

$$C_{P,a}(T_2 - T_1) + \Delta H + C_{P,b}(T_4 - T_3) = C_{P,a}(T_2 - T_1) + C_{P,a}\,\mathrm{d}T + \Delta H + \mathrm{d}\,\Delta H + C_{P,b}(T_4 - T_3) - C_{P,b}\,\mathrm{d}T$$

From this equation, therefore,

$$\begin{aligned} \mathrm{d}\,\Delta H &= C_{P,b}\,\mathrm{d}T - C_{P,a}\,\mathrm{d}T \\ &= (C_{P,b} - C_{P,a})\,\mathrm{d}T \end{aligned} \tag{5.23}$$

whence,

$$\frac{\mathrm{d}\,\Delta H}{\mathrm{d}T} = C_{P,b} - C_{P,a} = C_P(\text{products}) - C_P(\text{reactants}) = \Delta C_P \tag{5.24}$$

These equations, similar in form to the heat capacity equations for the pure substances, express the fundamental relation for the change of heat of reaction with temperature. If ΔC_P equals zero, that is, if the products and the reactants in the reaction have the same heat capacity, the heat of reaction does not vary with temperature. If the change in heat capacity is not independent of the temperature, the equation

$$\mathrm{d}\,\Delta H = \Delta C_P\,\mathrm{d}T \tag{5.25}$$

must be integrated.

Integration is simplified for the special case in which ΔC_P is independent of the temperature, that is, when it remains constant in the temperature range over which equation (5.25) is to be integrated. If the heat of reaction at temperature T_1 is ΔH_1 and that at T_2, ΔH_2, then, from equation (5.25),

$$\begin{aligned} \int_{H_1}^{H_2} \mathrm{d}\,\Delta H &= \Delta C_P \int_{T_1}^{T_2} \mathrm{d}T \\ \Delta H_2 - \Delta H_1 &= \Delta C_P(T_2 - T_1) \end{aligned} \tag{5.26}$$

When the heat capacities change with temperature and the heat capacity of the substances entering into the reaction may be represented over the indicated temperature range by the equation

$$C_P(\text{reactants}) = a' + b'T + c'T^2$$

and that of the products leaving the reaction by the equation

$$C_P(\text{products}) = a'' + b''T + c''T^2$$

the increase in heat capacity becomes

$$\begin{aligned} \Delta C_P = C_P(\text{products}) &- C_P(\text{reactants}) \\ &= (a'' - a') + (b'' - b')T + (c'' - c')T^2 \\ &= \alpha + \beta T + \gamma T^2 \qquad (5.27) \end{aligned}$$

Equation (5.27) may be combined with equation (5.25) to give a general expression for the heat of reaction as a function of temperature.

These principles will be applied to the calculation of the heat of freezing of water at −10°c.

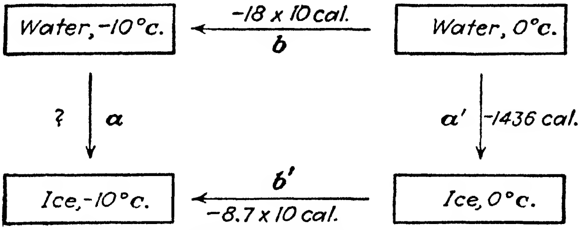


FIG. 5.5.—The change of heat of freezing of water with temperature. The molar heat of freezing at −10°c.

Heat of Freezing of Water at −10°c.—The heat capacity of liquid water at atmospheric pressure is 18 calories per mole. The mean heat capacity of ice over the range −10 to 0° is 2.03 joules per gram, or 8.7 calories per mole. At 0°, the heat of melting of ice is 1436 calories per mole.

Two methods may be followed in obtaining the heat of freezing of water at 10°c: (1) a repetition of the method used in deriving equation (5.26); (2) equation (5.26) itself.

1. Two paths between the states, water at 0°c and ice at −10°c, are path $(a + b)$ and path $(a' + b')$ in Fig. 5.5. When 1 mole of water is frozen to ice at 0°, 1436 calories of heat are evolved and $a' = -1436$ cal. If the ice is cooled to −10°, 8.7 × 10 calories of heat are evolved and $b' = -87$ cal. Similarly, when the mole of water is cooled without freezing to −10°, 18 × 10 calories of heat are evolved and $b = -180$ cal. But the change in heat content along the two paths is identical; hence,

$$\begin{aligned} a + b &= a' + b' \\ a &= -1436 - 87 + 180 \text{ cal} \\ &= -1343 \text{ cal} \end{aligned}$$

2. For the reaction

$$H_2O(\text{liq}) = H_2O(\text{c})$$

the increase in heat capacity ΔC_P when the "reactants" $H_2O(\text{liq})$ are converted to the "products" $H_2O(\text{c})$ is given by

$$C_{\text{ice}} - C_{\text{water}} = (8.7 - 18) \text{ cal/mole} = -9.3 \text{ cal/mole}$$

From equation (5.26), when T_2 is 0°C and T_1 is −10°C,

$$\begin{aligned} \Delta H_2 &= -1436 \text{ cal} \\ -1{,}436 - \Delta H_1 &= -93(10) \\ -\Delta H_1 &= 1436 - 93 \\ \Delta H_1 &= -1343 \text{ cal} \end{aligned}$$

ΔH_1 is identical with *a* above.

General Heat of Reaction Equation.—Between any two temperatures T_1 and T_2, the change in the heat of reaction at constant pressure may be obtained by integration of equation (5.25) between limits. Thus,

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

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_P \, dT \tag{5.28}$$

If the integration is performed between the limits $T_1 = 0$, $\Delta H_1 = \Delta H_0$, and $T_2 = T$, $\Delta H_2 = \Delta H_T$, equation (5.28) becomes

$$\Delta H_T - \Delta H_0 = \int_0^T \Delta C_P \, dT$$

Or, omitting the subscript $_T$,

$$\Delta H = \Delta H_0 + \int \Delta C_P \, dT \tag{5.29}$$

Equation (5.29) is mathematically equivalent to the general integration of equation (5.25) to give

$$\Delta H = \int \Delta C_P \, dT + I \tag{5.30}$$

where the integration constant I is identical with ΔH_0, which is interpreted as the heat of reaction at the absolute zero. However, we must emphasize the fact that, if the values of ΔC_P do not represent the heat capacities of the substances at low temperatures, ΔH_0 cannot represent the true heat of reaction at zero absolute temperature but is merely a useful integration constant.

When the value of ΔC_P is obtained from the empirical heat capacities of the reactants and the products of a reaction as in equation (5.27), it will yield values of ΔH over the same temperature range as that for which the heat capacity equations are valid. In general, equations of this type that hold above room temperature do not hold in the neighborhood of the absolute zero. Under these restrictions, equations (5.27) and (5.29) may be combined to give

$$\Delta H = \Delta H_0 + \int (\alpha + \beta T + \gamma T^2)\, dT$$

$$\Delta H = \Delta H_0 + \alpha T + \tfrac{1}{2}\beta T^2 + \tfrac{1}{3}\gamma T^3 \tag{5.31}$$

This general heat of reaction equation is used later in setting up free energy equations.

Heat of Formation of Gaseous Water.—We have given equation (2.10) for the formation of water vapor at 25° under the saturation pressure. When the water vapor is under standard conditions, that is, under a standard fugacity of 1 atmosphere, we find[1]

$$H_2(g, f = 1) + \tfrac{1}{2}O_2(g, f = 1) = H_2O(g, f = 1);$$

$$\Delta H^\circ_{298.16} = -57{,}798 \text{ cal} \tag{5.32}$$

If we know in addition the heat capacities of hydrogen, oxygen, and water, we can calculate the value of ΔH° at other temperatures. From equation (5.24), we see that

$$\Delta C_P = c(H_2O) - [c(H_2) + \tfrac{1}{2}c(O_2)] \tag{5.33}$$

When the heat capacity equations from Table 3.3 for these gases are substituted in equation (5.33), we obtain

For $H_2O(g)$,

$$c_P = 7.256 + 2.298 \times 10^{-3}T + 2.83 \times 10^{-7}T^2$$

For H_2,

$$-c_P = -6.9469 + 0.1999 \times 10^{-3}T - 4.808 \times 10^{-7}T^2$$

For $\tfrac{1}{2}O_2$,

$$-\tfrac{1}{2}c_P = -3.074 - 1.551 \times 10^{-3}T + 4.615 \times 10^{-7}T^2$$

$$\Delta C_P = -2.7649 + 0.9469 \times 10^{-3}T + 2.637 \times 10^{-7}T^2 \tag{5.34}$$

This value of ΔC_P may now be substituted in equation (5.31), whence we obtain

$$\Delta H^\circ = \Delta H^\circ_0 - 2.7649T + 0.4735 \times 10^{-3}T^2 + 0.879 \times 10^{-7}T^3 \tag{5.35}$$

as a general equation for the heat of formation of water vapor at unit fugacity. The integration constant ΔH°_0 may be evaluated from the known value of ΔH° at 25°c, namely, −57,798. Substituting this value and the value $T = 298.16$ in equation (5.35) and solving for ΔH°_0, we have

---

[1] ROSSINI, F. D., *J. Research Natl. Bur. Standards*, **22**, 407 (1939).

$$\begin{aligned}\Delta H_0^\circ &= -57{,}798 + 2.7649(298.16) - 0.4735 \times 10^{-3}(298.16)^2 \\ &\qquad - 0.879 \times 10^{-7}(298.16)^3 \\ &= -57{,}798 + 824.4 - 42.1 - 2.3 \\ &= -57{,}018 \text{ cal}\end{aligned}$$

The general heat of reaction equation, therefore, becomes

$$\Delta H^\circ = -57{,}018 - 2.7649T + 0.4735 \times 10^{-3}T^2 + 0.879 \times 10^{-7}T^3 \quad (5.36)$$

It may be used to calculate the heat of formation of water vapor at any temperature for which the heat capacity equations are valid. Thus, at 400°K, we have

$$\begin{aligned}\Delta H_{400}^\circ &= -57{,}018 - 1106.0 + 75.8 + 5.6 \\ \Delta H_{400}^\circ &= -58{,}043 \text{ cal}\end{aligned}$$

The calculation is here carried out in some detail so that the student may observe the influence of the various terms in equation (5.36) on the final result. At higher temperatures, the T^2 and T^3 terms assume more importance.

Maximum Flame Temperature.—The foregoing principles may be applied to the calculation of maximum flame temperatures. If, in a certain combustion, the heat of combustion is not lost to the surroundings, the temperature of the substances remaining after the combustion must rise as this heat is absorbed by these substances, until all the heat of combustion is absorbed. It is evident that the maximum temperature thus reached is dependent on the heat capacity of the substances that absorb the heat; if any inert body with an appreciable heat capacity is present, the maximum flame temperature will be less than that attained in the absence of this inert body. If the heat of reaction is ΔH and C_P is the heat capacity of the substances remaining after the reaction,

$$H_{T_m} - H_{T_1} = \Delta H = \int_{T_1}^{T_m} C_P \, dT \quad (5.37)$$

where T_1 is the initial temperature and T_m the maximum temperature.

As a simple example, consider the burning of methane in pure oxygen. We shall assume that the gases are present in stoichiometric proportions and that the reaction is complete so that the only substances present after the reaction are carbon dioxide and water. The heat of combustion previously given was for the production of gaseous carbon dioxide and liquid water, but in the flame the water is vaporized. Some of the heat will, therefore, be absorbed in the evaporation of water. Two methods of calculation are possible: Either we may calculate the heat absorbed by liquid water up to 100°C, then the latent heat of evaporation at 100°, and then the heat absorbed by the steam from 100°C to the maximum temperature; or we may calculate the latent heat of evaporation of water at room temperature and then the heat absorbed by the vapor from room temperature to the maximum temperature. In our example, we shall follow the second alternative. For the combustion of methane at 25°C,

$$CH_4 + 2O_2 = CO_2 + 2H_2O(\text{liq}); \qquad \Delta H = -212{,}800 \text{ cal} \qquad (5.38)$$

For the vaporization of water at 25°C,

$$H_2O(\text{liq}) = H_2O(\text{g, 1 atm}); \qquad \Delta H = 10{,}520 \text{ cal}$$

For 2 moles of water,

$$\Delta H = 21{,}040 \text{ cal}$$

On the assumption that the only substances left after the reaction are 1 mole of carbon dioxide and 2 moles of water and that 25°C = 300°K, the heat absorbed is

$$\Delta H = 21{,}040 + 2\int_{300}^{T_m} c(H_2O)\, dT + \int_{300}^{T_m} c(CO_2)\, dT = 212{,}800 \text{ cal} \qquad (5.39)$$

Because the heat capacity equations of Kelley[1] may be more safely extrapolated than those of Table 3.3, we shall use Kelley's equations here. For 2 moles of water,

$$2c(H_2O) = 16.44 + 0.30 \times 10^{-3}T + 2.68 \times 10^{-6}T^2$$

and, for CO_2,

$$\begin{array}{l} c(CO_2) = 10.34 + 2.74 \times 10^{-3}T \phantom{{}+ 2.68 \times 10^{-6}T^2} - 195{,}500T^{-2} \\ \hline \Sigma C_P = 26.78 + 3.04 \times 10^{-3}T + 2.68 \times 10^{-6}T^2 - 195{,}500T^{-2} \end{array}.$$

From equation (5.39), therefore,

$$212{,}800 - 21{,}040 = \int_{300}^{T_m} \sum C_P\, dT$$

$$191{,}760 = [26.78T + 1.52 \times 10^{-3}T^2 + 0.89 \times 10^{-6}T^3 + 195{,}500T^{-1}]_{300}^{T_m}$$

$$\begin{aligned} 26.78T_m + 1.52 \times 10^{-3}T_m^{\,2} + 8.9 \times 10^{-7}T_m^{\,3} & \\ + 195{,}500T_m^{-1} &= 191{,}760 + 8{,}030 + 140 + 20 + 650 \\ &= 200{,}600 \end{aligned}$$

When this equation is solved by the method of successive approximations, the maximum temperature is found to be a little less than 4200°K. Observe that the T^{-1} term is not important at high temperatures.

The above calculation is based on the premise that the combustion of

---

[1] KELLEY, K. K., *U. S. Bur. Mines, Bull.* 371 (1934).

methane goes to completion and that, at the high temperatures resulting from the combustion, the indicated products of combustion are stable. This assumption is obviously untrue at the extreme temperature of 4200°K. Some of the carbon dioxide and the water dissociate, absorbing heat during the dissociation, so that the observed maximum temperature would fall far below that indicated by the above temperature.

Furthermore, the maximum temperature is lowered greatly if the methane is burned in air rather than in pure oxygen. With every 21 moles of oxygen in air are found 79 moles of other gases, mostly nitrogen, so that about 7.5 moles of other gases will be found with the final product in equation (5.38). Under these conditions, the calculated maximum flame temperature becomes 2330°K rather than 4200°. Even at these temperatures, there will be some dissociation of the water and carbon dioxide. This dissociation which results in heat absorption by the gases will result in a greater *apparent heat capacity,* in accordance with the principles outlined earlier. Using this apparent heat capacity in the calculation, Ribaud[1] found the calculated value of

TABLE 5.6.—MAXIMUM FLAME TEMPERATURES* FOR THE COMBUSTION OF GASES IN AIR

Gas	°C	Gas	°C
Hydrogen	2040	Propane	1915
Carbon monoxide	2090	Butane	1915
Methane	1870	Acetylene	2210

* RIBAUD, *Chaleur et ind.*, **18**, 235, 295 (1937).

$$1870°\text{C} = 2140°\text{K}$$

instead of the value of 2330°K found on the assumption that there is no dissociation of the products of combustion. The correction for combustion in pure oxygen must obviously be much greater. Table 5.6 shows the maximum flame temperatures calculated for the combustion of several gases in air.

Problems

For data on heats of reaction not given in the tables of the text or in the problems, use standard sources such as F. R. Bichowsky and F. D. Rossini "Thermochemistry of Chemical Substances" (Reinhold Publishing Corporation, New York, 1936) (B-R); the tables of the American Petroleum Institute Research Project 44 at the National Bureau of Standards (API); compilations of K. K. Kelley in the bulletins of the Bureau of Mines; or the "International Critical Tables" (ICT). If you have not learned to use the tables, consult your instructor. Form the habit of recording the source, including volume and page, of each datum so that it may be checked when necessary. Note that the values for heats of combustion and formation in many tables represent the heat evolved.

---

[1] RIBAUD, *Chaleur et ind.*, **18**, 235, 295 (1937).

5.1. The heats of formation of the carbon compounds in B-R are based on diamond as the standard state for solid carbon. How will these values be changed when graphite is selected as the standard state?

5.2. Calculate the amount of energy required to transform 1 gram of ice at 0°c to steam at 150°c.

5.3. Calculate the heat of reaction at constant pressure ΔH for the following reactions. Record your answer in either calories or kilojoules, and indicate the source of your data.

$$\begin{aligned}
&H_2(g) + Cl_2(g) = 2HCl(g)\\
&2SO_2(g) + O_2(g) = 2SO_3(g)\\
&Ag^+(aq) + Cl^-(aq) = AgCl(c)\\
&K + H_2O(liq) = \tfrac{1}{2}H_2(g) + KOH(100\ aq)\\
&Na + H_2O(liq) = \tfrac{1}{2}H_2(g) + NaOH(100\ aq)\\
&Cu^{++}(aq) + Zn(c) = Zn^{++}(aq) + Cu(c)\\
&C_2H_5OH(liq) = C_2H_4(g) + H_2O(liq)\\
&C_2H_4(g) + H_2(g) = C_2H_6(g)
\end{aligned}$$

5.4. Calculate ΔH for the formation of liquid and gaseous methanol from the data in this chapter. Compare with the B-R values for the heat of formation, remembering that their values are based on carbon as diamond.

5.5. Naphthalene melts at 79.9°c. Select the necessary data, and calculate the heat absorbed in calories if 10 grams of molten naphthalene is allowed to crystallize at 50°c.

5.6. Using the value of $\Delta H^\circ_{298.16}$ for the formation of CO_2 given in equation (5.5) and the value

$$C(\text{graphite}) + \tfrac{1}{2}O_2(g) = CO(g); \qquad \Delta H^\circ_{298.16} = -26{,}416 \text{ cal}$$

calculate the standard heat of reaction at 25°c for the reaction

$$CO(g) + \tfrac{1}{2}O_2(g) = CO_2(g)$$

With this value and the heat capacity equations in Table 3.3, obtain the equation for ΔH° as a function of temperature.

5.7. From the data in Table 5.3, calculate the heat of reaction at 25°c for the isomerization of *n*-pentane to isopentane and to neopentane.

5.8. From the heats of formation of carbon monoxide (Prob. 5.6), carbon dioxide, and water, calculate the heat of reaction for the reaction

$$H_2(g) + CO_2(g) = H_2O(g) + CO(g)$$

Select the necessary data, and derive the equation for ΔH° as a function of temperature.

5.9. When methane is burned to carbon dioxide and liquid water,

$$\Delta H_{300} = -212{,}800 \text{ cal}$$

Calculate the maximum flame temperature when methane is burned in air. Consider air as 21 per cent oxygen and the remainder essentially nitrogen. Assume that the reactants are present in stoichiometric quantities and that the reaction is complete, without any dissociation.

5.10. The molar heat capacity of graphite according to K. K. Kelley [*U. S. Bur. Mines, Bull.* 371 (1934)] is represented to about 2 per cent by the equation

$$c_p = 2.673 + 0.002617T - \frac{116{,}900}{T^2} \text{ cal/deg}$$

between 273 and 1373°K and that of diamond between 273 and 1313°K is represented to about 3 per cent by the equation

$$c_P = 2.162 + 0.003059T - \frac{130{,}300}{T^2}\ \text{cal/deg}$$

For the transition

$$\text{C(graphite)} = \text{C(diamond)}; \qquad \Delta H^\circ_{298.16} = 453\ \text{cal}$$

Derive the complete equation for ΔH as a function of temperature for this transition.

5.11. Calculate the values for the heat of hydrogenation at 25°C of ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, and 1-octene to form the corresponding normal paraffins. How does the heat of hydrogenation vary with the length of the carbon chain?

5.12. On burning aluminum in a bomb calorimeter to form the oxide (corundum) P. E. Snyder and H. Seltz [*J. Am. Chem. Soc.*, **67**, 683 (1945)] obtain at 296.59°K

$$2\text{Al(c)} + \tfrac{3}{2}O_2\text{(g, 40 atm)} = Al_2O_3\text{(c)}; \qquad \Delta E = -1665.03\ \text{int kilojoules}$$

If $(\partial E/\partial P)_T$ for oxygen equals −6.51 joules per atmosphere per mole, calculate the value of ΔE at 296.59°K for the change

$$\tfrac{3}{2}O_2\text{(g, 1 atm)} = \tfrac{3}{2}O_2\text{(g, 40 atm)}$$

Calculate the value of ΔH_P at 296.59°K in kilojoules and in calories for the reaction

$$2\text{Al(c)} + \tfrac{3}{2}O_2\text{(g, 1 atm)} = Al_2O_3\text{(c)}$$

Select values for the heat capacities and calculate the value of ΔH° at 298.16°K. Snyder and Seltz obtain the value

$$\Delta H = -399.0_0 \pm 0.24\ \text{kcal}$$

5.13. The heats of reaction of magnesium and of magnesium oxide with 1 N hydrochloric acid as measured by C. H. Shomate and E. H. Huffman [*J. Am. Chem. Soc.*, **65**, 1625 (1943)] were as follows at 298.16°K:

$$\text{Mg} + 2\text{H}^+ = \text{Mg}^{++} + H_2; \qquad \Delta H = -111{,}322 \pm 41\ \text{cal}$$
$$\text{MgO} + 2\text{H}^+ = \text{Mg}^{++} + H_2O\text{(liq)}; \qquad \Delta H = -35{,}799 \pm 21\ \text{cal}$$

Calculate the value of ΔH for the formation of magnesium oxide.

5.14. According to B. F. Naylor [*J. Am. Chem. Soc.*, **67**, 150 (1945)], the molar heat content of solid magnesium fluoride is represented between 298.16° and the melting point, 1536°K, by the equation

$$MgF_2\text{(c)};\ H_T - H_{298.16} = 16.93T + 0.00126T^2 + \frac{220{,}000}{T} - 5{,}898\ \text{cal/mole}$$

and that of liquid magnesium fluoride between 1536 and 1800°K by the equation

$$MgF_2\ \text{(liq)};\ H_T - H_{298.16} = 22.57T + 2{,}450\ \text{cal/mole}$$

(*a*) From these equations, obtain the value for the molar heat of melting at 1536°K.

(*b*) From the heat content equations, derive the equations for the heat capacities of solid and liquid magnesium fluoride.

(*c*) Plot the heat contents of solid and liquid magnesium fluoride against temperature, and indicate on your graph the heat of melting of magnesium fluoride.

CHAPTER 6

HEAT OF SOLUTION. PARTIAL MOLAL HEATS

In the absence of specific interaction, the heat of solution of a solid in a liquid may be expected to equal the heat of melting of the solid at that temperature. A solution fulfilling these requirements is an example of an *ideal solution.* In such a solution, the dissolved solute molecules have no special attraction for the solvent molecules, and the heat of solution is independent of the final concentration of the solution. This means that there is no heat effect when more solvent is added to the solution, that is, there is no heat of dilution. These conditions do not obtain when an electrolyte is dissolved in water, the solution process being undoubtedly accompanied by hydration of the ions. In order to study the kind and magnitude of the heat effects found when electrolytes dissolve in water, we shall examine the behavior of aqueous potassium chloride solutions.

Apparent or Total Heat of Solution.—When 1 mole of KCl melts at 790°c, 6,400 calories of heat are absorbed. In order to calculate the heat of melting of KCl at room temperature, we must know the heat capacities of solid and liquid KCl between 20 and 790°c. Although data are not available on the heat capacity of liquid KCl, we may deduce from the corresponding data for AgCl, TlCl, and KNO_3 that liquid KCl has a higher heat capacity than solid KCl. If this is true, the heat of fusion of KCl at room temperature should be somewhat less than 6,400 calories (see Fig. 5.4). Actually, when KCl dissolves in 12 moles of water, only 3,786 calories of heat are absorbed, which is less than 60 per cent of the heat of fusion at 790°. Apparently, there are attractive forces between the water and salt that lessen the energy necessary to "melt" the salt into the salt solution. However, more energy is required if more water is used to dissolve the salt. If the mole of salt is dissolved in 100 moles of water, 4,391 calories of heat are absorbed; if it is dissolved in an infinite amount of water, 4,404 calories are absorbed. In 400 and 800 moles of water the heat of solution of KCl is at a maximum, 4,462 calories. These data are listed in Table 6.1. Column (2) gives the concentration of the final solution in terms of the mole ratio n_1/n_2, where n_1 represents the number of moles of water and n_2 the number of moles of KCl in the final solution; column (4) gives the corresponding heats of solution per mole of KCl ($n_2 = 1$).

Let us consider further the solution of 1 mole of KCl in 12 moles of water. The first of the K^+ ions and the Cl^- ions that dissolve enter pure water, forming an infinitely dilute solution of the ions in water. The molar heat of solution of these first ions must be that for the infinitely dilute solution of KCl, namely, 4,404 calories, as indicated in line *m*. When half the KCl has dissolved, the concentration of the solution is $n_1/n_2 = 24$, and the ions are now dissolving into a solution of this composition. The last of the KCl obviously dissolves in a salt solution in which the solution has the final concentration, namely, $n_1/n_2 = 12$. The heat effect for the whole process is a summation of all the heat effects, including those of the ions dissolving in pure water, those of the ions dissolving in all the intermediate concentrations, and those dissolving in the final solution. This value, from line *a*, is 3,786 calories. This heat is therefore, the *total heat of solution*. Because the first ions in dissolving absorbed more energy than the average, we may conclude that the last ions to dissolve required less energy than the average. As we shall see, the latter value is of the order of 3,400 calories.

TABLE 6.1.—HEAT OF SOLUTION OF POTASSIUM CHLORIDE IN WATER
(In defined calories)

Heat of fusion at 790°C: $KCl(c) = KCl(liq)$; $\Delta H = 6{,}400$ cal

Heat of formation at 18°C: $K(c) + \frac{1}{2}Cl_2(g) = KCl(c)$;

$\Delta H_f = H_f[KCl(c)] = -104{,}361$ cal

Number of moles of KCl $= n_2$; number of moles of water $= n_1$

H_f for water $= 0$, Q = heat of solution $= H_f(\text{solution}) - H_f[KCl(c)]$

	n_1/n_2, moles of water per mole of KCl	H_f(solution), heat of formation of solution per mole of KCl	Q/n_2, heat of solution per mole of KCl	n_2/n_1, moles of KCl per mole of water	Q/n_1, heat of solution per mole of water	$\Delta Q/\Delta n_1$	$\Delta Q/\Delta n_2$	$(\Delta Q/\Delta n_2) - 4{,}404$
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
a	12	−100,575	3,786	0.08333	315.5			
						30.7	3,420	−984
b	15	−100,483	3,878	0.06667	258.5			
						24.8	3,504	−900
c	20	−100,359	4,002	0.05000	200.1			
						16.8	3,670	−736
d	25	−100,275	4,086	0.04000	163.4			
						7.6	3,895	−609
e	50	−100,085	4,276	0.02000	85.52			
						2.3	4,161	−243
f	100	− 99,970	4,391	0.01000	43.91			
						0.58	4,332	− 72
g	200	− 99,912	4,449	0.005000	22.25			
						0.065	4,440	+ 36
h	400	− 99,899	4,462	0.002500	11.15			
						0	4,458	54
i	800	− 99,899	4,462	0.001250	5.578			
						−0.0088	4,469	65
j	1600	− 99,906	4,455	0.0006250	2.784			
						−0.0056	4 458	54
k	3200	− 99,915	4,446	0.0003125	1.389			
						−0.0028	4,451	47
l	6400	− 99,924	4,437	0.0001563	0.6933			
m	∞	− 99,957	4,404	0	0	0	4,404	0

Heats of Solution from Heats of Formation.—Table 6.1 was assembled from the data on the heat of formation[1] of solid potassium chloride and of the various solutions of the salt with water. The calculation of heats of solution from the tabulated heats of formations may be performed with confidence, for they were originally prepared from the experimental heat of solution data. The heat of formation tables represent convenient, concise summaries of the many separate experimental data.

For the formation of solid KCl at 18°c, we have

$$K(c) + \tfrac{1}{2}Cl_2(g) = KCl(c); \qquad \Delta H_f = -104{,}361 \text{ cal} \tag{6.1}$$

Similarly, for the formation of a solution of KCl in 200 moles of water, we have, from line *g* in column (3), Table 6.1,

$$\underset{0}{K(c)} + \underset{0}{\tfrac{1}{2}Cl_2(g)} + \underset{0}{200H_2O(liq)} = \underset{-99{,}912}{KCl(200H_2O)(liq)};$$
$$\Delta H_f = -99{,}912 \text{ cal} \tag{6.2}$$

In the preparation of the heat of formation tables for aqueous solutions, the heat of formation of the H_2O added as solvent was arbitrarily placed at zero. By subtracting equation (6.1) from equation (6.2), we have, at 18°c, for the heat of solution of KCl in 200 moles of water,

$$\underset{-104{,}361}{KCl(c)} + \underset{0}{200H_2O} = \underset{-99{,}912}{KCl(200H_2O)(liq)};$$
$$\Delta H = Q = 4{,}449 \text{ cal} \tag{6.3}$$

The symbol[2] Q, instead of the usual symbol ΔH, will be used for this change in heat content at constant pressure and temperature to prevent possible confusion with the heats of formation and duplication of symbols in a following section.

Heat of Solution of Water in Potassium Chloride Solutions.—In the previous section, the mixing of solid potassium chloride and of liquid water to form the solution was discussed in terms of the dissolving of 1 mole of potassium chloride in various quantities of water. The solution process may also be considered from the point of view of the water added to the mixture to form the solution. In this example, however, a distinction is to be made: The solid potassium chloride "melts" into the solution to form the final liquid phase whereas the liquid water enters the solution without any change in phase. This distinction does not exist for all solutions; we shall later consider the mutual solution of benzene and toluene for which arbitrary distinctions between "solvent"

---

[1] BICHOWSKY, F. R., and F. D. ROSSINI, "Thermochemistry of Chemical Substances," pp. 151–152, Reinhold Publishing Corporation, New York, 1936.

[2] Q corresponds to the *relative heat content* for which G. N. Lewis and M. Randall ("Thermodynamics and the Free Energy of Chemical Substances," Chap. VIII, McGraw-Hill Book Company, Inc., New York, 1923) use the symbol L.

and "solute" have no meaning. For the potassium chloride solution where the phases chosen as the *standard states* are pure solid potassium chloride and pure liquid water, special attention is usually concentrated on the salt. The heat effects attributed to the components of the solution take on a more symmetrical form when the reference standard states are, respectively, pure water and K^+ ions and Cl^- ions in an infinite amount of water to form an infinitely dilute solution of potassium chloride. However, this change in the selected standard state for the potassium chloride will not alter the heat effects attributed to the water itself.

Let us consider the heat effect produced *per mole of water* added to the solution. The observed heat effect when 12 moles of water and 1 mole of solid KCl form a solution is 3,786 calories. The heat effect *per mole of water* is 3,786/12 = 315.5 cal. This and other values per mole of water are indicated in column (6) in Table 6.1. Column (5) indicates the number of moles of KCl dissolved per mole of water; for line a, it is 0.08333 mole. From line g, column (4), 4,449 calories are absorbed when 200 moles of water dissolve 1 mole of KCl. The heat effect per mole of water is 4,449/200 = 22.25 cal, the amount of KCl per mole of water being 0.005 mole.

Column (4) gives the heat absorbed per mole of KCl, when the quantity of water varies as indicated in column (2). Column (6) gives the corresponding heat absorbed per mole of water, the quantity of KCl varying. These data are plotted in Fig. 6.1, those showing the variation of Q per mole of KCl with the number of moles of water, n_1, being plotted in Fig. 6.1a, and those for the variation of Q per mole of water with the number of moles of KCl, n_2, being plotted in Fig. 6.1b. The lack of agreement in the form of the two curves is evident.

Differential Heat of Solution of Water.—Both columns (4) and (6) in Table 6.1 list total heats of solution, the former the total heat absorbed per mole of KCl in the formation of the solution from the pure components, and the latter the total heat absorbed per mole of water. Suppose we wish to know, not the total heat absorbed, but the heat absorbed per mole of water when water is added to a solution rather than to pure potassium chloride. If 3 moles of water are added to a solution containing 12 moles of water and 1 mole of KCl, the heat effect is

$$Q_b - Q_a = 92 \text{ cal}$$

The heat effect per mole of water added while the number of moles of KCl remains unchanged ($n_2 = 1$) is

$$\frac{\Delta Q}{\Delta n_1} = \frac{Q_b - Q_a}{n_1(b) - n_1(a)} = \frac{3{,}878 - 3{,}786}{15 - 12} = \frac{92}{3} = 30.7 \text{ cal/mole} \qquad (6.4)$$

This value is the average heat of solution per mole of water in this concentration range. Similarly from lines d and e, Table 6.1, we have

$$\frac{\Delta Q}{\Delta n_1} = \frac{4{,}276 - 4{,}086}{50 - 25} = \frac{190}{25} = 7.6 \text{ cal/mole}$$

and from lines h and i,

$$\frac{\Delta Q}{\Delta n_1} = \frac{4{,}462 - 4{,}462}{800 - 400} = 0$$

Between $n_1/n_2 = 400$ and $n_1/n_2 = 800$, there is no apparent heat effect when 1 mole of water is added to the solution. Column (7) gives the various values of $\Delta Q/\Delta n_1$. It may be observed that, with more than 800 moles of water per mole of KCl, heat is evolved as more water is added.

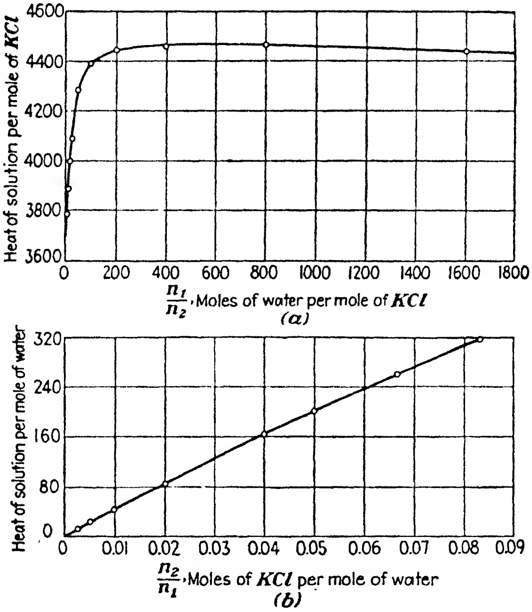


FIG. 6.1.—Heat of solution of potassium chloride and water.

The relation $\Delta Q/\Delta n_1$ does not give the true heat of solution of water at a particular concentration of solution; for, in the above calculations, finite quantities of water were added to produce finite changes in concentration. The true differential heat of solution is obtained when the finite quantities ΔQ and Δn_1 become the infinitesimals dQ and dn_1. The differential heat of solution of the water is defined by the derivative

$$\overline{Q_1} \equiv \left(\frac{\partial Q}{\partial n_1}\right)_{n_2,P,T} \tag{6.5}$$

where the subscripts indicate that the number of moles of potassium chloride and the pressure and temperature remain constant during the differentiation. In the case we are discussing, $n_2 = 1$, $P = 1$ atm, $T = 18°\text{C} = 291.16°\text{K}$. $\overline{Q}_1$ can be interpreted experimentally as the heat absorbed per mole of water at a given pressure, temperature, and number of moles of solute, when the quantity of added water is small enough not to change the concentration of the solution. It is the heat observed when 1 mole of water is added to an infinite quantity of solution of the specified concentration.

Table 6.2.—Relative Partial Molal Heat Contents of Potassium Chloride and Water in Aqueous Solutions of Potassium Chloride*

m = number of moles of KCl/1,000 g of water (molality)
n_1 = number of moles of water
n_2 = number of moles of KCl
Standard states: pure water; K^+ and Cl^- in ∞ moles of water

m Molality (1)	n_1/n_2, moles H_2O per mole of KCl (2)	$\overline{H}_1 - \overline{H}_1^0$, cal/mole of H_2O (3)	$\overline{H}_2 - \overline{H}_2^0$, cal/mole of KCl (4)
0	∞	0	0
0.01	5551	−0.0025	49
0.04	1388	−0.0079	63
0.09	617	−0.0064	63
0.16	347	+0.020	51
0.25	222	0.158	14
0.36	154	0.480	− 44
0.64	86.8	1.53	−165
1.00	55.5	3.57	−306
1.44	38.5	6.59	−442
1.96	28.3	11.58	−605

* Data from F. D. Rossini, *Bur. Standards J. Research*, **6**, 802 (1931).

The value of $(\partial Q/\partial n_1)_{n_2,P,T}$ can be obtained graphically from the plotted curve in Fig. 6.1*a*, for it is given by the slope of the curve at any value of Q and n. It may also be obtained analytically from the empirical equation representing the curve. It appears that $\Delta Q/\Delta n_1$ differs widely from $\partial Q/\partial n_1$ only at the concentrations where the curve changes direction abruptly. In Table 6.2, column (3), are listed some values of $\partial Q/\partial n_1$ here indicated under the notation $\overline{H}_1 - \overline{H}^0$. Inspection shows reasonable agreement between the values of $\Delta Q/\Delta n_1$ in Table 6.1 and the values of

$$\frac{\partial Q}{\partial n_1} = \overline{H}_1 - \overline{H}^0$$

in Table 6.2.

Differential Heat of Solution of Potassium Chloride.—From columns (5) and (6), Table 6.1, may be obtained the corresponding values for $\Delta Q/\Delta n_2$ for solutions containing a constant quantity of water ($n_1 = 1$). Thus, from lines *a* and *b*,

$$\frac{\Delta Q}{\Delta n_2} = \frac{258.5 - 315.5}{0.06667 - 0.08333} = \frac{57.0}{0.01666} = 3{,}420 \text{ cal}$$

This means that 3,420 calories are absorbed per mole of KCl dissolving into a solution containing 0.08333 to 0.06667 mole of potassium chloride per mole of water. It was pointed out earlier that the first potassium chloride to dissolve when the solution is prepared, dissolves into pure water with a molar heat of solution of 4,404 calories. The above calculation shows that the last to dissolve does so with a molar heat of solution of 3,420 calories. The observed total heat of solution is the summation of all the heat effects for the range of concentration up to the final concentration. It is, therefore, intermediate between these values, ranging in this concentration interval from 3,786 to 3,878 calories per mole of potassium chloride. The data in column (8) indicate the values of $\Delta Q/\Delta n_2$ for the entire concentration range.

The differential heat of solution of potassium chloride appears to pass through a maximum at a concentration lying between 0.0006 and 0.0012 mole of KCl per mole of water. Because a molal aqueous solution contains 1 mole of solute in 55.51 moles (1,000 grams) of water, the corresponding molalities of potassium chloride solution are 0.033 to 0.067 molal.

The true differential heat of solution of potassium chloride is represented by the derivative

$$\overline{Q_2} \equiv \left(\frac{\partial Q}{\partial n_2}\right)_{n_1,P,T} \tag{6.6}$$

This value may be obtained from the slope of the curve in Fig. 6.1*b* or from the empirical equation for the curve. The values for $\overline{Q_2}$, where KCl in infinite aqueous solution is the standard state, are given in column (4), Table 6.2. They may be compared with the corresponding values of $(\Delta Q/\Delta n_2) - 4{,}404$, obtained for finite concentration intervals, given in column (9), Table 6.1.

Partial Molal Quantities.—The limiting values of the differential molar heats of solution of the components in a solution at constant pressure, temperature, and composition as represented by the equations

$$\overline{Q_1} = \left(\frac{\partial Q}{\partial n_1}\right)_{n_2,P,T} \quad \text{and} \quad \overline{Q_2} = \left(\frac{\partial Q}{\partial n_2}\right)_{n_1,P,T}$$

are examples of quantities called by Lewis[1] *partial molal quantities*. Similarly, the *partial molal volumes* of the components in a solution are given by

$$\overline{V}_1 \equiv \left(\frac{\partial V}{\partial n_1}\right)_{n_2,P,T} \quad \text{and} \quad \overline{V}_2 \equiv \left(\frac{\partial V}{\partial n_2}\right)_{n_1,P,T} \tag{6.7}$$

In general, a partial molal quantity is the partial derivative of the quantity with respect to number of moles of one component of the solution, the pressure, temperature, and composition remaining constant. Following Lewis, we shall designate the partial molal quantities by the bar over the symbol, the subscript indicating the particular component referred to. For aqueous solutions, it is customary to designate the solvent water as the first component and the solute as the second component. However, in many solutions the distinction between solvent and solute is purely arbitrary. For a water solution, then, $\overline{H}_1$ represents the partial molal heat content of the water in the solution and $\overline{H}_2$ the partial molal heat content of the solute. At times, we may be interested in evaluating the partial change of the internal energy of a system with composition at constant volume and entropy. We have then the partial derivatives

$$\mu_1 = \left(\frac{\partial E}{\partial n_1}\right)_{n_2,V,S} \quad \text{and} \quad \mu_2 = \left(\frac{\partial E}{\partial n_2}\right)_{n_1,V,S} \tag{6.8}$$

These quantities are *not* called partial molal quantities. The term "partial molal" is reserved for *constant-temperature, constant-pressure processes.* With this understanding, we shall omit the qualifying subscripts in the subsequent discussion.

As we have stated earlier, the extensive properties of a substance in a standard state are indicated by the superscript ° as in the symbol H°. For a single phase of pure substance the partial molal value and the molar value of a property are identical, for

$$\overline{H}_1^\circ = \left(\frac{\partial H^\circ}{\partial n_1}\right) = \frac{H^\circ}{n_1} = H_1^\circ \tag{6.9}$$

Similarly, the partial molal heat content of the solute in a system containing one mole of K^+ ions and Cl^- ions in an infinite quantity of water may be expressed as

$$\overline{H}_2 = \left(\frac{\partial H}{\partial n_2}\right)_{n_1 \to \infty}$$

If this solution is selected for the standard state of potassium chloride, we have for the standard molar heat content of the potassium chloride

---

[1] LEWIS, G. N., *Proc. Am. Acad. Arts Sci.*, **43**, 273 (1907); *Z. physik. Chem.*, **61**, 144 (1907).

$$\overline{\text{H}^{\circ}} = \left(\frac{\partial H}{\partial n_2}\right)_{n_1=\infty} \tag{6.10}$$

If the pure potassium chloride is selected as the standard state, we have

$$\overline{\text{H}_2^{\circ}} = \left(\frac{\partial H^{\circ}}{\partial n_2}\right)_{n_1=0} = \text{H}^{\circ} \tag{6.11}$$

These two standard states evidently have different heat contents.

When a solution is made from the substances A and B in their standard states, their respective heat contents being H_1° and H_2°, the heat of solution may be represented by the equation

$$\underset{H_1^{\circ}}{n_1\text{A}} + \underset{H_2^{\circ}}{n_2\text{B}} = \underset{H}{\text{solution}}; \qquad \Delta H = H - (H_1^{\circ} + H_2^{\circ}) = Q \tag{6.12}$$

From equation (6.12), we have for the partial molal heat of solution of the solvent

$$\overline{\text{Q}_1} = \frac{\partial H}{\partial n_1} - \frac{\partial H_1^{\circ}}{\partial n_1} = \overline{\text{H}_1} - \overline{\text{H}_1^{\circ}} \tag{6.13}$$

for $\partial H_2^{\circ}/\partial n_1 = 0$. (Why?)

The difference between the partial molal heat content of the constituent A in the solution and in the standard state is called its *relative* partial molal heat content. Similarly,

$$\overline{\text{Q}_2} = \frac{\partial H}{\partial n_2} - \frac{\partial H_2^{\circ}}{\partial n_2} = \overline{\text{H}_2} - \overline{\text{H}_2^{\circ}} \tag{6.14}$$

Values of $\overline{\text{H}_2} - \overline{\text{H}_2^{\circ}}$, the relative partial molal heat content for KCl in aqueous solutions, are given in column (4), Table 6.2. If the standard state selected for the potassium chloride had been the solid, the listed values for $\overline{\text{H}_2} - \overline{\text{H}_2^{\circ}}$ would be increased by 4,404 calories, for, from Table 6.1, we have

$$\text{H}_f(\text{infinite dilution}) - \text{H}_f(\text{solid}) = 4{,}404 \text{ cal}$$

For convenience in comparison, molalities are converted to mole ratios in column (2), Table 6.2. Within the limits of the approximation involved in evaluating $\Delta Q/\Delta n$ instead of $\partial Q/\partial n$, the values in column (9), Table 6.1, are seen to correspond to those in column (4), Table 6.2.

Integral Heat of Solution of Benzene and Toluene.—In many solutions, especially those having constituents miscible in all proportions, the composition is best represented in terms of percentage. The whole composition range may then be shown on a single diagram. Weight percentages may be used but, in the majority of chemical problems, mole percentages are more instructive. If molalities are plotted, the properties of the pure solvent may be obtained at $m = 0$, but the properties of the pure solute cannot be represented on the same diagram. Thus, in Fig. 6.1*a* the heat of solution of water in the infinitely dilute solution cannot be made to fall on the diagram. On the contrary, when the composition is expressed in percentage (or fraction), the entire range of composition from pure A to pure B may be indicated on one diagram.

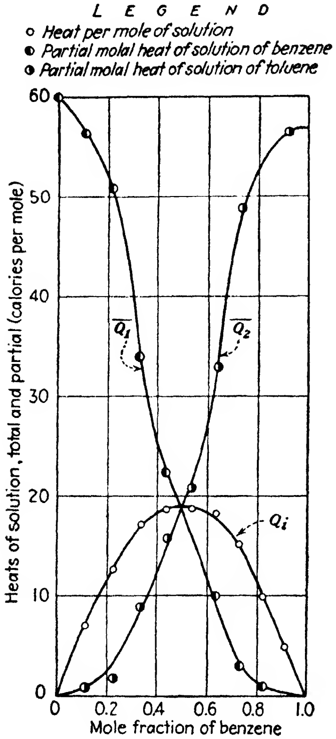


FIG. 6.2.—Heat of solution of benzene and toluene (in calories).

Benzene and toluene mix in all proportions. When their heat of mixing is plotted against mole fraction as in Fig. 6.2, the curve is fairly symmetrical; this method of plotting is, therefore, well suited to solutions of this type. The experimental heats of solution for this system in calories per gram of solution are given in column (2), Table 6.3. From these values and from the composition of the solution, expressed in columns (1) and (3) as weight fraction and mole fraction, respectively, may be calculated the corresponding heats of solution per mole of the mixture. The mole of mixture may be defined as follows: When n_1 moles of benzene and n_2 moles of toluene are mixed, the sum of n_1 and n_2 being unity, the final solution contains a number of molecules equal to the Avogadro number; therefore, 1 mole. In such a solution, we find from the definition of mole fraction

$$N_1 = \frac{n_1}{n_1 + n_2}, \qquad N_2 = \frac{n_2}{n_1 + n_2} \qquad (6.15)$$

that the number of moles of each constituent is equal to its mole fraction since $n_1 + n_2 = 1$.

The heat absorbed in the solution process depends on the quantity of solution produced. In the potassium chloride solution, the heat absorbed was listed both per mole of potassium chloride and per mole of water. For reasons that will appear, we shall discuss here the heat absorbed *per mole of solution.* This heat, corresponding to the total heat Q discussed earlier but referring always to 1 mole of solution, will be defined as the *integral heat of solution* Q_i. Values for this integral heat are given in column (4), Table 6.3. Where n_1 and n_2, respectively, are the number of moles of the two constituents of the solution, the integral heat Q_i is related to the total heat Q for $n_1 + n_2$ moles by the relation

$$\mathrm{Q}_i = \frac{Q}{n_1 + n_2} \tag{6.16}$$

Values for Q_i are plotted as ordinates against N_1 as abscissas in Fig. 6.2. At any composition N_1, the slope of the tangent to the curve gives values of $\partial \mathrm{Q}_i/\partial N_1$. This slope is related to the partial molal heat, which is $\partial \mathrm{Q}_i/\partial n_1$. In order to calculate the latter, we must find the relation between dN_1 and dn_1 at constant pressure and temperature.

TABLE 6.3.—HEATS OF SOLUTION OF BENZENE AND TOLUENE AT 17°C
(In calories)

Gram of benzene/gram of solution, weight fraction (1)	Heat absorbed*/gram of solution (2)	Mole fraction of benzene (3)	Q_i, heat absorbed per mole of solution (4)	$\bar{\mathrm{Q}}_1 = \bar{\mathrm{H}}_1 - \mathrm{H}_1^\circ$, cal/mole (5)	$\bar{\mathrm{Q}}_2 = \bar{\mathrm{H}}_2 - \mathrm{H}_2^\circ$, cal/mole (6)
0.00	0	0	0	60	0
0.10	0.080	0.116	7.24	57	1
0.20	0.144	0.228	12.81	51	2
0.30	0.198	0.336	17.31	34	9
0.40	0.219	0.440	18.83	23	16
0.50	0.223	0.541	18.85	17	21
0.60	0.220	0.639	18.30	10	33
0.70	0.186	0.734	15.22	3	49
0.80	0.124	0.825	9.99	1	55
0.90	0.063	0.914	5.00	0	57
1.00	0	0	0	0	57

* Data of G. C. Schmidt, *Z. physik. Chem.*, **121**, 221 (1926).

Partial Molal Quantities from Mole Fraction Diagrams.—Although the following relations are derived for partial molal heats, they apply also to other thermodynamic functions. We shall, therefore, analyze them in some detail.

On mixing n_1 moles of a substance A and n_2 moles of a substance B at constant pressure and temperature, the heat of solution is Q and we have

$$n_1\mathrm{A} + n_2\mathrm{B} = n_1 + n_2 \text{ moles of solution;} \qquad \Delta H = Q \tag{6.17}$$

For the formation of 1 mole of solution, the corresponding equation is

$$\left(\frac{n_1}{n_1 + n_2}\right)\mathrm{A} + \left(\frac{n_2}{n_1 + n_2}\right)\mathrm{B} = 1 \text{ mole of solution;}$$

$$\Delta H = \frac{Q}{n_1 + n_2} = \mathrm{Q}_i \tag{6.18}$$

Because $n_1/(n_1 + n_2)$ and $n_2/(n_1 + n_2)$ are the mole fractions N_1 and N_2, respectively, equation (6.18) may be written as

$$N_1\text{A} + N_2\text{B} = 1 \text{ mole of solution}; \qquad \Delta H = \text{Q}_i \tag{6.19}$$

Furthermore, from the definition of mole fraction, we have

$$\left.\begin{aligned} N_1 &= 1 - N_2 \\ N_2 &= 1 - N_1 \end{aligned}\right\} \tag{6.20}$$

Now the relation between $\partial Q/\partial N$ and $\partial Q/\partial n$ can be found from the relations between dN and dn and these in turn may be obtained from equations (6.15).

For the component A, we have, keeping n_2 constant,

$$\text{d}N_1 = \text{d}\left(\frac{n_1}{n_1 + n_2}\right) = \frac{(n_1 + n_2)\,\text{d}n_1 - n_1(\text{d}n_1)}{(n_1 + n_2)^2} = \frac{n_2}{(n_1 + n_2)^2}\,\text{d}n_1 \tag{6.21}$$

which may be rearranged to give

$$\frac{\text{d}N_1}{N_2} = \frac{\text{d}n_1}{(n_1 + n_2)} \tag{6.22}$$

For the partial molal heat of the component A, we have from equations (6.5) and (6.16), n_2 still being constant,

$$\overline{\text{Q}_1} = \frac{\partial Q}{\partial n_1} = \frac{\partial[(n_1 + n_2)\,\text{Q}_i]}{\partial n_1} = \text{Q}_i + (n_1 + n_2)\,\frac{\partial \text{Q}_i}{\partial n_1} \tag{6.23}$$

From equation (6.22), therefore,

$$\overline{\text{Q}_1} = \text{Q}_i + N_2\,\frac{\partial \text{Q}_i}{\partial N_1} = \text{Q}_i + (1 - N_1)\,\frac{\partial \text{Q}_i}{\partial N_1} \tag{6.24}$$

Similarly, for component B, n_1 now being constant, the partial molal heat is

$$\overline{\text{Q}_2} = \frac{\partial Q}{\partial n_2} = \text{Q}_i + N_1\,\frac{\partial \text{Q}_i}{\partial N_2} = \text{Q}_i + (1 - N_2)\,\frac{\partial \text{Q}_i}{\partial N_2} \tag{6.25}$$

The difference between $\overline{\text{Q}_1}$ and $\overline{\text{Q}_2}$ is found from equations (6.24) and (6.25) and the relation $\partial N_1 = \partial(1 - N_2) = -\partial N_2$ to be

$$\left.\begin{aligned} \overline{\text{Q}_1} - \overline{\text{Q}_2} &= \frac{\partial \text{Q}_i}{\partial N_1} \\ \text{and} \qquad & \\ \overline{\text{Q}_2} - \overline{\text{Q}_1} &= \frac{\partial \text{Q}_i}{\partial N_2} \end{aligned}\right\} \tag{6.26}$$

The evaluation of $\overline{\text{Q}_1}$ and $\overline{\text{Q}_2}$ can be made readily from the Q_i-mole-fraction curve. The method is illustrated in Fig. 6.3. At the mole fraction of the component A equal to $N_1 = x$, the integral heat of solution has the value

$$Q_i = \overline{ca} = \overline{fe} \tag{6.27}$$

The tangent to the curve at this point represented by the dotted line

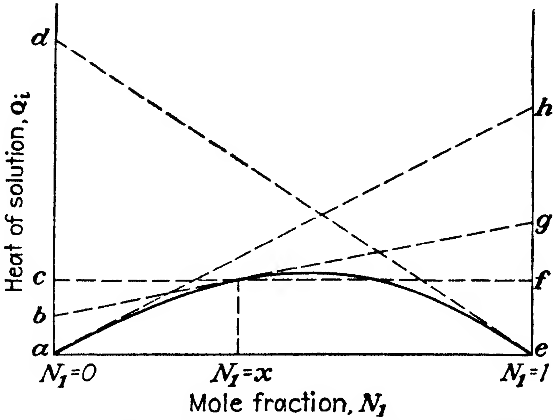


FIG. 6.3.—Partial molal heats from a mole-fraction diagram.

$\overline{bg}$ intercepts the axis $N_1 = 0$, $N_2 = 1$, at the point b and the axis $N_1 = 1$, $N_2 = 0$ at the point g. We shall show that

$$\frac{\partial Q}{\partial n_1} = \overline{Q_1} = \overline{ge} \tag{6.28}$$

and

$$\frac{\partial Q}{\partial n_2} = \overline{Q_2} = \overline{ba} \tag{6.29}$$

which represent the above intercepts.

The proof follows:

The slope of the tangent $\overline{bg}$ for $N_1 = x$ is given by

$$\frac{\partial Q_i}{\partial N_1} = \frac{\overline{gf}}{\overline{ex}} = \frac{\overline{gf}}{1 - N_1} = \frac{\overline{gf}}{N_2} \tag{6.30}$$

But, from equation (6.20),

$$dN_1 = -dN_2 \tag{6.31}$$

Hence, for $N_2 = 1 - x$,

$$\frac{\partial Q_i}{\partial N_2} = -\frac{\overline{gf}}{N_2} = \frac{-(\overline{cb})}{N_1} \tag{6.32}$$

When the values from equations (6.27) and (6.30) are substituted in equation (6.24), we have

$$\frac{\partial Q}{\partial n_1} = \overline{fe} + N_2 \frac{(\overline{gf})}{N_2} = \overline{ge}$$

and, from equations (6.25), (6.27), and (6.32),

$$\frac{\partial Q}{\partial n_2} = \overline{ca} + N_1 \frac{-(\overline{cb})}{N_1} = \overline{ba}$$

These equations are, respectively, equations (6.28) and (6.29).

The equations may be applied at the limit for pure A at which $N_1 = 1$, and $N_2 = 0$. Under these conditions,

$$\overline{Q_1} = \frac{\partial Q}{\partial n_1} = \overline{hc} \tag{6.33}$$

and

$$\overline{Q_2} = \frac{\partial Q}{\partial n_2} = 0 \tag{6.34}$$

Similarly, at the limit for pure B, $N_2 = 1$, $N_1 = 0$, and

$$\overline{Q_1} = \frac{\partial Q}{\partial n_1} = 0 \tag{6.35}$$

$$\overline{Q_2} = \frac{\partial Q}{\partial n_2} = \overline{da} \tag{6.36}$$

The partial molal heats of solution of benzene and of toluene are calculated in this manner from the intercepts of the tangents to the curve in Fig. 6.2. These values are listed in columns (5) and (6), Table 6.3, and they are plotted against mole fraction in Fig. 6.2. Observe that the two partial molal heat curves cross each other at the composition corresponding to the maximum integral heat where the slope of the tangent to the curve is zero. At this value, from equations (6.24) and (6.25),

$$\overline{Q_1} = \overline{Q_2} = Q_i$$

The three curves must, therefore, intersect at this composition.

The partial molal heat of solution of the benzene is at a maximum in the solution of nearly pure toluene and approaches zero as the solution approaches the composition of pure benzene. Similarly, for the toluene the partial molal heat of solution of toluene is at a maximum when the toluene dissolves into nearly pure benzene, and approaches zero when the toluene dissolves into a solution of nearly pure toluene.

Problems

6.1. Many data for solutions are reported *per gram of solution.* When we use the gram instead of the mole as the unit of substance and express concentrations in terms of weight fractions instead of mole fractions, the heats of solution or the volume change on solution per gram of solution may be plotted against weight fraction to give us *partial specific quantities* corresponding to the *partial molal quantities* defined in equations (6.5) to (6.7). The partial specific heat of solution and volume of solution may be defined by the following equations:

$$\frac{\partial Q}{\partial m} = \bar{\mathrm{q}}; \qquad \frac{\partial V}{\partial m} = \bar{\mathrm{v}} \tag{6.37}$$

where m is the mass of a component in grams and $\bar{\mathrm{q}}$ and $\bar{\mathrm{v}}$ are the partial specific quantities. Show that

$$\overline{\mathrm{q}_1} = q_i + w_2 \frac{\partial q_i}{\partial w_1} = q_i + (1 - w_1) \frac{\partial q_i}{\partial w_1} \tag{6.38}$$

$$\overline{\mathrm{q}_2} = q_i + w_1 \frac{\partial q_i}{\partial w_2} = q_i + (1 - w_2) \frac{\partial q_i}{\partial w_2} \tag{6.39}$$

where q_i is the heat of solution *per gram of solution* and w_1 and w_2 are the weight fractions of the first and second components of the solution. Show also that the corresponding partial molal heats are

$$\overline{Q_1} = M_1\overline{\mathrm{q}_1}; \qquad \overline{Q_2} = M_2\overline{\mathrm{q}_2} \tag{6.40}$$

where M_1 and M_2 are the molar weights of the two components.

6.2. For the benzene-toluene solutions listed in Table 6.3, plot the heat of solution per gram of solution, obtained from column (2), against the corresponding weight fraction of benzene obtained from column (1). Use the relations derived in Prob. 6.1, and calculate graphically the partial specific heats of solution of benzene and toluene at the concentrations given from the tangents to the curve. Obtain the partial molal heats of solution from these values and compare with those listed in columns (5) and (6), Table 6.3. Tabulate your results. Plot your values of the partial molal heats of solution against the corresponding mole fractions listed for these solutions in column (3).

6.3. Apply the method of Prob. 6.2 to the securing of the partial molal volumes of benzene and toluene in these same solutions. Schmidt [*Z. physik. Chem.*, **121,** 221 (1926)] gives the following data for the increase in volume when 1 gram of solution is prepared from benzene and toluene at 17°C. When the solutions contain 10, 20, 30, 40, 50, 60, 70, 80, and 90 per cent by weight of benzene, the increase in volume is 2.5, 5.1, 8.3, 9.0, 10.0, 9.5, 8.3, 7.2, and 4.0, all times 10^{-4} cc, respectively. Plot these data against weight fraction, and calculate graphically the partial molal volumes of benzene and toluene compared with those of the pure components. If the densities of benzene and toluene at 17°C are 0.88299 and 0.86956, respectively, what are the partial molal volumes of these components at each concentration and at infinite dilution? Plot $\overline{\mathrm{v}_1}$ and $\overline{\mathrm{v}_2}$ against mole fraction. How do the partial molal volumes of these substances at infinite dilution compare with their molar volumes as pure substances?

6.4. The apparent molar volume ϕ of a solute is frequently reported in the literature. It is defined in the equation

$$V = n_1\mathrm{v}_1 + n_2\phi \tag{6.41}$$

where n_1 and n_2 are the number of moles of solvent and solute, respectively, V is the volume of the solution, and v_1 the molar volume of the pure solvent. Show that the partial molal volume of the solute $\overline{\mathrm{v}_2}$ is related to the apparent molar volume by the equation

$$\overline{\mathrm{v}_2} = \phi + n_2 \frac{\partial \phi}{\partial n_2} \tag{6.42}$$

6.5. According to Longworth [*J. Am. Chem. Soc.*, **59,** 1483 (1937)], mixtures of $H^1{}_2O$ and $H^2{}_2O$ form perfect solutions, there being no volume change on mixing. If

$H^1{}_2O$ is component 1 and $H^2{}_2O$ is component 2, show that the volume v_i of a mole of solution is given by the relation

$$v_i = N_1 v_1 + N_2 v_2 = \frac{N_1 M_1 + N_2 M_2}{d}$$

where M_1 and M_2 are the molar weights of the two components, N_1 and N_2 are their mole fractions, and d is the density of the solution. If the atomic weights are $O = 16.0000$, $H^1 = 1.00786$, and $H^2 = 2.01419$ and the densities of $H^1{}_2O$ and $H^2{}_2O$ are, respectively, $d_4^{25} = 0.99705_5$ and $d_4^{25} = 1.10466$, what are the molar volumes of $H^1{}_2O$ and $H^2{}_2O$? What are the molar volume and density of natural water containing 0.017_5 mole per cent of $H^2{}_2O$?

CHAPTER 7

THE SECOND LAW OF THERMODYNAMICS

When one considers the entire period of time in which man has speculated and experimented on the material universe, one is impressed by the fact that the laws of the conservation of matter and of energy were formulated relatively recently. The conservation laws were not self-evident because the world is a continually changing world in which the natural processes involved in the changes tend to mask the laws of conservation. In terms of our present thinking, the changes occur because the world is not at equilibrium. Living things grow and die, water evaporates into the air and is precipitated again, summer and winter alternate and bring with them a whole series of changes. Even though we accept the laws of the conservation of matter and of energy as valid in the changing world, we must still consider whether any general principles apply to change itself. We suspect that such principles can be found because as chemists we know that, under given initial conditions, natural changes take place in a given direction. If these principles can be expressed in an energy law, the law will be as useful and fundamental as the laws of conservation. Before we discuss such a law, we shall first consider some of the aspects of change in more detail.

Spontaneous Processes.—Processes taking place in a system without the aid of an outside agency are called *spontaneous processes*. As illustrations, we shall consider several spontaneous processes involving energy.

1. *"Flow" of Energy from Higher Temperatures to Lower Temperatures.*—When two bodies at different temperatures are brought into thermal contact, the hotter body loses energy to the colder body. When no work is done in the process, all the energy lost by the hotter body flows to the colder body thus increasing the energy of the colder body. In agreement with the principles embodied in the first law of thermodynamics, there is here no net loss or gain of energy, yet the process is spontaneous with a fixed direction. Energy may be exchanged between colder and hotter bodies, but the net effect is to increase that of the colder body and to decrease that of the hotter body. Net energy exchanges that follow these rules are called *heat* in classical thermodynamics. They may be measured conveniently by a calorimeter.

These facts of energy flow may be used to define a state of *thermal equilibrium.* Two bodies are at thermal equilibrium when they are at the same temperature. They are at the same temperature if, when placed in thermal contact so that energy can pass freely between them, there is no net spontaneous flow of energy as heat from one body to the other. As we shall see, the flow of energy from bodies at a higher temperature to bodies at a lower temperature can be made to do useful work, if the flow takes place through a suitable heat engine.

2. *Flow of Liquid from a Higher Level to a Lower Level.*—The movement of a freely flowing liquid from higher levels to lower levels is a spontaneous process familiar to all observers. The process continues until the levels have become equalized. The system is then in mechanical equilibrium. Observe that in this spontaneous flow of liquids (as well as in the flow of gases in the two following examples) there is no heat effect. However, the liquid could have done work in passing from the higher to the lower level. Any general energy law that applies to all spontaneous processes must, therefore, apply to this one as well.

3. *Flow of Gases from Regions of Higher Pressure to Regions of Lower Pressure.*—Just as temperatures tend to equalize when energy can flow from one body to another, and liquid levels tend to equalize when the liquid can flow, so the pressures in a gaseous system tend to equalize when the gas is free to move. If, initially, part of the gas is at a higher pressure than another part, the gas moves from the region of higher pressure to the region of lower pressure until the pressures become equalized. Although some of the individual molecules of gas may be moving in a direction opposite to the direction of flow, the net effect of all the molecular movements is flow of the gas in the one definite direction. Here, again, the spontaneous processes tend to bring the system to mechanical equilibrium.

4. *Diffusion of Gases.*—In a gas that consists of more than one kind of molecules, the tendency for pressures to equalize is observed experimentally for each of the chemical constituents of the gas. The behavior of each constituent depends on its partial pressures in the different parts of the system and not on the total pressure of all the constituents. This fact is highly important in the application of thermodynamics to chemistry because there are so many chemical analogies to this behavior. If a volume of nitrogen and a volume of oxygen at the same pressure and temperature are brought into contact with each other, the system is not in complete equilibrium even though it is at thermal equilibrium and mechanical equilibrium in the usual sense. Spontaneously, the nitrogen diffuses into the oxygen, where its partial pressure was originally zero, until it is so distributed that its partial pressures in the different parts of the system are identical. Similarly, the oxygen diffuses into the nitrogen until it is also distributed throughout the system with a uniform partial pressure. Or, if, at a suitable high temperature, hydrogen is

separated from air by a palladium membrane permeable to hydrogen but not to air at that temperature, the hydrogen will diffuse through the palladium into the air until the partial pressures of the hydrogen on both sides of the membrane become equal. This diffusion takes place even though the total pressure of the gases on the one side becomes greater than that on the other side of the membrane. At first thought, we might consider this characteristic behavior outside the scope of thermodynamics because the heat absorbed or evolved during this redistribution of the gas or gases is negligible or zero and because, as in the case of the nitrogen and oxygen, the total pressure need not change during the process. However, the second law of thermodynamics applies also to such spontaneous processes.

5. *Chemical Reaction.*—Another type of spontaneous process that concerns us particularly is the usual chemical reaction. Unless we happen to start with equilibrium concentrations of the reacting substances, there is a tendency for the reaction to proceed in one direction or the other. Even when, under the experimental conditions, the reaction rate is exceedingly small, the tendency still exists. When a reaction rate is small, a catalyst is sometimes added. At other times, a new mechanism for the reaction is sought—a mechanism with more favorable rates. Thus, hydrogen reacts with oxygen at room temperature to form water at an exceedingly slow rate, but the reaction can be carried out even at room temperature in a suitable electrochemical cell. We must, however, not let the slowness of a rate disguise the reality of the tendency for the reaction to proceed in a definite direction.

In all the types of spontaneous processes considered, the tendencies of the process to go in a definite direction are not altered by the slowness of the rate. If a body at a higher temperature is separated from the body at the lower temperature by a thermal insulator so that the rate of heat flow becomes small, energy will still flow from the hotter to the colder body. If water at a higher level is throttled so that it flows very slowly, it will still flow toward the lower level. If a gas is throttled so that the rate of flow is small, it will still move from regions of higher pressure to regions of lower pressure. And, if two gases are separated by a small orifice so that diffusion becomes very slow, they will still diffuse until the partial pressures of the constituents become equalized. Thermodynamics deals primarily with the difference in properties of the initial and final states and makes its predictions about the direction of a process on the basis of the values of the properties at these states and not the rate at which the process or reaction occurs. For this reason, thermodynamics can help us determine whether, and to what extent, a given reaction can proceed and can, therefore, tell us whether the introduction of a catalyst would be useful.

Tendency toward Equilibrium.—Spontaneous processes and the tendency for them to proceed in a definite direction may be considered from another point of view. As spontaneous processes continue, they tend to run down so that they finally stop. Only when the system undergoing the process is replenished, can it continue indefinitely. Thus, if no new energy enters the system, the final result of energy flow from a hotter to a colder body is the cooling of the hotter body and the warming of the colder one. As a result of the process, the temperature difference between them finally becomes vanishingly small, and the two bodies are at thermal equilibrium.

The tendency toward equilibrium is also observed when liquids flow in a closed system. As enough water flows from the higher level to the lower level, the height of the water at the upper level falls and the height of the water at the lower level rises until the water has reached a common level. A waterfall can be maintained only if water is replenished at the higher level and removed at the lower level. Similarly, a thermal difference can be maintained between two bodies in thermal contact only if energy is supplied to the hotter body and removed from the colder body.

When gases flow from regions of higher pressure to regions of lower pressure or when they diffuse from regions of higher partial pressures to regions of lower partial pressures, there is a similar tendency for the higher pressures to decrease and the lower pressures to increase until the pressures or partial pressures have equalized. In the flow of gases or of liquids to lower levels or lower pressures, there is a tendency toward a mechanical equilibrium and the processes do not cease until mechanical equilibrium is reached.

Similar tendencies toward equilibrium exist in chemical systems. When hydrogen and oxygen react to form water, hydrogen and oxygen are consumed and water is produced. Unless the supply of the reacting gases is replenished, the reaction will stop when the concentrations of the reacting gases fall to the equilibrium concentrations. In this reaction, equilibrium at room temperature is reached only when the concentrations of hydrogen and oxygen have become vanishingly small, but the principle holds. Whatever the equilibrium concentrations for a particular reaction, the reaction can proceed only until the equilibrium conditions are reached. At the equilibrium state, the reactants may still be reacting, but the products of the reaction are reacting in the reverse direction at an equal rate. Hence, a spontaneous chemical reaction proceeds only to the state of chemical equilibrium.

Explosive reactions are subject to the same principles. If the quantity of explosive is limited, the explosion, however violent, can continue only until a chemical equilibrium is reached. During the explosion, the rate of reaction can increase as the reacting substances become hotter and hotter; hence, the equilibrium state is reached sooner.

There are some useful analogies between the diffusion of gases into each other and a chemical reaction. Both processes can take place at a constant temperature and a constant total pressure, that is, they may take place under conditions of thermal equilibrium and under conditions of mechanical equilibrium as measured by the usual devices. Only internally is there lack of equilibrium in the mixed gases. Indeed, the methods used for studying and expressing chemical equilibrium can be applied to diffusion problems. As a result, we can have greater confidence in the validity of the methods.

Work from Spontaneous Processes.—As was indicated in the previous sections, the spontaneous processes may be described in terms of a general tendency toward thermal, mechanical, or chemical equilibrium. Another general statement is that spontaneous processes in their movement toward equilibrium can furnish useful work. The mechanisms required to obtain the work may differ from process to process; hence, we shall consider various ones corresponding to the different types of spontaneous processes described earlier.

1. The undirectional flow of energy between two bodies at different temperatures can be made to do useful work if a suitable heat engine is devised for the purpose. All heat engines operate by absorbing energy at a higher temperature and discharging part of this energy at a lower temperature, the remainder of the energy being expended in doing work. In accordance with the first law, the total energy discharged by the engine at a lower temperature equals the total energy absorbed at the higher temperature. But, the first law does not tell us what fraction of the energy discharged at the lower temperature may be in the form of useful work. Carnot outlined an engine operating in a cycle between the two temperatures in an attempt to answer this problem. His cycle is interesting because it represented the first theoretical study of the work obtainable in a heat engine.

2. The spontaneous process, the waterfall, can be harnessed to perform useful work whether by the most primitive water wheel or the most modern turbine. Because of its availability and because of the simplicity of the machines required, the flow of water from higher to lower levels remains one of our important sources of energy for performing work.

3. Work may be secured from the movement of gases whether by a windmill, a gas turbine, a reciprocating engine, or by jet propulsion. Work may be done by the moving gases when no change in temperature is involved, but a stationary sample of gas can do work at constant temperature only if, in the process, energy is absorbed from some other

source. Otherwise, the temperature decreases. In practice, the majority of engines propelled by gases secure pressure differences partly as a result of high temperatures produced by chemical reactions. Such engines may be considered as heat engines or as chemical engines, but their efficiencies are not affected by the point of view from which one considers them.

4. In practice, it is difficult to devise an engine for securing useful work from the diffusion of gases. If one can find for each of the constituent gases of a mixture a membrane permeable only to that one gas, one can expand each constituent gas separately and thus carry out each expansion independently of the others. Such a mechanism is outlined in Fig. 12.1.

5. Work can be obtained from spontaneous chemical reactions as well as from other spontaneous processes, but the practical devices for obtaining the work are often difficult to produce. Electrochemical cells are one convenient device for obtaining work from a chemical reaction. But, whether or not a practical cell can be devised for any particular chemical reaction, the direction of a spontaneous process in a system depends on its initial and final states. Consequently, we can foresee the usefulness of a second law of thermodynamics which can make correct predictions on the basis of the change in state regardless of the manner in which we choose to carry on the process.

Heat and Work.—The law of the conservation of energy as expressed in the first law equation, $\mathrm{d}E = \mathrm{D}q - \mathrm{D}w$, equates the increase in energy with the difference in heat absorbed and work done. Consequently, it has become common practice to classify the energy exchanges by a system with its surroundings as heat and work. This classification, applying only to the process of exchange, can be made without any knowledge of how the energy is distributed within the system itself; hence, it cannot furnish information about the system or its tendency to change spontaneously. Heat and work were defined in Chap. 2.

One characteristic of heat as measured by the usual calorimetric process is that it passes from one system to another unaccompanied by material substance. Another characteristic is that it passes from regions of higher temperature to those of lower temperature. A system may exchange energy as heat even though it does not change in volume, does not gain or lose mass, and does not change in chemical composition. Whether it gains or loses energy as heat depends only on its relative temperature.

On the other hand, useful work is associated with the transport of matter. For example, a system does work when it expands against an opposing pressure, work that can be classified as $P\,\mathrm{d}V$ work. In the expansion, matter is transported into the new volume resulting from the expansion. Similarly, in the gaseous diffusion process described earlier, a gas is transported. This spontaneous transport, if suitably harnessed, can be used to perform useful work. Electrical work is the result of the transport of charged particles whether they are ions or electrons. Chemical work can also be considered from the point of view of transport of matter. In the chemical reaction, atoms are transported from a substance into a new substance which is separated or separable from the initial substance. Work can be derived from the reaction if a practical machine can be devised to harness the spontaneous process. For reacting gases, one such device would be the equilibrium box described in Chap. 12. For a reaction in an electrochemical cell, the transport of the reactants into the products of the reaction can be coupled with the movement of electrons in the external circuit and the movement of ions within the cell to do electrical work.

Limits of Work from a Spontaneous Process.—In the previous section, we found that work can be derived from spontaneous processes if they are suitably harnessed. As we shall see, the actual work done depends on the relations between system and surroundings during the change. Work from the net flow of energy alone between bodies at two different temperatures can be obtained only if a suitable heat engine is used to utilize the flow. Where no temperature difference exists, no work can be obtained from the heat engine. On the other hand, in spontaneous processes in which matter is transported, useful work can be done if no temperature gradients exist, or even in spite of temperature differences.

1. *Work from Spontaneous Heat Flow.*—If energy is allowed to flow from regions of higher temperature to regions of lower temperature unaccompanied by a flow of matter and in the absence of a heat engine, no work will result from the process. If the energy, which may be measured as heat, flows through a suitable heat engine, useful work is derived from the process. It appears, however, that heat engines with different efficiencies would produce different amounts of work from the flow of a definite amount of energy. Later, we shall consider the maximum ratio between the work and heat and shall find that this maximum ratio depends on the working temperatures of the heat engine. Hence, the work obtained may range from zero to a maximum.

2. *Work from Isothermal Spontaneous Processes.*—Work can also be obtained from isothermal spontaneous processes. Examples are spontaneous processes in which there is a tendency toward mechanical or chemical equilibrium. Consider a gaseous system containing a fixed amount of gas at a definite temperature and volume. The gas in this system will be at a definite pressure. If the gas is separated from the surroundings by a frictionless piston, the direction of the movement of the

piston will depend on the relative pressures on the two sides of the piston. As discussed in Chap. 2, if the pressure P of the gas is equal to an opposing pressure P', the system will be in mechanical equilibrium with its surroundings and no movement will take place. If P' is less than P, the gas will expand doing work equal to $P'\,\mathrm{d}V$ against the external pressure. If P' equals zero, no work is done; if P' approaches P, the actual work approaches the limiting value

$$\mathrm{D}w_r = P'\,\mathrm{d}V = P\,\mathrm{d}V$$

The work done by the gas cannot exceed $P\,\mathrm{d}V$ since, if expansion is to take place, P' must always be less than, even though only slightly less, P. If P' becomes greater than P, the movement of the piston is reversed and the gas becomes compressed, the work of the compression process being $P\,\mathrm{d}V$. Thus, where P and P' approach each other in value, the work of expansion in becoming equal to the reversible work also becomes equal to the work of compression. But P and V are properties of the gas. It appears, therefore, that the reversible work done by the gas in the isothermal expansion can be expressed in terms of properties of the gas itself.

The example chosen is instructive in another respect. The spontaneous process, the expansion of the gas, is most rapid when the opposing pressure is least and no work is done. As the opposing pressure P' approaches P, the pressure on the gas and the amount of work done increase but the rate of the process decreases. At the equilibrium state where P' equals P and the work done would be identical with the reversible work, there is really no work done at all because there is no movement of the piston. Thus, the reversible work must be regarded as a limit that the actual work may approach but never quite reach. Hence, we see that we can approach the reversible work only if we are willing to take infinite time. Fortunately, since the reversible work for the expansion of the gas may be expressed in terms of the properties P and V of the gas itself, we can calculate a value for the reversible work along any particular path without carrying on the experiment.

As another example of the limits of work from a spontaneous process, we may consider the work derivable from a chemical reaction carried out in an electrochemical cell. In Chap. 2, we found that the cell process can proceed spontaneously if the emf, $\boldsymbol{E}$, of the cell is positive. However, this spontaneous process will produce useful work only if the current operates against an opposing emf, $\boldsymbol{E}'$, in some engine capable of doing work. The amount of work done by the cell for the passage of a small amount of current will then be

$$\mathrm{D}w = \boldsymbol{E}'\,\mathrm{d}n$$

where dn is the number of faradays of electricity moving through the engine. If there is no opposing emf E', no work will be done. If $E' = E$, the cell will be in balance and no current will flow. But, if E' is less than E, work will be done by the spontaneous reaction, the amount of work becoming greater and greater as E' approaches E in value until a maximum work equal to $E\,dn$ is obtained. Thus, we find that the actual work obtained from the cell may range from zero to a reversible value determined by the way E varies with n. If E' becomes greater than E, the direction of electrical flow is reversed and work equal to $E\,dn$ is done on the cell.

These principles, here derived from the expansion of a gas and the operation of the cell, may be applied to the other spontaneous isothermal processes. For each process, we find that the actual work may vary from zero to a maximum, characteristic of the way the process is carried out. It appears that this maximum value may be expressed in terms of properties of the system and of their variation during the process, but that the actual work may not.

Types of Work.—All types of work can be expressed in terms of a potential and a quantity related to the amount of material transported. For pressure-volume work, an element of work Dw can be represented by the product of the pressure P and the volume change dV. The direction of the transport and, therefore, the sign of the work depend not on the absolute value of P for the system but on the value of P relative to the pressure P' of the surroundings. Thus, the sign of dV depends on whether P is greater than or less than P'. At equilibrium, the potentials of the system and its surroundings are equal and no transport takes place, and in the neighborhood of the equilibrium state the transport is almost reversible.

Similarly, the direction of transport of electric charges depends on the value of the electrical potential E relative to that of an opposing potential E'. Only when there is a difference in potential, will the charges move, the relative values of E and E' determining the direction of movement and the sign of dn. The transport becomes the more nearly reversible, the more nearly the potentials E and E' approach the same value.

The work of transport of a chemical substance may be expressed in terms of the quantity of substance dn and a potential called by Gibbs the chemical potential μ. As we shall see, the potential under the special experimental condition of constant temperature and constant pressure is represented by a function $\bar{F}$ called the partial molal free energy. This function will be discussed in more detail in later chapters. In a chemical reaction, the number of moles of the substance i transported may be represented in differential form as dn_i. Because in a chemical reaction new substances are produced and other substances are consumed, the chemical work will be the algebraic sum of the $\mu\,dn$ terms for the substances in the reaction, dn having a positive sign for each substance produced and a negative sign for each substance consumed in the reaction. If proper respect is paid to sign, we may write for chemical work from a reaction involving the 1st, 2nd, . . . and ith substances,

$$Dw = \mu_1\,dn_1 + \mu_2\,dn_2 + \cdots + \mu_i\,dn_i$$

For the transport of a single substance between a system and its surroundings, we find that the substance passes from regions of higher potential to those of lower potential and that equilibrium is reached when the substance has the same value of μ in all parts of the system.

The same point of view may be extended to other forms of work. A summary of the forms of work most commonly met in chemistry is given in Table 7.1, the potential and the quantity transported being indicated for each.

TABLE 7.1.—TYPES OF WORK

Type		Potential		Quantity	
Pressure—volume	$P\,dV$	Pressure	P	Volume	dV
Electrical	$E\,dn$	Electrical	E	Electric charge	dn
Surface	$\gamma\,dA$	Surface tension	γ	Area	dA
Gravitational	$h\,dm$	Gravitational	h	Mass	dm
Chemical	$\mu\,dn_i$	Chemical	μ	Amount of substance	dn_i

Reversible Processes.—Because the second law of thermodynamics is intimately connected with the idea of the reversible process, we shall review the general requirements for reversibility. If we start with a system at state 1 and allow it to change to state 2 and then change the system back to state 1, we might consider that we had reversed the initial change completely. This idea is correct as far as the system itself is concerned. If, however, we must produce changes in the surroundings to restore the system to its original state, the cycle of changes is not a reversible one.

Chemists are accustomed to considering a chemical reaction reversible if, by a change in experimental conditions such as pressure and temperature or by providing adding new reagents, they can restore the original reactants. In practice, this restoration requires labor by the chemists and the use of external sources of energy and materials or chemicals. Accordingly, even though the initial substances are restored, the reversal of the chemical reaction leaves the rest of the universe in a different state. Such a process is not a thermodynamically reversible one.

In thermodynamics, the term *reversible process* is used only for a change that can be reversed in such a way as to leave the surroundings as well as the system in a condition equivalent to the original condition in every respect. It does not follow, however, that there may not be more than one way of proceeding reversibly from one state to another, or that the reverse path must be identical with the original path. If the original state is restored by a reversible process that utilizes new substances or new machines, the cycle is still a thermodynamically reversible one, if all new substances as well as other parts of the environment are left in their initial conditions.

Previously, we considered the reversible expansion of a gas. As another example of a thermodynamically reversible process, we may consider the freezing of a liquid at constant temperature. In this process, energy as heat flows between system and surroundings during the change in state of the system. Let a system containing water be present in a surrounding, both system and surrounding being at 0°c and 1 atmosphere pressure. If 79.72 calories of heat are extracted from the water, 1 gram of the water freezes to ice. If the 79.72 calories of heat are restored to the system, the gram of ice melts to water, leaving the system in its original state. But, if heat is to flow from the system to the surroundings during the first change, the temperature of the surroundings must be slightly lower than that of the system; if heat is to flow back into the system, the temperature of the surroundings must be slightly higher. At the end of the two processes, the surroundings will be in approximately the same state as they were in the beginning. They will be more nearly the same, the smaller the temperature gradients permitted during the processes. But, as the temperature gradients become smaller, the rate of flow of the heat becomes smaller. Thus, the more nearly reversible the processes, the more time required. The truly reversible process is a limiting one, approached more nearly as the time, over which the process occurs, increases infinitely.

Thus, it appears that all natural processes are thermodynamically irreversible. Nevertheless, there are excellent reasons for studying reversible processes. Reversible processes define equilibrium conditions. From our knowledge of these limiting conditions, we can decide whether or not a given desired process is possible. The restriction of infinite time for the reversible process becomes important only when we actually attempt to carry out the process experimentally.

Second Law of Thermodynamics.—In the preceding sections we suggested that, from the experimentally observed tendencies toward thermal, mechanical, and chemical equilibrium, we should be able to formulate a second fundamental energy law, equal in importance to the first law of thermodynamics. In this section, we shall consider some verbal statements of such a law, postponing a mathematical statement until we have discussed another thermodynamic function called *entropy*. The second law of thermodynamics, like other natural laws, is a statement of experience. It is to be accepted because it represents the experimental facts. The following statements are alternative statements, emphasizing different experimental aspects but they are self-consistent. Consequently, as Planck has emphasized, either all are valid or none are valid, the test being whether or not they are in agreement with experiment.

1. *Actual processes are spontaneous processes, and the change is toward equilibrium.* It is not necessary that ultimate equilibrium be reached. However, if the statement is valid, the system after the process is nearer equilibrium than before. We have seen that spontaneous processes, when harnessed, can do useful work in their movement toward equilibrium. This fact will allow us later to evaluate quantitatively the distance of systems from equilibrium, and to express it in terms of properties of the systems.

2. *When any actual process occurs it is impossible to invent a means of restoring every system concerned to its original condition.* This statement by G. N. Lewis emphasizes another aspect of the tendency toward equilibrium. An actual process is a one-way process, the direction being toward rather than away from equilibrium. Consequently, if we wish to restore the original conditions of the system, we must do so at the expense of some other system. And, since every actual process is irreversible in the thermodynamic sense, the reversible process is a limiting one, which can be approached but never completely realized.

3. *Heat cannot of itself pass from a colder to a hotter body.* This statement of Clausius (1850) is more than a description of the direction of the flow of energy as heat. The phrase "of itself" means that the transfer of the energy to the higher temperature requires the aid of some agency that will become changed in the process. This early statement of Clausius is implicit in the more general statement 2.

4. *It is impossible by an inanimate material agency (an engine) to derive mechanical effect (work) from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.* According to this statement of Kelvin (1851), an engine cannot act as a refrigerator and use the energy absorbed in the refrigeration process to do useful work. Such an engine would operate contrary to statements 2 and 3.

5. *It is impossible to construct an engine which will work in a complete cycle and produce no effect except the raising of a weight and the cooling of a heat reservior.* This statement of Planck is equivalent to statement 4. The prohibited engine would not violate the first law, but it would enable man to derive work without limit from the energy of his surroundings.

6. *A transformation whose only final result is to transform into work heat extracted from a source which is at the same temperature throughout is*

impossible. According to this statement of Kelvin, a heat engine operating in an isothermal cycle cannot produce work. If a system in thermal equilibrium could move away from equilibrium, it would violate statements 1 and 2. Furthermore, energy does not flow as heat under isothermal conditions.

In the popular mind, the laws of thermodynamics are identified with their prohibition of perpetual motion. Violations of the first and second laws would produce, in the classification of Ostwald, perpetual motion of the *first kind* and the *second kind*, respectively. Another statement of the second law is that of Ostwald:

7. *It is impossible to construct a perpetual motion machine of the second kind.*

The principle of the conservation of energy indicates that perpetual motion of the first kind is impossible. If energy is neither created nor destroyed, no engine, however perfectly designed or operated, can do work (produce motion) without absorbing an equivalent amount of energy. Because friction cannot be eliminated entirely from an engine, the output of work must be slightly less than the energy absorbed, the remainder of the energy appearing as heat of friction. No perpetual-motion machine has been perfected; therefore, we have renewed confidence in the first law.

But the possibility of an engine producing work from isothermal cycles or from a transport of energy from lower to higher temperatures is not prohibited by the first law. An engine operating contrary to the preceding statements would not violate the first law but would represent perpetual motion of the second kind. There is here no question of creating new energy; the question is simply one of violating the laws of heat flow. Perpetual motion of the second kind would be just as useful to mankind as that of the first kind. If it were possible, an efficient engine could take heat from a heat reservoir at a prevailing temperature and convert part of it to work, cooling the reservoir in the process. The reservoir, being colder than its surroundings, would then absorb heat from its surroundings in accordance with the laws of heat flow. The net result of this process would be the gaining of useful work from a refrigeration process. Consider a ship in a constant-temperature sea, equipped with such an engine. It might use surrounding water, extract energy from it, thereby cooling it, discharge the colder water into the sea, and use the energy to do the work of driving the ship's propellers. The work done by the propellers could return the energy to the water, raise it to its original temperature, and leave the sea in its original state but the ship in a new position. Thus, the ship would move spontaneously without moving toward equilibrium as required by statement 1. Such perpetual motion is contrary to experience.

Carnot Cycle.—The work to be derived from the flow of energy from higher to lower temperatures was first studied by Nicholas Léonard Sadi Carnot, a French engineer, in 1824. He considered an ideal engine operating between two temperatures in a cycle with two reversible expansion states, one isothermal and one adiabatic, and two reversible compression stages, one isothermal and one adiabatic. Carnot discussed his cycle in terms of the then current but now abandoned caloric theory of heat, which considered heat as a substance. Later, when the first law became established, Clausius discussed the Carnot cycle in terms of heat as one aspect of energy change and subject to the first law. Other reversible cycles have been proposed and studied, but the Carnot cycle is so fundamental and instructive that it remains the one most used in connection with the second law.

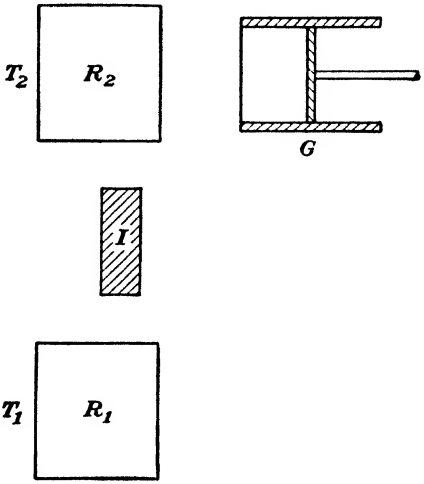


FIG. 7.1.—Apparatus for the Carnot cycle.

A Carnot engine may be idealized in terms of parts such as are shown in Fig. 7.1. The heat reservoir R_2 at the higher temperature T_2 is large enough so that finite amounts of heat may be withdrawn from or added to it without changing its temperature significantly. Similarly, the cold reservoir, R_1, at the lower temperature T_1, is large enough so that finite amounts of heat may be added to it or withdrawn from it without changing its temperature significantly. The cylinder G of the engine has a piston head and cylinder sides perfectly insulated so that heat is transmitted to or from the cylinder only through its bottom, which is a good thermal conductor. The insulating block, like the cylinder sides, is a perfect insulator. The working substance in the engine is enclosed in the cylinder G. In Chap. 4 we consider the Carnot cycle for an ideal gas, the various states reached by the gas being represented by the points

A, *B*, *C*, and *D*, in Fig. 4.5. A real gas, a liquid-vapor system, or a chemical system capable of doing $P\,dV$ work, a chemical system in an electric cell capable of doing $E\,dn$ work, or any other system capable of doing reversible isothermal work at different temperatures could be used in the cycle. Consider a liquid-vapor system as the working substance, the points *A*, *B*, *C*, and *D* in Fig. 7.2 representing the pressure and volume of the system at the end of the various stages. If liquid and vapor are in equilibrium at point *A*, the reversible expansion at the temperature T_2 will be isobaric as well as isothermal, the constant pressure being that of the saturated vapor at this temperature. During stage *AB*, the volume of the system increases as liquid is evaporated, heat q_2, equal to the heat of evaporation, being absorbed and work w_{BA}, represented graphically by the area *ABba*, being done. In stage *BC*, the reversible adiabatic expansion, the system cools until the temperature T_1 is reached. In this expansion q_{CB} equals zero and the work done w_{CB} is represented graphically by the area *BCcb*. The point *C* represents the end of the expansion processes. In stage *CD* the system is compressed isothermally and at a constant pressure equal to the vapor pressure at the temperature T_1, vapor condensing and heat being given to the cold reservoir. Since heat is lost by the system, the heat *absorbed* q_1 has a negative value.

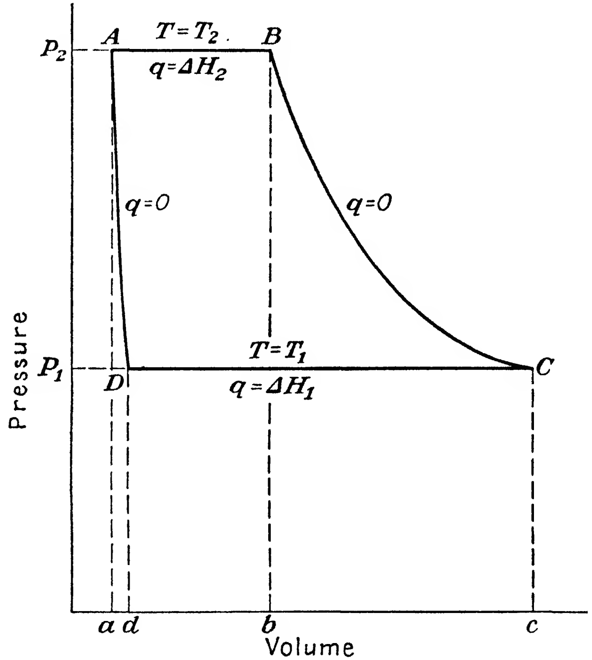


FIG. 7.2.—Carnot cycle for a one-component liquid-vapor system.

Similarly, the work done by the system is negative, the work w_{DC} being represented graphically by the area *CDdc* which is negative when read in the direction indicated. In stage *AD*, the compression is adiabatic, vapor condensing and the temperature rising to the original value T_2. Here q_{AD} is zero and the work done by the gas is negative, being represented by the area *DAad*. The energy changes for the entire cycle are summarized in Table 7.2, w_r being the net reversible work for the cycle.

At the end of the cycle, the working substance used in the Carnot engine has returned to its initial state with its initial energy. Since ΔE for the cycle is zero, we have from the first law

$$q_2 + q_1 = w_r \tag{7.1}$$

This equation is identical with equation (4.55) obtained in Chap. 4 for

TABLE 7.2.—ENERGY EXCHANGES IN THE CARNOT CYCLE

	Stages *AB* and *BC* Expansion (positive values)		Stages *CD* and *DA* Compression (negative values)	Cycle
Heat absorbed by working substance...	$(q_{BA} + 0)$	+	$(q_{DC} + 0)$	$= q_2 + q_1$
Work done by working substance...	$(w_{BA} + w_{CB})$	+	$(w_{DC} + w_{AD})$	$= w_r$
Work area....	$(ABba + BCcb)$	+	$(CDdc + DAad)$	$= ABCD$

the ideal gas in the Carnot cycle. However, equation (7.1) does not indicate what the relative values of q_2 (or q_1) and w_r shall be. When the ideal gas was used in the Carnot engine, we found that the relative values of q_2, q_1, and w_r are determined by the values T_2, T_1, and $T_2 - T_1$ as in equation (4.56), the temperatures being measured on the ideal gas scale. However, the first law would be satisfied if the reversible work from the transport of a definite amount of energy by the liquid-vapor system differed from that obtained with the ideal gas, even though both operated in cycles between the same temperature limits.

Nevertheless, several deductions may be made from the first law. Equation (7.1) is a statement of equality for a reversible process. It is still valid if the cycle is reversed and the path *ADCBA* is followed. Thus, if the system is expanded over the path *ADC*, it absorbs heat q_1 from the cold reservoir R_1 and does work equal to w_{CDA} so that the numerical values of both q_1 and w_{CDA} are positive. Over the compression path *CBA*, work is done on the system and heat is given to the hot reservoir R_2; hence, both q_2 and w_{ABC} have negative values. This reversed cycle is a refrigeration cycle, net work being done on the system, heat being absorbed at the lower temperature and evolved at the higher temperature.

Furthermore, since ΔE is zero even though a cycle is not carried out reversibly, we have from the first law

$$q_2 + q_1 = w \tag{7.2}$$

When the cycle is not carried out reversibly, the actual work w, obtained when a given amount of energy q_2 is absorbed at the higher temperature, is less than that for the reversible cycle. In the most completely irreversible cycle, no work is done, so that, from equation (7.2)

$$q_2 = -q_1 \tag{7.3}$$

Thus, the actual work may vary from zero to the value w_r, and the energy discharged to the cold reservoir will vary accordingly.

Maximum Work from the Carnot Cycle.—If the verbal statements of the second law of thermodynamics given in a previous section are valid, all Carnot engines operating reversibly between the same temperatures must have the same efficiency. Suppose that a Carnot engine with a liquid-vapor system or any other real system had an efficiency different from that of the engine using an ideal gas. These engines could then be coupled so that the less efficient one operating as a heat engine drives the more efficient one as a refrigeration engine. The net result would be the transfer of energy from the lower temperature to the higher temperature in contradiction to statement 3. Or, the coupled engines could do work and at the same time act as a refrigerator contrary to statements 4 and 5. If we are not to have perpetual motion of the second kind, all the reversible engines must have the same efficiency.

Coupled reversible engines can also be used to show that w_r must be proportional to q_2 (or q_1). If each of two engines absorbs the heat q_2 so that the total heat absorbed is $2q_2$, each must do the work w_r so that the total work is $2w_r$. There is no limit to the number of reversible engines that may be coupled in this way, hence w_r must be proportional to q_2.

A similar argument will lead to the conclusion that a Carnot engine operating irreversibly between two temperatures cannot be more efficient than a reversible engine. An actual engine operating in a cycle between the two temperatures can only approach the reversible cycle as a limit, and such an engine produces less work than the reversible engine, the value ranging from zero to the maximum value w_r. Consequently, a reversible engine coupled with an actual engine cannot transport as much energy back to the hot reservoir as is lost by this reservoir, and statements 1 and 2 apply. In an actual process, the tendency is toward thermal equilibrium, energy being transported from the higher to the lower temperature.

Thermodynamic Temperature Scale.—In the previous discussion we considered the relations between q_2, q_1, and w_r for Carnot engines operating between the fixed temperatures T_2 and T_1, but we have paid no attention to the actual temperature values beyond indicating that T_2 is greater than T_1. Suppose that the temperatures T_2 and T_1 approach a common value so that the expansion is carried out at the same temperature as the compression. In Fig. 4.5 or 7.2, this would mean that the stages AB and DC become identical and that the stages BC and AD vanish. Under these conditions, q_2 becomes identical with $-q_1$, and w_r vanishes as required by statement 6. Thus, it can be shown that w_r varies in some way with the difference in temperature, $T_2 - T_1$. Because the heat absorbed (q_2) during expansion at the higher temperature T_2 is greater than the heat absorbed ($-q_1$) during expansion,[1] at the lower temperature T_1 and because w_r is related to the difference between T_2 and T_1 it seems reasonable to establish a temperature scale that is directly proportional to the heats absorbed during expansion at the several temperatures. Let us, therefore, following Kelvin, who proposed such a temperature scale in 1851, define *relative* values of T_2 and T_1 by the ratio

$$\frac{q_2}{-q_1} = \frac{T_2}{T_1} \tag{7.4}$$

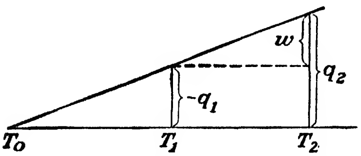


FIG. 7.3.—Relations between heat absorbed and work done in the Carnot cycle.

Observe that equation (7.4) defines merely the relative values of the temperatures and not their absolute values. As a consequence of equations (7.1) and (7.4), we have the ratios

$$\frac{q_2}{T_2} = \frac{-q_1}{T_1} = \frac{w_r}{T_2 - T_1} \tag{7.5}$$

(The student should derive this equation.) Temperature defined in this way is called *thermodynamic temperature.* It is independent of the working substance used in the reversible Carnot engine and dependent only on the relative values of q_2, q_1, and w_r. The relations among these various quantities are illustrated by the triangular diagram in Fig. 7.3 which expresses in geometric form all the relations in equation (7.5). For example, if $-q_1$ is half as great as q_2, T_1 is half as great as T_2 on the thermodynamic scale, and $w_r = -q_1 = \frac{1}{2}q_2$. As was stated previously, when T_1 approaches T_2, $-q_1$ approaches q_2 in value and w_r vanishes. The diagram, however, emphasizes an additional relation. It places

---

[1] Remember that q_1 was defined as the heat absorbed during *compression* at the lower temperature T_1.

zero on the thermodynamic temperature scale as the temperature at which $-q_1$ becomes zero and w_r becomes equal to q_2. In terms of the Carnot cycle, this means that when the cold reservoir is at zero temperature all the heat absorbed at the temperature T_2 can be completely converted to work. At any other value for T_1, w_r must be less than q_2, the difference being equal to $-q_1$.

Equation (7.5) in which T represents thermodynamic temperature is identical with equation (4.56) in which T represents temperature on the ideal gas scale. This fact is not surprising when one considers that an ideal gas in the Carnot engine would give the same relative temperatures as any other substance. In fact, Kelvin chose a form for his thermodynamic temperature scale that would reproduce the ideal gas scale. However, since equations (7.5) and (4.56) define only relative and not absolute values of T, more than one thermodynamic temperature scale can be used.

In the following chapter we shall consider how thermodynamic temperatures may be derived from data on the real gases by methods involving the second law. The values of certain reference temperatures on a thermodynamic scale may also be determined from the limiting values of PV for gases at these temperatures by the method discussed in Chap. 4. By international agreement, the size of the degrees on all temperature scales is defined in terms of the difference in temperatures of freezing water and boiling water at 1 standard atmosphere. If T_1 represents the former and T_2 the latter temperature, we have by definition for the centigrade thermodynamic scale, $T_2 - T_1 = 100$. The value of PV for a gas acting as an ideal gas is found to be 1.36609 times greater at the steam point than at the ice point so that, from the ideal gas equation,

$$\frac{(PV)_{i,T_2}}{(PV)_{i,T_1}} = 1.36609 = \frac{T_2}{T_1} \tag{7.6}$$

The value for T_1, the ice-point temperature, obtained from this ratio and the defined size of degree, is found to be 273.16°, as in equation (4.3). In honor of Kelvin's fundamental work on the scale, the thermodynamic centigrade scale is called the Kelvin scale, symbol °K. It is related to the usual centigrade scale by the relations 0°K = −273.16°C,

$$273.16°\text{K} = 0°\text{C},$$

and 373.16°K = 100°C.

The thermodynamic temperature scale in terms of the Fahrenheit degree is called the Rankine scale, symbol °R. There being 180 Fahrenheit degrees between freezing water and boiling water, we have, by definition, for these temperatures on the Rankine scale, $T_2 - T_1 = 180°$. From equation (7.6), one can calculate absolute values for T_1 and T_2

in the Rankine scale and relate them to the corresponding temperatures in °F. Thus, 0°R = −459.69°F, the freezing point of water being at 32°F = 491.69°R.

Entropy.—Let us consider again the first law equation in differential form

$$dE = Dq - Dw$$

in which Dq and Dw, unlike dE, are not properties of a system but depend on the path along which the change in E occurs. The different types of work included in the work term, Dw, may be those listed in Table 7.1 or additional terms of a similar type. In irreversible processes, we found that the actual work is measured in terms of changes in the surroundings and not in terms of the system itself. Thus, the work of expansion depends on the value P', a pressure of the surroundings, and the electrochemical work on the value of $\boldsymbol{E}'$, the counter emf. Only when a process is reversible, are the several work terms measured in terms of the properties of the system, varying in a definite way for each path over which the change takes place. Then we have

$$dE = Dq_r - Dw_r \tag{7.7}$$

in which

$$Dw_r = P\,dV + \boldsymbol{E}\,dn + \cdots \tag{7.8}$$

where P, $\boldsymbol{E}$, etc., are intensive properties and dV, dn, etc., are definite changes in extensive properties of the system. But, since Dw_r is measurable in terms of the properties of the system and dE is a property of the system, Dq_r must also be measurable in terms of some property or properties of the system which vary in a definite way for each path. By analogy with the work terms in Table 7.1, we may, therefore, hope to express Dq_r in the form $Y\,dX$ where Y is some intensive property of the system and X some extensive property. Since temperature plays a role in heat flow similar to the role of pressure in work of expansion, we may substitute the temperature T for Y and consider whether the change in some quantity, an extensive property of the system, could not bear the same relation to heat flow as dV plays in the work of expansion. Let such an X-property be designated by the symbol S, the change in the property being dS. This quantity will then be defined in part by the equation

$$Dq_r \equiv T\,dS \tag{7.9}$$

From this definition and from equation (7.7), we have

$$dS = \frac{Dq_r}{T} = \frac{dE + Dw_r}{T} \tag{7.10}$$

The function S, defined above, was first introduced by Clausius and named *entropy*.

Entropy as a Property.—If the entropy S is an extensive property, a characteristic function of a system, just as we found the functions V, E, H, C_P, and C_V to be, the value of the integral of dS between two states will equal the difference between the values of S in the two states. Thus,

$$\int_1^2 \mathrm{d}S = S_2 - S_1 = \Delta S \tag{7.11}$$

Consequently for the reversible, isothermal process, T being constant, we have from equation (7.9)

$$\int \mathrm{D}q_r = T \int \mathrm{d}S$$
$$q_r = T\,\Delta S \tag{7.12}$$

For the reversible adiabatic process between two states, q_r and Dq_r being zero and T being finite, we have from equation (7.9)

$$\mathrm{D}q_r = 0 = T\,\mathrm{d}S$$
$$\mathrm{d}S = 0$$

and

$$S_2 = S_1 \tag{7.13}$$

We have seen how q_r and w_r, and consequently Dq_r and Dw_r, have values in a given change that depend on the path over which the change takes place. Thus, Dq_r and Dw_r in equation (7.10) may have many values. But, if entropy is a characteristic function, its value must be independent of the path. Consider the change from state A to state C in the Carnot diagram, Fig. 4.3 or 7.2, by the path ABC or ADC, the values of q_r and w_r being different for the two paths. For the isothermal stage AB from equation (7.12),

$$S_B - S_A = \frac{q_2}{T_2}$$

For the adiabatic stage BC from equation (7.13),

$$S_C - S_B = 0$$

Thus, for the change from A to C along path ABC,

$$S_C - S_A = S_B - S_A = \frac{q_2}{T_2} \tag{7.14}$$

Similarly, for the stage AD along the second path,

$$S_D - S_A = 0$$

for the isothermal stage DC,

$$S_C - S_D = -\frac{q_1}{T_1}$$

and for the change from A to C along path ADC,

$$S_C - S_A = S_C - S_D = -\frac{q_1}{T_1} \tag{7.15}$$

But, from equation (7.5), the reversible heats and the temperatures are related in such a way that $q_2/T_2 = -q_1/T_1$. Hence, the difference between S_C and S_A as determined along the reversible path ABC is identical with that determined along the path ADC. It can be shown that, along any other reversible path between states A and C, the entropy change as defined by equation (7.9) has the same value. Hence, the change in entropy is indeed dependent only on the states and not on the path. Furthermore, entropy is an extensive property, depending on the amount of substance considered; 2 moles of a substance under given conditions have exactly twice the entropy of 1 mole under the same condition, just as they have twice the volume, energy, or heat capacity. However, we are warned by equation (7.10) that, although the energies of the two systems added to each other are additive, the entropy of the combined system is not necessarily the sum of the entropies of the two separate systems. Even though the energies are additive, the entropies will be additive only when there is no possibility of reversible work being done as a result of a combination of the two systems for, as equation (7.10) shows, the entropy change depends on the possibility of reversible work during the change as well as on the intrinsic energy of the system.

Earlier, we stated that the differential equation (7.9) defined the entropy only in part. It defines changes in the entropy and not the absolute value of entropy for any state of the system. On integration of equation (7.9), we have

$$S = \int \frac{\mathrm{D}q_r}{T} + I \tag{7.16}$$

as the indefinite integral, the value of the integration constant I remaining unknown. As will appear, an additional principle, called the third law of thermodynamics, is required to help us determine the absolute value of I. The value of the integral being determinable, we can, with this new principle, obtain absolute values for the entropy S.

Total Entropy Change in Reversible Processes.—Later, we shall focus our attention on the system alone. For the present, however, it will be instructive to consider entropy change in both system and surroundings. It will simplify our consideration of reversible and irreversible processes if we assume surroundings that, within themselves, absorb or evolve any heat reversibly. Let primes designate the quantities for the surroundings, dS' being the entropy change and T' the temperature of the surroundings, and $\mathrm{D}q'$ being the heat absorbed by the surroundings. Where heat is transferred from system to surroundings, $\mathrm{D}q$ and $\mathrm{D}q'$ must be equal in numerical value but opposite in sign so that

$$\mathrm{D}q = -\mathrm{D}q'$$

The entropy change of the surroundings for the heat absorbed $\mathrm{D}q'$ at the temperature T' will, therefore, be

$$\mathrm{d}S' = \frac{\mathrm{D}q'}{T'} = \frac{-\mathrm{D}q}{T'} \tag{7.17}$$

The entropy changes for both system and surroundings in certain typical reversible processes will be considered in turn.

1. *Adiabatic Reversible Processes.*—In an adiabatic process $\mathrm{D}q = 0$, but only if the process is reversible so that $\mathrm{D}q_r$ also equals zero will the entropy change for the system be zero. Such a process with no entropy change is called *isentropic.* Examples are the stages BC and DA, Figs. 4.5 and 7.2, in the reversible Carnot cycle. These stages are isentropic stages, stages of constant entropy. For them, since $\mathrm{d}S = 0$, we have from equation (7.10)

$$\mathrm{d}S = 0 = \frac{\mathrm{d}E + \mathrm{D}w_r}{T} = \frac{\mathrm{d}E + P\,\mathrm{d}V}{T}$$

And, since T is not zero,

$$\mathrm{d}E + P\,\mathrm{d}V = 0$$

Hence,

$$P\,\mathrm{d}V = -\mathrm{d}E$$

the work being done at the expense of the internal energy. In consequence, the temperature must decrease during an expansion. For an ideal gas, the relations for adiabatic expansion were given in equation (4.45). Since the system is insulated from the surroundings during the process and no heat is exchanged, the entropy of the surroundings also remains unchanged so that $\mathrm{d}S$ equals zero, $\mathrm{d}S'$ equals zero, and, hence,

$$\mathrm{d}S + \mathrm{d}S' = 0 \tag{7.18}$$

2. *Isothermal Reversible Process.*—If system and surroundings are at exactly the same temperature, no heat will flow from one to the other and they will be in equilibrium in this respect. Heat will be transferred reversibly only as a limiting process under the influence of a vanishingly small temperature difference. Examples are the stages AB and CD in the reversible Carnot cycle. Since the temperature remains constant, we may evaluate the entropy change from either $\mathrm{D}q_r/T$ or q_r/T and, since $T = T'$, we have, for the system, $\mathrm{d}S = \mathrm{D}q_r/T$, or $\Delta S = q_r/T$, and, for the surroundings, $\mathrm{d}S' = -\mathrm{D}q_r/T$ or $\Delta S' = -q_r/T$. For both system and surroundings, we have

$$\left.\begin{aligned} dS + dS' &= \frac{Dq_r}{T} - \frac{Dq_r}{T} = 0 \\ \Delta S + \Delta S' &= 0 \end{aligned}\right\} \tag{7.19}$$

3. *Reversible Heat Transfer between Two Temperatures.*—Earlier we found that energy is transferred reversibly as heat from one temperature to another only when reversible work is also done. Since the reversible Carnot engine is one device for making the transfer reversibly, it may be used to illustrate the entropy changes involved in the reversible transfer of heat between two temperatures. At the higher temperature T_2, the engine (system) absorbs heat q_2 isothermally and reversibly during the expansion so that its entropy change, ΔS_2, during this stage is

$$\Delta S_2 = \frac{q_2}{T_2}$$

The entropy change for the reservoir (surroundings) during the same stage is

$$\Delta S_2' = \frac{-q_2}{T_2}$$

At the lower temperature, T_1, the corresponding entropy changes are

$$\Delta S_1 = \frac{q_1}{T_1}; \qquad \Delta S_1' = \frac{-q_1}{T_1}$$

From these relations, it appears that at neither temperature is there a total entropy change for

$$\Delta S_2 + \Delta S_2' = \frac{q_2 - q_2}{T_2} = 0$$

$$\Delta S_1 + \Delta S_1' = \frac{q_1 - q_1}{T_1} = 0$$

But there were also no entropy changes during the adiabatic stages, so that, for each of the four stages in the reversible Carnot cycle the sum of the entropy changes of system and surroundings is zero.

If entropy is a property of the system, it should be unchanged at the end of the cycle. The sum of the entropy changes of the system itself is

$$\Delta S_{BA} + \Delta S_{CB} + \Delta S_{DC} + \Delta S_{AD} = \frac{q_2}{T_2} + 0 + \frac{q_1}{T_1} + 0$$

But, from equation (7.4),

$$\frac{q_2}{T_2} + \frac{q_1}{T_1} = 0$$

So that for the cycle

$$\Delta S = 0 \tag{7.20}$$

4. *Reversible Chemical Reactions.*—In Chap. 2, Table 2.1, we considered three different processes for the reaction of zinc and copper sulfate to form copper and zinc sulfate. Process *b*, being carried out in a reversible cell, may be used to illustrate the entropy change in a reversible chemical reaction. Since the necessary data are given in Table 2.1, we shall use them in calculating numerical values for the entropy changes. The reaction is isothermal, being carried out at 18°C which is 291°K. It is also carried out at constant pressure (atmospheric pressure), but the change in volume is negligible so that $P\,\mathrm{d}V$ work may be neglected. Consequently, for the reaction as written in equation (2.28),

$$\begin{aligned} \Delta E &= \Delta H = -51{,}400 \text{ cal} \\ w_r &= nFE = 51{,}070 \text{ cal} \\ q_r &= \Delta E + w_r = -330 \text{ cal} \end{aligned}$$

and

$$\Delta S = \frac{q_r}{T} = \frac{-330}{291} = -1.13 \text{ cal/deg}$$

For the surroundings, we have $q' = +330$ cal so that the entropy change for the surroundings is

$$\Delta S' = \frac{q'}{T'} = \frac{330}{291} = 1.13 \text{ cal/deg}$$

As in the other reversible processes, the total entropy change is zero, for

$$\Delta S + \Delta S' = -1.13 + 1.13 = 0 \tag{7.21}$$

Similarly, if the cell reaction were reversed, the entropy change for the reverse reaction would be 1.13, that of the surroundings, −1.13. For the complete cycle, there would again be no entropy change.

In all the different types of reversible processes considered in this section, we found that the entropy of a system may change for any single process but that for the complete cycle, the system being again brought into its original state

$$\mathrm{d}S = 0 \tag{7.22}$$

Or for any single process, the entropy change of both system and surroundings is

$$\mathrm{d}S + \mathrm{d}S' = 0 \tag{7.23}$$

These statements, therefore, appear suitable for a mathematical expression of the second law of thermodynamics.

Total Entropy Change in Irreversible Processes.—In irreversible, spontaneous processes, we found that less than the reversible work is done and that less than the reversible heat is absorbed. The irreversible heat Dq_i and the irreversible work Dw_i are subject to the first law equation

$dE = Dq_i - Dw_i$. This equation combined with the corresponding equation for a reversible change in state of a system under comparable conditions yields

$$Dq_r - Dq_i = Dw_r - Dw_i \tag{7.24}$$

But, since $Dw_i < Dw_r$, Dq_i must be less than Dq_r.

In the irreversible process, the heat absorbed by the surroundings, Dq' will be equal to $-Dq_i$ and not to $-Dq_r$. These facts have an important bearing on the entropy changes accompanying irreversible processes. The entropy change for the system will, as before, be measured by the quantity Dq_r/T, but the entropy change of the surroundings will be measured in terms of a different quantity, namely, Dq'/T' which equals $-Dq_i/T'$. Hence, the total entropy change for a process need no longer be equal to zero. Examination of some typical irreversible processes for specific conditions will enable us to see in what respects dS and dS' differ.

1. *Irreversible Adiabatic Processes.*—Reversible adiabatic processes are isentropic, but irreversible adiabatic processes are not. For the latter, there is no heat exchange between system and surroundings so that $Dq = -Dq' = 0$. As a consequence, we find from equation (7.17) that the entropy change of the surroundings, dS', equals 0. But since $Dw_r > Dw_i$ and $Dq_i = 0$, it appears from equation (7.24) that Dq_r must equal some positive number. Hence, Dq_r/T, which measures the entropy change of the system, also equals some positive number, and

$$dS > 0 \tag{7.25}$$

As a result, the total entropy change of system and surroundings must be positive since

$$dS + dS' > 0 \tag{7.26}$$

Inequalities such as those expressed in equations (7.25) and (7.26) are found for all processes not completely reversible. The maximum irreversibility occurs when the work done is at a minimum, that is, when $Dw_i = 0$. An example of such a process is the expansion of an ideal gas into a vacuum. For such a gas, $dE = 0$, $Dw_i = 0$, and hence from the first law, $Dq_i = 0$. This expansion will also be isothermal; hence, the entropy of expansion for an ideal gas can be calculated from equation (4.40) for the isothermal and reversible expansion of the gas. If the gas is not ideal, there will be a Joule effect; dE will still be zero, for $dE = Dq_i - Dw_i = 0 - 0 = 0$, but the expansion will not be isothermal. Consequently, the gas in its final state will differ in temperature from the first state, and a modified equation must be used to calculate the reversible heat absorbed and the entropy change for the process. In any case, the change in entropy of the gas will be greater than zero.

The entropy change could, of course, be determined by carrying out expansion reversibly or by recompressing the gas reversibly to its former state. If this process had been carried out reversibly, the gas in expanding would have pushed back the surroundings, thereby producing an entropy change in the surroundings. As a result, dS' would have had a value equal but opposite in sign to dS. When the gas expands into the vacuum, however, there is no further change in the entropy of the surroundings, for the change in entropy of the surroundings occurred when the vacuum was created.

2. *Isothermal Heat Transfer.*—The laws of energy flow as heat require that there be a temperature gradient. The isothermal transfer of heat is a limiting, reversible process. It was treated in the previous section. It is tabulated here merely to remind us that, if heat is to flow irreversibly between system and surroundings, T and T' cannot be equal and the process cannot be isothermal.

3. *Irreversible Energy Transfer between Two Temperatures.*—The reversible Carnot cycle enables us to transfer energy as heat from one temperature to another without entropy change, if we transfer only part of the energy absorbed at the higher temperature to the reservoir at the lower temperature and utilize the rest of the energy to do useful work. The maximum irreversibility will occur when no work is done in the process. By such a process, let a system at the temperature T lose heat to its surroundings, the heat being lost reversibly within the system. For the system, the change in entropy is $\mathrm{d}S = \mathrm{D}q/T$, the change being negative because heat is evolved so that the numerical value of Dq is negative. For the surroundings at its temperature T', the entropy change is, from equation (7.17), $\mathrm{d}S' = -\mathrm{D}q/T'$. The total entropy change becomes

$$\mathrm{d}S + \mathrm{d}S' = \frac{\mathrm{D}q}{T} - \frac{\mathrm{D}q}{T'} > 0 \tag{7.27}$$

That the total entropy change must have a positive value will be clear from the following considerations. Since $T > T'$, the fraction $\mathrm{D}q/T$ must be smaller numerically than $\mathrm{D}q/T'$. But, since Dq has a negative value because of the direction of heat flow, the sum of the fractions is positive. Only when $T = T'$ (isothermal transfer) or when

$$\frac{\mathrm{D}q}{T} = \frac{-\mathrm{D}q'}{T'}$$

(as in the Carnot cycle) will there be no increase in total entropy when heat is transferred.

If $T' > T$ so that heat flows from the surroundings to the system, the total entropy change will again be positive. In this process, the loss in entropy of the surroundings will be numerically smaller than the gain in entropy of the system. It appears that, in heat flow, the body at the higher temperature does not lose so much entropy as is gained by the body at the lower temperature.

4. *Irreversible Chemical Reactions.*—As an example of an irreversible reaction, we shall consider the reaction between zinc and copper sulfate previously discussed, but now carried out according to process *a* in which no work is done. If the reactants are mixed directly and the reaction allowed to go on at constant temperature and constant pressure, the $P\,\mathrm{d}V$ work still being negligible, we have, from the data in Table 2.1,

$$\Delta E = \Delta H = q_i = -51{,}400 \text{ cal}$$
$$w_i = 0$$
$$q_r = -330 \text{ cal}$$

As before,

$$\Delta S = \frac{q_r}{T} = -1.13 \text{ cal/deg}$$

However, for the surroundings in this irreversible process, $q' = -q_i$, so the entropy change of the surroundings is

$$\Delta S' = \frac{q'}{T'} = \frac{51{,}400}{291} = 176.6 \text{ cal/deg}$$

The total entropy change for the reaction carried out irreversibly in this way is

$$\Delta S + \Delta S' = \frac{-330 + 51{,}400}{291} = \frac{51{,}070}{291} = 175.5 \text{ cal/deg} \qquad (7.28)$$

In this as in other irreversible processes, there is a change in total entropy, positive in value. The student should compare the above equations for the irreversible process with the corresponding equations, leading to equation (7.21), for the reversible process.

The total entropy change for all the different types of irreversible processes considered may be stated in the form of the inequality

$$\mathrm{d}S > 0 \qquad (7.29)$$

Or, in terms of the entropy change for both system and surroundings, we have

$$\mathrm{d}S + \mathrm{d}S' > 0 \qquad (7.30)$$

These inequalities, showing a general increase in entropy in irreversible processes, may be compared with the equality in equations (7.22) and (7.23) showing no entropy change for processes carried out reversibly.

Entropy and the Second Law.—In all the reversible processes considered, the sum of the entropy changes of the system and the surroundings was found to be zero; the total entropy *remained unchanged.* On the contrary, in all the irreversible processes, the total entropy *increased.* However, before we make a general statement about entropy, we should consider several implicit assumptions made in discussion. One implicit assumption was that, for the combined system and surroundings, the total energy remained constant. In other words, in the given processes the surroundings exchanged energy only with the system. If the surroundings exchanged energy with a second system during a process, its entropy change would not have been determined by the term Dq'/T'. A second implicit assumption was that the total volume of system and surroundings remained constant, that the surroundings increased or decreased in volume only to the extent that the system decreased or increased in volume. Any further change in volume of the surroundings during a process would have resulted in an entropy change different from Dq'/T'. Where the subscripts E and V mean, as before, constant energy and constant volume, the general statement for entropy change in a process may be expressed in the form

$$\Sigma \, dS_{E,V} \geqq 0 \qquad (7.31)$$

where the equality sign applies to the reversible process and the inequality sign to the irreversible process. Equation (7.31) is *a mathematical statement of the second law of thermodynamics.* It is consistent with and more precise than the verbal statements of the second law given earlier.

In the discussion of the reversible and irreversible processes leading to equation (7.31), the assumption was made explicitly that the surroundings absorbed heat within itself reversibly. Its entropy change could then be represented by $dS' = Dq'/T'$. Suppose that this is not true and that there are additional irreversible processes within the surroundings themselves. By the previous methods, one can show that such processes result in entropy changes still more positive in value than those derived for reversible absorption. Each additional irreversibility serves to make the total entropy change more positive. Equation (7.31) is, therefore, not limited by this assumption.

In a previous section, several verbal statements of the second law were given. Statement 3, that of Clausius, when expressed in terms of the entropy function, forbids the total entropy change from being negative in value. The consequence of the flow of heat from a colder to a hotter body would, as equation (7.27) shows, result in a decrease in entropy. The other statements would also, if violated, result in a decrease in entropy. We have found that the total entropy change at constant energy and constant volume cannot be negative for, in real processes, that is, processes more or less irreversible, the total entropy change is always positive under these conditions. For reversible processes, which are limiting processes, entropy change is reduced to zero, but never less than zero. In the words of Clausius, "Die Energie der Welt ist konstant; die Entropie der Welt strebt einem Maximum zu."

Entropy and Equilibrium.—Since reversible processes are carried out through a series of equilibrium states, equation (7.31) may be used as a criterion of equilibrium between system and surroundings. It may also serve as a criterion of equilibrium for the system itself if the proper conditions are observed. In the reversible processes previously considered, the change in entropy of the system was found to be zero, positive, or negative, depending on the process, but the system did not remain at constant energy and volume in all these processes. When the conditions of constant energy and volume apply, the entropy of the system does not change during a reversible process.

Consider a system that can do the reversible work

$$\mathrm{D}w_r = P\,\mathrm{d}V + \mathrm{D}w' \tag{7.32}$$

where $\mathrm{D}w'$ stands for all other reversible work than $P\,\mathrm{d}V$ work. The first law equation may be combined with equations (7.9) and (7.32) to give an important equation

$$\mathrm{d}E = \mathrm{D}q_r - \mathrm{D}w_r = T\,\mathrm{d}S - P\,\mathrm{d}V - \mathrm{D}w' \tag{7.33}$$

which represents a combination of the first and second laws. From equation (7.33) is obtained a general statement for the entropy change of a system

$$\mathrm{d}S = \frac{\mathrm{d}E + P\,\mathrm{d}V + \mathrm{D}w'}{T} \tag{7.34}$$

When the conditions of constant energy and volume are imposed on equation (7.34), it becomes

$$\mathrm{d}S_{E,V} = \frac{\mathrm{D}w'}{T} \tag{7.35}$$

Thus, when a system at constant energy and volume is not at equilibrium the work $\mathrm{D}w'$ that the system may do in moving toward equilibrium along a reversible path is a measure of the entropy change. Both $\mathrm{D}w'$ and T are positive in value and $\mathrm{d}S_{E,V}$ is, therefore, also positive. On the other hand, at equilibrium the system cannot do work, $\mathrm{D}w'$ is zero, and $\mathrm{d}S_{E,V}$ is zero. These statements involve the second law and show how it may be used to describe the tendency toward equilibrium.

In the reversible adiabatic expansion, there was no entropy change in the system nor was there any Dw' work done. The system was, therefore, at equilibrium throughout the change. The increase in volume during expansion was accompanied by an equivalent decrease in energy, but the system by itself has no tendency to undergo this change. There is no spontaneity to this process. Thus, for a simple system that cannot do net work Dw', the entropy change, from equation (7.34) is

$$dS = \frac{dE + P\,dV}{T} \tag{7.36}$$

emphasizing again the fact that the entropy is a property of a system.

Consider, however, a system of two different gases in two separate containers but at the same pressure and temperature. If a stopcock connecting the two containers is opened, the two gases will diffuse into each other until the partial pressure of each gas has been equalized throughout the system. Obviously, the initial system was not at equilibrium for the diffusion proceeds spontaneously even though the total volume and the total energy remain constant. If the diffusion process is suitably harnessed, each of the gases can do work of diffusion as its partial pressure changes from the initial value to the equilibrium value and its volume changes from that of the initial container to that of the whole system. Since the work for gas A is $p_A\,dV_A$ and that of gas B is $p_B\,dV_B$, the work of diffusion is

$$Dw' = p_A\,dV_A + p_B\,dV_B$$

But, when $dE = 0$ and the total volume remains constant so that $dV = 0$, this equation, combined with equation (7.34), becomes

$$dS_{E,V} = \frac{p_A\,dV_A + p_B\,dV_B}{T} = \frac{Dw'}{T}$$

This latter equation, equivalent to equation (7.35), tells us more than that there is an increase in entropy. From it, we can calculate the numerical value for the entropy change.

Equilibrium at Constant Temperature.—We have found that, under the condition of constant energy and constant volume, the entropy change of a system is a measure of the reversible work obtainable from the process. If no such work is possible, the entropy change is zero and the system is at equilibrium. Either the entropy change or the reversible work may, therefore, be taken as a criterion of equilibrium. In practice, however, most processes of interest to the chemist are not carried out at constant energy and volume. The typical chemical reaction in open vessels takes place at constant pressure (atmospheric pressure) and, when suitably thermostated, at constant temperature. For these conditions, the entropy of the system is not the measure of the reversible work and of equilibrium. For example, the reaction between zinc and copper sulfate was carried out at constant pressure and constant temperature but with a volume change so small that the reaction may be considered a constant-volume reaction. However, in this reaction the energy of the system does not remain constant, the change being a decrease of 51,400 calories. A consequence is that the reaction may proceed spontaneously even though the entropy change of the system is negative.

Consider again a system and that part of its surroundings exchanging energy and volume with it. Where, as before, the surroundings absorb the heat $\mathrm{D}q'$ at the temperature T', the increase in entropy of the surroundings is $\mathrm{d}S' = -\mathrm{D}q/T'$ as in equation (7.17). At the same time, $\mathrm{D}q$ is related by the first law to the increase in energy of and the work done by the system as in the equation

$$\mathrm{D}q = \mathrm{d}E + \mathrm{D}w$$

Then, for the entropy change of the surroundings in terms of the changes in the system, we have

$$\mathrm{d}S' = \frac{-\mathrm{D}q}{T'} = \frac{-\mathrm{d}E - \mathrm{D}w}{T'} \tag{7.37}$$

But, from equation (7.31) we have, for the total entropy change,

$$\Sigma\, \mathrm{d}S_{E,V} = \mathrm{d}S + \mathrm{d}S' \geqq 0$$

This equation, when combined with equation (7.37), becomes

$$\sum \mathrm{d}S_{E,V} = \mathrm{d}S - \frac{\mathrm{d}E + \mathrm{D}w}{T'} \geqq 0 \tag{7.38}$$

Equation (7.38) is valid even though the system and surroundings are at different temperatures. However, in a constant-temperature process in which the surroundings are at the temperature of the system, $T' = T$ and equation (7.38) becomes, when rearranged

$$T\,\mathrm{d}S - \mathrm{d}E - \mathrm{D}w \geqq 0 \tag{7.39}$$

or

$$T\,\mathrm{d}S - \mathrm{d}E \geqq \mathrm{D}w \tag{7.40}$$

The equality sign applies, as before, for the reversible process, $\mathrm{D}w$ then being the reversible work. But the changes in energy and entropy do not depend on the path, being determined by the isothermal change in state of the system. Hence, the work in the irreversible path as indicated by the inequality sign is less than the reversible work, which then must be the maximum work for the isothermal change. Equation (7.40) is important and represents the combined first and second laws for an isothermal change. When combined with equation (7.32), we obtain for the reversible path

$$T\,dS - dE - P\,dV = Dw' \tag{7.41}$$

This equation is fundamental for equilibrium within a system. When the system is at equilibrium, it cannot do any net reversible work so that Dw' equals zero. At equilibrium, therefore,

$$T\,dS - dE - P\,dV = 0 \tag{7.42}$$

Entropy and Probability.—The second law of thermodynamics and the entropy function take on more meaning when they are viewed in the light of the atomic (molecular) theory and the kinetic theory. The molecules are small, and the number present in any measurable sample is enormous. One may imagine them to follow the laws of mechanics (and where necessary the quantum mechanics) and still be unable to give a detailed description of the position, energy, and velocity of the individual molecules. However, when the methods of statistics are applied to large numbers of molecules assumed to follow the laws of mechanics, the results have a surprising certainty. The statistical mechanics adopts the hypothesis of molecular chaos in which each molecule has no preference for any statistical state available to it. But, though a single molecule has an equal probability of being in each state available to it, the system as a whole will have a probability experimentally indistinguishable from the maximum probability W, which then becomes descriptive of the system.

A system of molecules that has an initial distribution of molecules differing from the most probable distribution will change spontaneously until the molecules attain the most probable distribution. Thus, the probability of the statistical mechanics appears to be related to the entropy of thermodynamics, both increasing as a system tends toward equilibrium at constant energy and volume.

As we have seen, entropy is an extensive property depending on the amount of substance in a system. For 2 moles of a substance, the entropy is double that for 1 mole at the same conditions. If two systems of a single substance with the entropies S' and S'', respectively, are combined into one system, the entropy S of this system is the sum of the entropies of the component systems. Thus,

$$S = S' + S'' \tag{7.43}$$

However, from statistical mechanics we find that the maximum probability, W, for a macroscopic system of molecules is, for practical purposes, equal to the number of ways of realizing the system of molecules. When two systems with the probabilities W' and W'', respectively, are combined into one system, the probability W of this system is the product of the probabilities of the component systems. Thus,

$$W = W' \times W'' \tag{7.44}$$

Boltzmann, therefore, suggested that the entropies are proportional to the logarithms of the probabilities, for from equation (7.44)

$$\ln W = \ln (W' \times W'') = \ln W' + \ln W'' \tag{7.45}$$

His well-known equation, relating entropy and probability, is

$$S = \boldsymbol{k} \ln W \tag{7.46}$$

where $\boldsymbol{k}$ is the proportionality constant. Equation (7.46) fulfills the requirements of additive systems since, for the two separate systems, we have

$$\begin{aligned} S' &= \boldsymbol{k} \ln W' \\ S'' &= \boldsymbol{k} \ln W'' \end{aligned}$$

and, for the combined system,

$$S' + S'' = \boldsymbol{k}(\ln W' + \ln W'') = \boldsymbol{k} \ln(W' \times W'')$$

which, from the relations in equations (7.43) and (7.45), is equal to equation (7.46).

When the value for $\boldsymbol{k}$ is properly chosen, equation (7.46) yields values for entropies equal to those obtained from thermal measurements and its validity has become well established. Since W is a pure number, $\boldsymbol{k}$ has the same dimensions as S. Its values are expressed in energy units per degree. If the temperature scale used in the statistical mechanics is the thermodynamic temperature scale, the value for $\boldsymbol{k}$ is found to be that of the *gas constant per molecule*. It is related to $\boldsymbol{R}$, the gas constant per mole by the equation

$$\boldsymbol{R} = N\boldsymbol{k} \tag{7.47}$$

where N is the Avogadro number. The constant $\boldsymbol{k}$ is called the *Boltzmann constant*.

Equation (7.46) is instructive in another respect. It contains no additive constant. Consequently, when $W = 1$, $\ln W = 0$, and S becomes zero. But W equals 1 only when there is but one way of realizing the system and the positions and energies of all the molecules are known. Under these conditions, the system has lost its randomness.

Equation (7.46), therefore, anticipates the third law of thermodynamics, which deals with the conditions under which the entropy becomes zero.

Distribution of Molecules in Space.—Some of the aspects of probability may be illustrated by the simple example of the distribution of a gas between two equal volumes V_1 and V_1'. As was indicated earlier, any single molecule a has an equal probability of being in either V_1 or V_1'. Hence, its probability of being in V_1 may be expressed as $\frac{1}{2}$ and the molecule may be expected to spend equal time in V_1 and V_1'. If a second molecule b is also present, the probability of finding both molecules in V_1 becomes $(\frac{1}{2})^2$ or $\frac{1}{4}$, since there are now four possible distributions, namely, (1) both a and b in V_1, (2) a in V_1 and b in V_1', (3) b in V_1 and a in V_1', and (4) both a and b in V_1'. There is only one chance in four of finding both a and b in V_1. These possibilities are outlined in Fig. 7.4. If there are 3 molecules, a, b, and c, there are 2^3 or 8 different ways of realizing the system, and the probability of finding all 3 molecules in V_1 is $(\frac{1}{2})^3$ or $\frac{1}{8}$. With 4 molecules, there are 2^4 or 16 different ways of realizing the system, and the probability of finding all 4 molecules in V_1

1 molecule
a

V_1	V_1'
a	
	a

2 molecules
a, b

V_1	V_1'
ab	
a	*b*
b	*a*
	ab

3 molecules
a, b, c

V_1	V_1'
abc	
ab	*c*
ac	*b*
bc	*a*
a	*bc*
b	*ac*
c	*ab*
	abc

4 molecules
a, b, c, d

V_1	V_1'
abcd	
abc	*d*
abd	*c*
acd	*b*
bcd	*a*
ab	*cd*
ac	*bd*
ad	*bc*
bc	*ad*
bd	*ac*
cd	*ab*
a	*bcd*
b	*acd*
c	*abd*
d	*abc*
	abcd

FIG. 7.4.—Possible distribution of molecules between equal volumes, V_1 and V_1'.

is reduced to $\frac{1}{16}$. It becomes clear that, if there are two ways of realizing a system for a single molecule, the number of ways for N molecules is 2^N, and the probability of finding all N molecules in the one statistical state is $(\frac{1}{2})^N$. These results are summarized in column (2) of Table 7.3. From this table, we see that for 10 molecules there is only 1 chance in 1,024 of finding all 10 molecules in V_1. With 20 molecules, there is only 1 chance in 1 million; for 40 molecules, 1 chance in 1 million million or 10^{12}. Even with as few as 20 or 40 molecules, the chance of finding all the molecules in V_1 is highly improbable. With the large number of molecules involved in chemical problems, the improbability becomes so great as to be considered an impossibility.

TABLE 7.3.—STATISTICAL DISTRIBUTION OF GASEOUS MOLECULES BETWEEN TWO EQUAL VOLUMES

Number of molecules in V_2, N	Number of combinations of molecules in $V_1 = \frac{1}{2}V_2$, 2^N	Number of combinations in which the number of molecules in V_1 is			Fraction of the combinations in which the number of molecules in V_1 is		
		Exactly $0.5N$	$0.45N$–$0.55N$	$0.4N$–$0.6N$	Exactly $0.5N$	$0.45N$–$0.55N$	$0.4N$–$0.6N$
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
1	2						
2	4	2	....	....	0.500		
3	8						
4	16	6	....	....	0.375		
6	64	20	....	....	0.313		
8	252	70	....	....	0.278		
10	1024	252	....	672	0.250	.....	0.66
20	1.049×10^6	0.1848×10^6	0.5201×10^6	0.7726×10^6	0.176	0.497	0.74
30	1.074×10^9	0.1551×10^9	....	0.8640×10^9	0.145	.....	0.80
40	1.100×10^{12}	0.1379×10^{12}	0.6272×10^{12}	0.9304×10^{12}	0.125	0.57	0.84
100	1.268×10^{30}	0.1009×10^{30}	0.9236×10^{30}	1.223×10^{30}	0.080	0.72	0.97

A further study of the distribution of 4 molecules between V_1 and V_1' is instructive, for it illustrates the behavior of gaseous systems containing larger numbers of molecules. From the different arrangements of the molecules in Fig. 7.4, it appears that there is 1 arrangement in which all the molecules are in V_1, and 1 in which none are in V_1; 4 arrangements in which 3 molecules are in V_1, and 4 in which 1 molecule is in V_1; and 6 arrangements in which 2 molecules are in V_1. The numbers of the different arrangements

$$1 + 4 + 6 + 4 + 1 = 2^4 = 16$$

correspond to the coefficients of a binomial raised to the fourth power.

The number of arrangements, 6, in which exactly one-half the molecules are in V_1 is listed in column (3), Table 7.3. The fraction representing the relative number of these arrangements is $\frac{6}{16} = 0.375$, which is listed in column (6). For 6 molecules, for which the total number of arrangements is 64, the number in which exactly 3 of the molecules are in V_1 is 20, the fraction being 0.313. As N increases, it is evident that the fraction of arrangements in which the division of the molecules in V_2 is exactly even between V_1 and V_1' decreases. However, the certainty of an essentially even distribution increases. Thus, if a 20 per cent fluctuation from the even distribution is permitted, the fraction of the arrangements within these limits increases steadily as is indicated by columns (5) and (8). For 10 molecules, the arrangement in which 4, 5, or 6 molecules are in V_1 are 672/1,024 of the total, or 65.6 per cent. For 20 molecules, the fraction of the arrangements between $0.4N$ and $0.6N$ increases to 773,000/1,049,000, or 0.74, and for 40 molecules to 0.84. For 100 molecules, the fraction of the arrangements containing between 40 and 60 molecules has increased to 0.97. Because of this rapid increase to an almost even distribution with so few as 100 molecules, one is not surprised by the statement by Mayer[1] that "for a liter of gas at standard conditions, for which $N \cong 10^{22}$, the chance of finding a deviation of more than one part in a million from the normal in one-half of the flask is only one chance in $10^{10^{10}}$."

Entropy and the Number of Ways of Realizing a System.—There is another aspect to the improbability of deviation from the most probable distribution. The statistical states of the system represented by most probable distribution are such a large fraction of the total number of states that W may be represented in entropy calculations, either by the total number of states, or by the number of states represented by the most probable distribution. Consequently, when there are two ways of realizing a system and the number of particles N is a sufficiently large number, W is increased by a factor 2^N and the entropy is increased by the amount

$$\Delta S = k \ln 2^N \tag{7.48}$$

For 1 mole of substance, N becomes the Avogadro number $\mathbf{N}$ so that from equations (7.47) and (7.48)

$$\Delta s = k \ln 2^{\mathbf{N}} = \mathbf{N}k \ln 2 = R \ln 2 \tag{7.49}$$

Similarly, if the number of ways of realizing a system is increased by g, the entropy increase for 1 mole is

$$\Delta s = k \ln g^{\mathbf{N}} = R \ln g \tag{7.50}$$

---

[1] MAYER, JOSEPH E., and MARIA G. MAYER, "Statistical Mechanics," p. 77, John Wiley & Sons, Inc., New York, 1940.

Equation (7.50) finds application when we consider the problem of absolute entropy values in connection with the third law of thermodynamics.

Entropy of Expansion of an Ideal Gas.—Consider the isothermal expansion of an ideal gas, from an initial volume V_1 as in Fig. 7.5, to a final volume V_2, which is double V_1. The gas being ideal, there is no change in energy E of the gas during the expansion. Then, we may expect an entropy change only as a result of an increase in volume. When the gas was in V_1, it had a value of $W = W_1$ determined by its number of molecules N, its energy E, and its volume V_1. In accordance with what we found earlier about the distribution of the gas, it was at its most probable distribution, that is, it was distributed evenly in the various parts of V_1. If now the gas is expanded to the volume V_2, E remaining constant, it is in an extremely improbable state, for all the molecules are in one-half the total volume. The gas will redistribute itself until it is evenly distributed in V_2, that is, until it has reached its most probable distribution and $W = W_2$. This is a spontaneous process at constant energy E and constant volume V_2. It results in an increase in S, the value of which is to be calculated. It also results in an increase in probability, the probabilities W_1 and W_2 being related by the equations

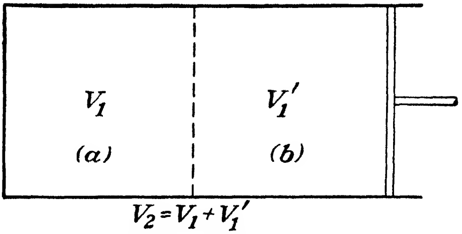


FIG. 7.5.—Distribution of molecules in a volume, V_2.

$$\left.\begin{aligned} W_1 &= (\tfrac{1}{2})^N W_2 \\ 2^N W_1 &= W_2 \end{aligned}\right\} \qquad (7.51)$$

Where the increase in entropy is $\Delta S = S_2 - S_1$, we have, from equation (7.46),

$$\begin{aligned} S_2 &= k \ln W_2 = k \ln (2^N W_1) \\ S_1 &= k \ln W_1 = k \ln [(\tfrac{1}{2})^N W_2] \\ \Delta S &= S_2 - S_1 = k(\ln W_2 - \ln W_1) = k \ln \frac{W_2}{W_1} \\ &= k \ln \frac{2^N W_1}{W_1} = k \ln 2^N \end{aligned} \qquad (7.52)$$

Where n is the number of moles of gas and $\mathbf{N}$ the Avogadro number, we have $N = n\mathbf{N}$ so that equation (7.52) becomes

$$S_2 - S_1 = nNk \ln 2$$
$$= nR \ln 2 \tag{7.53}$$

Equation (7.53) could also have been obtained from equation (7.49) which was derived for 1 mole of gas.

The entropy increase may also be calculated from equations (7.12) and (4.40) to be

$$S_2 - S_1 = \frac{q_r}{T} = \frac{w_r}{T} = \frac{nRT \ln \dfrac{V_2}{V_1}}{T}$$
$$= nR \ln \frac{V_2}{V_1} \tag{7.54}$$
$$= nR \ln 2 \tag{7.55}$$

since $V_2 = 2V_1$. Equations (7.53) and (7.55) for the increase in entropy for this isothermal expansion are identical.

Problems

7.1. Revise the following statements so that they are free from contradiction:

(*a*) In a reversible process, the increase in entropy is equal to $\int (dq_r/T)$.

(*b*) In a reversible process, the total entropy does not change.

7.2. (*a*) Calculate the work (in calories) done by a perfect gas in expanding isothermally and reversibly at 20°C from 1 liter and 1 atmosphere to 2 liters. What are the values of the heat absorbed, the entropy change, the change in internal energy ΔE, and the change in heat content ΔH for this process?

(*b*) What is the work done by 1 liter of a perfect gas at 1 atmosphere and 20°C in expanding into a liter vacuum so that the final volume is 2 liters? How much heat is absorbed in this process? What is the entropy change? Explain. Compare the values of w, q, ΔS, ΔE, and ΔH from this process with those in (*a*).

7.3. Derive the equation

$$\frac{w_r}{q_2} = \frac{T_2 - T_1}{T_2}$$

7.4. Derive the equation

$$-\frac{w_r}{q_1} = \frac{T_2 - T_1}{T_1}$$

7.5. A mole of a perfect gas at 300°K expands reversibly and isothermally from 20 to 40 liters. How much work, in calories, will be done by the gas? Will heat be absorbed in this reversible process? Will there be an increase or decrease in the entropy of the gas?

7.6. The entropy change in Prob. 7.5 is not zero, and yet the expansion is a reversible process. Explain. Will the surroundings undergo a change in entropy in this process? If so, what will be the sign and quantity of the change?

7.7. A mole of nitrogen at 0°C occupying 10 liters (state 1) is to be expanded to a volume of 20 liters at 100°C (state 2). An infinite number of paths from state 1 to state 2 are possible. Consider the following important paths: (*a*) The gas is expanded isothermally and reversibly at 0°C to the volume of 20 liters and then heated to 100°C, and (*b*) the gas at a volume of 10 liters is heated from 0 to 100°C and is then expanded isothermally to 20 liters. Compare the numerical values for the change in internal energy of the gas, the heat absorbed from the surroundings, and the work done by the gas obtained by following paths (*a*) and (*b*), respectively. Assume that the ideal gas law holds for nitrogen at these temperatures, that the heat capacity at constant volume is independent of the volume, and that

$$c_P = 6.524 + 0.00125\ T$$

7.8. Assume that liquid toluene and liquid xylene mix without an appreciable heat of solution and without a volume change. Will there be a change in internal energy ΔE? In heat content ΔH? In entropy ΔS? Will there be any work done in the process?

7.9. Five ideal gas molecules are distributed between two equal volumes. Prepare a chart showing the probability of finding 5, 4, 3, 2, 1, or none of these molecules in the one volume V_1. Plot this probability as ordinate against number of molecules as abscissa. What is the probability of finding other than a 2:3 or 3:2 distribution of the molecules between the two volumes?

7.10. The volume of a mole of an ideal gas is increased tenfold. What is the increase in entropy (in calories per degree)? What is the increase in entropy per molecule?

7.11. What will be the entropy changes resulting from the reversible adiabatic and isothermal expansions described in Probs. 4.7, 4.10, 4.11, and 4.14?

7.12. (*a*) A liter of perfect gas at 0°c and 1 atmosphere pressure is expanded isothermally. To what volume must it expand to produce an entropy increase of 0.1 calorie per degree?

(*b*) The temperature of the gas in (*a*) is raised to 100°c at constant volume. When the gas is expanded isothermally at this temperature, what will be its final volume when the entropy increases 0.1 calorie per degree during the expansion?

(*c*) The temperature of the gas in (*a*) is raised to 100°c at constant pressure. What will be its volume? When the gas is now expanded isothermally at 100°c, what will be its final volume when the entropy increases 0.1 calorie per degree during the expansion? What will be the relative increase in volume?

(*d*) Explain the results of (*a*), (*b*), and (*c*) in terms of probabilities.

7.13. (*a*) A liter of nitrogen and a liter of oxygen at 0°c and 1 atmosphere pressure are allowed to diffuse into each other. What is the value for the change in entropy for this process? Assume that the gases are ideal diatomic gases.

(*b*) A liter of nitrogen and a liter of oxygen at 100°c and 1 atmosphere pressure are allowed to diffuse into each other. What is the value for the change in entropy for this process?

(*c*) Does the temperature of the gases in (*a*) and (*b*) enter into the calculations? Explain.

CHAPTER 8

APPLICATIONS OF ENTROPY. SOME ENTROPY FUNCTIONS

The entropy function assumes relatively simple forms for systems that do no chemical or other work except work of expansion. For a change in state of such a system along any reversible path, the work done is $\mathrm{D}w_r = P\,\mathrm{d}V$ and the heat absorbed during the change is

$$\mathrm{D}q_r = T\,\mathrm{d}S$$

Since, according to the first law,

$$\mathrm{d}E = \mathrm{D}q_r - \mathrm{D}w_r$$

we have for the system

$$\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V \tag{8.1}$$

Equation (8.1), based on the first and second laws of thermodynamics, is fundamental for systems under the indicated conditions. All the variables in it are properties and depend only on the state of the system. Therefore, if we know the value of $\mathrm{d}E$ for any path and know how P changes with V along that path, we can evaluate $T\,\mathrm{d}S$. Or, if we can evaluate $T\,\mathrm{d}S$ and $P\,\mathrm{d}V$, we have the value for $\mathrm{d}E$. These relations enable us to determine the entropies of pure substances.

Efficiency of the Heat Engine.—Heat engines may operate in cycles other than the Carnot cycle, but the maximum work produced by one operating between the temperatures T_2 and T_1 is equal to that produced by an engine operating reversibly in the Carnot cycle. The energy, equal to the heat q_2, some of which is to be expended as work, may be obtained from a chemical process such as the combustion of coal at the temperature T_2. According to the theory of the Carnot cycle, some of this energy, equal to $-q_1$ must be discharged at the temperature T_1, the difference between q_2 and $-q_1$ being available as work. The *conversion factor* is defined by the ratio w/q_2, the maximum value being, from equation (7.5)

$$\frac{w_r}{q_2} = \frac{T_2 - T_1}{T_2} \tag{8.2}$$

Now the temperature T_1 at which the engine discharges the $-q_1$ calories of heat is dependent on the temperature of the surroundings of the engine.

If the engine is operating rapidly, so that heat accumulates around the engine, T_1 may be considerably higher than the temperature of the surroundings. The temperature T_1 cannot be lower than that of the surroundings for an engine operating continuously. From equation (8.2), the ratio expressing the maximum conversion factor for an engine operating between 0 and 100° is

$$\frac{373 - 273}{373} = \frac{100}{373} = 0.268$$

Only 27 per cent of the energy absorbed as heat at the higher temperature can be converted to work under these conditions. If the conversion factor is to be increased, the ratio $(T_2 - T_1)/T_2$ must be made as large as possible. The maximum limiting conversion factor is unity; under this condition all the energy would appear as work.

The ratio $(T_2 - T_1)/T_2$ can approach unity only when $T_2 - T_1 \doteq T_2$, that is, when T_2 is very large compared with T_1. This limit could be achieved if T_1 approached zero. However, T_1 cannot be lower than the temperature of the surrounding of the heat engine so that its lower limit is predetermined. Practical attempts to increase the efficiency of a heat engine must, therefore, be directed toward increasing T_2.

Much progress has been made in increasing the efficiency of steam engines by increasing the temperature of the saturated steam. Because the increased temperature results in increased boiler pressures, the strength of the boiler imposes limitations on the attainment of high temperatures with steam. In recent installations, pressures up to 2,300 pounds per square inch and temperatures up to 1000°F or 540°C have been obtained. If T_1 is assumed to be 300°K, the maximum conversion of such an engine is $(w/q_2) = \frac{513}{813} = 0.63$. The actual conversion from coal to electrical output is 33.5 per cent, a record for a steam plant. It should be pointed out here that it is the higher temperatures that are important, the higher corresponding pressures being incidental. In an effort to secure the desirable high temperatures without the undesirable high pressures, installations have been made in which higher boiling liquids such as diphenyl and mercury are substituted for the high pressure steam with actual conversions up to 37.5 per cent.

Refrigerating Engine.—In a refrigerating engine, the Carnot cycle is reversed: q_1 calories of heat are withdrawn from the cold reservoir R_1 at the temperature T_1, and work $-w$ is done on the refrigerating gas to transport this heat to the hot reservoir R_2 at the temperature T_2. According to equation (7.1), the heat discharged at the higher temperature will be

$$-q_2 = q_1 - w$$

and, according to equation (7.5) the ratio of the reversible work done by the engine to the heat absorbed from the cold reservoir is

$$-\frac{w_r}{q_1} = \frac{T_2 - T_1}{T_1} \tag{8.3}$$

From this relation, we see that the minimum work required to remove heat from a cold reservoir at $T_1 = 273°\text{K}$ and discharge the heat to the surroundings of the refrigerator at $T_2 = 300°\text{K}$ is indicated by the ratio

$$-\frac{w_r}{q_1} = \frac{300 - 273}{273} = \frac{27}{273} = 0.1; \qquad -w_r = 0.1q_1$$

One calorie of work is required to remove 10 calories of heat from the refrigerator. If the cold reservoir of the refrigerator is at $-73°\text{C}$ or $200°\text{K}$, and $T_2 = 300°\text{K}$,

$$-\frac{w_r}{q_1} = \frac{100}{200} = 0.5; \qquad -w_r = 0.5q_1$$

If T_1 is $100°\text{K}$, $-w_r = 2q_1$. As T_1 approaches 0, we have, at the limit,

$$-\frac{w_r}{q_1} = \frac{T_2 - 0}{0} = \infty$$

At zero absolute, therefore, the work required to remove heat from a substance acting as the cold reservoir becomes infinitely large. For this reason, the second law has been called the "principle of unattainability of the absolute zero" of temperature.

The work required to transport a given quantity of heat from the lower to the higher temperature becomes greater as the temperature of the cold reservoir decreases or as that of the hot reservoir increases. The efficiency of the refrigerating machine, therefore, becomes less when the cooling coils of the refrigerator are so covered that they cannot transmit the heat $-q_2$, which equals the sum of the heat pumped out of the refrigerator and the work done, to the surroundings of the refrigerator at the lowest possible temperature. It is not popularly understood that, in the operation of the domestic refrigerator, heat is added to the room in which the refrigerator stands.

Kelvin suggested an interesting possible application of the refrigerating machine to the heating of buildings. For example, with an outdoor temperature of $-10°\text{C}$ and an indoor temperature of $20°\text{C}$, the minimum work required to extract 1,000 calories of heat from the out of doors is

$$\frac{30}{263} \times 1{,}000 = 114 \text{ cal}$$

and the heat delivered indoors would be

$$1{,}000 + 114 = 1{,}114 \text{ cal}$$

If the work, say in the form of electrical energy, had been converted to heat directly by means of a resistance coil, only 114 calories would have been added to the room.

Change of Entropy with Temperature.—From the definition of entropy, it is evident that the change in entropy resulting from a change of temperature may be calculated from the heat for the reversible process. When a system changes temperature through absorption of heat, the change in entropy can be calculated from the heat capacity if the system absorbs the heat reversibly. However, if irreversible processes occur within the system during the absorption of heat, the change in entropy cannot be calculated from the actual heat absorbed. For example, for systems at constant pressure, the *actual* heat absorbed for a process is represented by $\mathrm{d}H = \mathrm{D}q_P$. The *reversible* heat is represented by $\mathrm{D}q_r = T\,\mathrm{d}S$. But, $\mathrm{d}H$ and $T\,\mathrm{d}S$ are not equal except under equilibrium conditions or in simple systems where no chemical reactions occur.

Consider a simple system consisting of some pure chemical substance. This system may absorb heat reversibly, the rate of temperature increase depending on the heat capacity of the substance. The heat will be absorbed reversibly if no temperature gradients exist in the substance itself or between the substance and the body donating heat to it. Under these conditions, the system absorbs heat infinitely slowly, the heat absorbed being

$$\mathrm{D}q = C\,\mathrm{d}T = T\,\mathrm{d}S \tag{8.4}$$

where C is the heat capacity of the substance.

If, in practice, the system absorbs the heat at a finite rate, its change in entropy will still be given by the relation $\mathrm{d}S = \mathrm{d}q/T$; for the entropy is a property of the system, and the *same amount* of heat will be absorbed for the spontaneous as for the reversible process. The difference in entropy between the reversible process and the irreversible process will occur not in the substance itself but in the surroundings. In the former process, the entropy loss by the surroundings will exactly equal the gain by the system; in the latter process, the surroundings, losing heat at a higher temperature, will not lose so much entropy as is gained by the system. This irreversible process results in a total increase in entropy, as in equation (7.27). In any event, the chemical substance has the change in entropy indicated by equation (8.4). For a simple system, therefore, we have, from this equation,

$$\frac{\mathrm{d}S}{\mathrm{d}T} = \frac{C}{T} \tag{8.5}$$

or

$$\mathrm{d}S = C\frac{\mathrm{d}T}{T} = C\,\mathrm{d}\ln T \tag{8.6}$$

Values of C are usually available for the common experimental conditions of *constant volume* or *constant pressure.* For these two conditions, we have from equations (3.2) and (3.5), respectively,

$$C = \left(\frac{\partial E}{\partial T}\right)_V$$

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

When these values are introduced into equations (8.5) and (8.6), we have, *at constant volume,*

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V \tag{8.7}$$

$$\mathrm{d}S_V = C_V\,\mathrm{d}\ln T \tag{8.8}$$

and, *at constant pressure,*

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P \tag{8.9}$$

$$\mathrm{d}S_P = C_P\,\mathrm{d}\ln T \tag{8.10}$$

The same equations may be derived in a more formal manner. From equation (8.1),

$$T\,\mathrm{d}S = \mathrm{d}E + P\,\mathrm{d}V \tag{8.11}$$

At constant volume, $\mathrm{d}V$ is zero, and, from equation (3.1),

$$\mathrm{d}E = \mathrm{d}E_V = \mathrm{D}q_V,$$

so that

$$T\,\mathrm{d}S_V = \mathrm{d}E_V = \mathrm{D}q_V \tag{8.12}$$

Similarly, at constant pressure, $\mathrm{d}E + P\,\mathrm{d}V = \mathrm{d}E_P + P\,\mathrm{d}V_P = \mathrm{d}H_P$ and from equation (3.4), $\mathrm{d}H_P = \mathrm{D}q_P$, so that

$$T\,\mathrm{d}S_P = \mathrm{d}E_P + P\,\mathrm{d}V_P = \mathrm{d}H_P = \mathrm{D}q_P \tag{8.13}$$

Thus, for such systems, the heat absorbed is the same whether it is absorbed reversibly or irreversibly, the value depending only on whether the process was carried out at constant volume or constant pressure, or any other condition that fixes the value of $P\,\mathrm{d}V$ for the change. For these processes, $\mathrm{D}q = \mathrm{D}q_r = T\,\mathrm{d}S$.

Since the heat absorbed produces a rise in temperature, it is related to the heat capacity of the system by equations (2.7), (3.3), and (3.5), so that

$$\mathrm{D}q = C\,\mathrm{d}T = T\,\mathrm{d}S \tag{8.14}$$

$$\mathrm{D}q_V = \mathrm{d}E_V = C_V\,\mathrm{d}T = T\,\mathrm{d}S_V \tag{8.15}$$

$$\mathrm{D}q_P = \mathrm{d}H_P = C_P\,\mathrm{d}T = T\,\mathrm{d}S_P \tag{8.16}$$

Equation (8.14) may be arranged to give equations (8.5) and (8.6), equation (8.15) to give equations (8.7) and (8.8), and equation (8.16) to to give equations (8.9) and (8.10).

Because we shall need them later, we shall derive two other relations from equations (8.7) and (8.9). At constant temperature, that is, at some definite value of the temperature, the partial derivative of equation (8.7) with respect to volume is

$$\frac{\partial^2 S}{\partial T\,\partial V} = \frac{1}{T}\left(\frac{\partial C_V}{\partial V}\right)_T = \frac{1}{T}\,\frac{\partial^2 E}{\partial T\,\partial V} \tag{8.17}$$

and the partial derivative of equation (8.9) with respect to pressure is

$$\frac{\partial^2 S}{\partial T\,\partial P} = \frac{1}{T}\left(\frac{\partial C_P}{\partial P}\right)_T = \frac{1}{T}\,\frac{\partial^2 H}{\partial T\,\partial P} \tag{8.18}$$

These equations are used later.

Isothermal Change of Entropy with Volume and Pressure.—At the beginning of the chapter, we pointed out that equation (8.1) was set up for a reversible process, but that it now contains only the terms E, T, S, V, and P, all of which are properties. It may, accordingly, be applied to a system that undergoes any change reversible or irreversible, *so long as the reversible system was not able to do work* Dw' *other than the work of expansion.* This qualification must not be overlooked, for it is contained implicitly in equation (8.1) and in all other equations derived from it. Equation (8.1) may be applied to simple systems that do not undergo chemical changes and that do only work of expansion. In general, when chemical changes occur, other work, such as electrical work, can be derived from the process.

Even though equation (8.1) is restricted in its application, it may be extremely useful, for any real process may be subdivided into separate stages. If the chemical reaction is presumed to go on at some constant temperature under specified conditions of pressure and volume, the substances to be used in the reaction can be brought to the reaction conditions in accordance with the requirements of equation (8.1) and allowed to react while doing other work w'. The products of the reaction may then be changed from the reaction conditions to the final condition in accordance with equation (8.1).

We have found that the internal energy function E is particularly useful under experimental conditions of constant volume, and the heat content function H is especially adapted to conditions of constant pressure. From the definition of H, it follows that

$$\mathrm{d}H = \mathrm{d}E + \mathrm{d}(PV) = \mathrm{d}E + P\,\mathrm{d}V + V\,\mathrm{d}P$$

and, therefore,

$$\mathrm{d}H - V\,\mathrm{d}P = \mathrm{d}E + P\,\mathrm{d}V$$

If $\mathrm{d}H - V\,\mathrm{d}P$ is substituted for $\mathrm{d}E + P\,\mathrm{d}V$ in equation (8.1), we have the relation

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}P \tag{8.19}$$

Equation (8.1) may be solved for P, and equation (8.19) for V to give the corresponding equations

$$P = T\frac{\mathrm{d}S}{\mathrm{d}V} - \frac{\mathrm{d}E}{\mathrm{d}V} \tag{8.20}$$

and

$$V = \frac{\mathrm{d}H}{\mathrm{d}P} - T\frac{\mathrm{d}S}{\mathrm{d}P} \tag{8.21}$$

If $\mathrm{d}E/\mathrm{d}V$ and $\mathrm{d}H/\mathrm{d}P$ are evaluated experimentally, values of $\mathrm{d}S/\mathrm{d}V$ and $\mathrm{d}S/\mathrm{d}P$ may be obtained. However, $\mathrm{d}S/\mathrm{d}V$ and $\mathrm{d}S/\mathrm{d}P$ at constant temperature can be more readily evaluated from the following relations:

When equation (8.20) is differentiated with respect to temperature at a definite volume, we obtain

$$\left(\frac{\partial P}{\partial T}\right)_V = T\frac{\partial^2 S}{\partial V\,\partial T} + \left(\frac{\partial S}{\partial V}\right)_T - \frac{\partial^2 E}{\partial V\,\partial T} \tag{8.22}$$

When equation (8.21) is differentiated with respect to temperature at a definite pressure, we obtain

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial^2 H}{\partial P\,\partial T} - T\frac{\partial^2 S}{\partial P\,\partial T} - \left(\frac{\partial S}{\partial P}\right)_T \tag{8.23}$$

Comparison with equations (8.17) and (8.18) shows that the second and fourth terms in equation (8.22) cancel, as do also the second and third terms in equation (8.23), so that we have the important relationships

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{8.24}$$

and

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{8.25}$$

These relations enable us to evaluate $(\partial S/\partial V)_T$ and $(\partial S/\partial P)_T$, for $(\partial P/\partial T)_V$ and $-(\partial V/\partial T)_P$ can be measured readily.

Thermodynamic Equations of State.—If equations (8.24) and (8.25) are combined, respectively, with equations (8.20) and (8.21), the "thermodynamic equations of state"

$$P = T\left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial E}{\partial V}\right)_T \tag{8.26}$$

and

$$V = \left(\frac{\partial H}{\partial P}\right)_T + T\left(\frac{\partial V}{\partial T}\right)_P \tag{8.27}$$

are obtained. Comparison of equations (8.20) and (8.21) with (8.26) and (8.27) shows that the latter are slightly less general than the former. However, they are frequently more useful, for experimental data on the change of pressure with temperature of substances at constant volume or on the thermal expansion of substances at constant pressure are relatively easily obtained. Indeed, it is easier to obtain values of $(\partial E/\partial V)_T$ and $(\partial H/\partial P)_T$ by use of these equations than to determine the values experimentally. We are familiar with equations of state that express the relationship between the properties P, V, and T for a given amount of the substance. Equations (8.26) and (8.27) contain also the properties E and H, respectively, and are called the "thermodynamic equations of state."

Equations (8.26) and (8.27) may be applied to any simple system and, therefore, to a gas that obeys the ideal gas equation $P\mathrm{v} = RT$. For such a gas,

$$P = \frac{RT}{\mathrm{v}}; \qquad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{\mathrm{v}} \tag{8.28}$$

and

$$\mathrm{v} = \frac{RT}{P}; \qquad \left(\frac{\partial \mathrm{v}}{\partial T}\right)_P = \frac{R}{P} \tag{8.29}$$

When these values are substituted in equations (8.26) and (8.27) we obtain the ideal gas relations

$$\left(\frac{\partial E}{\partial V}\right)_T = 0 \tag{8.30}$$

and

$$\left(\frac{\partial H}{\partial P}\right)_T = 0 \tag{8.31}$$

These relations are equations (4.6) and (4.8). We see here that they follow from the ideal gas equation and the laws of thermodynamics.

For real gases that are not represented by the ideal gas equation, equations (8.30) and (8.31) are not valid.

Thermodynamic Temperatures from Gas Thermometers.—Equations (4.56) and (7.5), namely,

$$\frac{q_2}{T_2} = \frac{-q_1}{T_1} = \frac{w_r}{T_2 - T_1}$$

are identical, holding, respectively, for the ideal gas and any substance in the Carnot cycle, but the temperature used in deriving equation (4.56) was that on the ideal gas scale and not that on the thermodynamic scale. Therefore, the identity of the two equations indicates the identity of the two temperature scales. Consequently, an ideal gas thermometer could be used to indicate thermodynamic temperatures. In a gas thermometer containing a definite amount of ideal gas, PV is directly proportional to the ideal gas and thermodynamic temperature T. Thus, if the measured pressure-volume product at the temperature T_1 is P_1V_1 and that at the temperature T_2 is P_2V_2, we have

$$\left.\begin{aligned} P_2V_2 &= nRT_2 \\ P_1V_1 &= nRT_1 \end{aligned}\right\} \tag{8.32}$$

In a *constant-volume thermometer*, V and n are constant so that

$$\frac{P_2}{P_1} = \frac{T_2}{T_1} \ (V \text{ and } n \text{ const}) \tag{8.33}$$

A real gas does not obey equations (8.32). Let the real gas be represented by the equations

$$\left.\begin{aligned} P_2V_2 &= nR\theta_2 \\ P_1V_1 &= nR\theta_1 \end{aligned}\right\} \tag{8.34}$$

The "real gas temperatures" θ_1 and θ_2 in equations (8.34) are not identical with the thermodynamic temperatures T_1 and T_2 in equations (8.32); relative values of θ_1 and θ_2 are what are measured by the observed pressure ratio in a real gas constant-volume thermometer since, from equations (8.34)

$$\frac{P_2}{P_1} = \frac{\theta_2}{\theta_1} \ (V \text{ and } n \text{ const}) \tag{8.35}$$

Since equations (8.33) and (8.35) give only relative values of T and θ an additional relation is required to fix the two temperature scales. If the pressures P_1 and P_2 are measured at the ice point and the steam point, respectively, we have by definition

$$T_2 - T_1 = 100° = \theta_2 - \theta_1 \tag{8.36}$$

Then, for the ideal gas pressures,

$$\frac{P_2 - P_1}{P_1} = \frac{100}{T_1}$$

and, for the real gas pressures,

$$\frac{P_2 - P_1}{P_1} = \frac{100}{\theta_1}$$

We must now find a relation between the real gas pressures and the thermodynamic or ideal gas temperature T. Equation (8.26) furnishes such a relation. It may be rearranged to

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

which, when divided by T^2, becomes

$$\frac{T\left(\frac{\partial P}{\partial T}\right)_V - P}{T^2} = \left[\frac{\partial\left(\frac{P}{T}\right)}{\partial T}\right]_V = \frac{\left(\frac{\partial E}{\partial V}\right)_T}{T^2}$$

This equation may be rearranged to

$$\partial\left(\frac{P}{T}\right)_V = \left(\frac{\partial E}{\partial V}\right)_T\left(\frac{\partial T}{T^2}\right)_V = -\left(\frac{\partial E}{\partial V}\right)_T \partial\left(\frac{1}{T}\right)_V$$

and integrated between the limits P_1, T_1 and P_2, T_2 to give at constant volume

$$\frac{P_2}{T_2} - \frac{P_1}{T_1} = -\int_{T_1}^{T_2}\left(\frac{\partial E}{\partial V}\right)_T d\left(\frac{1}{T}\right) \tag{8.37}$$

Comparison of equation (8.37) for the real gas with equation (8.33) for the ideal gas shows that the integral is a measure of the deviation of the real gas from the ideal gas equation. If the value of $(\partial E/\partial V)_T$ is zero, as it is for the ideal gas, the integral becomes zero and equation (8.37) reduces to equation (8.33). Equation (8.35) may be combined with equation (8.37) to give relations between θ, the "temperature" measured by the constant-volume gas thermometer, and T, the thermodynamic temperature.[1] With a constant-volume helium thermometer, the values of θ are about 0.02° greater than the corresponding values of T; with a constant-volume nitrogen thermometer, the values of θ are about 0.8°

---

[1] Discussion and application of these and other relations between gas scale temperatures and thermodynamic temperatures may be found in papers by W. T. Wensel, F. G. Keyes, J. R. Roebuck and T. A. Murrell, J. A. Beattie, and others in "Temperature, Its Measurement and Control in Science and Industry," Reinhold Publishing Corporation, New York, 1941.

smaller than those of T. At the ice point, the helium thermometer gives $\theta = 273.184°$ and the nitrogen thermometer gives $\theta = 272.380°$.

Corresponding equations may be derived for θ as measured by a *constant-pressure gas thermometer* and the thermodynamic temperature. From equations (8.32), we have for the ideal gas

$$\frac{V_2}{V_1} = \frac{T_2}{T_1} \text{ (}P\text{ and }n\text{ const)} \tag{8.38}$$

and, from equations (8.34), we have for the real gas

$$\frac{V_2}{V_1} = \frac{\theta_2}{\theta_1} \text{ (}P\text{ and }n\text{ const)} \tag{8.39}$$

In general, the relative values and, therefore, the absolute values of θ are not the same for the constant-pressure thermometer as for the constant-volume thermometer containing the same gas. As before, absolute values of θ and T may be obtained from relative values by use of equation (8.36) which fixes the size of the degree on each scale. A relation between V and T for the real gas is given by equation (8.27). From this equation by the methods previously used in deriving equation (8.37), we have

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

and

$$\partial\left(\frac{V}{T}\right)_P = \left(\frac{\partial H}{\partial P}\right)_T \partial\left(\frac{1}{T}\right)_P \tag{8.40}$$

But from equation (4.33), $(\partial H/\partial P)_T = -\mu C_P$, where μ is the Joule-Thomson coefficient. Equation (8.40), therefore, becomes, when integrated between the limits V_1, T_1 and V_2, T_2 at constant pressure,

$$\frac{V_2}{T_2} - \frac{V_1}{T_1} = -\int_{T_1}^{T_2} \mu C_P \, d\left(\frac{1}{T}\right) \tag{8.41}$$

As in equation (8.37), the integral measures the deviation of the real gas from ideal behavior. In a helium constant-pressure thermometer, the values of θ are approximately 0.15° greater than those for T, the value at the ice point being $\theta = 273.320°$. For the nitrogen constant-pressure thermometer, the values of θ are approximately 1° smaller, the value at the ice point being $\theta = 272.479°$.

Relation between Heat Capacity at Constant Pressure and Constant Volume.—In equation (3.16), we presented the difference between heat capacity at constant pressure and that at constant volume as

$$C_P - C_V = \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P \tag{8.42}$$

This relation was derived on the basis of the first law of thermodynamics. However, the value of P derived from equation (8.26), which is based on the second law, can be substituted in equation (8.42) to give

$$\begin{aligned} C_P - C_V &= \left[\left(\frac{\partial E}{\partial V}\right)_T + T\left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial E}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P \\ &= T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P \end{aligned} \tag{8.43}$$

Equation (8.43), as it stands, can be applied to gases for which the change of pressure with temperature is readily measured. However, this derivative is not so readily measured for condensed phases, especially solids. Following the method illustrated in Chap. 1, we have, for a pure substance whose pressure is a function of temperature and volume alone,

$$dP = \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT \tag{8.44}$$

But, for a constant-pressure process, $dP = 0$; and we obtain, from equation (8.44),

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P \tag{8.45}$$

When equation (8.45) is substituted in equation (8.43), we have

$$C_P - C_V = T\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P^2 \tag{8.46}$$

Let the coefficient of thermal expansion α and the compressibility β be defined by the relations

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P; \qquad \beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{8.47}$$

Substituting these relations in equation (8.46), we have

$$\begin{aligned} C_P - C_V &= T\frac{1}{\beta V}(\alpha^2 V^2) \\ &= \frac{\alpha^2 VT}{\beta} \end{aligned} \tag{8.48}$$

This equation for 1 mole of substance was introduced earlier [equation (3.24)]. As stated there, the equation is useful in calculating $c_P - c_V$ for solids.

Entropy of an Ideal Gas.—From the first law equation, we derived equation (8.1), which applies to systems in which the only work done is that of expansion. Equation (8.1) may be rearranged in the form

$$dS = \frac{dE}{T} + \frac{P\,dV}{T} \tag{8.49}$$

This equation may be applied to 1 mole of perfect gas. For such a gas, we have $P = RT/\mathrm{v}$ and, from equation (4.42), $d\mathrm{E} = \mathrm{c}_V\,dT$. Hence, the change in entropy per mole may be expressed as

$$d\mathrm{s} = \mathrm{c}_V \frac{dT}{T} + R\frac{d\mathrm{v}}{\mathrm{v}} = \mathrm{c}_V\,d\ln T + R\,d\ln \mathrm{v} \tag{8.50}$$

For the ideal gas with constant heat capacity, equation (8.50), when integrated, becomes

$$\mathrm{s} = \mathrm{c}_V \ln T + R\ln \mathrm{v} + \mathrm{s}_0' \tag{8.51}$$

where s_0' is an integration constant.

The entropy may also be expressed in terms of the variables P and T (or P and V). When v is in cubic centimeters and P in atmospheres, $\mathrm{v} = RT/P$, R being 82.057 cubic centimeter atmospheres per degree. Similarly, from equation (4.26), $\mathrm{c}_V = \mathrm{c}_P - R$, where R is in the same units as heat capacity. When these values are substituted in equation (8.51), we obtain

$$\begin{aligned}\mathrm{s} &= (\mathrm{c}_P - R)\ln T + R\ln\frac{RT}{P} + \mathrm{s}_0' \\ &= \mathrm{c}_P \ln T - R\ln P + R\ln R + \mathrm{s}_0' \end{aligned} \tag{8.52}$$

If entropy is to be expressed in calories per degree, the first R in the $R\ln R$ term must be expressed in this unit, but, from the derivation of equation (8.52) the second R must be expressed in the units of $P\mathrm{v}/T$. Thus, for the pressure and volume units chosen,

$$R\ln R = 1.9872 \ln 82.057 = 8.7584$$

The integration constant s_0' was first evaluated by Sackur and, more exactly, by Tetrode from the statistical mechanics. The constant has the value

$$\mathrm{s}_0' = \frac{3}{2}R\ln M + \frac{5}{2}R + R\ln\frac{(2\pi k)^{3/2}}{h^3 N^{5/2}} \tag{8.53}$$

where M is the molar weight of the gas in grams, h is Planck's constant in erg seconds, k is the Boltzmann gas constant in ergs per degree, and the other symbols have their usual meaning. The last term of equation (8.53), a constant for all gases, has the value

$$R\ln(3.12185 \times 10^{-4}) = -16.0408 \text{ cal/deg}$$

From equations (8.52) and (8.53), the molar entropy for the pressure in atmospheres is

$$\begin{aligned} \mathrm{s} &= \tfrac{3}{2}R \ln M + \mathrm{c}_P \ln T - R \ln P + \tfrac{5}{2}R + 8.7584 - 16.0408 \\ &= \tfrac{3}{2}R \ln M + \mathrm{c}_P \ln T - R \ln P + \tfrac{5}{2}R - 7.282 \qquad (8.54) \end{aligned}$$

Similarly, from equations (8.51) and (8.53), the entropy in terms of molar weight, temperature, and volume in cubic centimeters is

$$\mathrm{s} = \tfrac{3}{2}R \ln M + \mathrm{c}_V \ln T + R \ln \mathrm{v} + \tfrac{5}{2}R - 16.041 \qquad (8.55)$$

For the ideal monatomic gas, c_V and c_P have the values $\tfrac{3}{2}R$ and $\tfrac{5}{2}R$, respectively. These are also the values for that part of the heat capacity of polyatomic gases attributed to the increase in translational energy of the gas with temperature. Furthermore, $\tfrac{5}{2}R$ has the value of 4.968 calories per degree. Consequently, the Sackur-Tetrode equation for the molar entropy of a gas in calories per degree may be placed in one of the following forms:

For volume in cubic centimeters,

$$\left.\begin{aligned} \mathrm{s} &= \tfrac{3}{2}R \ln M + \tfrac{3}{2}R \ln T + R \ln \mathrm{v} + \tfrac{5}{2}R - 16.041 \\ \mathrm{s} &= \tfrac{3}{2}R \ln M + \tfrac{3}{2}R \ln T + R \ln \mathrm{v} - 11.073 \end{aligned}\right\} \qquad (8.56)$$

and, for pressure in atmospheres,

$$\left.\begin{aligned} \mathrm{s} &= \tfrac{3}{2}R \ln M + \tfrac{5}{2}R \ln T - R \ln P + \tfrac{5}{2}R - 7.282 \\ \mathrm{s} &= \tfrac{3}{2}R \ln M + \tfrac{5}{2}R \ln T - R \ln P - 2.314 \end{aligned}\right\} \qquad (8.57)$$

These equations were derived with the aid of the ideal gas equation and the heat capacities of a monatomic gas. They may be applied in the calculation of the entropies of monatomic gases; they may also be used to calculate the translational entropy of polyatomic gases. If the gases are not ideal, a calculation of the entropy difference between the ideal state and the real state of the gas enables one to obtain the translational entropy of the real gas. However, the equations are not applicable over too wide a range of temperature and pressure. Thus, at $P = 1$ and $T < 1$, $\ln P$ becomes zero and $\ln T$ becomes negative so that the entropy in equation (8.57) might become negative. Or if P is increased steadily, s might become negative. It does not follow, however that a substance can have a negative entropy. Instead, we must conclude that under these conditions the substance is no longer an ideal gas, or even a gas at all, so that these gas equations no longer apply to it.

From equations (8.51) and (8.52) or equations (8.54) and (8.55), may be derived a number of relations for the change in entropy of an ideal gas under various conditions. Where s_1 is the molar entropy of the gas in the first state and s_2 that for the gas in the second state, the changes in entropy under the indicated conditions are as follows:

At constant temperature, equation (8.51) yields, for the entropy change on expansion,

$$s_2 - s_1 = R \ln \frac{v_2}{v_1} \tag{8.58}$$

When equation (7.54) for the isothermal entropy of expansion is applied to 1 mole of gas, it becomes equation (8.58). Similarly, from equation (8.52),

$$s_2 - s_1 = -R \ln \frac{P_2}{P_1} = R \ln \frac{P_1}{P_2} \tag{8.59}$$

This equation follows from equation (8.58) or (7.54), since

$$\left(\frac{v_2}{v_1}\right) = \left(\frac{P_1}{P_2}\right)$$

for the perfect gas at constant temperature.

At constant volume, the change in entropy with temperature is, from equation (8.51),

$$s_2 - s_1 = c_V \ln \frac{T_2}{T_1} \tag{8.60}$$

This equation is obtained also when equation (8.8) is integrated for 1 mole of perfect gas.

At constant pressure, the change in entropy with temperature is, from equation (8.52),

$$s_2 - s_1 = c_P \ln \frac{T_2}{T_1} \tag{8.61}$$

This equation is also obtained when equation (8.10) is integrated for 1 mole of gas.

For a *reversible adiabatic expansion*, $q_r = 0$ and $s_2 = s_1$ so that equation (8.51) yields

$$c_V \ln \frac{T_2}{T_1} = -R \ln \frac{v_2}{v_1} \tag{8.62}$$

This equation is identical with equation (4.47).

Equations (8.54) and (8.55) contain a term for the molar weight of the gas. They may, therefore, be used to calculate the change in entropy of a gas with mass. For example, the difference in translational entropy between two isotopic species of gas at the same temperature and pressure (and volume) is given by

$$s_2 - s_1 = \frac{3}{2} R \ln \frac{M_2}{M_1} \tag{8.63}$$

where M_1 and M_2 are the molecular weights of the two isotopic species of the gas. However, equation (8.63) does not give the entropy change on the mixing of two isotopes. The expression for the entropy of mixing of two molecular species is derived in Chap. 14.

Entropy of Real Gases.—Though equation (8.50) is subject to the restrictions of the ideal gas, equation (8.49) is subject *only* to the condition that work of expansion is the only work done.

A number of gases that are ideal enough to expand approximately in accordance with the ideal gas law have a heat capacity dependent on the temperature. If the heat capacity is a function of the temperature, we have, on integration of equation (8.50),

$$\mathrm{s} = \int \frac{\mathrm{c}_V\, dT}{T} + R \ln \mathrm{v} + \mathrm{s}_0' \tag{8.64}$$

Equation (8.64) may also be expressed in the form

$$\mathrm{s} = \int \frac{\mathrm{c}_P\, dT}{T} - R \ln P + \mathrm{s}_0 \tag{8.65}$$

where $\mathrm{s}_0 = \mathrm{s}_0' + R \ln R$.

This equation may be applied to nitrogen. From Table 3.3, it appears that the constant c in the heat capacity equation is small enough to be neglected at moderate temperatures. Hence,

$$\mathrm{c}_P = 6.524 + 1.250 \times 10^{-3}T$$

and the change in entropy with temperature is

$$\begin{aligned} \mathrm{s}_2 - \mathrm{s}_1 &= \int_{T_1}^{T_2} \left(\frac{6.524}{T} + 0.001250\right) dT \\ &= 6.524 \ln \frac{T_2}{T_1} + 0.001250(T_2 - T_1) \end{aligned} \tag{8.66}$$

In general, the change in entropy with temperature at constant pressure is given by

$$\mathrm{s}_2 - \mathrm{s}_1 = \int_{T_1}^{T_2} \frac{\mathrm{c}_P\, dT}{T} = \int_{T_1}^{T_2} \mathrm{c}_P\, d \ln T \tag{8.67}$$

This equation follows from equation (8.10). If the heat capacity cannot be represented satisfactorily by an algebraic equation, the integration may be performed graphically. Equation (8.67) may be applied to liquids and solids as well as to gases.

The entropies of real gases can be obtained more accurately by the following method: The translational entropy of the ideal gas plus a small correction for nonideality of the gas gives the translational entropy of the real gas. The entropy of rotation of the gas molecules and the entropy of vibration of the atoms can be calculated from the energy levels obtained from band or Raman spectra according to the methods of Giauque[1] and others. These rotational and vibrational entropies can then be added to the translational entropies, as calculated by the above methods, to give the entropy of the gas. The entropy of nuclear spin and the entropy of mixing of isotopes may be similarly added to give the total entropy of the gas. The values obtained in this way are more accurate than those obtained by any other method. Because the nuclear spin entropies of the reactants in a chemical reaction are identical with those of the products of the reaction, the nuclear spin entropy is usually not included in tabulated entropy values.

Entropy Change in Isothermal Reactions.—For an isothermal reversible reaction, the change in entropy can be calculated directly from the calorimetric value of the heat of the reaction and the temperature; for, from equation (7.12), $\Delta S = q_r/T$. The melting of ice at 0° under a pressure of 1 atmosphere is such a process. Here the heat of melting, $\Delta H = 1{,}436$ cal, is the reversible heat q_r and we have

$$H_2O(c) = H_2O(liq); \qquad \Delta H = 1{,}436 \text{ cal}$$

$$\Delta S = \frac{1{,}436}{273.16} = 5.257 \text{ cal/deg} \tag{8.68}$$

The quantity of entropy corresponding to 1 calorie per degree centigrade is frequently called the "entropy unit" (eu). There will obviously be a different entropy unit if the energy is expressed in joules or foot-pounds or if the temperature is expressed in degrees Fahrenheit absolute. The term entropy unit for the calorie per degree is, therefore, not justifiable logically but it is met in practice.

For a chemical reaction proceeding reversibly at constant temperature and constant pressure, the entropy change can be obtained from the calorimetric heat of reaction $\Delta H = q_P$ in exactly the same way. If the constant-pressure reaction (or the constant-volume reaction) is not thermodynamically reversible, the calorimetric heat of the reaction cannot be used directly in the calculation of the entropy change for the process. Only when the constant pressure process is reversible can we write $q_P = q_r$. Under this condition, from equations (2.34) and (7.12),

$$\Delta H = T\,\Delta S \tag{8.69}$$

In reactions that are not reversible, q_P and q_r are not equal. The difference between q_P and q_r (ΔH and $T\,\Delta S$) at constant temperature is called the *free energy change;* in the reversible process there is no change in free energy. The free energy function is discussed later in more detail.

---

[1] GIAUQUE, W. F., *J. Am. Chem. Soc.*, **52**, 4808, 4816 (1930).

Entropy Change in Actual Irreversible Processes.—It is evident from the above relations between q_P and q_r that the entropy change for a thermodynamically irreversible process cannot be obtained from the calorimetric heat of reaction. It is evident, also, that the difference between q_P and q_r might be used as a measure of the distance of a chemical reaction from the reversible equilibrium state. For this reason, a knowledge of the entropy change in a reaction is useful, for it permits calculation of q_r from the relation $q_r = T\,\Delta S$. This value can then be used for comparison with q_P for the reaction.

Because the entropy is a property with a definite value for each state of the substance, knowledge of the entropies of the substances entering into and resulting from a reaction permits easy calculation of the change in entropy resulting from the reaction. In this way, we can predict beforehand whether or not a given chemical reaction will proceed. In recent years, great progress has been made toward obtaining the entropy of the simpler chemical compounds. One method depends on measurement of heat capacities down to low temperatures, the entropy for each phase being obtained from the relation in equation (8.67). When phase changes occur, the entropy of transition, calculated by the method of equation (8.68), must be added to the entropy calculated from heat capacities to give the total entropy of the phase present at the higher temperatures. In the other method applicable to gases, the entropy is obtained from spectroscopic data. Because more entropy data are becoming available, the entropy function is coming into more general use. The entropy values, together with the calorimetric heat of reaction at constant pressure, permit the calculation of the free energy of reactions and therefore of the equilibrium constants, which are directly related to the free energies, under conditions where a direct measurement is difficult. Some of the uses of the entropy function will appear as we apply it.

Entropy of Crystallization of Water at −10°.—The entropy of freezing of water to ice at −10° cannot be calculated from the heat of crystallization because the crystallization at this temperature does not proceed reversibly. Undercooled water freezes spontaneously to ice if a small crystal of ice is present or is formed as a nucleus for the crystallization of the water. For convenience, we shall assume that the heat capacities of ice and of water are constant over the temperature interval −10 to 0°C. In Chap. 5, the molar heat capacities of water and ice within this range are given as 18 and 8.7 calories per degree, respectively.

For finite temperature intervals the change of entropy with temperature is, from equation (8.10) or (8.67),

$$\mathrm{s}_2 - \mathrm{s}_1 = \int_{T_1}^{T_2} c_P \, d \ln T \qquad (8.70)$$

When the heat capacity is constant, this equation becomes simplified to

$$s_2 - s_1 = c_P \int_{T_1}^{T_2} d \ln T = c_P \ln \frac{T_2}{T_1} \tag{8.71}$$

Between the temperature limits of -10 and 0°C, we have, on transformation to common logarithms,

$$\begin{aligned} s_2 - s_1 &= c_P \times 2.303 \log \frac{273.16}{263.16}, \\ &= c_P \times 2.303(2.43642 - 2.42022) = c_P \times 0.0373 \end{aligned}$$

Between these temperatures, the molar entropy change for ice is

$$s_{273} - s_{263} = 8.7 \times 0.0373 = 0.324 \text{ cal/deg}$$

and that for water is

$$s_{273} - s_{263} = 18.0 \times 0.0373 = 0.671 \text{ cal/deg}$$

These entropy changes correspond, except for sign, to steps b' and b in Fig. 8.1. The entropy change for the reversible melting (step a') is found in equation (8.68) to be 5.257 calories per degree. From these values, the molar entropy of freezing of water to ice at -10°C (step a) is seen to be

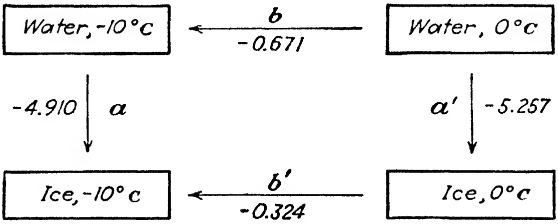


FIG. 8.1.—Entropy changes per mole of water (in calories per degree).

$$\begin{aligned} a &= a' + b' - b \\ &= -5.257 - 0.324 - (-0.671) \\ &= -4.910 \text{ cal/deg} \end{aligned}$$

The entropy of fusion of ice at -10° is opposite in sign; it equals $+4.910$ calories per degree per mole.

The same results are obtained when this process is described in the form of chemical equations. We have then

$$\begin{aligned} H_2O(c, 273^\circ) &= H_2O(c, 263^\circ); & \Delta S &= -0.324 \text{ cal/deg} \\ H_2O(liq, 263^\circ) &= H_2O(liq, 273^\circ); & \Delta S &= 0.671 \text{ cal/deg} \\ \underline{H_2O(liq, 273^\circ)} &\underline{= H_2O(c, 273^\circ);} & \underline{\Delta S} &\underline{= -5.257 \text{ cal/deg}} \\ H_2O(liq, 263^\circ) &= H_2O(c, 263^\circ); & \Delta S &= -4.910 \text{ cal/deg} \end{aligned} \tag{8.72}$$

The value of the entropy change for the crystallization of water at 263.16°K enables us to calculate the heat of crystallization for the reversible reaction at this temperature. We have, from equation (7.12),

$$q_r = T\,\Delta S = 263.16 \times -4.910 = -1{,}292 \text{ cal}$$

This may be compared with the corresponding calorimetric heat of melting at constant pressure $q_P = \Delta H = -1{,}343$ cal, calculated in Chap. 5.

Problems

8.1. (*a*) What is the maximum conversion factor of a steam engine with a condenser at 30°C and a boiler at 150°C? At 200°C?

(*b*) What is the pressure of saturated steam at 200°C? If mercury were used in the boiler at this pressure, what would be the maximum conversion factor of the engine?

8.2. A refrigerating machine maintains a refrigerator at 32°F in a room at 86°F. What is the minimum amount of work required to remove 1 kilocalorie of heat from the refrigerator? How much heat is given to the room in this process? If the refrigerator is maintained at 14°F in the same room, how much work is required to remove the kilocalorie of heat? How much heat is given to the room?

8.3. (*a*) The entropy of a mole of oxygen at 25°C and 1 atmosphere pressure is 49.003 calories per degree. Using the heat capacity equation from Table 3.3, calculate the entropy of oxygen at 100°C.

(*b*) Assuming that oxygen expands as a perfect gas, calculate the entropy of a mole of oxygen at 0.1 atmosphere and 25°C.

(*c*) What will be the entropy of oxygen at 100°C and 0.1 atmosphere?

8.4. The molar heat of melting of iodine at its melting point 113.6°C is

$$3{,}740 \pm 20 \text{ cal.}$$

What is the entropy of melting of iodine?

8.5. Assume the entropy of iodine at 25° to be 27.9 calories per degree per mole. With the aid of the heat capacity equation of iodine in Prob. 3.9, calculate the entropy of solid iodine at 113.6°C.

8.6. Combine the results of Probs. 8.4 and 8.5 to obtain the entropy of liquid iodine at its melting point 113.6°C.

8.7. Calculate the minimum work in kilowatt-hours that would be necessary to separate, by an isothermal reversible process, 1,000 cubic feet of air at 20°C and 1 atmosphere into nitrogen and oxygen, each at 1 atmosphere. Assume that the ideal gas law holds and that air is 21 per cent oxygen and 79 per cent nitrogen.

8.8. Calculate the entropy change for the separation of each gas in Prob. 8.7 from the mixture.

8.9. What will be the minimum amount of work required by a reversible refrigerator cycle that adds 1,000 calories of heat to a room at 20°C, the temperature of the out of doors (refrigerator) being 10°C (50°F)? 0°C? −10°C (14°F)? −20°C (−4°F)? How many kilowatt-hours of electricity are required to do this work? What will be the cost if the price of electricity is $1\frac{1}{2}$ cents per kilowatt-hour? Compare with the cost of 1,000 calories of heat obtained from natural gas (1,100 Btu/cu ft) at 60 cents per 1,000 cubic feet.

8.10. By the methods used in deriving equation (1.11) or (8.45), show that

$$\left(\frac{\partial T}{\partial P}\right)_S = -\left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial T}{\partial S}\right)_P \tag{8.73}$$

From equation (8.73) derive the relation

$$C_P = T\frac{(\partial V/\partial T)_P}{(\partial T/\partial P)_S} \tag{8.74}$$

8.11. It appears from equation (8.74) in Prob. 8.10 that heat capacity can be calculated from the measured values for the coefficient of thermal expansion and from the adiabatic temperature-pressure coefficient. Values of these coefficients have been measured by J. S. Burlew [*J. Am. Chem. Soc.*, **62,** 681, 690, 696 (1940)] for benzene and toluene. The adiabatic (isentropic) change of temperature with pressure for benzene is represented between 5 and 80°c by the equation

$$\left(\frac{\partial T}{\partial P}\right)_S = 2.12695 \times 10^{-2} + 10.6806 \times 10^{-5}t + 2.7715 \times 10^{-9}t^3 \text{ deg/bar}$$

where t is in degrees centigrade. Similarly, the coefficient of thermal expansion of benzene is represented by the equation

$$1{,}000\left(\frac{\partial V}{\partial T}\right)_P = 1.2965 + 3.503 \times 10^{-3}t + 1.779 \times 10^{-5}t^2 \text{ cc/deg gram}$$

From these equations, calculate the heat capacity of benzene in absolute joules and in defined calories per gram at 20, 50, and 80°c.

NOTE: 1 bar = 10^6 dynes/cm^2.

8.12. Calculate the difference in entropy between Ne^{20} and Ne^{22} at 25°c and 1 atmosphere.

8.13. From the data in Table 5.1, calculate the values for the entropy of evaporation of liquid water to form saturated vapor at 0, 25, 50, 75, and 100°c.

8.14. The heat content of compounds at high temperature is frequently expressed in terms of $\mathrm{H}_T - \mathrm{H}_{298.16}$ where H_T is the molar heat content at the temperature T and $\mathrm{H}_{298.16}$ is the molar heat content in the standard state at 298.16°K. From the relations in equation (8.9), (8.10), or (8.16), show that

$$d\mathrm{s} = \frac{1}{T}\,d(\mathrm{H}_T - \mathrm{H}_{298.16})$$

Integrate the right side of the equation by parts and show that the increase in entropy between the temperatures $T = 298.16$ and $T = T$ is

$$\mathrm{s}_T - \mathrm{s}_{298.16} = \frac{\mathrm{H}_T - \mathrm{H}_{298.16}}{T} + \int_{298.16}^{T} \frac{\mathrm{H}_T - \mathrm{H}_{298.16}}{T}\,d\ln T$$

8.15. The molar heat capacity equation for manganese dioxide between 298 and 780°K is given by G. E. Moore [*J. Am. Chem. Soc.*, **65,** 1398 (1943)] as

$$c_P = 16.60 + 2.44 \times 10^{-3}T - \frac{388{,}000}{T^2}$$

From this equation, derive the equation for the molar entropy increment for manganese dioxide at the temperature T.

$$\mathrm{s}_T - \mathrm{s}_{298.16} = 38.223 \log T + 2.24 \times 10^{-3}T + \frac{194{,}000}{T^2} - 97.491$$

If the value of $\mathrm{s}_{298.16}$ is 13.9 ± 0.4 calories per degree, what is the value of s at 500°c?

CHAPTER 9

EQUILIBRIUM IN SIMPLE SYSTEMS

The first law equation may be combined with the second law relation $\mathrm{D}q_r = T\,\mathrm{d}S$ to give the equation

$$\mathrm{d}E = T\,\mathrm{d}S - \mathrm{D}w_r \tag{9.1}$$

Under the restriction that the only work is work of expansion, we derived equation (8.1), which is

$$\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V \tag{9.2}$$

The restriction above bars the application of equation (9.2) to a reaction system in which other work, such as electrical work, can be performed. The equation can be applied, however, to systems, including heterogeneous systems, that do not undergo chemical reaction and to mixtures in which no chemical reaction occurs.

From equation (8.1) was derived the equation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{9.3}$$

which is equation (8.24). The partial change of entropy with volume can, therefore, be obtained from experimental data on the partial change of pressure with temperature.

Clausius-Clapeyron Equation.—Let us consider a system composed of a pure substance that may be present in two or more phases. If two phases coexist over long periods of time, either an equilibrium between the two must exist or the rate of transformation of one phase to the other must be infinitely slow. If the rate is slow enough, the two phases may exist independently of each other so that they may be considered as two separate constituents of the system. Among the different phases that may be present in a simple system are several solid phases, a liquid phase, a gas phase, and sometimes an intermediate phase such as the liquid crystal phase. The transformation between two solid phases is usually called a "transition," that between a solid and liquid, a "melting" or "freezing," that between solid and gas, a "sublimation," and that between liquid and gas, a "vaporization" or "evaporation." All these equilibrium transformations of the various phases can take place at constant pressure. The heats of transformation may, therefore, be heats at constant pressure and, at the same time, reversible heats. Under these conditions,

$$q_P = \Delta H_P = q_r \tag{9.4}$$

These equilibrium processes may be carried out at constant temperature as well as at constant pressure. For the isothermal processes, we have, from equation (7.12),

$$q_r = T\,\Delta S$$

so that, *at constant pressure*,

$$\Delta H_P = T\,\Delta S_P \tag{9.5}$$

If two phases of a pure substance are present at the temperature T, each possesses an entropy value characteristic of the state of the substance and of the quantity of the phase. The entropy of the system varies with the relative quantities present; it will increase if the phase with the lower specific entropy is converted to the phase with the higher specific entropy. But the volume of the system depends in the same way on the relative amounts of the two phases present. The volume increases if the phase with the lower specific volume is converted to the phase with the higher specific volume. At constant temperature, therefore, both entropy and volume depend directly on the relative quantities of the two phases so that the derivative $(\partial S/\partial V)_T$ may be written more simply as

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\Delta S}{\Delta V}\right)_T \tag{9.6}$$

The equilibrium systems are also characterized by the fact that the pressure of the system does not depend on the volume of the system but only on its temperature. This follows from the fact that the equilibrium pressure is independent of the relative amounts of the two phases present. If the pressure does not vary with the quantity of the two phases, it cannot vary with the volume. The equilibrium pressure of a water and vapor system at 20°c is the same whether 90, 50 or 10 per cent of the water is in the form of vapor, the remainder being present in the liquid phase. The volume of the system depends on the relative amounts of vapor and liquid, for the volume occupied by a gram of saturated water vapor at this temperature is approximately 58,000 ml compared with a volume of 1 ml for the liquid. At the same time, the entropy of the system depends on the relative amounts of liquid and gas whose molar entropies differ by the entropy of evaporation of the liquid.

Because the pressure of the equilibrium system is a function of the temperature alone, we may remove the restriction of constant volume from equation (9.3) and combine with it (9.6) to obtain

$$\frac{dP}{dT} = \left(\frac{\Delta S}{\Delta V}\right)_T \tag{9.7}$$

This equation, when combined with equation (9.5), gives

$$\frac{dP}{dT} = \left(\frac{\Delta H}{T\,\Delta V}\right)_{P,T} \tag{9.8}$$

the well-known Clausius-Clapeyron equation, which was first deduced from the Carnot cycle by Clapeyron and later derived from thermodynamics by Clausius. Equation (9.8) is exact, containing no approximations. We shall, therefore, call it the exact form of the Clausius-Clapeyron equation.

The changes represented by ΔS and ΔH accompany the volume change in the system. All these changes result from the transformation of one phase to the other *at the pressure P and the temperature T*. The functions H, S, and V are extensive properties that may represent any amount of the substance. If ΔH is the heat of melting of 1 mole, ΔV is the volume change when 1 mole of the solid is melted to form 1 mole of the liquid. If 1 gram of the substance is considered, ΔH is the change in heat content per gram and ΔV the change in specific volume of the substance.

Equation (9.8) may be used directly without integration for processes in which dP/dT is approximately constant over the range considered. For example, for the equilibrium,

$$H_2O(c) = H_2O(liq)$$

dP/dT can be calculated from the known values of ΔH, T, and ΔV at the pressure P and the temperature T. In a numerical solution of the problem, consistent units must be used. If P is expressed in atmospheres and the molar volumes of water and ice in cubic centimeters, ΔH must be expressed as the molar heat of melting in cubic-centimeter–atmospheres. However, since the specific data are commonly reported for water, we have for the specific quantities[1] at $T = 273.16°\text{K}$,

$$\Delta H = 333.6 \text{ joules} = 333.6 \times 9.870 \text{ cm}^3\text{-atm/gram}$$
$$\Delta V = V_l - V_c = 1.0001 - 1.0908 = -0.0907 \text{ cm}^3\text{/gram}$$

The change in melting point with pressure is, therefore, given by

$$\frac{dT}{dP} = \frac{273.2 \times (-0.0907)}{333.6 \times 9.870} = -0.00753 \text{ deg/atm}$$

---

[1] Data from the "International Critical Tables," McGraw-Hill Book Company, Inc., New York, 1926.

The freezing point of water under its own vapor pressure (4.6 mm) is evidently different from the freezing point of water exposed to air at a pressure of 1 atmosphere. The latter freezing point defines 0° on the centigrade scale. If we neglect any freezing point lowering because of the dissolving of air in water, we see that water under a pressure of 4.6 mm will freeze at +0.0075°c.

Here the melting temperature decreases with rising pressure; for ΔV for water is negative, water being denser than ice. Antimony also furnishes an exception to the general rule that the solid state is denser than the corresponding liquid state. Because ΔH and T are always positive, the sign of dP/dT must correspond to the sign of ΔV. If dP/dT, T, and ΔV are measured directly, the heat of melting can be calculated. This method of obtaining heats of melting is especially useful at high pressures, where direct determination of the heat of melting is difficult.

The other forms of ice (high pressure) are denser than water so that, for them, ΔV for the melting is positive and the melting point is raised by increased pressure in the normal manner.

Clausius-Clapeyron Equation and Vapor Pressures.—In a system where equilibrium exists between a liquid and its vapor or between a solid and its vapor, the equilibrium pressure, called the "vapor pressure," changes rapidly with temperature and not at all linearly. Thus, the vapor pressure of water[1] on going from 0 to 1°c increases 0.343 mm; the increase between 50 and 51°c is 4.69 mm, and that between 100 and 101°c is 27.51 mm. The value of dP/dT in atmospheres per degree at 0° is 0.0004373, and that at 1° is 0.0004662, an increase of nearly 7 per cent for the 1° interval. At 50 and 100°, the values of dP/dT are 0.00604 and 0.03570 atmosphere per degree, respectively. It is evident that for this liquid-vapor equilibrium dP/dT does not remain constant over wide temperature ranges so that equation (9.8) must be integrated. However, it cannot be integrated unless ΔH and ΔV can be expressed as functions of temperature or pressure.

When one phase is gaseous and the other condensed, ΔV may be expressed as a function of temperature and pressure by the use of two simple approximations. Because the molar volume of a gas is large compared with that of the liquid (or solid), the change in volume ΔV is approximately that of the gas itself, so that, for the evaporation of 1 mole

$$\Delta \mathrm{v} = \mathrm{v}_g - \mathrm{v}_l \doteq \mathrm{v}_g \tag{9.9}$$

But the molar volume v_g of a gas is given approximately by the ideal

---

[1] From the data of N. S. Osborne and C. H. Meyers, *J. Research Natl. Bur. Standards*, **13**, 1 (1934).

gas equation, so that

$$\Delta\mathrm{v} \doteq \frac{RT}{P} \tag{9.10}$$

When this value of $\Delta\mathrm{v}$ is substituted in equation (9.8), $\Delta\mathrm{H}$ being the molar heat of evaporation (or sublimation), it becomes

$$\frac{dP}{dT} = \frac{\Delta\mathrm{H}P}{RT^2} \tag{9.11}$$

which is readily transformed to

$$\frac{dP/P}{dT} = \frac{d\ln P}{dT} = \frac{\Delta\mathrm{H}}{RT^2} \tag{9.12}$$

Equation (9.12) can be integrated whenever $\Delta\mathrm{H}$ is a known function of T. When $\Delta\mathrm{H}$ does not vary with temperature, equation (9.12) may be transformed to

$$d\ln P = \frac{\Delta\mathrm{H}}{R}\frac{dT}{T^2} \tag{9.13}$$

which becomes, on integration,

$$\ln P = -\frac{\Delta\mathrm{H}}{R}\frac{1}{T} + I' \tag{9.14}$$

On transforming to common logarithms, we have

$$\log P = -\frac{\Delta\mathrm{H}}{2.3026R}\frac{1}{T} + \frac{I'}{2.3026} \tag{9.15}$$

$\Delta\mathrm{H}$ and R must be expressed in the terms of the same energy unit. If $\Delta\mathrm{H}$ is in calories, R has the value 1.9872 calories per degree and 2.3026 R becomes 4.5757. Where the integration constant I' equals $2.3026I$, equation (9.15) becomes

$$\log P = \frac{-\Delta\mathrm{H}}{4.5757}\frac{1}{T} + I \tag{9.16}$$

which is frequently written in the form

$$\log P = \frac{-A}{T} + B \tag{9.17}$$

These equations are equations for a straight line of the type $y = ax + b$. If $\log P$ is plotted as ordinate against $1/T$ as abscissa, the resulting curve is a straight line with a negative slope equal to A (or $\Delta\mathrm{H}/4.5757$) and an intercept on the $1/T$-axis equal to B. The numerical value of B depends on the units in which P is expressed. When P is expressed in millimeters of mercury, B is greater by 2.8808 (which is log 760) than when P is expressed in atmospheres. In the "International Critical Tables," where the joule is the energy unit and R is assumed to be 8.315 joules per degree, vapor pressure equations are usually given in the form

$$\log P_{\text{mm}} = -0.05223 \frac{A}{T} + B \tag{9.18}$$

This equation corresponds to (9.16), for here A = ΔH(in joules), and $(1/2.3026R) = 0.05223$ degree per joule.

These equations are used to express vapor pressure data in spite of the computational labor required to solve equations involving logarithms and reciprocals of the absolute temperature. For several good reasons, physical chemists choose functions that can be plotted to give straight lines. When inaccurate vapor pressure data are plotted on a log P *vs.* $1/T$ diagram, they are identified by their refusal to fall on or near a straight line. The straight line permits more accurate interpolation between experimental points, and it usually permits more accurate extrapolation for values lying outside the experimental values. In addition, fewer *good* data are required to establish a straight line than any other type of curve.

The Clausius-Clapeyron equation is frequently met in the form of the definite integral. If equation (9.13) is integrated between the temperatures T_1 and T_2 where the vapor pressures are P_1 and P_2, ΔH remaining constant, we have

$$\ln \frac{P_2}{P_1} = -\frac{\Delta\text{H}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{\Delta\text{H}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{9.19}$$

When R is expressed in calories per degree, equation (9.19) may be transformed to

$$\log \frac{P_2}{P_1} = \frac{\Delta\text{H}}{4.5757}\left(\frac{T_2 - T_1}{T_1 T_2}\right) \tag{9.20}$$

This equation rests on all the approximations used in transforming equation (9.8) to equation (9.13).

Validity of the Integrated Clausius-Clapeyron Equation.—In deriving equation (9.13), we made three assumptions, namely, that the specific volume of liquid is negligible compared with that of the vapor, that the volume of the vapor can be expressed by the ideal gas equation, and that the heat of evaporation is not a function of the temperature. At low pressures, the molar volume of the gas is large, and the first approximation can be justified. However, a gas in equilibrium with its liquid, especially at the higher pressures, cannot be ideal. The presence of the liquid indicates that attractive forces exist among the molecules, great enough to liquefy the gas when the molecules approach each other closely. Furthermore, the heat of evaporation is not independent of the temperature; and it cannot be, so long as the heat capacities of gas and liquid are not equal. The heat of evaporation changes with temperature according to the relation $d\,\Delta H = \Delta C_P\, dT$, derived as equation (5.25). The heat of evaporation of water changes from 10,800 calories per mole at 0° to 9,700 calories per mole at 100°, as indicated in Table 5.1.

At the critical point, which is the highest point on the vapor pressure curve, the heat of evaporation vanishes and the specific volumes of gas and liquid become equal to each other so that we have $\Delta H = 0$ and $\Delta V = 0$. Equation (9.8), therefore, becomes

$$T\frac{dP}{dT} = \frac{0}{0} \tag{9.21}$$

where 0/0 is indeterminate. This relation is evidently greatly different from the relation in equation (9.11).

In spite of these difficulties, the integrated equation fits the experimental vapor pressure data surprisingly well over a wide temperature range, even near the critical point. If the experimental data are plotted on a log P *vs.* $1/T$ diagram, they fall on a line approximately linear or with but a slight curvature. We, therefore, conclude that the approximations involved in the above assumptions tend to cancel each other, so that the final equation is better than either of the assumptions made in deriving it.

General Vapor Pressure Equations.—When accurate vapor pressure data over an extended range of temperature are plotted on a log P *vs.* $1/T$ diagram, a slight curvature is usually found. This curvature can be partially accounted for in terms of a variation of ΔH with temperature. If ΔH varies with temperature, according to equation (5.31), we have

$$\Delta H = \Delta H_0 + \alpha T + \tfrac{1}{2}\beta T^2 + \tfrac{1}{3}\gamma T^3 \tag{9.22}$$

When this value of ΔH is substituted in equation (9.13), we obtain

$$d \ln P = \frac{1}{R}\left(\frac{\Delta H_0}{T^2} + \frac{\alpha}{T} + \frac{\beta}{2} + \frac{\gamma T}{3}\right) dT$$

When integrated, this equation becomes

$$\ln P = \frac{1}{R}\left(-\frac{\Delta H_0}{T} + \alpha \ln T + \frac{\beta}{2} T + \frac{\gamma}{6} T^2\right) + I \tag{9.23}$$

This is an equation of the type

$$\log P = \frac{-A}{T} + B \log T + CT + DT^2 + E \tag{9.24}$$

When the energy unit is the calorie, the constants of equation (9.24) are related to those of equation (9.23) by the following:

$$A = \frac{\Delta H_0}{4.5757}; \quad B = \frac{\alpha}{1.9872}; \quad C = \frac{\beta}{2 \times 4.5757};$$
$$D = \frac{\gamma}{6 \times 4.5757}; \quad E = \frac{I}{2.3026} \tag{9.25}$$

Empirical equations, such as (9.24), are used to represent vapor pressures accurately. Other empirical equations represent slight modifications. Thus, Keyes[1] has used equations of the type

$$\log P = \frac{-A}{T} + CT + DT^2 + E \tag{9.26}$$

which contains all but the log T term of equation (9.24).

Although equations, such as (9.24) and (9.26), with more than two constants may be fitted accurately to vapor pressure data, they are not easy to use in the usual numerical computations. A three-constant equation corresponding in simplicity to the two-constant equation (9.17) is the Antoine equation[2] used as a vapor pressure equation at the National Bureau of Standards. This equation has the form

$$\log P = a - \frac{b}{c + t} \tag{9.27}$$

Comparison with equation (9.17) shows that the constant a corresponds to B, the numerical value of both being greater by log 760 = 2.8808 when pressures are given in millimeters rather than in atmospheres. Similarly, the constant b corresponds to A. The constant c corresponds to the ice point temperature, 273.16°, but in practice its values are somewhat lower. In this equation, the temperature t is in degrees centigrade. The Antoine equation also appears in an alternative form

$$\log P = a - \frac{b}{T - c'} \tag{9.28}$$

where T, as before, is the temperature in degrees Kelvin. The constant c' is related to c by the equation

$$T - c' = t + c \tag{9.29}$$

Heat of Evaporation from Vapor Pressure.—The latent heat of evaporation of the liquid ΔH can be calculated from vapor pressures with the aid of the above equations. If two vapor pressures are known, the constant value of ΔH is obtained from equation (9.16) or (9.20). If the vapor pressures are expressed in the form of equation (9.24), the value of ΔH as a function of the temperature is obtained. The relations of

---

[1] For example, see *J. Am. Chem. Soc.*, **40**, 42 (1918).

[2] ANTOINE, C., *Compt. rend.*, **107**, 681 (1888).

equations (9.25) may be used to calculate the constants of equation (9.22).

Because of the approximations made in deriving the integrated Clausius-Clapeyron equation, the heat of evaporation calculated from vapor pressures has, in general, a higher value than the calorimetric value. At moderate pressures, it has the right order of magnitude. Where direct calorimetric data do not exist, the integrated Clausius-Clapeyron equation furnishes a good method for estimating heat of evaporation. Where vapor pressures are accurately known, so that dP/dT can be evaluated with good precision, and the specific volume of the vapor is known, the heat of evaporation can be calculated from the exact differential form of the Clausius-Clapeyron equation. Because this form of the equation includes no approximations, the accuracy of the heat of evaporation calculated by its use is limited only by the accuracy of the vapor pressure and specific volume data.

Estimation of Vapor Pressures from Limited Data.—We have stated that, when experimental values of log P are plotted against $1/T$, the points lie approximately on a straight line; with the more accurate data, a curve is required to fit the experimental points. If a straight-line equation is used to fit the curve there are systematic positive and negative deviations of the experimental points from the straight line. When the data are not sufficiently accurate and the experimental points scatter about any line, the equation for a straight line is often as accurate as the experimental points.

Only two experimental points are required to establish a straight line. If the normal boiling point of a liquid is known, and in addition the boiling point at some lower pressure, these values of P_1, T_1 and P_2, T_2 can be substituted in equation (9.16) to evaluate the constants $\Delta\text{H}/4.5757$ and I. The vapor pressure at any other temperature can then be calculated.

If the heat of evaporation ΔH and the boiling point T_B are known, I can again be evaluated. At the normal boiling point, P is 1 atmosphere, and we have, from equation (9.16),

$$I = \frac{\Delta\text{H}}{4.5757T_B} \tag{9.30}$$

If the pressure is stated in millimeters, $P = 760$ mm at the boiling point, and

$$I = \log 760 + \frac{\Delta\text{H}}{4.5757T_B}$$

$$I = 2.8808 + \frac{\Delta\text{H}}{4.5757T_B} \tag{9.31}$$

By making an additional assumption, we can estimate the vapor pressure curve of a liquid, knowing only the boiling point. For a "normal" liquid, Trouton found that the molar heat of evaporation divided by the boiling temperature on the absolute scale is a constant with a value of about 21 calories per degree. Associated liquids such as water and ammonia have a volume of $\Delta H/T_B$ of about 26 calories per degree. Trouton's rule is discussed in more detail later. If we accept his value of 21 calories per degree, we have, from equation (9.30), for a normal liquid (when P is in atmospheres),

$$I = \frac{21}{4.576} = 4.589$$

If P is in millimeters, we have, from equation (9.31),

$$I = 2.881 + 4.589 = 7.470$$

The heat of evaporation can also be estimated from the known boiling point and the relation $\Delta H/T_B = 21$.

Let us apply the method to ethyl iodide, which has a boiling point of 72.5°C. Using Trouton's rule, we have

$$\Delta H = 21(72.5 + 273.2) = 7{,}260 \text{ cal/mole}$$

The vapor pressure equation becomes

$$\log P_{\text{mm}} = -\frac{1{,}587}{T} + 7.470$$

At 30°C, we find that $\log P_{\text{mm}} = 7.470 - 5.234$ and

$$P = 172 \text{ mm}$$

The experimental value[1] is 167.5 mm. Agreement to this degree of precision may be expected.

Dühring's Rule.—An empirical rule proposed by Dühring[2] in 1878 has proved useful in the estimation of vapor pressures over large temperature ranges. Though it does not give the highest precision, it gives values that are approximately correct. Dühring's rule indicates a relation between the boiling temperatures of two different substances at different pressures. When one substance has a vapor pressure P_1 at the temperature t_1, a second substance has the same vapor pressure at the temperature θ_1. At the temperature t_2, the first substance has a vapor pressure of P_2; the second substance has the same pressure at the temperature θ_2. These temperatures are related to each other by the equation

$$\frac{t_2 - t_1}{\theta_2 - \theta_1} = K \tag{9.32}$$

---

[1] "International Critical Tables," Vol. 3, p. 217.

[2] "Neue Grundgesetze zur rationalen Physik und Chemie," Leipzig, 1878.

which is an equation for a straight line. The straight line is plotted in Fig. 9.1 where the t's are plotted as ordinates and the θ's as abscissas. The slope of the line is equal to K.

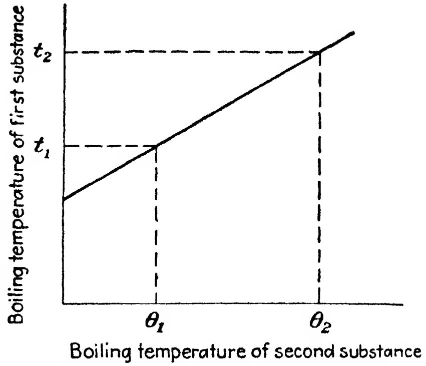


FIG. 9.1.—Dühring's rule relations.

According to this rule, which Dühring proposed after a study of about 50 substances with differing chemical and physical properties, the whole vapor pressure curve of a substance can be obtained from two experimental points by using some known vapor pressure curve as a

TABLE 9.1.—BOILING TEMPERATURES OF WATER CALCULATED BY DÜHRING'S RULE WITH ETHANOL AS REFERENCE SUBSTANCE. RATIOS OF ABSOLUTE BOILING POINTS OF WATER AND ETHANOL AT VARIOUS PRESSURES

(The reference temperatures are in **bold-faced** type)

Temperature of ethanol		Vapor pressure, mm	Temperature of water			Ratio of absolute boiling point, T'/T
			Calculated temperature, t, °C	Observed temperature		
T, °K	t, °C (θ)			t', °C	T', °K	
273.2	0	12.2	13.84	14.3	287.5	1.052
283.2	10	23.6	24.84	24.9	298.1	1.053
293.2	20	43.9	35.84	35.7	308.9	1.054
303.2	30	78.8	46.84	46.8	320.0	1.055
313.2	40	135.3	57.84	57.9	331.1	1.057
323.2	**50**	222.2	**68.84**	**68.84**	**342.0**	1.058
333.2	60	352.7	79.84	79.8	353.0	1.059
343.2	70	542.5	90.84	90.83	364.0	1.061
348.2	75	666.1	96.34	96.34	369.5	1.061
351.5	**78.32**	760.0	**100.00**	**100.00**	**373.2**	1.062
353.2	80	812.6	101.84	101.88	375.1	1.062

reference. The rule holds best when the reference substance is similar to the substance whose vapor pressure curve is desired, but the rule holds fairly well even when a metal such as mercury is compared with an associated liquid such as water. Table 9.1 shows the degree of correspondence when alcohol is compared with water at various temperatures. For alcohol the temperatures selected for substitution in equation (9.32) are $\theta_1 = 50°$, $\theta_2 = 78.32°$. At these temperatures the vapor pressures are 222.2 and 760 mm respectively. From the vapor pressure tables for water in the "International Critical Tables"[1] the temperatures corresponding to these pressures are 68.84 and 100°, designated by t_1 and t_2, respectively. We have, then,

$$K = \frac{t_2 - t_1}{\theta_2 - \theta_1} = \frac{100 - 68.84}{78.32 - 50} = 1.100$$

Any boiling temperature of water t is related to the corresponding boiling temperature of alcohol θ by the equation

$$t = K\theta + (t_1 - K\theta_1) \tag{9.33}$$

which is obtained by rearranging equation (9.32). When the proper values are substituted in equation (9.33), we have

$$t = 1.100\theta + 13.84$$

The fourth column of Table 9.1 gives the boiling temperatures of water calculated from this equation. The fifth column gives the corresponding temperatures obtained by interpolation in the vapor pressure table for water. Except at the lower temperatures the degree of correspondence is good.

Some of the approximations on which Dühring's rule rests will become evident from the derivation of the rule from equation (9.20). Using primes to designate the reference substance, we have

$$\log \frac{P_2'}{P_1'} = \frac{\Delta H'}{4.5757}\left(\frac{T_2' - T_1'}{T_1'T_2'}\right)$$

and, for the other substance,

$$\log \frac{P_2}{P_1} = \frac{\Delta H}{4.5757}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

Now, if the temperatures are so selected that $P_1 = P_1'$ and $P_2 = P_2'$, $\log P_2'/P_1' = \log P_2/P_1$, and

$$\Delta H'\left(\frac{T_2' - T_1'}{T_1'T_2'}\right) = \Delta H\left(\frac{T_2 - T_1}{T_1 T_2}\right) \tag{9.34}$$

---

[1] Vol. 3, pp. 211–212.

If we designate $(T_2' - T_1')$ by $(t_2 - t_1)$ and $(T_2 - T_1)$ by $(\theta_2 - \theta_1)$, we obtain, from equation (9.34),

$$\frac{(t_2 - t_1)}{(\theta_2 - \theta_1)} = \frac{\Delta H}{\Delta H'} \frac{T_1'T_2'}{T_1T_2} \tag{9.35}$$

Comparison with equation (9.32) shows that if Dühring's rule is valid the following equation must hold:

$$\frac{\Delta H}{\Delta H'} \times \frac{T_1'}{T_1} \times \frac{T_2'}{T_2} = K \tag{9.36}$$

The last column of Table 9.1 shows how closely the ratio between the absolute boiling temperatures remains the same for the different pressures.

TABLE 9.2.—HEATS OF EVAPORATION OF ETHANOL AND WATER AT VARIOUS PRESSURES
(In calories per mole)

Vapor pressure, mm	Temperature, °C		Molar heat of vaporization		ΔH′/ΔH
	Ethanol	Water	Ethanol ΔH	Water ΔH′	
12.2	0	14.3	10,130	10,620	1.048
43.9	20	35.7	10,020	10,410	1.039
135.3	40	57.9	9,910	10,170	1.026
352.7	60	79.8	9,690	9,940	1.026
760	78.3	100	9,410	9,720	1.032

Table 9.2 shows similarly how the different values of the ratio ΔH′/ΔH for water and ethanol vary with temperature. These data indicate the accuracy with which vapor pressures may be calculated from Dühring's rule. Although the agreement is not too close, the method is useful, for vapor pressures calculated in this way are more accurate than many published vapor pressure data.

The equation of Dühring may be applied to solutions as well as to pure liquids. Thus, a 20 per cent aqueous NaCl solution has vapor pressures of 14.8 and 760 mm at the temperatures 20 and 104.72°,[1] respectively. The boiling temperatures of pure water at these pressures are 17.30 and 100°, respectively. Using equation (9.32), we find that the temperature of pure water corresponding to a boiling temperature of 50° for the salt solution is 46.57°C. At 46.57°C, pure water has a vapor pressure of 77.9 mm. Compare this pressure with the tabulated value for the vapor pressure of the salt solution at 50°C, namely, 78.1 mm. Similarly, the total pressures[2] (including the partial pressures of water

---

[1] "International Critical Tables," Vol. 3, p. 370.

[2] *Ibid.*, p. 362.

and ammonia) of an aqueous 20 per cent solution of NH_3 at 0 and 50°C are 81.75 and 783.5 mm, respectively. The pressure at 30°C is 351.6 mm. If water is used as the reference substance, its temperature corresponding to 30° is 79.52°, at which temperature the vapor pressure is 348.3 mm. The deviation here is 3.3 mm, or 1 per cent.

Baker and Waite[1] report that " . . . the relationships expressed by Dühring's rule appear to hold for unsaturated aqueous solutions where the solute does not exert an appreciable vapor pressure, more accurately than data which have been determined without regard to (1) whether the concentration is high or low, (2) whether or not the solute ionizes, (3) whether or not the molecules or ions of the solute take up water of hydration or association. It is not at all necessary that the solution be 'ideal' to conform rigorously to the law." Leslie and Carr[2] investigated the applicability of the rule to organic substances *vs.* water. They found it to hold for all types of binary systems including those whose components are partly or completely soluble and whose boiling point curves show a maximum or minimum or neither. They concluded that "the generalization of Dühring's rule is as accurate as most data on vapor pressures recorded in the literature."

Entropy of Evaporation.—The evaporation of a liquid at a pressure equal to its saturated vapor pressure is an equilibrium process and, therefore, a reversible process. At the same time, if the evaporation is carried out isothermally, it is a constant-pressure process. For this, as for any other reversible process at constant pressure, we may write

$$q_P = \Delta H, \qquad \Delta S = \frac{\Delta H}{T} \tag{9.37}$$

When a mole of water is transformed to a mole of vapor at the normal boiling point, we have

$$H_2O(\text{liq, 1 atm}) = H_2O(\text{g, 1 atm});$$
$$\Delta s_{373.16} = \frac{9{,}717.1}{373.16} = 26.040 \text{ cal/deg}$$

From equation (9.37), it appears that the entropy of evaporation is identical with Trouton's "constant." Trouton found empirically that $\Delta H/T$ for a number of liquids at their normal boiling points were approximately constant at 21 calories per degree, but that water and other associated liquids gave abnormally high "constants" of the order of 26 calories per degree. Table 9.3 lists the values of the entropy of evaporation, the Trouton constant, for a number of hydrocarbons.

---

[1] BAKER, E. M., and V. H. WAITE, *Chem. Met. Eng.*, **25**, 1137 (1921).

[2] LESLIE, E. N., and A. R. CARR, *Ind. Eng. Chem.*, **17**, 810 (1925).

Observe the general increase of entropy of evaporation at one atmosphere pressure with the increase in boiling point.

TABLE 9.3.—HEAT AND ENTROPY OF EVAPORATION OF SOME HYDROCARBONS*
(For the evaporation of 1 mole of the liquid to the gas at the saturation pressure and at the indicated temperature)

Compound	Formula	Normal boiling point at 1 atm, °c	Heat of evaporation, ΔH, at saturation pressure, kcal		Entropy of evaporation, ΔS, at saturation pressure at the normal boiling point, cal/deg
			At 25°c	At normal boiling point	
Methane	CH_4	−161.6	......	1.955	17.52
Ethane	C_2H_6	− 88.9	......	3.514	19.07
Propane	C_3H_8	− 42.1	3.605	4.487	19.42
n-Butane	C_4H_{10}	− 0.50	5.035	5.352	19.63
2-Methylpropane (isobutane)	C_4H_{10}	− 11.72	4.570	5.089	19.47
n-Pentane	C_5H_{12}	36.08	6.316	6.160	19.92
2-Methylbutane (isopentane)	C_5H_{12}	27.86	5.878	5.842	19.41
2,2-Dimethylpropane (neopentane)	C_5H_{12}	9.45	5.205	5.438	19.24
n-Hexane	C_6H_{14}	68.74	7.540	6.935	20.28
n-Heptane	C_7H_{16}	98.43	8.735	7.660	20.61
n-Octane	C_8H_{18}	125.66	9.915	8.360	20.96
n-Nonane	C_9H_{20}	150.80	11.099	9.030	21.30
Benzene	C_6H_6	80.10	8.090	7.353	20.81
Methylbenzene (toluene)	C_7H_8	110.62	9.080	8.00	20.85
Ethylbenzene	C_8H_{10}	136.19	10.097	8.60	21.01
1,2-Dimethylbenzene (*o*-xylene)	C_8H_{10}	144.42	10.381	8.80	21.07
1,3-Dimethylbenzene (*m*-xylene)	C_8H_{10}	139.10	10.195	8.70	21.10
1,4-Dimethylbenzene (*p*-xylene)	C_8H_{10}	138.35	10.128	8.62	20.95

* American Petroleum Institute Research Project 44 of the National Bureau of Standards. Selected Values of Properties of Hydrocarbons. Table 1m, Heat and Entropy of Vaporization, at 25°c and the Normal Boiling Point, Mar. 31, 1944; Table 2m, *ibid.*, Mar. 31, 1944; Table 3m, *ibid.*, Mar. 31, 1944; Table 4m, *ibid.*, Mar. 31, 1945; Table 5m, *ibid.*, June 30, 1944, revised Mar. 31, 1945.

Table 9.3 also lists values for the heat of evaporation at the saturation pressure, both at 25°c and at the normal boiling point. For all the liquids, the heat of evaporation is greater at the lower temperature. In general, the heat of evaporation of a liquid increases somewhat with decreasing temperature because the liquid has a greater heat capacity than the vapor. For water, an "associated" liquid, this increase is greater than normal, because decreasing temperature favors association in the liquid state. The change of heat of evaporation of water with temperature was indicated in Table 5.1. It is evident, therefore, that the entropy of evaporation must increase at the lower temperatures both because ΔH increases and because T decreases. Thus, for the change in entropy on the evaporation of a mole of water, we have, at 50°C,

$$\Delta S_{323.16} = \frac{10{,}257}{323.16} = 31.740 \text{ cal/deg mole}$$

and, at 0°C,

$$\Delta S_{273.16} = \frac{10{,}767}{273.16} = 39.416 \text{ cal/deg mole}$$

At the critical temperature where ΔH is zero, the entropy of evaporation must vanish. Because the entropy of evaporation of a liquid decreases with increasing temperature, as shown above, it is evident that Trouton was required to fix a reference temperature.

We should point out here that the normal boiling temperature is an accidental point determined by the pressure defined as standard. A change in the standard pressure would result in changes in the absolute boiling temperatures and in the entropy of evaporation. Trouton's rule fails for low-boiling and high-boiling liquids. Thus liquid oxygen boiling at 90°K with a heat of vaporization of 815 calories has the low entropy change of 9.06 calories per degree per mole. Hildebrand[1] concluded that the reason for the general increase of entropy of evaporation with temperature is to be found in the decrease in the equilibrium concentration of the vapor with temperature at constant pressure.

Hildebrand-Trouton Rule.—Various equations have been derived to express the general increase of entropy of evaporation at the normal atmospheric pressure with increase in boiling point. The rule of Hildebrand proposes that comparison of entropies of evaporation at *constant pressure* be abandoned in favor of comparison of the entropy changes at temperatures where the vapors have *equal concentrations.* We may consider the entropy of evaporation as including the entropy increase on the separation of the molecules of liquid to form gas and the entropy increase on expansion of the gas. For associated liquids, an additional component of the entropy of evaporation is the entropy of dissociation of the liquid into simpler gas molecules. As we saw in equation (7.54) or (8.58), the entropy of a gas increases with volume at constant temperature, the increase for a mole of perfect gas being given by

---

[1] HILDEBRAND, J. H., *J. Am. Chem. Soc.*, **37**, 970 (1915).

$$\Delta \mathrm{s} = R \ln \frac{\mathrm{v}_2}{\mathrm{v}_1} = 4.576 \log \frac{\mathrm{v}_2}{\mathrm{v}_1} \tag{9.38}$$

On the assumption that v_1 for the various gases is essentially the volume of their liquids, it appears from equation (9.38) that the entropy of expansion of the various gases will be the same when they have equal molar volumes (concentrations). When entropies of expansion are compared at the normal boiling points, the final gas volumes may be far from equal. Thus the molar volume of a perfect gas at 273°K is 22.4 liters; but at the boiling point of oxygen, 90°K, it is 7.4 liters, and at the boiling point of cadmium, 1040°K, it is 85.3 liters. At these temperatures the respective concentrations of vapor are 0.0446, 0.135, and 0.0117 mole per liter.

The Clausius-Clapeyron equation (9.11) may be written in the form

$$\frac{dP}{P} = \frac{\Delta \mathrm{H}}{RT} \frac{dT}{T}$$

whence,

$$\frac{d \ln P}{d \ln T} = \frac{d \log P}{d \log T} = \frac{\Delta \mathrm{H}}{RT} = \frac{\Delta \mathrm{s}}{R} \tag{9.39}$$

This equation shows that if $\Delta \mathrm{s}$ is to remain constant, $d \log P/d \log T$ must be the same for all liquids. This is not true at normal boiling points. However, Hildebrand found that when he plotted $\log P$ *vs.* $\log T$ for liquids ranging in boiling point from nitrogen to zinc the slopes of all the curves for normal liquids, $d \log P/d \log T$, were the same at the same concentration of vapor.

The ideal gas equation may be written in the form

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

On the $\log P$ *vs.* $\log T$ vapor pressure diagram, the line of equal concentration of vapor is given by the equation

$$\log P = \log (CRT) = \log T + \log (CR) \tag{9.40}$$

Hildebrand arbitrarily chose $C = 0.00507$ mole per liter; for at this value, if P is in millimeters, $\log (CR) = 0.5$. His values of $\Delta \mathrm{s}/R$ are given in column (3) of Table 9.4. They are constant for the normal liquids although the evaporation temperatures range from 55 to 1130°K. Column (5) lists the values of $\Delta \mathrm{s}/R$ of the different substances at the pressure of 100 mm. Observe the increase of $\Delta \mathrm{s}/R$ with temperature at constant pressure.

Earlier, we found that the vapor pressure curve can be estimated for a liquid if only the normal boiling point is known, provided that the liquid is normal enough to permit estimation of the heat of vaporization from Trouton's rule. Hildebrand's rule permits a more accurate estimation of this quantity provided that some reference substance is available. The two substances will have the same entropy of evaporation at the same concentration of vapor. If the value of ΔH for the reference substance at this concentration and temperature is known, $\Delta H/T$ for the unknown at the same values can be calculated.

TABLE 9.4.—HILDEBRAND-TROUTON ENTROPY OF EVAPORATION CONSTANTS* FOR VARIOUS SUBSTANCES COMPARED AT EQUAL CONCENTRATIONS AND AT EQUAL PRESSURES

Substance	C = 0.00507 mole/liter		P = 100 mm	
	T_C,† °K	$\Delta H/RT_C = \Delta S/R$	T_P,‡ °K	$\Delta H/RT_P = \Delta S/R$
(1)	(2)	(3)	(4)	(5)
Nitrogen	55	13.8	63	11.0
Oxygen	75	13.8	81	11.4
Chlorine	194	13.9	200	13.5
Pentane	256	13.5	260	13.2
Isopentane	258	13.7	262	13.5
Hexane	286	13.6	289	13.3
Carbon tetrachloride	294	13.5	295	13.4
Benzene	298	13.7	299	13.7
Fluorobenzene	303	13.7	304	13.7
Stannic chloride	329	13.6	328	13.6
Octane	338	13.8	339	13.9
Bromonaphthalene	486	13.8	472	14.1
Mercury	560	13.1	533	13.5
Cadmium	988	13.2	908	14.8
Zinc	1130	13.2	1030	15.1
Ammonia	200	16.2		
Water	325	16.0		
Ethyl alcohol	307	16.7		

* HILDEBRAND, J. H., *J. Am. Chem. Soc.*, **37**, 970 (1915).

† T_C = temperature at which C = 0.00507 mole/liter.

‡ T_P = temperature at which P = 100 mm.

Problems

9.1. The vapor pressures of water at the temperatures 0, 25, 50, 75, and 100°C are given by Osborne and Meyers, *loc. cit.*, as 0.006027, 0.031222, 0.12170, 0.38043, and 1.00000 atmosphere, respectively. Assuming that water vapor behaves as an ideal gas, calculate the molar volume of the water vapor under the above conditions.

9.2. The observed specific volumes of water vapor at 0, 25, 50, 75, and 100°C are 206,288, 43,401, 12,045, 4,133.2, and 1,673.0 cm^3 per gram, respectively. Calculate the molar volumes at these temperatures, and compare with those derived with the ideal gas equation in Prob. 9.1.

9.3. Calculate dP/dT for the water-vapor equilibrium at 0°, using the value of heat of evaporation in Table 5.1 and equation (9.11). What approximations were made in this calculation? Compare with the experimental value of dP/dT.

9.4. Using the vapor pressure data in Prob. 9.1, calculate the mean values of the heat of evaporation of water over the temperature intervals 0 to 25, 25 to 50, 50 to 75, and 75 to 100°, with the aid of the integrated Clausius-Clapeyron equation. Compare these values with the experimental values in Table 5.1.

9.5. (*a*) Using the exact form of the Clausius-Clapeyron equation, calculate the heat of evaporation of water at 100°C and compare with the calorimetric value.

(*b*) Perform this calculation, using the same vapor pressure data and the approximate form of the Clausius-Clapeyron equation. Explain any discrepancies between this result and the result secured in (*a*).

9.6. The vapor pressure of nitrous oxide, N_2O, according to H. J. Hoge [*J. Research Natl. Bur. Standards*, **34,** 281 (1945)] is represented between the triple point, 182.351°, and 240°K by the equation

$$\log P_{\text{atm}} = 4.1375 - \frac{656.60}{T - 26}$$

At the normal boiling point, the molar heat of evaporation is 3,956 calories per mole according to Hoge and 3,958 calories per mole according to Blue and Giauque. Calculate a value for the heat of evaporation of N_2O with the exact form of the Clausius-Clapeyron equation, deriving a value of dP/dT from the vapor pressure equation, a value of v_l from "International Critical Tables" (Vol. 3, p. 229), and a value of v_g with the aid of the virial coefficient B which, according to H. L. Johnston and H. R. Weimer [*J. Am. Chem. Soc.*, **56,** 625 (1934); **57,** 2737 (1935)], has the value

$$B = 32 - \frac{56{,}115.0}{T} + \frac{3.9424 \times 10^6}{T^2} - \frac{3.9145 \times 10^{11}}{T^4} + \frac{3.0747 \times 10^{15}}{T^6}$$

9.7. The change in vapor pressure of 1-butene with temperature at 266.722°K according to J. G. Aston *et al.* [*J. Am. Chem. Soc.*, **68,** 52 (1946)] is $(dP/dT) = 29.362$ mm/deg, the vapor pressure being 0.99279 atmosphere. The molar volume of the liquid is 0.090 liter. The molar heat of evaporation at this temperature is 5,236.1 calories. Calculate values for the molar volume of the gas and the second virial coefficient B.

9.8. Using the appropriate value of the heat of evaporation of ethanol in Table 9.2 and the observed boiling point 78.3°C, calculate the vapor pressure of ethanol at 60°C. Compare with the observed value.

9.9. From the "International Critical Tables" (Vol. 3, p. 205), obtain the vapor pressure equation for liquid zinc for the range 600 to 985°C, and calculate the vapor pressure of zinc at 600°C.

9.10. The boiling point of *n*-propyl alcohol is 97.19°C. At 40° its vapor pressure is 50.2 mm. Using water as a reference liquid, apply Dühring's rule, and estimate the vapor pressure of *n*-propyl alcohol at 70°C. The observed vapor pressure is 239.0 mm.

9.11. Using the reference temperatures for *n*-propyl alcohol given in Prob. 9.10, calculate the vapor pressure of *n*-propyl alcohol at 70°C, with the aid of the Clausius-Clapeyron equation. Compare with the results in Prob. 9.10.

CHAPTER 10

FREE ENERGY

In the preceding chapter, we considered some reversible processes in simple two-phase systems, the only work being work of expansion. The systems were at equilibrium internally during the reversible processes and could do no net work w'. Thus, at 0° and 1 atmosphere pressure, there is no tendency for ice to melt or water to freeze even though the transition results in a change in volume. The phase transitions—melting, evaporation, sublimation, and transition between crystalline phases—are equilibrium processes. They take place at a constant temperature if the pressure is maintained at a constant value, there being a definite temperature of transition corresponding to each pressure. But the usual experimental condition for chemical reactions is also that of constant temperature. Therefore, a more general study of equilibrium at constant temperature is desirable.

Equilibrium in Simple Systems at Constant Temperature.—In simple systems capable of work of expansion only, reversible processes at constant temperature are changes at equilibrium. In Chap. 7, we found that entropy is a criterion of reversibility and of equilibrium under the conditions of constant energy and constant volume, the change in entropy being measured by the net work w' for a reversible process and being zero for a process at equilibrium. However, in phase transitions (and chemical reactions) at constant temperature there is an entropy change measured by the heat of the reversible reaction, since $q_r = T\,\Delta S$.

Consider an isothermal process in a simple system for which w_r equals $\int P\,dV$, there being no net work w'. Then, for the reversible process, that is, an equilibrium process, we have
At constant volume,

$$q_r = q_V = \Delta E_V \tag{10.1}$$

At constant pressure,

$$q_r = q_P = \Delta E_P + P\,\Delta V_P = \Delta H_P \tag{10.2}$$

The temperature being constant and q_r being equal to $T\,\Delta S$, we have from equations (10.1) and (10.2) for the equilibrium conditions at constant volume

$$\Delta E_{V,T} = T\,\Delta S_{V,T}$$
$$\Delta E_{V,T} - T\,\Delta S_{V,T} = 0 \tag{10.3}$$

and at constant pressure,

$$\Delta H_{P,T} = T\,\Delta S_{P,T}$$
$$\Delta H_{P,T} - T\,\Delta S_{P,T} = 0 \tag{10.4}$$

The subscripts are used to emphasize the conditions under which these equilibrium equations are valid. The equations are important, having a more general validity than might be expected from the conditions for which they were derived. As we shall find later, they apply also to any system in internal equilibrium, the net work w' being zero under these conditions.

It will be instructive to apply equation (10.4) to the data for the freezing of water to ice at 1 atmosphere pressure. In Chap. 5 we found the molar heat of freezing of water at 0°c and −10°c to be −1,436 and −1,343 calories, respectively. In Chap. 8, we found the molar entropy change for the freezing at these temperatures to be −5.257 and −4.910 calories per degree, respectively. Hence, at 0°c for the equilibrium process,

$$\begin{aligned}\Delta H_{273.16} - T\,\Delta S_{273.16} &= -1{,}436 - 273.16(-5.257)\\ &= -1{,}436 + 1{,}436 = 0\end{aligned}$$

At −10°c, the freezing is not an equilibrium process but a spontaneous process. At this temperature,

$$\begin{aligned}\Delta H_{263.16} - T\,\Delta S_{263.16} &= -1{,}343 - 263.16(-4.910)\\ &= -1{,}343 + 1{,}292 = -51 \text{ cal}\end{aligned}$$

Thus, for the equilibrium process, equation (10.4) applies and for the spontaneous process

$$\Delta H_{P,T} - T\,\Delta S_{P,T} < 0$$

This is a general result for changes at constant pressure and constant temperature. The difference, $\Delta H - T\,\Delta S$, is zero at equilibrium, negative for spontaneous changes, and positive for changes that would go spontaneously in the reverse direction. Thus, for the freezing of water above 0°c, the difference is positive and the spontaneous process is the melting of ice, not the freezing of water. The same principles apply to the difference expressed in equation (10.3). At constant volume and constant temperature, the difference is zero at equilibrium, negative for a spontaneous process, and positive for a process spontaneous in the reverse direction.

Free Energy Functions.—The quantities, $\Delta E_{V,T} - T\,\Delta S_{V,T}$ and $\Delta H_{P,T} - T\,\Delta S_{P,T}$, which indicate the equilibrium conditions for a system in terms of the thermodynamic properties of the system at constant temperature, are so important that they are represented as the changes in two functions A and F. Thus, let A be such a function that its change at constant volume and constant temperature is

$$\Delta A_{V,T} = \Delta E_{V,T} - T\,\Delta S_{P,T} \tag{10.5}$$

and let F be such a function that its change at constant pressure and constant temperature is

$$\Delta F_{P,T} = \Delta H_{P,T} - T\,\Delta S_{P,T} \tag{10.6}$$

The values of $\Delta A_{V,T}$ and $\Delta F_{P,T}$ can then serve as criteria of equilibrium at the indicated conditions.

In Chap. 2 we found that a general function H, defined as $E + PV$, took on a particularly useful form at constant pressure. Accordingly, we look for general definitions of the functions A and F that lead to equations (10.5) and (10.6) respectively.

Two such functions are defined by the equations

$$A \equiv E - TS \tag{10.7}$$
$$F \equiv H - TS \tag{10.8}$$

Since $H = E + PV$, the F function may be written

$$F = E - TS + PV \tag{10.9}$$

and F is related to A by

$$F = A + PV \tag{10.10}$$

Because H, E, T, and S, are *properties* of a system, F and A are also properties whose values are defined by the state of the system. H, E, and S are extensive properties, and T is an intensive property; consequently, F and A are extensive properties, dependent on the amount of material considered in a process. For processes occurring at constant pressure, which is the common experimental condition, we have found the heat of reaction to be represented by ΔH_P and not by ΔE_P. Similarly, under conditions of constant volume, ΔE_V not ΔH_V represents the heat of the process. A comparison with equations (10.5) and (10.6) suggests that the F function is the important function under the condition of constant temperature and constant pressure and that the A function is the more useful under the condition of constant temperature and constant volume at which no work of expansion of the system occurs.

The function $E - TS$, here designated as A, was called the "free energy" by Helmholtz. This name and the symbol F have been generally adopted for it by the European school of chemical thermodynamics. However, as Gibbs and later Americans have pointed out, the function $H - TS$ is much the more useful function under the common condition of constant pressure. This function, called the "thermodynamic potential" by Gibbs and the "free energy" by Noyes and Lewis, has been called the *free energy* by the followers of Noyes and Lewis. The symbol F was adopted for it, the symbol A being used for the function $E - TS$. Our definition of the A and F functions[1] follows the practice of the American school, as does our naming of the functions. The A function, following this practice, is called the *work content* or, occasionally, the *Helmholtz free energy.* Our F function is called simply the *free energy.* This function is frequently called the "Lewis free energy," the "Gibbs function," or the "Gibbs free energy." Many represent it by the symbol G.

Free Energy Functions at Constant Temperature.—The free energy functions are in their most useful form for reactions at constant temperature. The restriction of constant temperature does not interfere with the use of the functions in chemical thermodynamics, for most of the chemical reactions can be and are investigated under isothermal conditions. In the initial state a system has definite values of the properties T, P_1, V_1, S_1, E_1, H_1, A_1, and F_1. After an isothermal change the system in the final state has the corresponding properties T, P_2, V_2, S_2, E_2, H_2, A_2, and F_2. We are here concerned with the change in the *work content* and in the *free energy.* From equation (10.7), the isothermal change in the work content is

$$A_2 - A_1 = E_2 - E_1 - T(S_2 - S_1)$$

This may be written in the equivalent form

$$\Delta A = \Delta E - T\,\Delta S \tag{10.11}$$

In the differential form, equation (10.11) becomes

$$dA = dE - T\,dS \tag{10.12}$$

From equation (10.8), we have, for the isothermal change in free energy, the corresponding equation

$$F_2 - F_1 = H_2 - H_1 - T(S_2 - S_1)$$

---

[1] The British *Joint Committee of the Chemical Society, The Faraday Society, and The Physical Society* on "Symbols of Thermodynamical and Physicochemical Quantities and Conventions Relating to Their Use" selects the symbol A as the preferred symbol for the $E - TS$ function, with F as a nonpreferred alternate. It also selects the symbol G for the $H - TS$ function called the "Gibbs function" or the "Lewis free energy." Following European practice, it recommends the symbol F only as an optional symbol for the $E - TS$ function [*Chemistry & Industry*, **56**, 860 (1937)].

which in accordance with our conventions is written

$$\Delta F = \Delta H - T\,\Delta S \tag{10.13}$$

In the differential form, this equation becomes

$$\mathrm{d}F = \mathrm{d}H - T\,\mathrm{d}S \tag{10.14}$$

From equation (10.10), we have, similarly,

$$\Delta F = \Delta A + \Delta(PV) \tag{10.15}$$

The free energy functions, as has been indicated, are especially useful in the study of systems at constant temperature. When a system with a definite amount of substance changes from one state to another at a different temperature, the heat absorbed and the work done along different reversible paths may differ, for part of the work may be done as the result of the transport of energy from one temperature to the other. The energy transported, and consequently the work done, are not properties of the system itself, since some of the energy transported may come from the surroundings. On the other hand, if the two states of the system are at the same temperature, there is no work associated with the transport of energy between two temperatures and all the work can then be accounted for in terms of the work potentials and the quantities transported. As we found in Chap. 7, the actual work done depends on the opposing potentials; it may range from zero, as in the completely irreversible process, to a maximum, as for the reversible process.

Since the first law equation holds for reversible processes as well as for other processes and since $\mathrm{D}q_r = T\,\mathrm{d}S$, we have

$$\mathrm{d}E = \mathrm{D}q_r - \mathrm{D}w_r = T\,\mathrm{d}S - \mathrm{D}w_r$$

For the change from one state to another at constant temperature, the integral of $T\,\mathrm{d}S$ being $T\,\Delta S$ under these conditions, this differential equation becomes

$$\Delta E = T\,\Delta S - w_r$$

When this equation is combined with equation (10.11) we obtain

$$\Delta A = \Delta E - T\,\Delta S = -w_r$$

or

$$-\Delta A = w_r \tag{10.16}$$

Since, at constant temperature, the reversible work is the maximum work for the process, we see that the decrease in the Helmholtz free energy or work content is a measure of the reversible work, the maximum for the isothermal process.

If the process is carried out in an irreversible manner, the change in A (which is a property of the system) will be definite, just as the maximum work obtainable from the process is definite; but this change in A will exceed the work actually done, that is, $-\Delta A > w$. There is, accordingly, a definite loss in ability to do work whenever a process proceeds irreversibly. Equation (10.16) tells us also that, when a system does work, its work content, its ability to do work, decreases.

The relation of ΔF at constant temperature to the total reversible work w_r may be obtained from equations (10.15) and (10.16), whence

$$\Delta F = -w_r + \Delta(PV)$$

This equation does not appear to be immediately useful, but it becomes so when the special restriction of constant pressure is imposed on it so that $\Delta(PV)$ becomes $P\,\Delta V$, the reversible work of expansion of the system against an external pressure equal to P. Under these conditions, the equation becomes

$$-\Delta F_P = w_r - P\,\Delta V = w' \tag{10.17}$$

where w' is the *net* reversible work, the *maximum useful work* for the isothermal isobaric process. The work of expansion cannot be classed as useful work. In a reaction taking place in an open vessel, it is required to push back the atmosphere during the process. It cannot be used for any other purpose.

Let us apply these relations to the isothermal reaction

$$\mathrm{Zn + 2HCl = ZnCl_2 + H_2}$$

This reaction may proceed in an electrolytic cell, in a beaker, or in some closed vessel. When the reaction is carried out reversibly in a cell at constant pressure, the total work obtainable is the sum of the electrical work w_e and the work of expansion of the evolved hydrogen $P\,\Delta V$. The useful work from the process is the electrical work w_e; it is expressed by the relation

$$w_e = w_r - P\,\Delta V = w' \tag{10.18}$$

Because the process is carried out reversibly, we have, from equations (10.16) to (10.18),

$$-\Delta F_P = -\Delta A_P - P\,\Delta V = w_e \tag{10.19}$$

Now, if the reaction is carried out in an open vessel against atmospheric pressure by a direct mixing of zinc and acid, the electrical or useful work obtained is nil, the only work done being $P\,\Delta V$, the work of expansion of the hydrogen. The decrease in free energy $-\Delta F$ is the same as in the reaction carried out reversibly, even though no useful work was actually obtained.

If the reaction is carried out reversibly at constant volume, there is no work of expansion, $P\,\Delta V = 0$, the electrical work at constant volume is the total work, and

$$-\Delta A_V = w_{e,V} \tag{10.20}$$

If the reaction proceeds by direct mixing in a closed tube, the electrical or useful work is nil, as is also the total work, but a loss in ability to do work has occurred. The decrease in Helmholtz free energy is still $-\Delta A_V$. Thus, at constant pressure the actual useful work may range all the way from zero to the maximum value $-\Delta F_P$, and at constant volume the useful work may range from zero to the maximum value $-\Delta A_V$.

Free Energy as Criterion for Equilibrium.—In the first section we considered equilibrium in simple systems and found that at constant temperature two functions serve as criteria for equilibrium. One of these is identified with the A function for constant volume and the other with the F function for constant pressure. We shall now see how these functions serve as criteria for equilibrium in more complicated systems including those in which chemical processes may take place.

Equation (7.40), based on the first and second laws is a general equation for isothermal processes, relating the change in entropy and energy of a system in any isothermal process to the work done. Thus,

$$T\,\mathrm{d}S - \mathrm{d}E \geqq \mathrm{D}w \tag{10.21}$$

the equality sign applying to a reversible path and the inequality sign to an irreversible path. But the total work $\mathrm{D}w$ is the sum of any work of expansion $P\,\mathrm{d}V$ against the surroundings and the net work $\mathrm{D}w_n$, which represents the work the system does as a result of its tendency toward internal equilibrium. Thus,

$$\mathrm{D}w = P\,\mathrm{d}V + \mathrm{D}w_n \tag{10.22}$$

When the process is carried out reversibly, $\mathrm{D}w$ becomes $\mathrm{D}w_r$ and $\mathrm{D}w_n$ becomes the net reversible work $\mathrm{D}w'$ defined earlier. Equation (10.22) then becomes equation (7.32), or, when integrated at constant pressure, it expresses the relation in equation (10.17). When equations (10.21) and (10.22) are combined, we have

$$T\,\mathrm{d}S - \mathrm{d}E - P\,\mathrm{d}V \geqq \mathrm{D}w_n \tag{10.23}$$

which becomes a measure of equilibrium within a system at constant temperature. We shall consider in turn the relations at constant volume and constant pressure, both at constant temperature as required by the conditions under which equation (10.21) [equation (7.40)] was derived.

1. *Isothermal Change at Constant Volume.*—In a change at constant volume, dV equals zero and the total work equals the net work so that Dw equals Dw_n. A system *at equilibrium* within itself can do no work so that from either equation (10.21) or (10.23)

$$T\,dS - dE = 0 \tag{10.24}$$

This equation corresponds to equation (10.3) derived earlier.

If the system is *not at equilibrium*, the change may take place reversibly or irreversibly. Along any reversible isothermal path $Dw = Dw_r = Dw'$, the work being positive in value if the system can move spontaneously toward equilibrium. Thus, for a reversible path,

$$T\,dS - dE = Dw_r = Dw' > 0 \tag{10.25}$$

If the system changes along an irreversible path, the work done is less than Dw'. But dS and dE do not depend on the path so that, for the irreversible path,

$$T\,dS - dE > Dw \geqq 0 \tag{10.26}$$

From equation (10.12), the left side of these equations equals $-dA$ so that, for the system at equilibrium, $dA = 0$ and for a system that can change spontaneously toward equilibrium either by a reversible or an irreversible path

$$dA = -Dw_r = -Dw' < 0$$

These statements may be combined to give the criterion for equilibrium at constant volume and constant temperature

$$dA_{V,T} \leqq 0 \tag{10.27}$$

the equality applying for the system at equilibrium and the inequality sign for the change toward equilibrium. A spontaneous change at constant volume is one that can proceed with a decrease in Helmholtz free energy, the decrease being a measure of the reversible work for the change.

2. *Isothermal Change at Constant Pressure.*—In a change at constant pressure, $dE + P\,dV$ equals dH so that equation (10.23) becomes

$$T\,dS - dH \geqq Dw_n \tag{10.28}$$

At equilibrium, the net work is zero and equation (10.28) becomes

$$T\,dS - dH = 0 \tag{10.29}$$

This equation corresponds to equation (10.4) derived earlier.

If the system is *not at equilibrium* but proceeds to equilibrium reversibly, the net work is the reversible net work Dw' and equation (10.28) becomes

$$T\,dS - dH = Dw' > 0 \tag{10.30}$$

If the change toward equilibrium takes place along an irreversible path, the value of Dw_n is less than that for Dw' so that, from equations (10.28) and (10.30),

$$T\,dS - dH > Dw_n \geqq 0 \tag{10.31}$$

Comparison of these equations with equation (10.14) shows that, for a system at equilibrium, $dF = 0$ and that, for a change toward equilibrium, $dF = -Dw' < 0$. These statements may be combined into the criterion for equilibrium at constant temperature and constant pressure

$$dF_{P,T} \leqq 0 \tag{10.32}$$

the equality sign holding for equilibrium and the inequality sign for the change toward equilibrium. This equation has immediate application to chemistry. If a chemical reaction is to proceed spontaneously, it is necessary that the change in free energy be negative. Those reactions can proceed spontaneously that do so with a decrease in free energy. When no free energy change occurs, the reaction is at equilibrium; when the reaction would result in an increase in free energy, the reverse reaction is the reaction that proceeds spontaneously.

It is only for an isothermal change that we may write dF or dA equal to zero for equilibrium at constant pressure and volume, respectively. However, these criteria are adequate for chemical purposes, for the question usually proposed in chemistry is whether or not a reaction will proceed at a given temperature. If the reactants cannot form the desired products at that temperature by an isothermal process, they also cannot by another process, for the initial and final free energies are independent of the path over which the reaction proceeds. Free energies do change with temperature, as we shall see below.

General Free Energy Equations.—When the free energy equations are differentiated, we obtain from equations (10.7) to (10.9) the general equations

$$dA = dE - T\,dS - S\,dT \tag{10.33}$$

and

$$dF = dH - T\,dS - S\,dT \tag{10.34}$$

$$= dE + P\,dV + V\,dP - T\,dS - S\,dT \tag{10.35}$$

Reversible work, as in equations (10.17) and (7.32), may be expressed as the sum of the work of expansion and other reversible work, the net work. Thus, in differential form,

$$Dw_r = P\,dV + Dw'$$

Then, we have from a combination of the first and second law equations, as in equation (7.33),

$$dE = T\,dS - P\,dV - Dw'$$

which may be written in the forms

$$dE - T\,dS = -P\,dV - Dw' \tag{10.36}$$

and

$$dE + P\,dV - T\,dS = -Dw' \tag{10.37}$$

On combining equation (10.33) with (10.36) and (10.35) with (10.37), we have, respectively,

$$dA = -S\,dT - P\,dV - Dw' \tag{10.38}$$

and

$$dF = -S\,dT + V\,dP - Dw' \tag{10.39}$$

Equations (10.38) and (10.39) are general equations, derived without any qualifying restrictions. From them, we can secure the equations for use under restricted conditions.

In many of the equations we have assumed that Dw' is zero. The processes for which this assumption is valid are those in which all the work[1] may be expressed as a function of P and V, and equilibrium processes, in which $w' = 0$. In the special case of reactions in balanced electric cells, w' also equals zero. Spontaneous reactions may yield no work w', but they must be considered separately because in such processes the $S\,dT$ and $P\,dV$ terms are not those of the reversible process, for S does not vary with T nor P with V in the same manner as in reversible processes.

Free Energy Change in Simple Systems.—In simple systems that do not undergo chemical reaction, the only work done is that against pressure. There is no other work such as electrical work, work of solution, or surface work. For these systems, $Dw' = 0$, and equations (10.38) and (10.39) become simplified to

$$dA = -S\,dT - P\,dV \tag{10.40}$$

and

$$dF = -S\,dT + V\,dP \tag{10.41}$$

When both temperature and volume remain constant, we have $dA_{T,V} = 0$, which is equation (10.27); when both temperature and pressure are constant, we have $dF_{T,P} = 0$, which is equation (10.32).

---

[1] For constant-temperature processes, such as we are considering in the preceding equations, Dw' is measured by the exact differentials $-dA$ and $-dF$ at constant volume and constant pressure, respectively. However, we shall continue to use the notation Dw' to express small values for the net work.

1. *Isothermal Processes,* dT = 0.—For processes that occur at constant temperature, the above equations take on the simple forms

$$dA_T = -P\,dV_T$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \qquad (10.42)$$

and

$$dF_T = V\,dP_T$$

$$\left(\frac{\partial F}{\partial P}\right)_T = V \qquad (10.43)$$

These two derivatives can be readily evaluated from available experimental data.

2. *Constant-volume Processes,* dV = 0.—If the volume is kept constant instead of the temperature, it is evident that equation (10.40) becomes

$$dA_V = -S\,dT_V$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \qquad (10.44)$$

It is apparent from equation (10.41) that the F function does not take on a simple form for constant-volume processes. It is therefore not used under these conditions.

The entropy of a substance is therefore a measure of the change of A with temperature at constant volume; it can be evaluated from $(\partial A/\partial T)_V$. Its value is also expressed in terms of E and A by equation (10.7), whence,

$$-S = \frac{A - E}{T} \qquad (10.45)$$

This value may be substituted in equation (10.44) to give the Gibbs-Helmholtz relation for the constant-volume process

$$\left(\frac{\partial A}{\partial T}\right)_V = \frac{A - E}{T} \qquad (10.46)$$

3. *Constant-pressure Processes,* dP = 0.—If the pressure is kept constant, equation (10.41) becomes

$$dF_P = -S\,dT_P$$

$$\left(\frac{\partial F}{\partial T}\right)_P = -S \qquad (10.47)$$

Under these conditions, the A function does not assume a simple form, and the entropy is a measure of the change of F with temperature. Again, the entropy is given by the relation in equation (10.8), namely,

$$-S = \frac{F - H}{T} \tag{10.48}$$

This may be combined with equation (10.47) to give the Gibbs-Helmholtz equation for the constant-pressure process

$$\left(\frac{\partial F}{\partial T}\right)_P = \frac{F - H}{T} \tag{10.49}$$

Tabulated Thermodynamic Relations.—We have derived only a few of the many mathematical relations between the properties of a system, such as P, V, T, H, E, S, A, and F. A very great number of relations exist between these properties, many of which are useful though more

TABLE 10.1

$$(\partial T)_P = -(\partial P)_T = 1$$
$$(\partial V)_P = -(\partial P)_V = (\partial V/\partial T)_P$$
$$(\partial S)_P = -(\partial P)_S = C_P/T$$
$$(\partial E)_P = -(\partial P)_E = C_P - P(\partial V/\partial T)_P$$
$$(\partial H)_P = -(\partial P)_H = C_P$$
$$(\partial F)_P = -(\partial P)_F = -S$$
$$(\partial A)_P = -(\partial P)_A = -[S + P(\partial V/\partial T)_P]$$

$$(\partial V)_T = -(\partial T)_V = -(\partial V/\partial P)_T$$
$$(\partial S)_T = -(\partial T)_S = (\partial V/\partial T)_P$$
$$(\partial E)_T = -(\partial T)_E = T(\partial V/\partial T)_P + P(\partial V/\partial P)_T$$
$$(\partial H)_T = -(\partial T)_H = -V + T(\partial V/\partial T)_P$$
$$(\partial F)_T = -(\partial T)_F = -V$$
$$(\partial A)_T = -(\partial T)_A = P(\partial V/\partial P)_T$$

$$(\partial S)_V = -(\partial V)_S = (1/T)[C_P(\partial V/\partial P)_T + T(\partial V/\partial T_P^2)]$$
$$(\partial E)_V = -(\partial V)_E = C_P(\partial V/\partial P)_T + T(\partial V/\partial T)_P^2$$
$$(\partial H)_V = -(\partial V)_H = C_P(\partial V/\partial P)_T + T(\partial V/\partial T)_P^2 - V(\partial V/\partial T)_P$$
$$(\partial F)_V = -(\partial V)_F = -[V(\partial V/\partial T)_P + S(\partial V/\partial P)_T]$$
$$(\partial A)_V = -(\partial V)_A = -S(\partial V/\partial P)_T$$

$$(\partial E)_S = -(\partial S)_E = (P/T)[C_P(\partial V/\partial P)_T + T(\partial V/\partial T)_P^2]$$
$$(\partial H)_S = -(\partial S)_H = -VC_P/T$$
$$(\partial F)_S = -(\partial S)_F = -(1/T)[VC_P - ST(\partial V/\partial T)_P]$$
$$(\partial A)_S = -(\partial S)_A = (1/T)\{P[C_P(\partial V/\partial P)_T + T(\partial V/\partial T)_P^2] + ST(\partial V/\partial T)_P\}$$

$$(\partial H)_E = -(\partial E)_H = -V[C_P - P(\partial V/\partial T)_P] - P[C_P(\partial V/\partial P)_T + T(\partial V/\partial T)_P^2]$$
$$(\partial F)_E = -(\partial E)_F = -V[C_P - P(\partial V/\partial T)_P] + S[T(\partial V/\partial T)_P + P(\partial V/\partial P)_T]$$
$$(\partial A)_E = -(\partial E)_A = P[C_P(\partial V/\partial P)_T + T(\partial V/\partial T)_P^2]$$

$$(\partial F)_H = -(\partial H)_F = -V(C_P + S) + TS(\partial V/\partial T)_P$$
$$(\partial A)_H = -(\partial H)_A = -[S + P(\partial V/\partial T)_P][V - T(\partial V/\partial T)_P] + P(\partial V/\partial P)_T$$
$$(\partial A)_F = -(\partial F)_A = -S[V + P(\partial V/\partial P)_T] - PV(\partial V/\partial T)_P$$

are little used. We have illustrated the general methods used in deriving the relations and could, if necessary, derive the others by the same methods. However, Bridgman[1] presented a method and table that permit a ready calculation of the various interrelationships. This method is applied below.

In terms of the general properties X, Y, and Z, Table 10.1 gives values for $(\partial X)_Y$, $(\partial X)_Z$, $(\partial Y)_X$, $(\partial Y)_Z$, and so forth, for which we may write

$$\left(\frac{\partial X}{\partial Y}\right)_Z = \frac{(\partial X)_Z}{(\partial Y)_Z}$$

From the table, we see that, in general,

$$(\partial X)_Z = -(\partial Z)_X$$

Thus, if we wish to obtain $(\partial F/\partial P)_T$, we find

$$(\partial F)_T = -V, \qquad (\partial P)_T = -1, \qquad \text{and} \qquad \left(\frac{\partial F}{\partial P}\right)_T = V$$

which is equation (10.43). Similarly, from the table,

$$(\partial F)_P = -S, \qquad (\partial T)_P = 1$$

so that

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

which is equation (10.47).

Free Energy Change in Chemical Reactions.—The differential free energy equations already derived are general and can be applied to chemical reactions as well as to simple substances. In chemistry, we deal principally with constant-pressure reactions for which the change of free energy ΔF is the difference between the free energy of the products of the reaction and the free energy of the reactants. At constant pressure, the $H - TS$ function is, therefore, much more useful than the $E - TS$ function. Accordingly, we shall restrict our discussion to the F function. However, when desired, the corresponding equations for the A function may be derived by analogous methods.

Consider a chemical system in which a change in free energy occurs because of the chemical reaction, pressure and temperature remaining constant. In the initial state, the system is characterized by functions such as F_1, H_1, S_1, P, and T. In the final state, these functions have the values F_2, H_2, S_2, P, and T. From Equation (10.8), we have, therefore,

$$\begin{array}{c} F_2 = H_2 - TS_2 \\ \underline{F_1 = H_1 - TS_1} \\ F_2 - F_1 = H_2 - H_1 - T(S_2 - S_1) \end{array} \qquad (10.50)$$

---

[1] BRIDGMAN, P. W., *Phys. Rev.* (2), 3, 273 (1914).

We have used the symbol Δ to denote change in a function because of the chemical reaction. Under this notation, equation (10.50) becomes

$$\Delta F = \Delta H - T\,\Delta S \tag{10.51}$$

which is a fundamental equation for the free energy change of a chemical reaction at constant temperature. The free energy change can be evaluated if ΔH and ΔS are known, the heat of reaction if ΔF and ΔS are known, and the entropy change if ΔF and ΔH are known, the last being given by the relation [compare equation (10.48)]

$$-\Delta S = \frac{\Delta F - \Delta H}{T} \tag{10.52}$$

In a reaction system for which the reversible work is given by

$$P\,\Delta V + w'$$

w' being all forms of reversible work other than that of expansion, and $q_r = T\,\Delta S$, we have, from the first law equation,

$$\Delta E = q_r - w_r = T\,\Delta S - P\,\Delta V - w' \tag{10.53}$$

But, at constant pressure,

$$\Delta H = \Delta E + P\,\Delta V \tag{10.54}$$

If equations (10.53) and (10.54) are combined with (10.51), we have

$$\Delta F = -w'$$

which is the equation derived earlier as equation (10.17).

Free Energy Change in Equilibrium Reactions at Constant Pressure. We have seen that equilibrium reactions are characterized by having $w' = 0$. Let us see how the free energy change of such a reaction (at constant temperature and pressure) changes with temperature and with pressure. On differentiating equation (10.51) with respect to temperature, we have

$$\frac{d\,\Delta F}{dT} = \frac{d\,\Delta H}{dT} - T\frac{d\,\Delta S}{dT} - \Delta S \tag{10.55}$$

But, from equation (10.4) or (10.29), for an equilibrium process at constant pressure and the temperature T

$$\Delta H_P = T\,\Delta S_P \qquad \text{and} \qquad \frac{d\,\Delta H_P}{dT} = T\frac{d\,\Delta S_P}{dT}$$

so that equation (10.55) becomes

$$\left(\frac{d\,\Delta F}{dT}\right)_P = -\Delta S \tag{10.56}$$

TABLE 10.2.—THE FREE ENERGY FUNCTIONS AND THE MAXIMUM WORK

Maximum work $= \mathrm{D}w_r = -\mathrm{d}E + T\,\mathrm{d}S$

Maximum useful work $= \mathrm{D}w_r - P\,\mathrm{d}V = \mathrm{D}w'$

Conditions	Work content function A	Free energy function F
Defining equation	$A \equiv E - TS$	$F \equiv H - TS$ $\equiv E + PV - TS$
General differential equation	$\mathrm{d}A = \mathrm{d}E - T\,\mathrm{d}S - S\,\mathrm{d}T$ $= -\mathrm{D}w_r - S\,\mathrm{d}T$	$\mathrm{d}F = \mathrm{d}E + P\,\mathrm{d}V + V\,\mathrm{d}P - T\,\mathrm{d}S - S\,\mathrm{d}T$ $\mathrm{d}F = -\mathrm{D}w_r + P\,\mathrm{d}V + V\,\mathrm{d}P - S\,\mathrm{d}T$ $= -\mathrm{D}w' + V\,\mathrm{d}P - S\,\mathrm{d}T$
For constant temperature	$\mathrm{d}A = -\mathrm{D}w_r$	$\mathrm{d}F = -\mathrm{D}w' + V\,\mathrm{d}P$
At constant volume	$\mathbf{d}\boldsymbol{A_V} = \mathbf{-(D}\boldsymbol{w_r}\mathbf{)}_{\boldsymbol{V}} = \mathbf{-(D}\boldsymbol{w'}\mathbf{)}_{\boldsymbol{V}}$	$\mathrm{d}F_V = -(\mathrm{D}w')_V + V\,\mathrm{d}P$ $= \mathrm{d}A_V + V\,\mathrm{d}P$
At constant pressure	$\mathrm{d}A_P = -(\mathrm{D}w_r)_P$	$\mathbf{d}\boldsymbol{F_P} = \mathbf{-(D}\boldsymbol{w'}\mathbf{)}_{\boldsymbol{P}}$ $= \mathbf{d}\boldsymbol{A_P} + \boldsymbol{P}\,\mathbf{d}\boldsymbol{V}$
For a chemical reaction:		
At constant temperature	$\Delta A = -w_r$ $= \Delta E - T\,\Delta S$	$\Delta F = -w_r + \Delta(PV)$ $= \Delta E + \Delta(PV) - T\,\Delta S$
At constant volume	$\boldsymbol{\Delta A_V} = \boldsymbol{-(w_r)_V} = \boldsymbol{-(w')_V}$	$\Delta F_V = -(w_r)_V + V\,\Delta P$
At constant pressure	$\Delta A_P = -(w_r)_P$	$\boldsymbol{\Delta F_P} = \boldsymbol{-(w_r)_P + P\,\Delta V} = \boldsymbol{-w'}$
No net work, $-w' = 0$:		
At constant temperature	$\mathbf{d}\boldsymbol{A_T} = \boldsymbol{-P}\,\mathbf{d}\boldsymbol{V}$	$\mathbf{d}\boldsymbol{F_T} = \boldsymbol{V}\,\mathbf{d}\boldsymbol{P}$
At constant volume	$\mathbf{d}\boldsymbol{A_V} = \boldsymbol{-S}\,\mathbf{d}\boldsymbol{T}$	$\mathrm{d}F_V = V\,\mathrm{d}P - S\,\mathrm{d}T$
At constant pressure	$\mathrm{d}A_P = -P\,\mathrm{d}V - S\,\mathrm{d}T$	$\mathbf{d}\boldsymbol{F_P} = \boldsymbol{-S}\,\mathbf{d}\boldsymbol{T}$
For constant temperature, when $w = 0$ (no net work):		
At constant volume	$\mathbf{d}\boldsymbol{A_{V,T}} = \mathbf{0}$	$\mathrm{d}F_{V,T} = V\,\mathrm{d}P$
At constant pressure	$\mathrm{d}A_{P,T} = -P\,\mathrm{d}V$	$\mathbf{d}\boldsymbol{F_{P,T}} = \mathbf{0}$
For a chemical reaction at equilibrium, $w' = 0$, and at constant temperature:		
At constant volume	$\boldsymbol{\Delta A_{V,T}} = \mathbf{0}$	$\Delta F_{V,T} = V\,\Delta P$
At constant pressure	$\Delta A_{P,T} = -P\,\Delta V$	$\boldsymbol{\Delta F_{P,T}} = \mathbf{0}$

which is analogous to equation (10.47). When equation (10.52) is combined with equation (10.56), we have the Gibbs-Helmholtz equation for the chemical reaction

$$\left(\frac{\mathrm{d}\,\Delta F}{\mathrm{d}T}\right)_P = \frac{\Delta F - \Delta H}{T} \tag{10.57}$$

which is analogous to equation (10.49).

The above equations have been derived for the restricted condition of the equilibrium reaction. However, they now contain only functions that are properties of the systems under consideration. These properties are not subject to the path over which the reaction occurs, and the equations may therefore be applied to nonequilibrium reactions. The application of these equations is discussed later.

In a spontaneous process the actual net work may be zero, but the final free energies and entropies and volumes have values depending only on the final state. The values of the $V\,\mathrm{d}P$ and the $S\,\mathrm{d}T$ terms differ for the irreversible and reversible processes, but in such a manner as to produce the same value of $\mathrm{d}F$ for the process.

Summary.—The relations between the maximum total work, the maximum net work, and the free energy functions A and F have been derived and discussed for various restrictive conditions such as those of constant temperature, constant volume, and constant pressure. Some of these equations are assembled in Table 10.2. As we have stated, the free energy function F is most useful under the experimental condition of constant pressure and temperature, whereas the total work function A is more useful at constant volume. The more useful and commonly used functions are emphasized in the table by bold-faced type.

Problems

10.1. Calculate the change in free energy ΔF (in calories) for the following reactions at 100°C:

(a) H_2O(liq) = H_2O(g, 0.9 atm)
(b) H_2O(liq) = H_2O(g, 1.0 atm)
(c) H_2O(liq) = H_2O(g, 1.1 atm)

Explain, with the aid of the free energy function, which of these reactions are possible.

10.2. For the isothermal expansion of a mole of an ideal gas, show that the increase in free energy is

$$F_2 - F_1 = \mathbf{R}T \ln \frac{P_2}{P_1}$$

10.3. Derive equation (10.42)

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

and equation (10.44)

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

from the relations in Table 10.1.

10.4. At 100°C what is the change in free energy (in calories) of 1 mole of liquid water when the pressure is increased by 1 atmosphere? Assume the water to be essentially incompressible.

10.5. What is the change in free energy when 1 mole of water at 100°C and 1 atmosphere is changed to steam at the same temperature and pressure? What is the change in A?

10.6. Combining the results from Probs. 10.4 and 10.5, calculate the change in free energy when 1 mole of water at 2 atmospheres and 100°C is changed isothermally to steam at 1 atmosphere pressure.

10.7. For a chemical reaction at constant volume, show that

$$\left(\frac{d\,\Delta A}{dT}\right)_V = \frac{\Delta A - \Delta E}{T} \tag{10.58}$$

Explain the meaning of ΔA and ΔE for such a process.

10.8. For a cell in which the reaction is

$$\tfrac{1}{2}H_2(g, P = 1) + AgCl(c) = HCl(aq, a = 1) + Ag(c)$$

the standard emf at 25°C is 0.2225 int volt. What is the value of the standard free energy change for the reaction? The value of ΔA?

10.9. Is there a change in free energy for the mixing of toluene and xylene described in Prob. 7.8? Explain.

10.10. What is the change in free energy as a result of the separation of the nitrogen and oxygen from air, as described in Prob. 8.7, for nitrogen? For oxygen?

10.11. How does the free energy F of a perfect gas change with temperature at constant pressure? At constant volume?

10.12. How does the Helmholtz free energy (total work function) A of a perfect gas change with temperature at constant pressure? At constant volume? Compare with the results from Prob. 10.11.

10.13. In thermodynamic calculations, the Berthelot equation of state for gases

$$Pv = RT\left[1 + \frac{9}{128}\frac{P}{P_c}\frac{T_c}{T}\left(1 - 6\frac{T_c^2}{T^2}\right)\right] \tag{10.59}$$

is frequently used to evaluate the deviation of the real gas from ideal behavior when other data are lacking. In this equation, P_c and T_c are the critical pressure and critical temperature, respectively. Show the relation between the correction term in equation (10.59) and the second virial coefficient B.

10.14. For nitrogen, calculate values of the second virial coefficient B from the critical data and the Berthelot equation at the temperatures −150, −100, −50, 0, 50, 100, 300, and 600°C and compare with the values of B read from Fig. 4.3. What percentage error is introduced into the molar volume when the Berthelot equation is used to calculate the molar volume at these temperatures? Compare the molar volumes with those obtained in Prob. 4.17.

10.15. The density of propylene gas is 1.9149 grams per liter at 0°C and 1 atmosphere according to T. Batuecas [*J. chim. phys.*, **31,** 165 (1934)]. Calculate for this gas

(a) The molar volume of the gas.
(b) The second virial coefficient B.
(c) The compressibility factor $P\mathrm{v}/RT$.
(d) The value of $\mathrm{F}_2 - \mathrm{F}_1$ for the isothermal expansion of the gas from $P = 1$ to $P = 0.5$.

10.16. For a real gas obeying the Berthelot equation (10.59) in Prob. 10.13, show that the thermal expansion is expressed by

$$\left(\frac{\partial \mathrm{v}}{\partial T}\right)_P = \frac{R}{P}\left(1 + \frac{27}{32}\frac{P}{P_c}\frac{T_c{}^3}{T^3}\right)$$

What are the values of $(\partial \mathrm{s}/\partial P)_T$ and of $(\partial \mathrm{E}/\partial P)_T$ for a Berthelot gas and for an ideal gas. Integrate the expressions for $(\partial \mathrm{s}/\partial P)_T$ between the pressures $P = 0$ and $P = P$, and obtain the entropy difference

$$\mathrm{s}_{\text{ideal}} - \mathrm{s}_{\text{Berthelot}} = \frac{27RT_c{}^3P}{32T^3P_c}$$

remembering that, at $P = 0$, the Berthelot gas becomes identical with the ideal gas. Derive the corresponding expression for $\mathrm{F}_{\text{ideal}} - \mathrm{F}_{\text{Berthelot}}$.

CHAPTER 11

FREE ENERGY CHANGE IN CHEMICAL REACTIONS

The free energy of a system depends on the pressure, temperature, and composition of the system, as indicated in the general equation (10.39). As we shall show later, the net work w' in a chemical reaction results from a change in composition of the system; it is, therefore, of special interest to chemists who are concerned with producing desired substances. When temperature and pressure are kept constant, there will still be a change in the free energy function F if a change in composition produces net work.

Free Energy of Reaction.—Consider a reaction system containing a moles of the substance A and b moles of the substance B, the molar free energy of the former being $\mathrm{F_A}$ and that of the latter, $\mathrm{F_B}$. If these substances react at constant pressure and temperature, according to the chemical equation

$$a\mathrm{A} + b\mathrm{B} = d\mathrm{D} + e\mathrm{E} \tag{11.1}$$

d moles of the substance D and e moles of the substance E are formed, having the molar free energies $\mathrm{F_D}$ and $\mathrm{F_E}$, respectively. In accordance with our previous conventions, the free energy change for the reaction is given by

$$\Delta F = F_2 - F_1 \tag{11.2}$$

Because F_1, the free energy of the system in the initial state with the composition $a\mathrm{A} + b\mathrm{B}$, equals $a\mathrm{F_A} + b\mathrm{F_B}$ and F_2, the free energy in the final state with the composition $d\mathrm{D} + e\mathrm{E}$, equals $d\mathrm{F_D} + e\mathrm{F_E}$, equation (11.2) may be expressed in the form

$$\Delta F = (b\mathrm{F_D} + e\mathrm{F_E}) - (a\mathrm{F_A} + b\mathrm{F_B}) \tag{11.3}$$

This change in free energy accompanying the isothermal constant-pressure chemical reaction is called the *free energy of reaction.*

For a process at constant pressure and temperature, such as the one above, we have seen that the decrease in free energy equals the maximum net work, the reversible work. According to equation (10.17), this relation may be expressed as $-\Delta F = w'$. For the special case of a reaction at equilibrium, there is no net work; hence, $w' = 0$, and $\Delta F = 0$. A reaction may proceed spontaneously if it can do the net work w', that is, if a decrease in free energy results from the reaction. If there is to be an increase in free energy, w' must be negative; that is, work must be done on the reaction system, and the reaction cannot be spontaneous in the forward direction. Instead, the spontaneous reaction will be the reverse reaction for which the sign of the free energy change is reversed.

The ice-water transformation at 1 atmosphere pressure is an equilibrium reaction used to define 0°c. Since the reaction is at equilibrium, $\Delta F = 0$, as indicated by the equation

$$H_2O(c) = H_2O(liq); \qquad \Delta F_{273.16} = \mathrm{F}_{\mathrm{water}} - \mathrm{F}_{\mathrm{ice}} = 0 \tag{11.4}$$

At some other temperature or pressure, the free energy change is not zero, for the free energy of water changes with pressure and temperature, according to equations (10.43) and (10.47). The free energy of ice also changes with pressure and temperature but at a rate different from that of liquid water, for the specific volumes and entropies of ice and water differ. Ice and water can be at equilibrium only at temperatures and corresponding pressures at which the free energy functions of the two have the same value. In Chap. 10, we found for the freezing of water to ice at -10°c that $\Delta H - T\,\Delta S$, which equals ΔF and, therefore, $\mathrm{F}_{\mathrm{ice}} - \mathrm{F}_{\mathrm{water}}$, had the value, -51 calories per mole. Hence, under these conditions, a mole of water has 51 calories more free energy than a mole of ice. If we know the free energy of water as a function of pressure and temperature, and also the corresponding free energy function for ice, we can calculate the complete pressure-temperature curve for the ice equilibrium.

The combustion of graphite is a spontaneous process. At 25°c and at a constant pressure of 1 atmosphere, the free energy change for the formation of carbon monoxide[1] from graphite and oxygen is given by the equation

$$C(\text{graphite}) + \tfrac{1}{2}O_2(g, 1\text{ atm}) = CO(g, 1\text{ atm}); \qquad \Delta F = -32{,}808\text{ cal} \tag{11.5}$$

The formation of 1 mole of carbon monoxide from the elements results in a decrease in free energy of 32,808 calories. This value represents the maximum useful work that can be done in the formation of carbon monoxide at constant pressure and temperature. If the forward reaction is the spontaneous one, as in equation (11.5), the reverse reaction will not occur. When equation (11.5) is reversed, so that the decom-

---

[1] WAGMAN, D. D., J. E. KILPATRICK, W. J. TAYLOR, K. S. PITZER, and F. D. ROSSINI, *J. Research Natl. Bur. Standards*, **34**, 143 (1945). Strictly speaking, this free energy value is for fugacities equal to 1 atmosphere rather than for pressures equal to 1 atmosphere.

position reads from left to right, it becomes

$$CO(g,\ 1\ atm) = C(graphite) + \tfrac{1}{2}O_2(g,\ 1\ atm); \qquad \Delta F = 32{,}808\ cal \quad (11.6)$$

Here the free energy change is positive; the forward reaction will not take place spontaneously. At 25°C and 1 atmosphere pressure, carbon monoxide will not decompose spontaneously into the elements.

Free Energy of Formation.—Equation (11.5) states specifically that a mole of carbon monoxide has a free energy content 32,808 calories less than the elements of which it is composed at 25°C and 1 atmosphere. In terms of equation (11.3)

$$\Delta F = -32{,}808\ cal = F_{CO} - (F_C + \tfrac{1}{2}F_{O_2}) \qquad (11.7)$$

We may set up a table of *relative* free energy values for compounds by arbitrarily setting the free energies of the elements at zero. When this substitution is made in equation (11.7), $F_C = 0$, $\frac{1}{2}F_{O_2} = 0$, and

$$F_{CO} = \Delta F = -32{,}808$$

at the specified temperature and pressure. This value for a mole of carbon monoxide and the corresponding values calculated for the other compounds are called their *free energies of formation.* This procedure is exactly analogous with that used for setting up heats of formation in Chap. 5. If we wish to obtain the *absolute* free energy of formation of carbon monoxide from this value, we must know the absolute free energies of the elements carbon and oxygen at the experimental conditions, 25°C and 1 atmosphere pressure. This means in turn that we must have absolute values of H (and E). For most purposes, absolute free energies are not required; the relative values permit us to calculate the free energies of reaction for all reactions at the experimental conditions for which the free energies of formation are known.

Addition of Free Energy Equations.—Free energy equations may be added by the methods used for obtaining heats of reaction in the thermochemical equations previously written. Thus, if we know the free energy of formation of carbon dioxide at 25°C and 1 atmosphere pressure to be $\Delta F = -94{,}260$ cal, we may, on combining this value with that in equation (11.6), obtain the free energy of combustion of carbon monoxide to dioxide as illustrated below:

$$\begin{array}{rll} C + O_2 = CO_2; & \Delta F = -94{,}260\ cal & (11.8) \\ CO = C + \tfrac{1}{2}O_2; & \Delta F = 32{,}808\ cal & (11.6) \\ \hline CO + \tfrac{1}{2}O_2 = CO_2; & \Delta F = -61{,}452\ cal & (11.9) \end{array}$$

Under the experimental conditions, 25°C and 1 atmosphere pressure, at which the free energies of formation in equations (11.5) and (11.8) were measured, we find that carbon monoxide burns to the dioxide with a decrease in free energy of 61,452 calories. This isothermal reaction is therefore capable of doing this quantity of useful work for every mole of carbon monoxide burned if the reaction can be made to proceed reversibly. Unfortunately, such a process has not yet been devised.

Standard States.—Because the free energy change in a reaction is the difference between the free energy of the products of the reaction and that of the reactants, it is affected by any of the factors that change the free energies of any of the constituents of the reaction. Free energies are dependent on the temperature; hence, the free energy change in a reaction will, in general, change with the temperature. If free energies of reaction are reported, the temperature at which the reactions occur must be specified; and if tables of free energies of formation are prepared, some standard temperature must obviously be chosen. The temperature of 25°c has quite generally been selected for this purpose. Unless otherwise specified, we shall use this temperature as that of the standard state.

The pressure also has its influence on the free energy of reaction. According to equation (10.43), the change in free energy of a substance with pressure is measured by the specific volume. Because their molar volume is relatively small, solids and liquids do not show a large change of free energy with pressure. In describing the standard state of a pure liquid or a stable solid, therefore, it is usually sufficient to specify the temperature.

Gases, however, have molar volumes much larger than those of the condensed phases, and their change in free energy with pressure is appreciable. For this reason, it is necessary to specify the pressure as well as the temperature of the different reacting substances. Indeed, the partial pressures in the reacting system must be considered in some detail; for, though all the constituents usually have the same temperature, they do not necessarily have the same partial pressures. In describing the state of a gas, therefore, its partial pressure is specified as well as its temperature, the standard pressure usually selected being 1 atmosphere. At times, the standard pressure selected for gases is not that of the gas at a pressure of 1 atmosphere but at a fugacity of 1 atmosphere. For dissolved substances, the standard state frequently selected is that of unit activity. The concepts of activity and of fugacity will be developed later. Because the difference in free energy between the standard states of unit fugacity and unit pressure are not great for a gas that is nearly ideal, we shall not always distinguish between the two standard states at this point. The student is warned, however, that some of the data we use are for the standard state of unit fugacity.

When the reactants and the products of a reaction are all at their standard states, the free energy change of the reaction becomes the *standard free energy change* designated by a superscript °. Thus, since the partial pressures of the gases in equation (11.9) are 1 atmosphere, we may write, for the free energy of this reaction,

$$\Delta F^{\circ}_{298.16} = -61{,}452 \text{ cal}$$

The standard free energy change in equation (11.9) results from the reaction of 1 mole of pure carbon monoxide and $\frac{1}{2}$ mole of pure oxygen, each at a partial pressure of 1 atmosphere. These initial conditions are different from those which obtain when a mixture of 1 mole of carbon monoxide and $\frac{1}{2}$ mole of oxygen under a total pressure of 1 atmosphere reacts. When the pure gases mix, there is a free energy change of mixing equal to the loss in reversible net work w'. The mixing of the pure gases is a spontaneous process proceeding with a loss in free energy in accordance with the rules previously stated. This free energy of mixing is included in the value −61,452 calories for the free energy of the reaction. There is a free energy of mixing even though there is no significant heat of mixing. On the other hand, these gases are so nearly ideal that their heat of mixing is negligible compared with their heat of combustion. For this reason, we have discussed the standard state in more detail here than we did earlier in connection with the heat content change ΔH.

When pure solids and liquids are diluted with solvents to form solutions, their concentrations change with an accompanying change in their free energies. There is a free energy of formation of the solutions even though there is no heat of solution ΔH. In addition, there may be free energy changes resulting from specific interaction between the solvent and solute. The partial molal free energy of a substance in solution differs, therefore, from the molar free energy of the substance in the pure state. Either state may be chosen as the standard reference state. These questions will be considered in more detail in the discussion of solutions.

Change of Free Energy of a Gas with Pressure.—For a simple substance the change of free energy with pressure was given by equation (10.43) as

$$\left(\frac{\partial F}{\partial P}\right)_T = \qquad (11.10)$$

For pure solids and liquids, this change in free energy becomes a significant contributing factor to the free energy only if the pressure change is relatively great, for their specific volume V is small. With gases, however, rather small pressure changes may make large changes in the free energy, especially at the lower pressures where the molar volume is large. Let us consider n moles of a perfect gas whose pressure and volume are related by the ideal gas equation, so that $V = nRT/P$. If this value of V is substituted in equation (11.10) it can be integrated between the states 1 and 2 at the temperature T to give the equation

$$F_2 - F_1 = \int_{P_1}^{P_2} V\,dP = nRT \ln \frac{P_2}{P_1} \tag{11.11}$$

It is evident that the change of free energy with pressure depends not on the absolute value of the pressures but on their ratio and that the free energy change depends directly on the absolute temperature. For 1 mole of gas the change in free energy accompanying a tenfold pressure drop at 25°c is

$$\begin{aligned} F_2 - F_1 &= 2.3026 \times 1.9872 \times 298.16 \log 0.1 \\ &= 4.5757 \times 298.16 \times (-1) = -1{,}364 \text{ cal} \end{aligned}$$

Because the mole of gas at a partial pressure of 1 atmosphere has 1,364 calories more free energy than it has at 0.1 atmosphere, it is apparent that the state of a gas must be carefully defined in free energy calculations.

Free Energy Change in Galvanic Cell Reactions.—In Chap. 10, we indicated that the free energy represents the maximum energy available as useful work and that, in some reactions, the useful work may be obtained in the form of electrical work. In terms of the electronic theory, it is entirely reasonable for chemical free energy to appear as electrical energy, for all oxidation-reduction reactions involve a transfer of electrons and a resulting electric current. The electrical work is represented by the equation

$$w_e = nFE$$

where E represents the emf of the galvanic cell, F the faraday constant, and n the number of equivalents passing through the cell. If the reaction is carried out reversibly at constant temperature, the work and, therefore, E are at a maximum, and the maximum work is a measure of the decrease in free energy. At constant pressure, the decrease in the free energy is

$$-\Delta F = w' = w_e = nFE \tag{11.12}$$

and at constant volume the decrease in work content, or "Helmholtz free energy," is

$$-\Delta A = w_r = w_e = nFE \tag{11.13}$$

Insofar as ΔA_V differs from ΔF_P, the emf of the cell at constant volume must differ from that at constant pressure. The galvanic cell offers a convenient method for obtaining free energies, for the reversible emf of a cell can be measured with a potentiometer. If the emf is zero, the cell is at equilibrium and there is no change in free energy.

From the relation in equation (11.12), it is evident that free energies of reaction may be obtained directly from emf measurements. Reversible cells furnish one of the most accurate methods for deriving the free energy values. When the emf of a cell is expressed in international volts and the faraday constant has the values indicated in Chap. 1, the free energy change for the cell reaction becomes

$$\Delta F = -n96{,}501E \text{ int joules} \tag{11.14}$$
$$\Delta F = -n23{,}068E \text{ cal} \tag{11.15}$$

Values for the emf of a reversible cell may be obtained from the appropriate values for the single electrode potentials by the methods previously discussed for the addition of the chemical equations and discussed in greater detail in Chap. 20. Thus, for the formation of silver chloride at 25°c, we have, from the half-cell reactions,

$$\text{Ag(c)} + \text{Cl}^- = \text{AgCl(c)} + \text{e}^-; \qquad E^\circ = -0.2225 \text{ volt} \tag{11.16}$$
$$\tfrac{1}{2}\text{Cl}_2\text{(g)} + \text{e}^- = \text{Cl}^-; \qquad E^\circ = 1.3587 \text{ volts} \tag{11.17}$$
$$\text{Ag(c)} + \tfrac{1}{2}\text{Cl}_2\text{(g)} = \text{AgCl(c)}; \qquad E^\circ = 1.1362 \text{ volts} \tag{11.18}$$

As before, the superscript ° is used to show that the indicated value of E is for the reactants and products in their standard states. Because there is one equivalent of electricity passing through the cell in this reaction, n is unity and the free energy change for reaction (11.18) is

$$\Delta F^\circ = -23{,}068 \times 1.1362 = -26{,}210 \text{ cal}$$

The formation of solid silver chloride from the elements is, therefore, a spontaneous reaction.

Change of Emf with Temperature.—The change of the emf of a galvanic cell with temperature may be obtained by substituting the value for ΔF in equation (11.12) in (10.57). As a result, we have

$$\left(\frac{\mathrm{d}\,\Delta F}{\mathrm{d}T}\right)_P = -nF\left(\frac{\mathrm{d}E}{\mathrm{d}T}\right)_P = \frac{-nFE - \Delta H}{T} \tag{11.19}$$

This equation may be rearranged in the form

$$nFE + \Delta H = nFT\left(\frac{\mathrm{d}E}{\mathrm{d}T}\right)_P \tag{11.20}$$

or the form

$$E = -\frac{\Delta H}{nF} + T\left(\frac{\mathrm{d}E}{\mathrm{d}T}\right)_P \tag{11.21}$$

These equations may be used to calculate dE/dT if ΔH and E are known or to calculate ΔH if E and dE/dT are known. It is possible for some reactions to get a more accurate value for ΔH by this method than by a direct calorimetric one.

Free Energy and the Heat of Reaction.—In an attempt to formulate a rule concerning the direction of chemical reactions, Berthelot stated that spontaneous reactions proceed so as to form the substance, or substances, which involves the evolution of the maximum amount of heat. This "principle" has been mistakenly called the "principle of maximum work." As was previously deduced, the maximum work in a reaction depends not on the heat evolved but on the change in free energy. The principle of Berthelot is, therefore, in error whenever the maximum heat evolved does not give the results predicted by the free energy change.

The relation between the change in free energy and the heat of reaction for an isothermal reaction at constant pressure was given by equation (10.51), which becomes, on change of sign,

$$-\Delta F = -\Delta H + T\,\Delta S \tag{11.22}$$

$T\,\Delta S$ equals the absorption of heat from the surroundings for the reversible process; if there is no change of entropy, that is, no exchange of heat between the reacting system and its surroundings, equation (11.22) becomes

$$-\Delta F = -\Delta H = w'$$

But $-\Delta H$ is the heat evolved by the process as carried out in a constant-pressure calorimeter. In a reversible process that proceeds without entropy change, all this energy would appear as useful work.

When heat is absorbed as the reversible process occurs, $T\,\Delta S$ is positive, and

$$-\Delta F > -\Delta H$$

that is, more work can be derived from the reversible process than would have been obtained if all the energy evolved as heat in the irreversible calorimetric process had appeared as work. On the other hand, if heat is evolved during the reversible process, $T\,\Delta S$ is negative, the work obtainable directly is less than the heat evolved in the calorimetric process, and

$$-\Delta F < -\Delta H$$

If the $T\,\Delta S$ energy is sufficiently large, ΔF and ΔH may be opposite in sign. It is in such cases that the use of the sign of ΔH as a criterion of the direction of reaction leads to erroneous conclusions. A reaction may proceed whenever the occurrence of the reaction would result in a free energy decrease; if so large an amount of heat is evolved by the reversible reaction that $T\,\Delta S > -\Delta F$, ΔH is positive. Such an example is found among the list of problems.

Some Numerical Relations between Free Energy and Heat Content. The relations between ΔF, ΔH, and $T\,\Delta S$ for some reactions are illustrated in Table 11.1. When 1 mole of graphite is burned to carbon dioxide under the standard conditions, the heat evolved is 94,052 calories. This value is very nearly equal to the decrease in free energy, which is 94,260 calories. Observe, however, that the work that might be obtained from the reversible combustion is 208 calories greater than the heat obtained from the irreversible combustion at 25°. In the reversible process, therefore, 208 calories of energy will be absorbed from the surroundings by the reacting system; this reversible heat $T\,\Delta S$ will be available for the performance of useful work so that $-\Delta F$ is greater than $-\Delta H$. Similarly, when graphite burns to carbon monoxide, the decrease in free energy is 32,808 calories; this quantity of work could be done in the reversible combustion. In this process, energy of the quantity $T\,\Delta S = 6{,}392$ calories would be absorbed from the surroundings. The decrease in heat content during the reaction is only 26,416 calories. If this process could be carried out reversibly and the free energy converted to heat in a room, more heat would be introduced into the room than if the irreversible combustion occurred within the room, the surroundings being required to donate energy in the former process.

TABLE 11.1.—CHANGES IN FREE ENERGY, HEAT CONTENT, AND ENTROPY FOR SOME REACTIONS*

[Standard conditions: 25°c and 1 atmosphere pressure (unit fugacity for gases)]

Reaction	$\Delta F°$, cal	$\Delta H°$, cal	$T\,\Delta S°$, cal	$\Delta S°$, cal/deg
C(graphite) + $\frac{1}{2}O_2$(g) = CO(g)	−32,808	−26,416	6,392	21.439
C(graphite) + O_2(g) = CO_2(g)	−94,260	−94,052	208	0.697
C(graphite) + $2H_2$(g) = CH_4(g)	−12,140	−17,889	− 5,749	−19.283
C(graphite) = C(diamond)	685	453	− 232	− 0.778
H_2(g) + $\frac{1}{2}O_2$(g) = H_2O(g)	−54,635	−57,798	− 3,163	−10.607
H_2(g) + $\frac{1}{2}O_2$(g) = H_2O(liq)	−56,690	−68,317	−11,627	−38.997
Ag(c) + $\frac{1}{2}Cl_2$(g) = AgCl(c)	−26,210	−30,342	− 4,132	−13.86

---

[*] The values for the reactions of carbon and hydrogen are from the tables of D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer, and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

In the above reactions where ΔS is positive, the reactions proceed with an increase in entropy. In the combustion of hydrogen to form liquid water, there is a decrease in $T\,\Delta S^\circ$ of 11,627 calories. From the principle of the entropy increase in spontaneous reactions, one might assume that the reaction would not be a spontaneous one. However, the reaction is spontaneous, for it results in a decrease in free energy of 56,690 calories. Under the experimental conditions of constant temperature and pressure, the decrease in free energy is the measure of the spontaneity of a reaction. The principle of the increase in entropy can be applied only to a process at constant energy and volume and not necessarily to one at constant pressure and temperature.

For the formation of solid silver chloride, we found the change in free energy at 25°c to be −26,210 calories. The heat of formation at constant pressure and 18°c is −30,300. Neglecting, for the present, any change of this heat of reaction with temperature in the interval 18 to 25°, we obtain a value of −4,092 calories for the value of $T\,\Delta S$. This quantity of energy will be evolved by the cell to the thermostat during the reversible process, while the maximum net work done by the cell is 26,210 calories. Here the reversible work is smaller than the change in heat content.

Free Energies from Thermal Data.—From the fundamental relation between the free energy, heat content, and entropy, we found, for the constant-pressure isothermal process

$$\Delta F = \Delta H - T\,\Delta S \tag{11.23}$$

which was derived earlier [equation (10.51)]. Because of this relationship, we may calculate the free energy change for any reaction for which we know the values of ΔH and ΔS. The entropy change in the reaction can be calculated from the individual entropies of the elements and compounds by the usual methods of combining the necessary chemical equations. Tables of standard entropies as well as of standard heats of formation prepared in this way, therefore, enable us to obtain the desired free energy values.

We are accustomed to the calculation of heat content from relative values of H. For various reasons, however, entropies of elements and compounds are reported on an absolute or a pseudoabsolute basis. By use of the third law of thermodynamics, which establishes the absolute value at the zero absolute of temperature, the standard entropy of a simple system, consisting of an element or a compound, can be obtained from the heat capacity data of the substance from low temperatures up to the standard temperature. Thus, from equation (8.10), the increase in entropy of 1 mole of simple substance, between two temperatures at constant pressure, is

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_P}{T} \, dT = \int_{T_1}^{T_2} c_P \, d \ln T \qquad (11.24)$$

Any change in phase that occurs in the simple substance is usually indicated by an abnormal heat capacity, as discussed in Chap. 5. When all heat effects are taken into account, the entropy of a simple substance at 25°c is the entropy of that substance in excess of the entropy value at the zero absolute. A second method for calculating the entropies of simple substances is based on an analysis of the band spectrum of the substance. As stated earlier, the precision of this method in many cases exceeds that of the method based on heat capacity data.

TABLE 11.2.—ENTROPIES OF SOME SUBSTANCES IN THEIR STANDARD STATES AT 25°C
(In calories per degree mole)

Substance* (formula)	$s^{\circ}_{298.16}$	Substance† (formula)	$s^{\circ}_{298.16}$
O_2(g)	49.003	Ca(c)	9.95
H_2(g)	31.211	CaO(c)	9.5
H_2O(g)	45.106	$CaCO_3$(calcite)	22.2
H_2O(liq)	16.716	Cl_2(g)	53.31
N_2(g)	45.767	HBr(g)	47.48
C(graphite)	1.3609	HCl(g)	44.66
C(diamond)	0.5829	HI(g)	49.36
CO(g)	47.301	Pb(c)	15.51
CO_2(g)	51.061	$PbCl_2$(c)	32.6
CH_4(g)	44.50	Ag(c)	10.21
		AgCl(c)	23.0

* Values for the substances in this column are from D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer, and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143, 1945.

† Values for the substances in this column are from K. K. Kelley, *U. S. Bur. Mines, Bull.* 434, revision of 1940, or from later data.

Tables of entropies based on either or both of these two methods are now available. A few entropy values are listed in Table 11.2.[1] Selecting the entropies of silver, chlorine, and silver chloride, we have for the reaction

$$Ag(c) + \tfrac{1}{2}Cl_2(g) = AgCl(c); \qquad \Delta S^{\circ}_{298.16} = -13.86 \text{ cal/deg} \qquad (11.25)$$

---

[1] Extensive entropy tables are given by W. M. Latimer, "Oxidation States of the Elements and Their Potentials in Aqueous Solution," Appendix V, p. 328, Prentice-Hall, Inc., New York, 1938, and by K. K. Kelley, "Contributions 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. References to the original literature are included. For the hydrocarbons, see Tables "t" of the "American Petroleum Institute Research Project 44 at the National Bureau of Standards." Entropy values are given up to 1500°K.

From this value, we find that, at 25°, $T\,\Delta S = -4{,}132$ cal. Compare this value with the value of $-4{,}092$ calories obtained earlier from the values of ΔF and ΔH. In this reaction the free energy value, obtained from emf measurements, and the entropy values are probably more accurate than the reported value for the heat of formation ΔH. In this case, therefore, we may obtain a revised value of ΔH. Thus,

$$\begin{aligned}\Delta H^\circ_{298.16} &= \Delta F^\circ + T\,\Delta S^\circ = -26{,}210 - 4{,}132 \\ &= -30{,}342 \text{ cal}\end{aligned} \tag{11.26}$$

This value of ΔH° is probably more precise than that obtained from the direct calorimetric measurement.

For many reactions, however, the free energy change is not obtained so readily or so precisely. Indeed, it is frequently impossible to measure ΔF directly. Under these circumstances, ΔF can be obtained from the experimental values of ΔH and ΔS. Thus, for the formation of methane, we have, from the calorimetric data,

$$\text{C(graphite)} + 2\text{H}_2\text{(g)} = \text{CH}_4\text{(g)}; \qquad \Delta H^\circ = -17{,}889 \text{ cal} \tag{11.27}$$

and from Table 11.2

$$\Delta S^\circ = s^\circ(\text{CH}_4) - s^\circ(\text{C}) - 2s^\circ(\text{H}_2) = -19.283 \text{ cal/deg}$$

From these values, we find, at 25°C = 298.16°K

$$\Delta F^\circ = -12{,}140 \text{ cal} \tag{11.28}$$

As we shall see in the following chapter, this value of the standard free energy of formation of methane may be used to calculate the equilibrium constant for reaction (11.27).

Free Energy Change as a Function of the Temperature.—For a chemical reaction at constant pressure, the variation of the free energy change with temperature was given in equations (10.56) and (10.57) as

$$\left(\frac{\partial\,\Delta F}{\partial T}\right)_P = -\Delta S = \frac{\Delta F - \Delta H}{T} \tag{11.29}$$

As the equation stands, it cannot be integrated, but it can be put into a form suitable for integration by the following steps:

$$\frac{\partial\,\Delta F}{\partial T} = \frac{\Delta F}{T} - \frac{\Delta H}{T}$$

Upon dividing by T and rearranging,

$$\frac{\partial\,\Delta F}{\partial T}\,\frac{1}{T} - \frac{\Delta F}{T^2} = -\frac{\Delta H}{T^2}$$

But,

$$\frac{\partial\,\Delta F}{\partial T}\frac{1}{T} - \frac{\Delta F}{T^2} = \frac{T(\partial\,\Delta F/\partial T) - \Delta F}{T^2} = \frac{\partial}{\partial T}\left(\frac{\Delta F}{T}\right)$$

Hence,

$$\frac{\partial}{\partial T}\left(\frac{\Delta F}{T}\right) = -\frac{\Delta H}{T^2} \tag{11.30}$$

Although we have dropped the subscripts indicating constant pressure, we understand that the restriction of constant pressure is still maintained. In rearrangement, we obtain

$$d\left(\frac{\Delta F}{T}\right) = -\Delta H\,\frac{dT}{T^2} \tag{11.31}$$

If ΔH depends on T, according to the equation

$$\Delta H = \Delta H_0 + aT + bT^2 + cT^3$$

equation (11.31) may be integrated to give

$$\int d\left(\frac{\Delta F}{T}\right) = -\int\left(\frac{\Delta H_0}{T^2} + \frac{a}{T} + b + cT\right)dT$$

$$\frac{\Delta F}{T} = \frac{\Delta H_0}{T} - a\ln T - bT - \frac{1}{2}cT^2 + I \tag{11.32}$$

Equation (11.32), when multiplied by T, becomes

$$\Delta F = \Delta H_0 - aT\ln T - bT^2 - \tfrac{1}{2}cT^3 + IT \tag{11.33}$$

Either equation (11.32) or (11.33) may be used to calculate the free energy at any temperature if the dependence of ΔH on the temperature is known, and if the value of ΔF at some one temperature is known so that the constant of integration I may be evaluated. A greater accuracy of calculation with less effort can frequently be achieved if equation (11.32) instead of equation (11.33) is used in carrying out a calculation.

In Chap. 5, we found that, for the reaction in which the change in heat capacity is represented by the equation

$$\Delta C_P = \alpha + \beta T + \gamma T^2$$

and the change of heat of reaction with temperature by the equation

$$\frac{d\,\Delta H}{dT} = \Delta C_P = \alpha + \beta T + \gamma T^2$$

the value of ΔH at any temperature is

$$\Delta H = \Delta H_0 + \alpha T + \tfrac{1}{2}\beta T^2 + \tfrac{1}{3}\gamma T^3$$

which is equation (5.31). In terms of the constants, α, β, and γ, the equation for the free energy becomes

$$\Delta F = \Delta H_0 - \alpha T \ln T - \tfrac{1}{2}\beta T^2 - \tfrac{1}{6}\gamma T^3 + IT \qquad (11.34)$$

Just as we were able to add heat capacity and heat of reaction equations, so we can add free energy equations if they are expressed in similar terms. These equations are used in subsequent calculations.

Free Energy Equation for the Formation of Water.—In Chap. 5, we found the heat of formation of water vapor at 25° to be

$$\Delta H^\circ_{298.16} = -57{,}798 \text{ cal}$$

and the value of the heat of formation as a function of temperature to be [equation (5.36)]

$$\Delta H^\circ = -57{,}018 - 2.7649T + 0.4735 \times 10^{-3}T^2 + 0.879 \times 10^{-7}T^3 \qquad (11.35)$$

In Chap. 12, we shall derive the value of the standard free energy of formation at 25°, namely,

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(g); \qquad \Delta F^\circ_{298.16} = -54{,}635 \text{ cal} \qquad (11.36)$$

With these values, we are prepared to evaluate the integration constant in the equation for the free energy of formation of water as a function of temperature.

Where ΔH has the value indicated in equation (11.35), we obtain from (11.31), for the constant-pressure reaction,

$$d\left(\frac{\Delta F^\circ}{T}\right) = \left(+\frac{57{,}018}{T^2} + \frac{2.7649}{T} - 0.4735 \times 10^{-3} - 0.879 \times 10^{-7}T\right) dT$$

which becomes, on integration,

$$\frac{\Delta F^\circ}{T} = -\frac{57{,}018}{T} + 2.7649 \ln T - 0.4735 \times 10^{-3}T - 0.440 \times 10^{-7}T^2 + I \qquad (11.37)$$

where $2.7649 \ln T = 6.3665 \log T$.

If we knew the temperature at which the reacting substances at their standard pressures are at equilibrium, we could substitute this value of T and the value $\Delta F = 0$ in equation (11.37), thereby obtaining a value for the integration constant I. For this reaction, the standard free energy at 25° is more accurately known than the equilibrium temperature, so that this value, from equation (11.36), will be used in evaluating I. Again, to show the relative importance at 25°c of the various terms in equation (11.37), we shall outline the calculation in some detail. From equation (11.37), therefore,

$$I = \frac{2{,}383}{298.16} - 6.3665 \log 298.16 + 0.4735 \times 10^{-3}(298.16) + 0.440 \times 10^{-7}(298.16)^2$$
$$= 7.992 - 15.754 + 0.141 + 0.004$$
$$= -7.617$$

Equation (11.37), therefore, becomes

$$\frac{\Delta F^\circ}{T} = -\frac{57{,}018}{T} + 6.3665 \log T - 0.4735 \times 10^{-3}T - 0.440 \times 10^{-7}T^2 - 7.617 \quad (11.38)$$

As stated earlier, this form of the equation is occasionally more convenient to use than the more explicit form

$$\Delta F^\circ = -57{,}018 + 6.3665T \log T - 0.4735 \times 10^{-3}T^2 - 0.440 \times 10^{-7}T^3 - 7.617T \quad (11.39)$$

In the above calculation, we have carried more significant figures than the accuracy of the heat capacity equations warrants. This was done to secure internal consistency so that a reverse calculation would reproduce the coefficients of equation (11.35). Equation (11.39), of course, cannot give more accurate free energy values at the higher temperatures than the accuracy of the heat capacity equations permits.

Problems

11.1. If the standard entropy of ethane is 54.85 calories per degree at 25°c, what is the entropy change for the reaction

$$2\text{C(graphite)} + 3\text{H}_2 = \text{C}_2\text{H}_6\text{(g)}$$

Select the necessary data, and calculate ΔF° and ΔH° for this reaction.

11.2. For a cell in which the reaction is

$$\text{Ag(c)} + \text{HgCl(c)} = \text{AgCl(c)} + \text{Hg(liq)}$$

R. H. Gerke [*J. Am. Chem. Soc.*, **44**, 1684 (1922)] found, at 25°c

$$E^\circ_{298.16} = 0.0455 \text{ int volt}, \qquad \frac{dE}{dT} = 0.000338 \text{ int volt/deg}$$

Calculate ΔF°, ΔH°, and ΔS° for this reaction. Compare the signs of ΔF and ΔH. Will the reaction proceed spontaneously from left to right? Explain.

11.3. Select the necessary data from the tables in the preceding chapters and from Prob. 5.8, and calculate the values of ΔH°, ΔF°, and ΔS° at 25°c for the reaction

$$\text{CO}_2\text{(g)} + \text{H}_2\text{(g)} = \text{CO(g)} + \text{H}_2\text{O(g)}$$

11.4. From the heat of reaction equation derived in Prob. 5.8 and the datum $\Delta F^{\circ}_{298.16} = 6{,}817$ cal, derive the free energy equation

$$\Delta F^{\circ} = 9{,}934 - 1.1858T \log T + 3.116_5 \times 10^{-3}T^2 - 5.25_2 \times 10^{-7}T^3 - 8.402T$$

for the reaction

$$H_2(g) + CO_2(g) = H_2O(g) + CO(g)$$

Calculate $\Delta F_{1{,}000}$.

11.5. From the datum $\Delta F^{\circ}_{298.16} = 685$ and the heat of reaction equation derived in Prob. 5.10, derive the free energy equation

$$\Delta F^{\circ} = 541 + 1.177T \log T - 0.000221T^2 + \frac{6{,}700}{T} - 2.438T$$

for the transition

$$\text{C(graphite)} = \text{C(diamond)}$$

11.6. The value for the heat of formation of hydrogen chloride gas at 25°C is −22,063 calories per mole. Calculate the values for the standard entropy of formation and the standard free energy of formation of hydrogen chloride at 25°C.

11.7. For the reduction of carbon dioxide to carbon monoxide by hydrogen (Prob. 11.3), calculate the values of ΔE° and ΔA°. Compare with the values of ΔH° and ΔF°. Explain.

11.8. If the formation of ethane as expressed in Prob. 11.1 is carried out at constant pressure, what will be the volume change for the reaction? What will be values of ΔA_P and ΔE_P for this reaction? If the reaction is carried out at constant volume, what will be the values of ΔF_V and ΔH_V?

11.9. Because the classical heat capacity expression

$$C_P = a + bT + cT^2 + dT^3 \cdots \qquad (11.40)$$

fails to express heat capacity data at high temperatures, G. C. Maier and K. K. Kelley [*J. Am. Chem. Soc.*, **54,** 3243 (1932)] propose the expression

$$C_P = a + bT - cT^{-2} \qquad (11.41)$$

J. Chipman and M. G. Fontana [*ibid*, **57,** 48 (1935)] find a better fit with experimental data when an equation of the type

$$C_P = a + bT + cT^{-\frac{1}{2}} \qquad (11.42)$$

is used. Derive the expressions for the heat content H and the free energy F corresponding to equations (11.41) and (11.42). Compare with the equations derived in the text from equation (11.40).

11.10. For substances at high temperature, the heat content relative to that at 25°C is frequently expressed in the form

$$H_T - H_{298.16} = aT + bT^2 + \frac{c}{T} + d \qquad (11.43)$$

Derive the corresponding equations for C_P and $S_T - S_{298.16}$. What additional information is needed if values of $F_T - F_{298.16}$ are to be derived from equation (11.43)?

CHAPTER 12

FREE ENERGY CHANGE AND THE EQUILIBRIUM CONSTANT

As chemists, we have used the equilibrium constant as a measure of equilibrium states and of the distance of reacting systems from equilibrium. Because the free energy also measures this distance from the equilibrium state at constant temperature, it must be related to the equilibrium constant. Let us consider the reaction between the perfect gases A and B, and D and E as expressed in the general chemical equation

$$a\text{A} + b\text{B} + \cdots = d\text{D} + e\text{E} + \cdots \tag{12.1}$$

the gases being at partial pressures equal to P'_{A}, P'_{B}, P'_{D}, and P'_{E}, respectively. The equation then indicates that a moles of the gas A at the partial pressure P'_{A} react with b moles of the gas B at the partial pressure P'_{B} to form d moles of the gas D at the partial pressure P'_{D} and e moles of the gas E at the partial pressure P'_{E}. We have chosen a reaction among ideal gases because the properties of a mixture of ideal gases can be calculated from the known properties of the component pure gases.

The relation between the free energy change and the equilibrium constant can be obtained directly from the relations derived in the previous chapter. It may also be obtained from a study of an "equilibrium box" (Fig. 12.1). Hitherto, we have used analytical methods in deriving thermodynamic formulas and have avoided the use of cycles. However, the equilibrium box may be useful in a physical interpretation of the derived formulas. We shall develop it first as an example of the general method and then derive the relations formally.

Equilibrium Box.—The reaction in equation (12.1) may be carried out isothermally, reversibly, and at the constant pressure P with the aid of an "equilibrium box" illustrated in Fig. 12.1. In the reaction chamber I, the gases are present at equilibrium, the equilibrium partial pressures of the gases being P_{A}, P_{B}, P_{D}, and P_{E}, respectively, and the total pressure being constant at the value P. The reacting gases A and B are present at their initial partial pressures P'_{A} and P'_{B} in the reservoirs II and III, respectively. The products of the reaction D and E are present at their final partial pressures P'_{D} and P'_{E} in the reservoirs IV and V, respectively. The initial and final pressures may equal P, but they may be given any arbitrary values.

The reaction may be carried out as follows: The gases A and B are changed from their initial pressures to their equilibrium partial pressures and added to the reaction chamber I where they react reversibly and at equilibrium to form the gases D and E. As they form, D and E are removed at their equilibrium partial pressures and changed to their final pressures. In this way, *a* moles of A and *b* moles of B are converted reversibly and isothermally into *d* moles of D and *e* moles of E.

Consider the detailed process for A. When *a* moles of the gas, initially stored in II at the pressure P'_A, are transferred at this pressure to VI, no work or free energy changes are involved: as piston II moves down, piston VI moves up. In VI, the gas is changed from its initial pressure to its equilibrium partial pressure, the molar volume of the gas changing from the initial value v'_A to the equilibrium value v_A. From equation (4.39), the work done by *a* moles of the gas in this isothermal expansion is

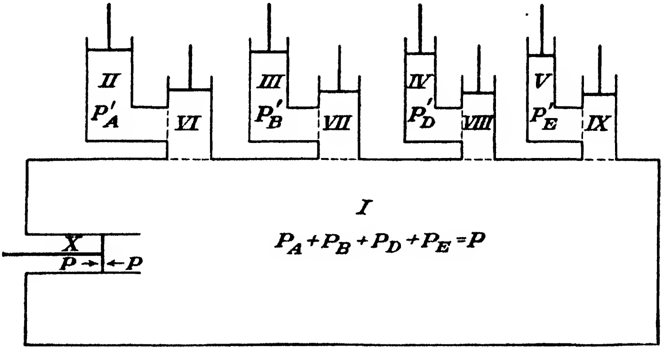


FIG. 12.1.—The equilibrium box. Key: (I) reaction chamber; (II), (III), (IV), (V), reservoirs for the gases A, B, D, and E, respectively; (VI), (VII), (VIII), (IX), piston chambers used to transfer the gases reversibly between the reservoir and the reaction chamber.

$$w_A = aRT \ln \frac{v_A}{v'_A} = aRT \ln \frac{P'_A}{P_A} \tag{12.2}$$

From equation (11.11), the free energy change in this process is

$$F_A - F'_A = aRT \ln \frac{P_A}{P'_A} \tag{12.3}$$

A comparison of equations (12.2) and (12.3) shows that the free energy change equals $-w_A$. The *a* moles of A are now transferred reversibly through a semipermeable membrane from VI to I at the equilibrium partial pressure P_A. The membrane, permeable only to A, permits A to pass at constant partial pressure from VI to I in spite of the presence of other gases in the reaction chamber. There is here no free energy change, there being no change in the partial pressure of A, but isobaric work is done on the gas. As A is transferred to I, the volume of I need not change for the gas is consumed in the reaction, but there is a change in volume of VI, a decrease equal to $-a\text{v}_A$ at the constant pressure P_A. In this constant-pressure process, the work done *by* the gas is

$$P\,\Delta V = -aP_A\text{v}_A = -aRT \tag{12.4}$$

in accordance with the gas laws.

In a similar way, b moles of B are introduced to the reaction chamber, there being work and free energy equations corresponding to equations (12.2) to (12.4). As the reaction proceeds at equilibrium, A and B are consumed and D and E are formed. The d moles of D and the e moles of E must then be removed and brought to their final pressures. The same operations are carried out as for A and B except that the direction is reversed. Thus, the work done by B in the transfer from VII to I at the equilibrium partial pressure is $-bRT$, being negative as in equation (12.4), but the work done by D and E in going from I to VIII and IX, respectively, is positive, the values being dRT and eRT.

The isobaric work, which does not involve a free energy change, is the sum of the isobaric work for the individual gases, namely,

$$w_P = -aRT - bRT + dRT + eRT = [(d + e) - (a + b)]RT \tag{12.5}$$

But the difference between $(d + e)$, the number of moles of gas produced, and $(a + b)$, the number of moles consumed, represents the increase in number of moles of gas as a result of the reaction. Let this increase Δn be defined as

$$\Delta n = (d + e) - (a + b) \tag{12.6}$$

It follows from equations (12.5) and (12.6) and the gas laws that

$$w_P = \Delta nRT = P\,\Delta V \tag{12.7}$$

where P is the total pressure of the reacting mixture and ΔV is the increase in volume as a result of the reaction, this increase being measured at the total pressure P. Only when there is no change in the number of moles as a result of the reaction will there be no external work w_P.

Now there was no spontaneity is the work of expansion w_P, for all this work is done at equilibrium pressures. On the other hand, the changes between the equilibrium and the initial or final pressures, though carried out reversibly, do not represent equilibrium processes. If more work can be secured from the expansion of the products of the reaction than is required to compress the reactants, useful net work results. The net work expression for B corresponding to equation (12.2) is

$$w_B = -bRT \ln \frac{P_B}{P'_B} \tag{12.8}$$

and the net work done by the products D and E between their equilibrium pressures and their final pressures is, respectively,

$$w_D = dRT \ln \frac{\mathrm{v}'_D}{\mathrm{v}_D} = -dRT \ln \frac{P'_D}{P_D} \tag{12.9}$$

and

$$w_E = -eRT \ln \frac{P'_E}{P_E} \tag{12.10}$$

From equation (10.16), the change in work content for this isothermal reaction is

$$\Delta A = -w_r = -w_P - w_A - w_B - w_D - w_E \tag{12.11}$$

The reaction is also an isobaric one so that, from equation (10.17), the change in the free energy is

$$\Delta F = -w' = -w_A - w_B - w_D - w_E \tag{12.12}$$

We have, then, for the reaction,

$$\begin{aligned} \Delta F &= aRT \ln \frac{P_A}{P'_A} + bRT \ln \frac{P_B}{P'_B} + dRT \ln \frac{P'_D}{P_D} + eRT \ln \frac{P'_E}{P_E} \\ &= RT \left[\ln \left(\frac{P_A}{P'_A} \right)^a + \ln \left(\frac{P_B}{P'_B} \right)^b + \ln \left(\frac{P'_D}{P_D} \right)^d + \ln \left(\frac{P'_E}{P_E} \right)^e \right] \\ \Delta F &= RT \ln \frac{P'^{\,d}_D P'^{\,e}_E}{P'^{\,a}_A P'^{\,b}_B} - RT \ln \frac{P_D{}^d P_E{}^e}{P_A{}^a P_B{}^b} = -w' \end{aligned} \tag{12.13}$$

Because the decrease in Helmholtz free energy equals the total work, we have, from equations (12.7), (12.11), and (12.12),

$$\Delta A = \Delta F - \Delta nRT$$

as may be deduced from the general relation $\Delta A = \Delta F - \Delta(PV)$.

Free Energy Change from the Partial Free Energies.—From equation (11.11), the change in free energy when a moles of the ideal gas A expand from a partial pressure of P'_A to a partial pressure P_A is given by

$$\int_{F_A'}^{F_A} dF_A = a \int_{P_A'}^{P_A} \mathrm{v}_A \, dP \tag{12.14}$$

If F'_A is the molar free energy of A at the partial pressure P'_A and if F_A is that of A at the equilibrium partial pressure, we have, from equation (12.14),

$$F_A - F'_A = a(\mathrm{F}_A - \mathrm{F}'_A) = aRT \ln \frac{P_A}{P'_A} \tag{12.15}$$

TABLE 12.1.—SUMMATION OF PARTIAL FREE ENERGY CHANGES FOR A REACTION

Step	Reaction	Free energy change
I	$a\mathrm{A}(P'_\mathrm{A}) = a\mathrm{A}(P_\mathrm{A})$	$\Delta F_\mathrm{I} = a(\mathrm{F}_\mathrm{A} - \mathrm{F}'_\mathrm{A})$
II	$b\mathrm{B}(P'_\mathrm{B}) = b\mathrm{B}(P_\mathrm{B})$	$\Delta F_\mathrm{II} = b(\mathrm{F}_\mathrm{B} - \mathrm{F}'_\mathrm{B})$
III	$a\mathrm{A}(P_\mathrm{A}) + b\mathrm{B}(P_\mathrm{B}) = d\mathrm{D}(P_\mathrm{D}) + e\mathrm{E}(P_\mathrm{E})$	$\Delta F_\mathrm{III} = 0$
IV	$d\mathrm{D}(P_\mathrm{D}) = d\mathrm{D}(P'_\mathrm{D})$	$\Delta F_\mathrm{IV} = d(\mathrm{F}'_\mathrm{D} - \mathrm{F}_\mathrm{D})$
V	$e\mathrm{E}(P_\mathrm{E}) = e\mathrm{E}(P'_\mathrm{E})$	$\Delta F_\mathrm{V} = e(\mathrm{F}'_\mathrm{E} - \mathrm{F}_\mathrm{E})$
Total	$a\mathrm{A}(P'_\mathrm{A}) + b\mathrm{B}(P'_\mathrm{B}) = d\mathrm{D}(P'_\mathrm{D}) + e\mathrm{E}(P'_\mathrm{E})$	$\Delta F = \Delta F_\mathrm{I} + \Delta F_\mathrm{II} + \Delta F_\mathrm{IV} + \Delta F_\mathrm{V}$

Corresponding equations may be written for the gases B, D, and E. Reaction (12.1) may be carried out by the reversible steps in Table 12.1, step III being the reversible reaction that occurs when all the gases are at their equilibrium pressures, so that $\Delta F = 0$. For the reaction indicated in equation (12.1), we have, therefore,

$$\begin{aligned} \Delta F &= \Delta F_\mathrm{I} + \Delta F_\mathrm{II} + \Delta F_\mathrm{IV} + \Delta F_\mathrm{V} \\ &= aRT \ln \frac{P_\mathrm{A}}{P'_\mathrm{A}} + bRT \ln \frac{P_\mathrm{B}}{P'_\mathrm{B}} + dRT \ln \frac{P'_\mathrm{D}}{P_\mathrm{D}} + eRT \ln \frac{P'_\mathrm{E}}{P_\mathrm{E}} \\ \Delta F &= RT \ln \frac{P'^{\,d}_\mathrm{D} P'^{\,e}_\mathrm{E}}{P'^{\,a}_\mathrm{A} P'^{\,b}_\mathrm{B}} - RT \ln \frac{P_\mathrm{D}{}^d P_\mathrm{E}{}^e}{P_\mathrm{A}{}^a P_\mathrm{B}{}^b} \end{aligned} \tag{12.16}$$

This equation is identical with equation (12.13) deduced from the operation of the equilibrium box.

Equilibrium Constant.—For an isothermal equilibrium process at constant pressure $\Delta F = 0$. Consequently, if the initial partial pressures of the reactants and the final partial pressures of the products of the reaction equal the equilibrium values, $\Delta F = 0$ for the reaction. Then, from equation (12.16),

$$RT \ln \frac{P_\mathrm{D}{}^d P_\mathrm{E}{}^e}{P_\mathrm{A}{}^a P_\mathrm{B}{}^b} = RT \ln \frac{P'^{\,d}_\mathrm{D} P'^{\,e}_\mathrm{E}}{P'^{\,a}_\mathrm{A} P'^{\,b}_\mathrm{B}}$$

and

$$\frac{P_\mathrm{D}{}^d P_\mathrm{E}{}^e}{P_\mathrm{A}{}^a P_\mathrm{B}{}^b} = \frac{P'^{\,d}_\mathrm{D} P'^{\,e}_\mathrm{E}}{P'^{\,a}_\mathrm{A} P'^{\,b}_\mathrm{B}} = K_P \tag{12.17}$$

where K_P is a constant called the *equilibrium constant* for the reaction. At constant temperature, we may vary the initial and final pressures in a reaction and still preserve equilibrium so long as the variation keeps constant the ratio

$$K_P = \frac{P_\mathrm{D}{}^d P_\mathrm{E}{}^e}{P_\mathrm{A}{}^a P_\mathrm{B}{}^b} \tag{12.18}$$

This is the relation known as the *law of mass action,* used widely by chemists in making calculations on equilibrium reactions. It was first derived not from thermodynamics but from kinetic considerations.

As early as the beginning of the nineteenth century, Berthollet called attention to the influence of quantity of reacting substances on a chemical reaction; but, unfortunately, he concluded that the influence of varying proportions of reactants resulted in compounds of varying composition. When the law of definite composition was established, the ideas concerning the effect of quantity of material on the course of a reaction were neglected for a half century. In 1863, Guldberg and Waage, using the concept "active mass," stated that the velocity of a chemical reaction depends on the products of the active masses of the reactants. If [A] and [B] represent the active masses of the reactants and [D] and [E] those of the products in a reaction

$$A + B = D + E$$

involving 1 mole of each of the reacting substance, the velocity of the forward reaction equals $p[A][B]$, and that of the reverse reaction $q[D][E]$, where p and q are constants characteristic of the reacting substances and of the temperature. For equilibrium,

$$p[A][B] = q[D][E]$$

or

$$\frac{[D][E]}{[A][B]} = \frac{p}{q} = K \qquad (12.19)$$

Equation (12.19) is a simplified form of (12.18), applying when the number of reacting moles, a, b, d, and e, are all unity. Guldberg and Waage suggested the use of concentration as a measure of active mass, or, as we would say now, of activity. We should take note that the law was derived for "active masses" and that it cannot be used in terms of concentration where concentration is not a measure of activity.

Standard Free Energy Change and the Equilibrium Constant.—In previous sections, we found that if reaction (12.1) is an equilibrium reaction the initial pressures of the reactants (P'_A and P'_B) and the final pressures of the products (P'_D and P'_E) are equilibrium pressures. Whenever these pressures are not equilibrium pressures, there is a free energy change. The greater the pressures of the reactants and the smaller the pressures of the products, the greater is the tendency for the reaction to proceed. This is readily explained from the kinetic point of view and just as readily from equation (12.16), which may be put in the form

$$\Delta F = RT \ln \frac{P'^d_D P'^e_E}{P'^a_A P'^b_B} - RT \ln K_P \qquad (12.20)$$

As P'_D and P'_E decrease and P'_A and P'_B increase, the fraction $P'^d_D P'^e_E / P'^a_A P'^b_B$ decreases, its logarithm decreases, and ΔF becomes more negative. From the thermodynamic as well as the kinetic standpoint, therefore, the reaction has a greater tendency to go. The tendency of a reaction to go depends on the initial and final concentrations or activities of reactants and products as well as on the value of the equilibrium constant, and there is a free energy change for each set of initial and final conditions. We must emphasize the fact that there are these different free energy changes even though temperature and pressure of the reaction remain unchanged. As equations (12.7) and (12.13) indicate, the total pressure P enters into the work of expansion but not the free energy of reaction.

If a standard state is selected for each constituent at which its initial or final pressure is unity, we have

$$P'_{\text{A}} = P'_{\text{B}} = P'_{\text{D}} = P'_{\text{E}} = 1$$

Under these conditions, equation (12.20) becomes

$$\begin{aligned} \Delta F &= \Delta F^\circ = 0 - RT \ln K_P \\ \Delta F^\circ &= -RT \ln K_P \end{aligned} \tag{12.21}$$

where ΔF° is the *standard free energy change* previously defined in Chap. 11. This standard free energy change is particularly useful because it can be calculated from, or used to calculate, the equilibrium constant.

We know that the numerical value of an equilibrium constant frequently depends on the units used. Each set of units implies a *different standard state* and the value of the standard free energy change changes with the shift in standard states. If the partial pressures P_{A}, P_{B}, and so forth, are expressed in millimeters then the standard state is taken as $P'_{\text{A}} = P'_{\text{B}} = 1$ mm. When we do not specify otherwise, we shall select 1 atmosphere pressure as the standard state of a gas.

Perhaps we should remind ourselves at this point that the free energy functions used in the derivations in this chapter are valid only for constant-temperature processes. Consequently, the equilibrium constant is a constant for the constant-temperature reaction and the standard free energy change refers to a reaction between substances in their standard states *at that temperature.* For simplicity, we have omitted the subscript $_T$, but it is implied in the preceding equations in this chapter.

Conventions in the Use of Equilibrium Constants.—In accordance with established usage, ΔF is positive when the final state has more free energy than the initial state. From equations (12.16) and (12.21), it appears that the free energy change is positive when $\ln K_P$ is negative, that is, when K_P has a fractional value. In the expression for K_P, the terms for the products of the reaction are uniformly written in the numerator and those for the reactants in the denominator of the mass action expression. This practice is necessary if the proper signs for ΔF are to be obtained. If the equilibrium concentrations of the products of the reaction are larger than the initial concentrations and those of the reactants are correspondingly smaller, the reaction may proceed from left to right spontaneously. Under these conditions, $K > 1$, $\ln K$ is positive, and ΔF has a negative value. This is in agreement with our previous statements on the free energy change of a spontaneous isothermal isobaric reaction.

We have stated earlier that free energies are additive extensive properties of systems. When two systems are added, therefore, the free energy of the resulting system is the sum of the two separate free energies. Thus, we have, for the formation of 1 mole of water vapor,

$$H_2 + \tfrac{1}{2}O_2 = H_2O(g); \qquad \Delta F_1 \tag{12.22}$$

and, for the formation of 2 moles of water,

$$2H_2 + O_2 = 2H_2O(g); \qquad \Delta F_2 = 2\Delta F_1 \tag{12.23}$$

But, from equation (12.18), we have, for (12.22),

$$K_1 = \frac{P_{H_2O}}{P_{H_2} \cdot P_{O_2}^{\frac{1}{2}}} \tag{12.24}$$

and, for equation (12.23),

$$K_2 = \frac{P_{H_2O}{}^2}{P_{H_2}{}^2 \cdot P_{O_2}} = (K_1)^2 \tag{12.25}$$

From equation (12.21), we have the confirming relation

$$\Delta F_2^\circ = 2\Delta F_1^\circ = -2RT \ln K_1 = -RT \ln K_1{}^2 = -RT \ln K_2 \tag{12.26}$$

When a chemical equation is doubled, the free energy change of the reaction is doubled but the equilibrium constant is squared. From the logarithmic relation between ΔF and K, we find in general that, if reactions (1) and (2) with free energy changes ΔF_1 and ΔF_2 and equilibrium constants K_1 and K_2, respectively, are added, the free energy and equilibrium constant for the resulting reaction are, respectively,

$$\left.\begin{aligned} \Delta F_3 &= \Delta F_1 + \Delta F_2 \\ K_3 &= K_1 \times K_2 \end{aligned}\right\} \tag{12.27}$$

Relations between the Equilibrium Constants Expressed in Different Units.—Because perfect gases do not affect each other, their activities are directly proportional to their partial pressures, or to their "concentrations" in moles per liter or to their mole fractions. These different methods of expressing activity and the corresponding constants K_P, K_C, and K_N are related. Concentrations are frequently expressed in moles per liter. If the total reaction volume is V, the number of moles of A being a, the concentration of A is given by $C_A = a/V$ [compare equation

(1.16)]. For all the constituent gases, we have, in this concentration unit,

$$C_A = \frac{a}{V}; \qquad C_B = \frac{b}{V}; \qquad C_D = \frac{d}{V}; \qquad C_E = \frac{e}{V} \tag{12.28}$$

In terms of concentration units the equilibrium constant K_C is written

$$K_C = \frac{C_D{}^d \cdot C_E{}^e}{C_A{}^a \cdot C_B{}^b} \tag{12.29}$$

From the definition of a mole fraction in equations (1.18) and (1.19), we have, for the constituent gases,

$$N_A = \frac{a}{a+b+d+e}; \qquad N_B = \frac{b}{a+b+d+e},$$
$$N_D = \frac{d}{a+b+d+e}; \qquad N_E = \frac{e}{a+b+d+e} \tag{12.30}$$

In terms of the mole fractions the equilibrium constant K_N is given by

$$K_N = \frac{N_D{}^d \cdot N_E{}^e}{N_A{}^a \cdot N_B{}^b} \tag{12.31}$$

From Dalton's law of partial pressures, we have, for perfect gases,

$$P_A = N_AP; \qquad P_B = N_BP; \qquad P_D = N_DP; \qquad P_E = N_EP \tag{12.32}$$

From the ideal gas equation [compare equation (1.17)], we have

$$P_A = C_ART; \qquad P_B = C_BRT; \qquad P_D = C_DRT;$$
$$P_E = C_ERT \tag{12.33}$$

The relation between the equilibrium constants in terms of partial pressures and mole fractions is obtained by combining equations (12.18) and (12.32). Thus,

$$K_P = \frac{P_D{}^d \cdot P_E{}^e}{P_A{}^a \cdot P_B{}^b} = \frac{(N_DP)^d \cdot (N_EP)^e}{(N_AP)^a \cdot (N_BP)^b} = \frac{N_D{}^d \cdot N_E{}^e}{N_A{}^a \cdot N_B{}^b} P^{(d+e)-(a+b)} \tag{12.34}$$

and, from equation (12.31),

$$K_P = K_N \cdot P^{(d+e)-(a+b)} \tag{12.35}$$

The relation between the equilibrium constants in terms of partial pressures and concentrations is obtained by combining equations (12.18) and (12.33). Thus,

$$K_P = \frac{(C_DRT)^d \cdot (C_ERT)^e}{(C_ART)^a \cdot (C_BRT)^b} = \frac{C_D{}^d \cdot C_E{}^e}{C_A{}^a \cdot C_B{}^b} \cdot (RT)^{(d+e)-(a+b)} \tag{12.36}$$

and, from equation (12.29),

$$K_P = K_C(RT)^{(d+e)-(a+b)} \tag{12.37}$$

Using the definition of Δn in equation (12.6), we have, for the various equilibrium constants,

$$K_P = K_N \cdot P^{\Delta n} = K_C(RT)^{\Delta n} \tag{12.38}$$

and, similarly,

$$K_N = K_C\left(\frac{RT}{P}\right)^{\Delta n} = K_C\left(\frac{V}{n}\right)^{\Delta n} \tag{12.39}$$

In some reactions the numerical values of the equilibrium constants expressed in the different units are identical. From equation (12.38), it follows that

$$K_P = K_N = K_C \tag{12.40}$$

when $\Delta n = 0$, that is, when there is no change in number of moles in the reaction and $d + e = a + b$. Another condition under which K_P and K_N are identical is that of unit pressure. K_P and K_C may also be identical when (RT) is unity. If the concentration is expressed in moles per liter and the pressure in atmospheres, $R = 0.08206$, and T must be $1/0.08206 = 12.2$°K. This last condition ($RT = 1$) is evidently not of practical importance.

Standard States and the Standard Free Energy Change.—Let us now study in more detail the influence of the choice of standard states on the value of the standard free energy change. From the relations in equations (12.15) and (12.16), it follows that the free energy change for reaction (12.1) may be expressed as

$$\Delta F = a(\mathrm{F_A} - \mathrm{F'_A}) + b(\mathrm{F_B} - \mathrm{F'_B}) + d(\mathrm{F'_D} - \mathrm{F_D}) + e(\mathrm{F'_E} - \mathrm{F_E}) \tag{12.41}$$

which may be written in the form

$$\Delta F = [(d\mathrm{F'_D} + e\mathrm{F'_E}) - (a\mathrm{F'_A} + b\mathrm{F'_B})] - [(d\mathrm{F_D} + e\mathrm{F_E}) - (a\mathrm{F_A} + b\mathrm{F_B})] \tag{12.42}$$

These equations show that the free energy change for the reaction is related to the change in free energy of the constituent gases. Thus, what appears in equation (12.41) for the gas A is the free energy difference $a(\mathrm{F_A} - \mathrm{F'_A})$. If this difference can be determined directly, it follows that the absolute values of the free energy of A in the initial and equilibrium states are not necessary. The definition $F = H - TS$, indicates that absolute values of F can be obtained when the absolute values of both H and S are available. These values are known only for a limited number of substances.

It is, of course, possible to prepare free energy of formation tables corresponding to the heat of formation tables if the elements in their standard states are assigned a free energy of zero. The free energy tables prepared for the compounds in this way represent the values relative to those of the elements. If the gases A, B, D, and E, in reaction (12.1), are compounds and not elements, their free energies, even when expressed in these relative values, will usually have values not equal to zero.

When the reactants and products of a reaction are in their standard states, their molar free energies F'_A, F'_B, F'_D, and F'_E become the standard molar free energies, and the free energy change for the reaction becomes the standard free energy change. Using the customary notation, we have, from equations (12.41) and (12.42),

$$\begin{aligned}\Delta F^\circ &= [d(\mathrm{F}^\circ_D - \mathrm{F}_D) + e(\mathrm{F}^\circ_E - \mathrm{F}_E)] - [a(\mathrm{F}^\circ_A - \mathrm{F}_A) + b(\mathrm{F}^\circ_B - \mathrm{F}_B)] \\ &= [(d\mathrm{F}^\circ_D + e\mathrm{F}^\circ_E) - (a\mathrm{F}^\circ_A + b\mathrm{F}^\circ_B)] - [(d\mathrm{F}_D + e\mathrm{F}_E) \\ &\qquad\qquad - (a\mathrm{F}_A + b\mathrm{F}_B)] \quad (12.43)\end{aligned}$$

It follows from equation (12.43) that, when the equilibrium free energies of the three substances A, B, and C, are fixed independently, $d\mathrm{F}_D$ must assume a unique value that preserves the constancy of the term $[(d\mathrm{F}_D + e\mathrm{F}_E) - (a\mathrm{F}_A + b\mathrm{F}_B)]$. Because F_D has a constant value for a mole of D under these conditions, the value of d, the number of moles of D, also must assume a unique value. This result is a necessary consequence if ΔF° for the reaction is to have a value dependent only on the initial and final conditions and independent of the path over which the reaction proceeds. This constancy may be used as the basis for another statement of the law of mass action.

The above relations were derived for an isothermal reaction. Under the condition of constant temperature, we have seen that it is possible to alter the free energy of a substance by changing its concentration. Let us consider a new standard state for the gas A, at which its initial partial pressure is $P^{\circ\prime}$ instead of P°, the temperature remaining unchanged. The corresponding molar free energies of A are designated $\mathrm{F}^{\circ\prime}_A$ and F°_A, respectively. Because the equilibrium free energy term in equation (12.43) is unchanged by this shift in standard state, the standard free energy of the reaction must change correspondingly. If the new value of the free energy change for the reaction is designated as $\Delta F^{\circ\prime}$, it follows that

$$\Delta F^{\circ\prime} - \Delta F^\circ = a(\mathrm{F}^\circ_A - \mathrm{F}^{\circ\prime}_A) \quad (12.44)$$

A shift in the standard state for any of the reactants or products of a reaction is, therefore, directly reflected in the value for the standard free energy of the reaction. Changes in standard state are frequently met in studies on solutions where the standard states are fixed arbitrarily. They are also common in studies of reactions where one or more of the reacting substances may be present in more than one phase. Thus, in a reaction involving water, we may select ice, liquid water, or water vapor as the standard state.

Solids, Liquids, and the Equilibrium Constant.—The basic equation (12.21), relating the standard free energy change for a reaction to the equilibrium constant, was derived for the reaction of ideal gases. It can also be applied to the reactions of solids and liquids whose vapors behave as ideal gases; for if the vapors are in equilibrium with each other in a reaction mixture, the solid and liquid phases in equilibrium with their respective vapors must also be in equilibrium with each other. However, in a mixture of ideal gases the vapor pressure of a pure solid or liquid at constant temperature remains constant, whereas the pressures of the gaseous constituents are variable. As a consequence the equilibrium concentration of the vapor from the pure solid or liquid is identical with its initial (or final) concentration. Thus, if the substance A in reaction (12.1) is a pure solid, the vapor pressure of A will fix both the initial and equilibrium pressures of A in the gas phase. Because $P'_\text{A} = P_\text{A}$, it follows from equation (12.15) that

$$a(\mathrm{F}_\text{A} - \mathrm{F}'_\text{A}) = aRT \ln 1 = 0 \tag{12.45}$$

It is the custom not to include the concentrations of pure solids or liquids in the expression for the equilibrium constant but, because their values remain constant, to "include them in the numerical value of the equilibrium constant." Thus, when the substance A is a pure solid or liquid, equation (12.18) becomes

$$K_P = \frac{P_\text{D}{}^d P_\text{E}{}^e}{P_\text{B}{}^b} \tag{12.46}$$

Let us define a new standard state for the substance A so that A is in its standard state when it is a pure solid with a vapor pressure of $P^{\circ\prime}$ rather than a gas at 1 atmosphere pressure. The change in the standard free energy of A accompanying this change in standard states, on comparison with equation (12.15), is seen to be

$$a(\mathrm{F}^{\circ\prime}_\text{A} - \mathrm{F}^{\circ}_\text{A}) = aRT \ln \frac{P^{\circ\prime}_\text{A}}{P^{\circ}_\text{A}} = aRT \ln P^{\circ\prime}_\text{A} \tag{12.47}$$

The standard free energy change of the reaction resulting from the change in the standard state of A becomes altered by this same quantity; for, from equation (12.44),

$$\Delta F^{\circ\prime} - \Delta F^{\circ} = a(\mathrm{F}^{\circ}_\text{A} - \mathrm{F}^{\circ\prime}_\text{A}) = aRT \ln \frac{1}{P^{\circ\prime}_\text{A}} \tag{12.48}$$

This factor $(1/P^{\circ\prime}_\text{A})^a$ is obviously responsible for the difference between equations (12.18) and (12.46).

Equilibrium Constant for the Formation of Water at 25°C.—The equilibrium conditions for the formation of water from hydrogen and oxygen may be deduced from the equilibrium constant of the reaction. This value in turn may be obtained from the standard free energy change for the reaction. We have shown how the standard free energy change may be calculated from the potential of a standard reversible cell with the aid of equation (11.12). This change, $\Delta F°$, may also be evaluated from the basic equation

$$\Delta F° = \Delta H° - T\,\Delta S° \tag{12.49}$$

if the necessary data are available.

The heat of formation of liquid water under standard conditions was given in equation (5.1) as $\Delta H_{298.16} = -68{,}317$ cal. In this reaction, at 25°C the hydrogen and oxygen gases and the liquid water were all in their standard states so that this value of the heat of reaction at constant pressure is the standard heat of reaction $\Delta H°$. The standard entropies of hydrogen and oxygen gases and liquid water at 25°C, from Table 11.2, are 31.211, 49.003, and 16.716 calories per degree per mole, respectively. The standard entropy change for the reaction is

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(liq); \qquad \Delta S° = \overset{\circ}{s}_{H_2O} - (\overset{\circ}{s}_{H_2} + \tfrac{1}{2}\overset{\circ}{s}_{O_2}) \tag{12.50}$$

Using the above data, we have

$$\Delta S° = -38.997 \text{ cal/deg} \tag{12.51}$$

At 298.16°K, $T\,\Delta S°$ has the value $-11{,}627$ calories. When this value and the value for $\Delta H°$ are substituted in equation (12.49), we have

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(liq); \qquad \Delta F° = -56{,}690 \text{ cal} \tag{12.52}$$

We have remarked that the standard free energy change measures the distance from equilibrium of the system in which the reactants and products are in their standard states. At 25°C, hydrogen and oxygen gases at 1 atmosphere are far from being in equilibrium with water. Consider a system of hydrogen, oxygen, and water that would be in equilibrium at this temperature, the equilibrium partial pressures of the hydrogen and oxygen being x and y atmospheres, respectively. In this system, the liquid water is in equilibrium with its vapor so that the free energy of the saturated vapor equals that of the liquid water. Thus,

$$H_2O(\text{g, satd vapor}) = H_2O(liq); \qquad \Delta F = 0 \tag{12.53}$$

The saturated vapor in turn is in equilibrium with the hydrogen and oxygen at their equilibrium partial pressures so that

$$H_2(x \text{ atm}) + \tfrac{1}{2}O_2(y \text{ atm}) = H_2O(\text{g, satd vapor}); \qquad \Delta F = 0 \tag{12.54}$$

From equations (12.53) and (12.54), it appears that liquid water is also in equilibrium with hydrogen at x atmospheres and oxygen at y atmospheres. These equations, when combined, become

$$H_2(x \text{ atm}) + \tfrac{1}{2}O_2(y \text{ atm}) = H_2O(\text{liq}); \qquad \Delta F = 0 \qquad (12.55)$$

Equation (12.55), or equations (12.53) and (12.54), may be subtracted from equation (12.52) to indicate a reaction with a free energy change identical with the standard free energy change. Thus,

$$H_2(1 \text{ atm}) + \tfrac{1}{2}O_2(1 \text{ atm}) = H_2(x \text{ atm}) + \tfrac{1}{2}O_2(y \text{ atm}); \qquad \Delta F = -56{,}690 \text{ cal} \qquad (12.56)$$

The free energy change in equation (12.56) is a measure of the net work of expansion of hydrogen from its standard state of 1 atmosphere to its equilibrium state of x atmospheres and of oxygen from its standard state of 1 atmosphere to its equilibrium state of y atmospheres. It appears, therefore, that equation (12.52) with the same value for the free energy change measures the same net work.

It will be instructive to express the free energy change for equation (12.56) in terms of the free energies of the reacting substances. Thus,

$$\begin{aligned}\Delta F &= [\mathrm{F}(H_2, x\,\text{atm}) - \mathrm{F}^\circ(H_2, 1\,\text{atm})] + [\tfrac{1}{2}\mathrm{F}(O_2, y\,\text{atm}) - \tfrac{1}{2}\mathrm{F}^\circ(O_2, 1\,\text{atm})] \\ &= -56{,}690 \text{ cal} \qquad (12.57)\end{aligned}$$

But, from equation (11.11), the isothermal change in free energy of the hydrogen is

$$\mathrm{F}(H_2, x \text{ atm}) - \mathrm{F}(H_2, 1 \text{ atm}) = RT \ln x \qquad (12.58)$$

and the corresponding change for the $\frac{1}{2}$ mole of oxygen is

$$\tfrac{1}{2}\mathrm{F}(O_2, y \text{ atm}) - \tfrac{1}{2}\mathrm{F}(O_2, 1 \text{ atm}) = \tfrac{1}{2}RT \ln y = RT \ln y^{\frac{1}{2}} \qquad (12.59)$$

From these equations, we have for the free energy change of reaction (12.56)

$$\Delta F = RT \ln x + RT \ln y^{\frac{1}{2}} = RT \ln xy^{\frac{1}{2}} = -56{,}690 \text{ cal} \qquad (12.60)$$

This result may be compared with that obtained by a more formal treatment of equation (12.52). The equilibrium constant for reaction (12.52) is related to its standard free energy change by equation (12.21) so that

$$\begin{aligned}\Delta F^\circ &= -RT \ln K_P = -2.3026RT \log K_P = -4.5757T \log K_P \\ &= -56{,}690 \text{ cal} \qquad (12.61)\end{aligned}$$

R being 1.9872 calories per degree. The liquid water being in its standard state, it follows from equation (12.46) that the equilibrium constant for reaction (12.52) is

$$K_P = \frac{1}{P_{H_2} \cdot P_{O_2}^{\frac{1}{2}}} = \frac{1}{xy^{\frac{1}{2}}} \tag{12.62}$$

From equations (12.61) and (12.62), we have

$$\Delta F^\circ = -RT \ln K_P = -RT \ln \frac{1}{xy^{\frac{1}{2}}} = RT \ln xy^{\frac{1}{2}} = -56{,}690$$

which was obtained previously [equation (12.60)] by a different method. The equilibrium constant for the formation of liquid water may be evaluated from equation (12.61). Thus,

$$\log K_P = \frac{56{,}690}{4.5757 \times 298.16} = 41.553$$

and

$$K_P = 3.57 \times 10^{41}$$

From these values and equation (12.62), we obtain

$$\log (P_{H_2} \cdot P_{O_2}^{\frac{1}{2}}) = -41.553 = \overline{42}.447$$

and

$$P_{H_2} \cdot P_{O_2}^{\frac{1}{2}} = xy^{\frac{1}{2}} = 2.80 \times 10^{-42} \tag{12.63}$$

It is evident that the partial pressures of hydrogen and oxygen in equilibrium with liquid water have extremely small values and that the reaction goes essentially to completion.

The above relations are for the equilibrium of hydrogen and oxygen with liquid water. In a reaction system in which the water is present as the vapor, the vapor at 1 atmosphere pressure is chosen as the standard state for water. This change in standard state produces a corresponding change in standard free energy in accordance with the discussion leading to equation (12.44). According to Osborne and Meyers,[1] the equilibrium vapor pressure of water at 25°c is 0.031222 atmosphere, or 23.729 mm. The change in free energy desired is, therefore, that for the change in standard states for water,

$$H_2O(\text{liq, 1 atm; vapor pressure} = 0.031222 \text{ atm}) = H_2O(\text{g, 1 atm}) \tag{12.64}$$

Three equivalent procedures may be used in evaluating this change in standard free energy from the experimental data. We shall indicate the optional methods of procedure as examples of general methods among which one may choose on the basis of simplicity or convenience.

---

[1] OSBORNE, N. S., and C. H. MEYERS, *J. Research Natl. Bur. Standards*, **13**, 11 (1934).

1. Remembering that water is a product of the reaction corresponding to D and not to A, we have from equations (12.43) and (12.44)

$$\Delta F^{\circ\prime} - \Delta F^{\circ} = \mathrm{F}^{\circ\prime}_{\mathrm{H_2O}} - \mathrm{F}^{\circ}_{\mathrm{H_2O}} \tag{12.65}$$

Because $P^{\circ\prime} = 1$ and $P^{\circ} = 0.031222$ atm, we have, by analogy with equation (12.47),

$$\begin{aligned}\mathrm{F}^{\circ\prime}_{\mathrm{H_2O}} - \mathrm{F}^{\circ}_{\mathrm{H_2O}} &= RT \ln \frac{1}{0.031222} \\ &= -4.5757 \times 298.16 \log 0.031222 \\ &= 2{,}054.0 \text{ cal}\end{aligned} \tag{12.66}$$

2. Let us consider the change in standard state for water as the result of two steps, the first being an equilibrium reaction with a free energy change of zero, and the second being the compression of the water vapor. Thus,

$$H_2O(\text{liq}) = H_2O(\text{g, } 0.031222 \text{ atm});$$

$$\Delta F = 0$$

$$H_2O(\text{g, } 0.031222 \text{ atm}) = H_2O(\text{g, } 1 \text{ atm});$$

$$\Delta F = \int \mathrm{v}\, dP = RT \ln \frac{1}{0.031222}$$

$$\begin{aligned}H_2O(\text{liq}) = H_2O(\text{g, } 1 \text{ atm}); \quad \Delta F &= -RT \ln 0.031222 \\ &= 2{,}054.0 \text{ cal}\end{aligned} \tag{12.67}$$

Equation (12.67) is equivalent to (12.66) above.

3. For the reaction

$$H_2O(\text{liq}) = H_2O(\text{g}), \qquad K_P = P_{H_2O} \tag{12.68}$$

we may write in a formal manner

$$\Delta F^{\circ} = -RT \ln K_P = -RT \ln P_{H_2O} \tag{12.69}$$

In equation (12.68), we have omitted the term for the liquid water from the equilibrium constant expression, as is customary for liquids and solids. The value of P_{H_2O} is the equilibrium value, 0.031222 atmosphere, and the value for ΔF° is the standard free energy change for reaction (12.68). We have, therefore,

$$\Delta F^{\circ} = -RT \ln 0.031222 = 2{,}054.0 \text{ cal} \tag{12.70}$$

in agreement with equations (12.66) and (12.67).

In these calculations, we have assumed that water vapor acts as a perfect gas. Rossini[1] reports a difference in free energy of the real and

---

[1] ROSSINI, F. D., *J. Research Natl. Bur. Standards*, **22**, 407 (1939).

ideal water vapor at a pressure of 0.031222 atmosphere equal to

$$F_{\text{ideal}} - F_{\text{real}} = 4.7 \pm 1.2 \text{ joules} = 1.1 \text{ cal} \qquad (12.71)$$

Because the real gas at 0.031222 atmosphere pressure has a free energy smaller by 1.1 calories than the ideal gas, the free energy change for bringing the gas to a fugacity (symbol f) of 1 atmosphere is obtained by combining equation (12.66), (12.67), or (12.70) with equation (12.71) to give the free energy change for the change of the standard state of water from that of the liquid to that of the vapor at unit fugacity. Thus,

$$\Delta F^\circ = 2{,}054.0 + 1.1 = 2{,}055.1 \text{ cal} \qquad (12.72)$$

Fugacity is defined in the following section.

We are now prepared to calculate the free energy of formation of water vapor at 25° and fugacity of 1 atmosphere by combining equations (12.52) and (12.72). Thus,

$$\begin{array}{l}
H_2(g, f = 1) + \tfrac{1}{2}O_2(g, f = 1) = H_2O(\text{liq}); \\
\qquad\qquad\qquad\qquad\qquad\qquad \Delta F^\circ = -56{,}690 \text{ cal} \\
H_2O(\text{liq}) = H_2O(g, f = 1); \\
\qquad\qquad\qquad\qquad\qquad\qquad \Delta F^\circ = 2{,}055 \text{ cal} \\
\hline
H_2(g, f = 1) + \tfrac{1}{2}O_2(g, f = 1) = H_2O(g, f = 1); \\
\qquad\qquad\qquad\qquad\qquad\qquad \Delta F^\circ = -54{,}635 \text{ cal} \quad (12.73)
\end{array}$$

This value of ΔF° was used in equation (11.36) to evaluate I in the general free energy equation for the formation of water vapor.

In equation (12.68) the equilibrium constant contains the term P_{H_2O} for the partial pressure of gaseous water in the numerator. Either the standard free energy value in equation (12.52) or that in (12.73) may be used in deriving the equilibrium pressures of the hydrogen and oxygen in the formation of water at 25°, but each value must be used with its corresponding equilibrium constant.

The calculations on the preceding pages illustrate the need for precise free energy data in calculating equilibrium constants. Rossini gives the "accuracy error" for the standard free energy of liquid water [equation (12.52)] as ±11 calories. Let us assume, therefore, that the last significant figure is uncertain; it is carried primarily so that a reversed calculation will permit the recovery of the original experimental values on which it is based. If the fifth significant figure in the value 56,690 is uncertain, the fifth figure in the value log $K_P = 41.553$ is also uncertain. Although the logarithm of K_P is given to *five* significant figures, the value of K_P itself will be available to only *three;* for it is the mantissa, and not the characteristic, that controls the number of significant figures in the value of K_P. If ΔF° is assigned a value of $-56{,}695$, an increase of 5 calories, log K_P becomes 41.556 and K_P becomes 3.60×10^{41}, an increase of 0.03, or 1 per cent in the value of K_P. In this example, an error of 0.01 per cent in ΔF becomes a 1 per cent error in K_P. The value of the absolute temperature, kept constant in the above calculation, also enters into equation (12.21). A doubling of the absolute temperature results in a halving of the value of log K for any given value of ΔF.

Fugacity.—The relation between the change in standard free energy for a reaction and the equilibrium constant was derived for the reactions of ideal gases and of solids or liquids whose vapors behave as ideal gases. For each simple constituent of an isothermal system, we may write $d\mathrm{F} = \mathrm{v}\, dP$, but only for the ideal gas may we place v equal to RT/P in order to obtain the integrated expression

$$\mathrm{F} - \mathrm{F}' = RT \ln \frac{P}{P'} \tag{12.74}$$

which we used in deriving the expression for the equilibrium constant.

However, there are many chemical systems in which these ideal conditions do not obtain. In such systems, the equilibrium "constant" in terms of partial pressures or concentrations does not remain constant with varying equilibrium conditions at constant temperature; consequently, the "constant" cannot be an exact measure of the standard free energy change of the reaction as required by equation (12.21). Several alternative procedures may be followed in applying the laws of thermodynamics to nonideal systems.

1. An empirical function for the relation between V and P for the nonideal system may be derived so that $\mathrm{v}\, dP$ may be integrated to give an exact value of $\mathrm{F} - \mathrm{F}'$. In general, the form of the empirical function will vary from substance to substance; thus, the combinations of the functions of the different substances in the chemical system may give complicated expressions that are not easy to apply.

2. The general form of equations (12.74) and (12.21), including the ideal gas constant R, may be preserved if another function is substituted for the pressure. This function will be empirical and the deviations from ideality will all be lumped into one term, but it will give the correct value of $\mathrm{F} - \mathrm{F}'$ for the isothermal process.

In accordance with the suggestion of Lewis, the second alternative has been almost universally followed by physical chemists. Lewis[1] proposed the use of the function *fugacity*, f, as a measure of the escaping tendency of a substance. Because the escaping tendency of an ideal gas is measured by the pressure, the fugacity is such a function that, for an ideal gas,

---

[1] LEWIS, G. N., *Proc. Am. Acad. Arts Sci.*, **37**, 49 (1901); *Z. physik. Chem.*, **38**, 205 (1901).

it is identical with the pressure. Let the fugacity of a mole of substance be defined in part by the differential equation

$$d\text{F} = RT\, d \ln f \tag{12.75}$$

This equation defines only the change in f and not its absolute value. For the isothermal process, we obtain, on integration,

$$\text{F} - \text{F}' = RT \ln \frac{f}{f'} \tag{12.76}$$

which is strictly analogous to equation (12.74). Observe, however, that equation (12.76) defines only the ratio f/f' and does not in itself permit the evaluation of either f or f'.

However, the requirement that the fugacity for an ideal gas shall equal its pressure permits us to fix the absolute value of the fugacity for a real gas. A real gas approaches ideal behavior as its pressure becomes reduced; hence, the fugacity of the real gas approaches the pressure as the pressure approaches zero. This statement in mathematical form is

$$\lim_{P=0} \frac{f}{P} = 1 \tag{12.77}$$

Activity.—Lewis also introduced another function, *activity*[1] (symbol, a), which is used as a relative function. For 1 mole of substance in an arbitrarily selected standard state with a free energy F° and a fugacity f°, the absolute value of the fugacity in atmospheres or any other unit will not necessarily be unity. However, the activity in this state, a°, is defined as equal to unity. In any other state, the substance has a value of the fugacity f which may be expressed in absolute units. The value of the activity in this state, however, is relative to the activity in the standard state (unity) as defined by the equation

$$a = \frac{f}{f^\circ} \tag{12.78}$$

A comparison with equation (12.76) shows that activity is also defined by the equation

$$\text{F} - \text{F}^\circ = RT \ln a \tag{12.79}$$

As this equation indicates, when a substance approaches the arbitrarily selected standard state, its free energy F becomes equal to F°, $\ln a = 0$, and $a = 1$. All values of a are therefore relative to this value at the standard state. In the arbitrarily selected standard state, f may have an absolute value different from unity. From equation (12.76),

---

[1] LEWIS, G. N., *Proc. Am. Acad. Arts Sci.*, **43**, 259 (1907); *Z. physik. Chem.*, **61**, 129 (1907).

however, it follows that a standard state exists in which $\mathrm{F} = \mathrm{F}' = \mathrm{F}^\circ$, $\ln f/f^\circ = 0$, $f/f^\circ = 1$; therefore, $f = f^\circ$.

Fugacities, Activities, and the Equilibrium Constant.—Because equations (12.76) and (12.79) have the same form as equation (12.15), it appears that all the thermodynamic equations derived for ideal gases with the aid of equation (12.15) may be generalized to include substances that do not obey the ideal gas laws. Equation (12.76) or (12.79) may be used in the derivations so that f or a will be substituted for P in all the derived equations. Thus, if the reactants A and B in equation (12.1) are initially in standard states with fugacities f°_{A} and f°_{B}, respectively, f_{A} and f_{B} being the corresponding equilibrium values, and if the products D and E are finally in standard states with fugacities f°_{D} and f°_{E}, respectively, the equilibrium values being f_{D} and f_{E}, we see by comparison with equations (12.16) and (12.18) that

$$\Delta F = RT \ln \frac{f^{\circ d}_{\mathrm{D}} f^{\circ e}_{\mathrm{E}}}{f^{\circ a}_{\mathrm{A}} f^{\circ b}_{\mathrm{B}}} - RT \ln K_f \qquad (12.80)$$

If the standard states are so chosen that $f^\circ_{\mathrm{A}} = f^\circ_{\mathrm{B}} = f^\circ_{\mathrm{D}} = f^\circ_{\mathrm{E}} = 1$, the free energy change becomes the standard free energy change and equation (12.80) becomes

$$\Delta F^\circ = -RT \ln K_f \qquad (12.81)$$

where

$$K_f = \frac{f_{\mathrm{D}}{}^d f_{\mathrm{E}}{}^e}{f_{\mathrm{A}}{}^a f_{\mathrm{B}}{}^b} \qquad (12.82)$$

Similarly, if equation (12.79) is used in the derivation, we have directly

$$\Delta F^\circ = -RT \ln K_a \qquad (12.83)$$

where

$$K_a = \frac{a_{\mathrm{D}}{}^d a_{\mathrm{E}}{}^e}{a_{\mathrm{A}}{}^a a_{\mathrm{B}}{}^b} \qquad (12.84)$$

Equations in terms of the functions activity and fugacity are extremely useful for they may be applied to reacting systems nonideal in behavior. However, the task of obtaining numerical values of the activity or fugacity to use in place of pressures or concentrations is not circumvented. When accurate values of the standard free energy are known, K_a and the resulting values of a can be calculated. We shall not discuss here the general methods for evaluating activities and fugacities. For purposes of illustration, we shall continue to use the approximate equations involving K_P, K_C, or K_N as occasion may require because values for pressures, concentrations, and mole fractions are more readily available than activity and fugacity data. In research, where a quantitative application of the laws of thermodynamics to real systems is desired, the more exact but less convenient equations will obviously be used.

✓**Fugacity of Water Vapor at 25°C.**—A single method of obtaining the fugacity of water at 25°C is presented here At this temperature we found in equation (12.72) that the free energy of water vapor with a fugacity of 1 atmosphere is 2.055.1 calories greater than the free energy of liquid water. But the fugacity of the liquid water is equal to the fugacity of the vapor in equilibrium with it so that we have

$$H_2O(g, f = 1) = H_2O(g, f \text{ of satd vapor}); \qquad \Delta F = \mathrm{F} - \mathrm{F}^\circ = -2{,}055.1 \text{ cal} \qquad (12.85)$$

where F is the molar free energy of the saturated vapor with the fugacity f and F° is the molar free energy of the water vapor in its standard state of unit fugacity. The value of f, the fugacity of the saturated vapor, and of the liquid water in equilibrium with it may be calculated from equations (12.76) and (12.85). Thus,

$$\mathrm{F} - \mathrm{F}^\circ = -2{,}055.1 = RT \ln \frac{f}{1}$$

whence,

$$\log f = \frac{-2{,}055.1}{4.5757 \times 298.16} = -1.5063$$

and

$$f = 0.03117 \text{ atm}$$

Compare this value with the pressure of 0.031222 atmosphere.

Or, using the value for the free energy change on going from the real to the ideal gas from equation (12.71), we have

$$\mathrm{F}_{\text{ideal}} - \mathrm{F}_{\text{real}} = RT \ln \frac{P}{f} = 1.1 \text{ cal}$$

$$\log 0.031222 - \log f = \frac{1.1}{4.5757 \times 298.16} = 0.0008_1$$

whence we have

$$f = 0.03116_4 \text{ atm}$$

Various Equilibriums and Their Equilibrium Constants.—Equilibrium constants and corresponding standard free energy changes can be expressed for many equilibriums that do not involve chemical change in the traditional sense. Some of these types are listed in Table 12.2. In general, the equilibrium constants expressed in terms of activities differ in numerical value from those expressed in the traditional units, for different standard states are usually selected. The equilibrium constants expressed in the different traditional units, P, C, and N, also differ in numerical value for the same reason.

TABLE 12.2.—VARIOUS EQUILIBRIUMS AND THEIR EQUILIBRIUM CONSTANTS

Number	Type	Example	Constant in terms of activities	Constant in conventional units
1	***Liquid*** and its ***vapor***	$H_2O(liq) = H_2O(g)$	$K_a = a_{(g)}$	$K = P_{H_2O}$
2	***Solvent*** and its ***vapor***	$H_2O(solvent) = H_2O(g)$	$K_a = a_{(g)}/a_{(solvent)}$	$K = P_{H_2O}/N_{H_2O}$
3	***Solute*** and its ***vapor***	$CO_2(in\ soln) = CO_2(g)$	$K_a = a_{(CO_2\ in\ gas)}/a_{(CO_2\ in\ soln)}$	$K = P_{CO_2}/N_{(CO_2\ in\ soln)}$ or $K' = P_{CO_2}/C_{(CO_2\ in\ soln)}$
4	***Solid*** and its ***vapor***	$H_2O(ice) = H_2O(g)$	$K_a = a_{(g)}$	$K = P_{H_2O}$
5	***Solid*** and its ***liquid***	$H_2O(ice) = H_2O(liq)$	$K_a = a_{(liq)}$	$K = 1$
6	***Solid*** and its ***solution***	*a.* $NaCl(c) = NaCl(in\ soln)$	$K_a = a_{(NaCl\ in\ soln)} = a_{Na^+} \cdot a_{Cl^-}$	No constant in these units
		b. $A(c) = A\ (in\ soln)$	$K_a = a_{(A\ in\ soln)}$; (if $a_{[A(c)]} = 1$)	$K = N_{A(in\ soln)}$, or $K' = C_{A(in\ soln)}$
7	Solute and two immiscible solvents	NH_3 (in chloroform) = NH_3 (in water)	$K_a = \dfrac{a_{(NH_3\ in\ water)}}{a_{(NH_3\ in\ chloroform)}}$	$K = \dfrac{C_{(NH_3\ in\ water)}}{C_{(NH_3\ in\ chloroform)}}$
8	Ionic equilibriums:			
	a. Water	$H_2O = H^+ + OH^-$	$K_a = a_{H^+} \cdot a_{OH^-}$, (if $a_{H_2O} = 1$)	$K = [H^+][OH^-]$
	b. A weak base	$BOH = B^+ + OH^-$	$K_a = \dfrac{a_{B^+} \cdot a_{OH^-}}{a_{BOH}}$	$K = \dfrac{[B^+][OH^-]}{[BOH]}$
	c. A weak acid	$HA = H^+ + A^-$	$K_a = \dfrac{a_{H^+} \cdot a_{A^-}}{a_{HA}}$	$K = \dfrac{[H^+][A^-]}{[HA]}$
	d. A slightly soluble salt	$AgCl(c) = Ag^+ + Cl^-$	$K_a = a_{Ag^+} \cdot a_{Cl^-}$	$K = [Ag^+][Cl^-]$

Change of the Equilibrium Constant with Temperature.—When both sides of equation (12.20) are divided by T, we obtain the equation

$$\frac{\Delta F}{T} = R \ln \frac{P_{\mathrm{D}}'^{d} P_{\mathrm{E}}'^{e}}{P_{\mathrm{A}}'^{a} P_{\mathrm{B}}'^{b}} - R \ln K_P \tag{12.86}$$

When this equation is differentiated with respect to the temperature, the first term on the right side becomes zero, for the partial pressures P'_{A}, P'_{B}, P'_{D}, and P'_{E} are fixed by the initial and final states of the reacting substances. These initial and final states are set up arbitrarily; they are, therefore, independent of the temperature. We have, accordingly,

$$\frac{\mathrm{d}(\Delta F/T)}{\mathrm{d}T} = \frac{\mathrm{d}(\Delta F^\circ/T)}{\mathrm{d}T} = -R\frac{\mathrm{d}\ln K_P}{\mathrm{d}T} \tag{12.87}$$

When this equation is combined with equation (11.30), we obtain

$$R\frac{\mathrm{d}\ln K_P}{\mathrm{d}T} = \frac{\Delta H}{T^2}$$

which may be rearranged to the equation, known as the van't Hoff equation

$$\frac{\mathrm{d}\ln K_P}{\mathrm{d}T} = \frac{\Delta H}{RT^2} \tag{12.88}$$

Corresponding equations may be obtained for the dependence of K_a and K_f on temperature.

The corresponding equations for K_C and K_N may be obtained from equation (12.38) by the following steps: Because

$$K_P = K_N P^{\Delta n} = K_C(RT)^{\Delta n}$$
$$\ln K_P = \ln K_N + \Delta n \ln P = \ln K_C + \Delta n \ln (RT)$$

On differentiating with respect to temperature and substituting in equation (12.88), we have

$$\frac{\mathrm{d}\ln K_P}{\mathrm{d}T} = \frac{\mathrm{d}\ln K_N}{\mathrm{d}T} + \Delta n\frac{\mathrm{d}\ln P}{\mathrm{d}T} = \frac{\mathrm{d}\ln K_C}{\mathrm{d}T} + \Delta n\frac{\mathrm{d}\ln (RT)}{\mathrm{d}T} = \frac{\Delta H}{RT^2} \tag{12.89}$$

Now, at constant pressure, the total pressure P is independent of the temperature, and

$$\frac{\mathrm{d}\ln P}{\mathrm{d}T} = 0$$

Consequently,

$$\frac{\mathrm{d}\ln K_N}{\mathrm{d}T} = \frac{\Delta H}{RT^2} \tag{12.90}$$

The value of $\mathrm{d}\ln (RT)/\mathrm{d}T$ is $1/T$; consequently,

$$\frac{\mathrm{d}\ln K_C}{\mathrm{d}T} + \frac{\Delta n}{T} = \frac{\Delta H}{RT^2}$$

Rearranging and using the relation, $P\,\Delta V = \Delta nRT$ from equation (12.7),

$$\frac{\mathrm{d}\ln K_C}{\mathrm{d}T} = \frac{\Delta H}{RT^2} - \frac{\Delta nRT}{RT^2} = \frac{\Delta H - P\,\Delta V}{RT^2} = \frac{\Delta E}{RT^2} \qquad (12.91)$$

We should point out here the necessary correspondence between the van't Hoff equation, in which the equilibrium constant is expressed in partial pressures, and the approximate form of the Clausius-Clapeyron equation, which also rests on the same ideal gas equation. From Table 12.2 the equilibrium constant for the reaction

$$H_2O(\mathrm{liq}) = H_2O(\mathrm{g})$$

is $K_P = P_{H_2O}$. A substitution of this value in equation (12.88) gives directly the Clausius-Clapeyron equation (9.12) as applied to vapor pressures.

Integration of the van't Hoff Equation.—The van't Hoff equation may be integrated as was the Clausius-Clapeyron equation. When ΔH does not vary with the temperature, we have, for either K_P or K_N,

$$\int \mathrm{d}\ln K = \frac{\Delta H}{R}\int\frac{\mathrm{d}T}{T^2} \qquad (12.92)$$

and

$$\ln K = -\frac{\Delta H}{R}\frac{1}{T} + I \qquad (12.93)$$

When integrated between the temperatures T_1 and T_2, equation (12.92) becomes

$$\ln\frac{K_2}{K_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

or, in terms of common logarithms,

$$\log\frac{K_2}{K_1} = \frac{\Delta H}{4.5757}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{\Delta H}{4.5757}\left(\frac{T_2 - T_1}{T_1T_2}\right) \qquad (12.94)$$

where ΔH is the heat of reaction in calories. This equation can be used to calculate the shift in equilibrium in any reaction for which the heat of reaction is known.

When ΔH varies with temperature, according to the equation

$$\Delta H = \Delta H_0 + aT + bT^2 + cT^3,$$

we obtain, instead of equation (12.92),

$$\mathrm{d}\ln K = \frac{1}{R}\left(\frac{\Delta H_0}{T_2} + \frac{a}{T} + b + cT\right)\mathrm{d}T$$

On integration, we obtain

$$\ln K = \frac{1}{R}\left(-\frac{\Delta H_0}{T} + a \ln T + bT + \frac{1}{2}cT^2\right) + I' \qquad (12.95)$$

When ΔH and R are in calories and natural logarithms are converted to common logarithms, equation (12.95) becomes

$$\log K = -\frac{\Delta H_0}{4.5757T} + \frac{a}{1.9872}\log T + \frac{b}{4.5757}T + \frac{c}{2 \times 4.5757}T^2 + I \qquad (12.96)$$

where $I = I'/2.3026$.

We have shown earlier that the coefficients, a, b, and c in the heat content equation may be obtained from the coefficients α, β, and γ, obtained from heat capacities. Thus, if the change in heat capacity as the result of a reaction is

$$\Delta C_P = \alpha + \beta T + \gamma T^2$$

the value of ΔH as a function of temperatures becomes

$$\Delta H = \Delta H_0 + \alpha T + \tfrac{1}{2}\beta T^2 + \tfrac{1}{3}\gamma T^3$$

ΔH_0 being the integration constant. If this value for ΔH is substituted in equation (12.88), we obtain, on integration,

$$\ln K = -\frac{\Delta H_0}{R}\frac{1}{T} + \frac{\alpha}{R}\ln T + \frac{1}{2}\frac{\beta}{R}T + \frac{1}{6}\frac{\gamma}{R}T^2 + I' \qquad (12.97)$$

Comparison with the constants in equation (12.95) confirms the relationships $\alpha = a$, $\tfrac{1}{2}\beta = b$, $\tfrac{1}{3}\gamma = c$.

Again, on dividing equation (12.97) by 2.3026, we obtain an equation of the type

$$\log K = -\frac{\Delta H'}{T} + A \log T + BT + CT^2 + I \qquad (12.98)$$

where

$$\Delta H' = \frac{\Delta H_0}{2.3026R}, \qquad A = \frac{\alpha}{R}, \qquad B = \frac{\beta}{2 \times 2.3026R}, \qquad C = \frac{\gamma}{6 \times 2.3026R}$$

and

$$I = \frac{I'}{2.3026}$$

Evaluation of I.—In an equation of the type of equations (12.96), (12.97), or (12.98), there is an integration constant I to be evaluated. The other constants may be derived from those of the heat of reaction equation. The same statement applies to equation (12.93) where ΔH is considered constant. Because of the relationship between $\Delta F°$ and $\ln K$, it is evident that the integration constant I is common to both functions. We have shown earlier how I may be evaluated if the value of ΔF° for some one temperature is known. But this is equivalent to saying that I may be evaluated if the value of K is known for some temperature. In practice, if the equilibrium constant can be measured accurately, I (and ΔF°) are evaluated with this datum. If equilibrium is difficult to secure or to measure, I is evaluated from the value of ΔF, which in turn may be obtained from ΔH and $T\,\Delta S$ or from the emf of a suitable cell.

Problems

12.1. From the equation $\Delta F^\circ = -RT \ln K$, calculate the change in ΔF° in calories if the value of K is doubled at 25°C. At 350°C.

12.2. What percentage error in the equilibrium constant will result from an error of 1 kilocalorie in the free energy of the reaction at 27°C? At 327°C? From an error of 100 calories at these temperatures? 10 calories? Tabulate your results

12.3. At 0°C, the value of ΔF° for a reaction is $-1{,}000$ calories. What is the value of K? What must be the value of ΔF° at the following temperatures if K is not to vary with temperature: 200, 400, 600, 800, 1000°C? Tabulate your results.

12.4. Will a reaction proceed if $\ln K > 0$? If $\ln K < 0$? Under what conditions? Explain.

12.5. If K_1 and K_2 are the equilibrium constants at the temperature T for the two reactions $2CO_2 = 2CO + O_2$ and $2H_2O = 2H_2 + O_2$, respectively, find the value of K_3, the equilibrium constant at the same temperature, for the reaction

$$H_2 + CO_2 = H_2O + CO$$

12.6. Some iodine and hydrogen were heated at 475°C in a bulb of 90 ml capacity until equilibrium was established. The equilibrium mixture was analyzed and found to consist of 4.60×10^{-4} mole of H_2, 6.0×10^{-5} mole of I_2, and 11.4×10^{-4} mole of HI.

(*a*) Calculate K_P, K_N, and K_C. Is the reaction influenced by total pressure?

(*b*) Calculate the equilibrium partial pressures in this experiment.

(*c*) Calculate the percentage decomposition of pure HI when heated at 475°C.

(*d*) Calculate the free energy change of the reaction if the products and reactants are considered at atmospheric pressure by calculating the free energy change of each of the products and reactants in passing from the "standard" to the equilibrium condition and then summing these free energy changes. Show that this sum corresponds to the equation

$$\Delta F^\circ = -RT \ln K_P$$

12.7. From the data in Prob. 11.6, calculate the numerical value of the equilibrium constant at 25°C for the reaction

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

12.8. From the free energy equation for the reaction

$$H_2(g) + CO_2(g) = H_2O(g) + CO(g)$$

derived in Prob. 11.4, calculate the value of the equilibrium constant for the reaction at the temperatures 298.16, 400, 600, 800, 1000, and 1500°K. (Indicate your calculations in tabular from.)

12.9. According to Rossini and Jessup [*J. Research Natl. Bur. Standards*, **21,** 491 (1938)], the change of free energy, as a function of both temperature and pressure, for the transition

$$\text{C(graphite)} = \text{C(diamond)}$$

is given by the equation

$$\begin{aligned}\Delta F = 541.82 + \frac{6{,}700}{T} + 1.17662T \log T - 2.43723T - 0.000221\,T^2 \\ - (0.045660 + 0.91236 \times 10^{-6}T - 0.7830 \times 10^{-10}T^2 \\ - 0.3623 \times 10^{-12}T^3)P + 0.19 \times 10^{-6}P^2 \text{ cal}\end{aligned}$$

where P is in atmospheres and T in degrees Kelvin. Calculate the value of ΔF for the following conditions, and state whether or not diamond is stable with respect to graphite under these conditions:

(*a*) 300°K and 1 atmosphere.
(*b*) 300°K and 1,000 atmospheres.
(*c*) 300°K and 10,000 atmospheres.
(*d*) 300°K and 20,000 atmospheres.
(*e*) 500°K and 1 atmosphere.
(*f*) 500°K and 1,000 atmospheres.
(*g*) 500°K and 10,000 atmospheres.
(*h*) 500°K and 20,000 atmospheres.

(Try sample calculations with a slide rule to discover which terms need more accurate computation.)

12.10. Solid ammonium hydrosulfide dissociates according to the equation

$$NH_4HS(c) = NH_3(g) + H_2S(g)$$

and the vapor phase contains practically no NH_4HS. The vapor pressure of this system has been measured over a temperature range by Isambert [*Compt. rend.*, **92,** 919 (1881)] and Walker and Lumsden [*J. Chem. Soc.*, **71,** 428 (1897)] and at 20°C by Magnusson [*J. Phys. Chem.*, **11,** 21 (1907)]. Isambert's data are given by Magnusson (*ibid*). Walker and Lumdsen give their data (p. 432) and compare with interpolated values of Isambert's data. Record the original data of Isambert and Walker and Lumsden, calculate the value of K_P at each temperature (slide rule), and plot log K *vs.* $1/T$. Draw the best line through these points, and calculate the heat of sublimation from its slope. Calculate the heat of this reaction from the heat of formation in some standard table, and compare. Calculate the standard free energy change for the sublimation at 298.1°K. Specify clearly the standard states you selected.

12.11. (*a*) From the value for standard free energy of formation of liquid water, at 25°C, calculate the value of the equilibrium constant for the dissociation of liquid water and the partial pressures of hydrogen and oxygen in equilibrium with the water at this temperature. What volume is required to hold 1 mole of oxygen at this pressure and temperature? Calculate the ratio of this volume to that of the earth.

(*b*) What is the corresponding value of the dissociation constant for gaseous water? How do the partial pressures of hydrogen and oxygen in equilibrium with water vapor at 25°C and 1 atmosphere pressure compare with those calculated in (*a*)? Explain any differences.

12.12. For the dissociation of triammonium phosphate trihydrate according to the reaction

$$(NH_4)_3PO_4 \cdot 3H_2O(c) = (NH_4)_2HPO_4(c) + 3H_2O(g) + NH_3(g) \qquad (12.99)$$

Huey and Tartar [*J. Am. Chem. Soc.*, **62,** 26 (1940)] find that the equilibrium partial pressures of water vapor and ammonia are represented by the equations

For H_2O,

$$\log P_{\text{mm}} = \frac{-2{,}239.0}{T} + 8.8353$$

For NH_3,

$$\log P_{\text{mm}} = \frac{-3{,}161.3}{T} + 11.2045$$

between 25 and 50°c. Write the equilibrium constant for equation (12.99). If the partial pressures of water vapor and ammonia are expressed in atmospheres, show that

$$\begin{aligned} \log K_P &= \frac{-9{,}878.3}{T} + 26.1872 \\ \Delta F^\circ &= 45{,}198 - 119.820T \text{ cal} \\ \Delta H &= 45{,}198 \text{ cal} \\ \Delta S &= \frac{\Delta H}{T} = 151.59 \text{ cal/deg} \end{aligned}$$

What are the values of K_P, ΔF°, ΔH°, and ΔS° at 25°c? Can the decomposition of the triammonium phosphate trihydrate proceed spontaneously at 25°? Under what conditions? What is the meaning of the standard free energy change for this reaction? The meaning of ΔS°?

12.13. For the equilibrium between the dimer and the monomer of benzoic acid in benzene solution F. T. Wall and F. W. Banes [*J. Am. Chem. Soc.*, **67,** 898 (1945)] report

$$(BzOH)_2 = 2BzOH; \qquad \log K = 3.383 - \frac{1{,}841}{T}$$

Calculate a value for the heat of dissociation of the dimer and values for the equilibrium constant at 25 and 50°c.

12.14. For the isomerization equilibrium between normal butane and isobutane

$$n\text{-}C_4H_{10} = i\text{-}C_4H_{10}$$

the values of the standard free energy change in kilocalories per mole for the temperatures 298.16, 600, and 1000°K are $\Delta F^\circ_{298.16} = -0.542$, $\Delta F^\circ_{600} = 0.59$, and $\Delta F^\circ_{1000} = 2.08$. For these temperatures, report in tabular form the values of $\Delta F^\circ/T$, $\log K$, and K, and the equilibrium mole fractions of n-butane and i-butane.

CHAPTER 13

IDEAL SOLUTIONS[1]

The concept of the ideal, or perfect, gas enables us to correlate the common properties of all gases and to make quantitative predictions, under many conditions, on the behavior of real gases. The concept of the ideal solution serves a similar useful function. It may be applied to gaseous solutions, usually called "gaseous mixtures," with an accuracy comparable with that of the ideal gas laws. Solutions of condensed phases, solids, and liquids are much more concentrated than gaseous solutions; hence, there is much more opportunity for specific interaction of the molecules in the former than in the latter. Nevertheless, there is much to be learned about the laws of solutions from the laws of ideal solutions, especially because dilute solutions tend to approximate the limiting ideal solution as concentration is decreased. Furthermore, where experimental data are lacking, we can frequently obtain approximate values by applying the laws of ideal solutions to liquid and solid solutions as well as to gaseous solutions.

Concentration Units for Ideal Solutions.—In setting up general rules for ideal solutions, we must determine first of all the units to be used in expressing the composition of the solution. The problem is illustrated by the data on the solubility of sulfur[2] in benzene and in toluene, in Table 13.1. In terms of weight percentages, sulfur is about equally soluble in benzene and toluene. The concentration of sulfur per unit volume of the solution differs, however, the liter of benzene containing more sulfur than the liter of toluene. In a volumetric unit, grams or moles per liter, the two solutions do not appear to have an equal "concentration" of sulfur. If the concentration of the sulfur is expressed in terms of mole fraction or in relative number of moles of "solute" and "solvent," the solutions again differ in apparent concentration, but here the toluene solution has the higher "concentration" of sulfur. Before we can set up criteria for the ideality of liquid solutions, we must, there-

---

[1] The student interested in ideal solutions is referred to the monograph by J. H. Hildebrand on "Solubility of Non-electrolytes," 2d ed., Reinhold Publishing Corporation, New York, 1936, which provides an excellent review of ideal and nonideal solutions and contains many references to the original literature. Some of the ideas developed in this chapter are treated in more detail in the monograph.

[2] *Ibid.*, p. 17.

fore, discover which of these methods of expressing concentration can be used to give general solubility equations applicable to all solutions in which specific interactions between solvent and solute do not occur. This question of the concentration unit does not arise for gaseous solutions because all ideal gases have equal molar volumes under similar conditions. In a mixture of ideal gases the numerical value of the relative abundance of the constituents is the same whether expressed in moles per liter, partial pressures, mole fractions, or partial volumes.

TABLE 13.1.—SOLUBILITY* OF SULFUR (S_8) AT 25°

Solvent	Weight per cent	Grams/liter	Mole per cent
Benzene	2.07	18.5	0.641
Toluene	2.02	17.8	0.735

* HILDEBRAND, J. H., "Solubility of Non-electrolytes," 2d ed., p. 17, Reinhold Publishing Corporation, New York, 1936.

In gaseous solutions, there is no distinction to be made between "solvent" and "solute." As we shall see, there is also no theoretical difference between solvent and solute in an ideal liquid solution because there is no abrupt change in properties of the solution when one substance is added gradually to the other until it is present in excess. For this reason, the terms "solvent" and "solute" will be used merely as terms of convenience without any implication of a theoretical difference between them.

Raoult's Law.—Unlike gases, liquids differ in molar volume. In a mixture of liquids, therefore, the volume ratio of the liquids in the solution differs from the mole ratio of the liquids. Let us consider the partial vapor pressure of one of the constituents, A, of the solution. We may expect this partial vapor pressure to be proportional either to the relative number of molecules of the type A or to the relative volume occupied by A in the solution. The relative number of moles of A is, by definition, the mole fraction of A, and the relative volume the volume fraction of A. Raoult[1] found empirically that the vapor pressure of a number of solutions varied with the mole fraction. This relation is, therefore, used as a basis for the definition of an ideal liquid solution.

The observed vapor pressure relation for solutions may be explained in the following way: If the constituents A and B in a solution are sufficiently alike so that the solute B does not change the field of force around A, the escaping tendency of A from the solution will depend only on the mole fraction of A. If half the molecules are A and half B, the mole

---

[1] *Compt. rend.*, **104**, 1430 (1887); *Z. physik. Chem.*, **2**, 353 (1888).

fraction of A in the solution is 0.5 and its escaping tendency is 0.5 that from pure A. The constituent A in the solution will therefore be in equilibrium with a vapor in which the partial pressure of A is 0.5 that of the vapor in equilibrium with pure A. This relation between the vapor pressure P_A of the constituent A and its concentration in the liquid solution is represented by the linear equation

$$P_A = P_A^\circ N_A \tag{13.1}$$

where P_A° is the vapor pressure of pure A at that temperature and N_A is the mole fraction of A in the liquid solution. This statement is known as *Raoult's law of vapor pressures.* For a second constituent B in the ideal solution the corresponding relation is

$$P_B = P_B^\circ N_B \tag{13.2}$$

The vapor pressure of A is not a strict measure of the free energy of A when the vapor itself does not behave as an ideal gas. Strictly speaking, the fugacity of A rather than its partial pressure is a measure of the free energy and consequently of the escaping tendency of A. If allowance is to be made for this departure of the vapor from the behavior of an ideal gas, the fugacity f must be substituted for the vapor pressure, and Raoult's law takes the form

$$f_A = f_A^\circ N_A \tag{13.3}$$
$$f_B = f_B^\circ N_B \tag{13.4}$$

Because equations (13.3) and (13.4) make the proper allowance for the departure of the vapors from ideal behavior in the gas phase, they may be used to detect departure from the laws of ideal solution in the liquid phase. Deviation of liquid solutions from the laws of ideal solutions is more frequent and more extensive than is the deviation of gaseous solutions from the ideal relations. This behavior follows from the fact that, in general, liquids are much more highly concentrated than gases. Because the nonideal solution effects in the liquid phase overshadow those in the gaseous phase, we shall utilize equations (13.1) and (13.2) rather than (13.3) and (13.4) as the defining equations for the ideal liquid solution. This decision parallels the one made earlier when, for the sake of simplicity, we used the ideal gas equations in the discussion of thermodynamic theory.

In a system in which the vapor pressures of the constituents A and B are proportional to their concentrations, as in equations (13.1) and (13.2), there can be no theoretical difference between solvent and solute. The equations for A and B have the same form, and they are linear over the entire concentration range from pure A ($N_A = 1$) to pure B ($N_A = 0$). This relation is shown in Fig. 13.1 where the equation for the constituent

A is plotted for the entire range in concentration, $N_A = 0$ to $N_A = 1$, the pressure ranging from $P = 0$ to $P = P°$ between these limits.

Because the vapor pressure here considered is an equilibrium pressure, an equilibrium constant can be written for the isothermal "reaction"

$$\text{A(in soln)} = \text{A(vapor)}; \qquad K_a = \frac{a_{(\text{A},g)}}{a_{(\text{A, in soln})}} \tag{13.5}$$

The activity of A in the vapor, if it behaves as an ideal gas, is directly proportional to the partial pressure of A; and the activity of A in the solution, if ideal, is directly proportional to the mole fraction of A in the solution. Therefore, for equation (13.5), we may write

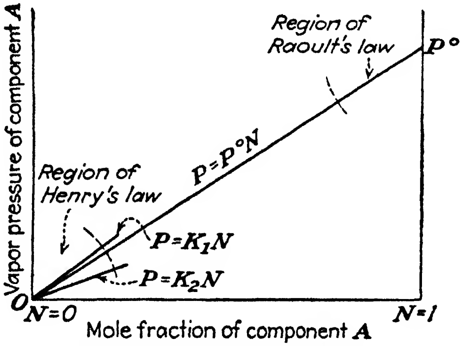


FIG. 13.1.—Vapor pressures according to Raoult's and Henry's laws.

$$K = kK_a = \frac{P_A}{N_A} \tag{13.6}$$

as in equilibrium 2 of Table 12.2. A comparison of equations (13.1) and (13.6) shows that the equilibrium constant K is identical with the vapor pressure of pure A at that temperature. For the ideal solution, therefore,

$$K = P° \tag{13.7}$$

Henry's Law.—The solubility of gases or vapors in a liquid may be expressed in many different units. The form in which Henry's law for the solubility of gases is expressed depends, therefore, on the units used. If, as before, we express the activity of a substance A in the gaseous phase in terms of its partial pressure P_A and its activity in the solution in terms of its mole fraction N_A, we have, for the equilibrium of A between gas and solution phases,

$$\text{A(in soln)} = \text{A(g)}; \qquad K_a = \frac{a_{(\text{A},g)}}{a_{(\text{A, in soln})}} \tag{13.8}$$

$$K = kK_a = \frac{P_A}{N_A} \tag{13.9}$$

Equation (13.9) may be selected as a statement of Henry's law. The law is similar to Raoult's law except that the constant K does not necessarily have the value P°. Figure 13.1 shows the form of the Henry's law equation when the constant K has values K_1 and K_2, which are, respectively, greater than and smaller than P°.

Correlation of Raoult's and Henry's Laws.—Traditionally, Raoult's law has been applied to the vapor pressures of water from aqueous solutions, especially from dilute solutions of nonvolatile solutes. In such solutions the concentration is usually expressed in terms of the solute, the term "dilute" meaning relatively little solute and a relatively large amount of water. Because a dilute solution of sugar in water means relatively little sugar, it must also mean a relatively large amount of water. The dilute sugar solution is, therefore, concentrated with respect to water. Under these conditions, Raoult's law is applied to the vapor pressure of the "solvent" in the concentration range where the mole fraction of the solvent approaches unity. This region is indicated in Fig. 13.1. In a solution of A approaching the composition of pure A, the molecules of A are in great excess so that the environment surrounding any particular molecule of A approaches that in pure A. These conditions are especially favorable for agreement with Raoult's law. Many substances in solution obey Raoult's law in the range $N \doteq 1$, when the solutions are not ideal over the whole concentration range.

Henry's law is usually applied to gases that are not too soluble; that is, to gases whose concentration in the solution is low. The gas or vapor A in equilibrium with A in the liquid solution is therefore classed as the solute, and its concentration range occurs in the neighborhood of $N_A = 0$. This is in contrast to the traditional Raoult's law region, which is in the neighborhood of $N_A = 1$. In a solution in which N_A approaches zero, the molecules of A are surrounded by those of the other constituent B, so that the environment of any particular molecule of A approaches that of pure B. From such an environment, the escaping tendency of A will not necessarily be identical with that from a solution of pure A, and the value of equilibrium constant K may differ somewhat from the value of P°. The deviation of K from P° in Henry's law may be taken as a measure of the difference in environment provided for molecules of A by an excess of B and A, respectively.

Ideal Solution.—An ideal gaseous solution may be defined as one in which the partial pressures of the constituents are proportional to their mole fractions over the entire concentration range. Similarly, the ideal liquid solution is defined as one in which the partial pressure of each constituent is proportional to its mole fraction over the entire concentration range. This is the relation defined by the Raoult's law equations.

If this relation is to hold, a molecule of A must have the same chance to escape from a solution in which it is surrounded by molecules of B as from a solution in which it is surrounded by its own kind of molecules. This requirement is a rigorous one. When it is met at some one temperature and pressure, it is reasonable to suppose that the forces about the individual molecules of A and B will be influenced in much the same way by a change of temperature or of pressure. If, because of the similarity between the molecules of A and B, it is possible to substitute molecules of A for those of B without changing the escaping tendency of the individual molecules of A or of B, an increase of temperature should not disturb this relationship. A solution that acts as an ideal solution at 25°c and 1 atmosphere pressure should be ideal at 50°c and 1 atmosphere. Similarly it should be ideal at 2 or 3 atmospheres pressure. These requirements may be included in the definition of the ideal solution as in the statement: *An ideal solution is one that obeys Raoult's law at all temperatures and all pressures.* As we shall see, such a solution is assembled from its constituent liquids without a heat of mixing and without a volume change on mixing.

Equations of the type of (13.1) and (13.2) contain only functions of one component of the solution. If the solution is ideal, the vapor pressure equation for A contains only terms that apply to the component A and that for B only terms that apply to the component B. This relation has important consequences. It enables us to predict the solubility and other properties of a substance in a number of different solvents without reference to the individual properties of these solvents.

Heat of Solution of Gases in Liquids.—The equilibrium constant defined in equation (13.8) for the solution equilibrium between A in the gas phase and A in the solution phase is the Henry's law constant. For the ideal solution, this constant is identical with the Raoult's law constant $P°$. For the ideal solution, therefore, from equations (13.6) and (13.7),

$$K = P° = \frac{P_A}{N_A} \tag{13.10}$$

To get a complete expression of the solubility as a function of temperature, all that we need do is to find how this equilibrium constant changes with temperature. From the van't Hoff equation (12.88) or (12.90) and equation (13.10), we have, for either K_P or K_N,

$$\mathrm{d} \ln K = \mathrm{d} \ln \frac{P_A}{N_A} = \frac{\Delta \mathrm{H}_A}{RT^2}\, \mathrm{d}T \tag{13.11}$$

and

$$\mathrm{d} \ln P_A^\circ = \frac{\Delta \mathrm{H}_A}{RT^2}\, \mathrm{d}T \tag{13.12}$$

But equation (13.12) is identical with the Clausius-Clapeyron equation (9.13) as applied to vapor pressures, $\Delta\mathrm{H}$ being the heat of evaporation at the temperature T. The change in heat content on evaporation of a mole of gas or vapor from the ideal solution is therefore identical with the heat of evaporation from its own liquid at the same temperature, and the heat of solution of the gas or vapor is identical with the heat of condensation of the gas at the same temperature. There is, therefore, no heat of mixing of the liquefied vapor and the solvent. The heat of evaporation is usually a function of the temperature because the heat capacities of liquid and vapor differ; it follows that the heat of solution of a gas varies with temperature in the same way. Because equations (13.11) and (13.12) contain only quantities that are functions of A, it follows that the heat of solution of the gas is independent of the particular solvent used to form the ideal solution with it and that it is independent of the concentration.

From equation (13.11), it appears that the heat of solution must remain constant over the entire concentration range. If $\mathrm{H}_{\mathrm{A}}^{\circ}$ is the molar heat content of the pure liquid A, $\mathrm{H}_{\mathrm{A}}^{*}$ that of the gas, and H_{A} that of the substance A in the solution, we have, for the heat of solution

$$\Delta H(\text{solution}) = \mathrm{H}_{\mathrm{A}} - \mathrm{H}_{\mathrm{A}}^{*}$$

and, for the liquefaction of the gas, $\mathrm{H}_{\mathrm{A}}^{\circ} - \mathrm{H}_{\mathrm{A}}^{*}$. These values being equal, we have

$$\Delta H(\text{solution}) = \mathrm{H}_{\mathrm{A}}^{\circ} - \mathrm{H}_{\mathrm{A}}^{*} = \mathrm{H}_{\mathrm{A}} - \mathrm{H}_{\mathrm{A}}^{*} \tag{13.13}$$

$$\mathrm{H}_{\mathrm{A}}^{\circ} = \mathrm{H}_{\mathrm{A}} \tag{13.14}$$

We find, therefore, that, in the solution, A has the same molar heat content as in the pure liquid.

These thermal relations may be expressed in terms of the partial molal heats defined in Chap. 6. If the values of H_{A}, H_{A}^{*}, and H_{A}° are the values of the heat content of n moles of A in the solution, gas, and pure liquid phases, respectively, we have from equation (13.14), at constant temperature and pressure

$$\frac{\partial H_{\mathrm{A}}}{\partial n_{\mathrm{A}}} = \frac{H_{\mathrm{A}}}{n_{\mathrm{A}}} = \overline{\mathrm{H}}_{\mathrm{A}} = \overline{\mathrm{H}}_{\mathrm{A}}^{\circ} = \mathrm{H}_{\mathrm{A}}^{\circ} \tag{13.15}$$

In the ideal solution, the partial molal heat content of A is constant over the entire concentration because it is equal to the molar heat content of pure A in the liquid phase. The simpler molar heat content is used throughout in this chapter because it is equal to the partial molal heat content. In ideal solutions at constant temperature and pressure, the heat content of A is directly proportional to the number of moles of A and independent of the number of moles of B. This statement may be expressed in the form

$$\left(\frac{\partial H_{\mathrm{A}}}{\partial n_{\mathrm{A}}}\right)_{n_{\mathrm{B}},P,T} = \left(\frac{\partial H_{\mathrm{A}}}{\partial n_{\mathrm{A}}}\right)_{n'_{\mathrm{B}},P,T} \tag{13.16}$$

The heat content will, of course, vary with temperature and with pressure in the usual way. An ideal gas has a molar heat content that is not dependent on the other ideal gases mixed with it, so that its partial molal heat content is also identical with the molar heat content over the entire concentration range. These relations are expressed in the equations

$$\frac{\partial H_{\mathrm{A}}^*}{\partial n_{\mathrm{A}}} = \frac{H_{\mathrm{A}}^*}{n_{\mathrm{A}}} = \overline{\mathrm{H}}_{\mathrm{A}}^* = \mathrm{H}_{\mathrm{A}}^* \tag{13.17}$$

Solubility of Gases.—We have seen that, according to Raoult's law, the equilibrium constant for the solution of a gas or vapor is identical with the vapor pressure P° of the pure liquid at that temperature. In Chap. 9, we observed that this pressure may be read directly from a log P *vs.* $1/T$ plot of the vapor pressure data. When $\Delta\mathrm{H}$ is not a function of temperature, we found this plot to be a straight line. The same results follow from equation (13.11) or (13.12), which may be written in the form

$$\frac{d \log P}{d(1/T)} = -\frac{\Delta\mathrm{H}}{2.303R} \tag{13.18}$$

In Chap. 9, we observed that $\Delta\mathrm{H}$ cannot remain constant, for it vanishes in the neighborhood of the critical point. Nevertheless, the log P *vs.* $1/T$ plot is approximately linear even up to the critical point because the other approximations made in deriving the integrated Clausius-Clapeyron vapor pressure equation compensate almost completely for the change of $\Delta\mathrm{H}$ with temperature.

Many gases whose solubilities we wish to study are above their critical temperatures in the temperature range for which we wish to know their solubilities. For such gases, Hildebrand[1] suggested that a fictitious value of P° may be obtained by an extrapolation of the linear log P *vs.* $1/T$ plot above the critical point. This value can then be used to give an estimated value for the solubility of a gas when no other data are available. Even though this value of P° represents the "vapor pressure" of a pure "liquid" at temperatures above the critical temperature where the liquid does not exist, it gives good estimates of the solubility of gases in solutions that do not depart too widely from ideality.[2]

[1] *Op. cit.*, p. 31.

[2] *Op. cit.*, Fig. 4, p. 30.

Certain rules for the solubility of gases in solutions that approach ideality may be deduced from the above considerations, and especially from equations (13.11) and (13.12).

1. *At a given temperature the solubility of a gas is independent of the solvent* and is, therefore, the same for all solvents. This follows directly from Raoult's law.

2. *The gas with the higher boiling point or critical temperature has a greater solubility than one with a lower critical temperature.* This follows because the gas with the higher critical temperature has the lower value of $P°$ at the solution temperature.

3. *The solubility of a gas decreases with increasing temperature.* This follows from equations (13.11) and (13.12) because the heat of evaporation ΔH is positive; hence $d \ln P°/dT$ is positive and $P°$ increases with increasing temperature. Therefore, P/N increases with temperature. If P is kept constant, the mole fraction of the substance in the solution must decrease.

The above rules apply quantitatively to systems that obey Raoult's law; they may be applied qualitatively to many other systems.

Solubility of Liquids.—If two liquids have properties similar enough so that their solutions obey Raoult's law, they must be miscible in all proportions. If the two liquids, when mixed, form two layers with different compositions, the mole fraction of the A in the two liquid phases must differ. But if the two liquid phases are to be in equilibrium with each other, they must be in equilibrium with the same gas phase. Because the mole fractions of A in the two liquid phases differ, the vapor pressure cannot be proportional to the mole fraction.

Partly miscible liquids cannot obey Raoult's law.

Heat of Solution of Solids in Liquids.—When a binary ideal solution is cooled sufficiently, one or both of the components crystallize out of the solution unless a glass is formed. If the two components are sufficiently similar, they are miscible in the solid phase as well as in the solution phase and a solid solution will be formed. If the two components differ sufficiently in molecular size or shape so that they do not fit into the same crystal lattice, the components that crystallize out of the solution may be pure A, pure B, or a mixture (eutectic) consisting of crystals of pure A and crystals of pure B. We shall study here this equilibrium between pure solids and the ideal liquid solution. The corresponding equilibrium for a solid solution can be treated by the same general methods if the proper equilibrium constant is used.

Let us consider the pure solid A, which dissolves in B at the temperature T, to form an ideal liquid solution of A and B. If the solution is saturated with respect to A, an equilibrium exists between solid A and

A in the solution for which an equilibrium constant may be written as follows:

$$\text{A(c)} = \text{A(in soln)}; \qquad K_a = \frac{a_{(\text{A in soln})}}{a_{(\text{A,c})}}; \qquad K = N_\text{A}$$

$$\Delta H(\text{solution}) = \text{H}_\text{A} - \text{H}^\circ_\text{A}(\text{c}) \tag{13.19}$$

where $\text{H}^\circ_\text{A}(\text{c})$ is the molar heat content of the pure solid A. The activity of A in the solution is proportional to N_A as indicated by Raoult's law. In pure solid A, the mole fraction of A is unity, so that the activity is also unity. This is in agreement with the convention of selecting the pure solid as the standard state of A. Equation (13.19) may also be obtained by the following method:

Let the dissolving of the solid be represented in two steps, the first being the evaporation of the solid and the second the solution of this gas. We have, for the former step,

$$\text{A(c)} = \text{A(g)}; \qquad K = \frac{P_\text{A}}{N^\circ_\text{A}} = P^s_A \tag{13.20}$$

Here the mole fraction of the solid is unity, $N^\circ_\text{A} = 1$, and the vapor pressure P_A must equal the saturation pressure P^s_A. For the dissolving of the gas, we have the reverse of equation (13.8), namely,

$$\text{A(g)} = \text{A(in soln)}; \qquad K = \frac{N_\text{A}}{P_\text{A}} \tag{13.21}$$

At equilibrium, $P_\text{A} = P^s_\text{A}$. On addition of equations (13.20) and (13.21), we obtain the value for the equilibrium constant in equation (13.19).

Let us now find the heat of solution of 1 mole of a solid in an ideal solution by the same steps. For the evaporation of the solid [equation (13.20)] the heat of the reaction is the heat of sublimation.

$$\Delta H = \text{H}_\text{A}(\text{g}) - \text{H}^\circ_\text{A}(\text{c}) \tag{13.22}$$

For the solution of the gas [equation (13.21)], the heat of the reaction is the heat of solution of the gas which, from equation (13.13), is identical with the heat of liquefaction of the gas.

$$\Delta H = \text{H}_\text{A}(\text{in soln}) - \text{H}_\text{A}(\text{g}) = \text{H}^\circ_\text{A}(\text{liq}) - \text{H}_\text{A}(\text{g}) \tag{13.23}$$

When equations (13.22) and (13.23) are added, we obtain, for the solution of the solid in equation (13.19),

$$\begin{aligned}\Delta H(\text{solution}) &= [\text{H}_\text{A}(\text{g}) - \text{H}^\circ_\text{A}(\text{c})] + [\text{H}^\circ_\text{A}(\text{liq}) - \text{H}_\text{A}(\text{g})] \\ &= \text{H}^\circ_\text{A}(\text{liq}) - \text{H}^\circ_\text{A}(\text{c})\end{aligned} \tag{13.24}$$

When equation (13.24) is compared with equation (13.19), we see that *in the ideal solution the heat of solution of a solid is identical with its heat* *of melting* at the same temperature. The substance A will absorb the same energy when it "melts" into an ideal solution containing both A and B as it will when it melts to form pure liquid A.

Equation (13.24) applies over the entire concentration range. Thus, the partial heat of solution of the solid is constant, and the molar heat content H_A of A in solution may be represented by the equations

$$\text{H}_A(\text{in soln}) = \text{H}_A^\circ(\text{liq})$$

$$\left(\frac{\partial H_A}{\partial n_A}\right)_{n_B} = \frac{H_A}{n_A} = \overline{\text{H}_A} = \text{H}_A^\circ(\text{liq}) \tag{13.25}$$

As for ideal gases, the simpler molar heats are identical with the partial molar heats. For the systems discussed in Chap. 6, the heat contents were not independent of the concentration and the partial molal heats were required to give the heat of solution at any given concentration

Solubility of Solids in Liquids.—From equation (13.19), it appears that at the temperature T, the solubility of a solid is constant. This conclusion is in agreement with experience. When the temperature changes at constant pressure, the solubility changes as required by the van't Hoff equation. From equations (12.90) and (13.19), we have the solubility equation

$$d \ln N_A = \frac{\Delta \text{H}_A}{RT^2} dT \tag{13.26}$$

As a first approximation, we may consider the heat of melting independent of the temperature. This assumption is legitimate at temperatures not too far removed from the melting point of the solid, especially because the differences in heat capacities of solids and liquids are not so great as the differences between the heat capacities of gases and condensed phases. The indefinite integral of equation (13.26) is

$$\ln N_A = -\frac{\Delta \text{H}_A}{R}\frac{1}{T} + I' \tag{13.27}$$

When $R = 1.9872$ cal/deg, 2.3026 R equals[1] 4.576 and, we have for 1 mole of A, on conversion to common logarithms,

$$\log N_A = -\frac{\Delta \text{H}_A}{4.576}\frac{1}{T} + I \tag{13.28}$$

This equation is analogous to equation (9.16) for the change of vapor pressure with temperature.

---

[1] In this chapter we shall use the value 4.576 rather than the more exact 4.5757. Equations based on the assumption of ideal solution are not exact enough to justify the use of the more exact value.

When $\log N_A$ is plotted against $1/T$, a straight line is obtained with the slope equal to $-\Delta H_A/4.576$ and the intercept at I. The value of I can be readily determined; for, at the melting temperature T_A of pure A, the "solution" becomes pure A, so that $N_A = 1$ and $\log N_A = 0$. From equation (13.28), therefore,

$$I = \frac{\Delta H_A}{4.576}\frac{1}{T_A} \tag{13.29}$$

This value of I may be substituted in equation (13.28) to give

$$\log N_A = -\frac{\Delta H_A}{4.576}\frac{1}{T} + \frac{\Delta H_A}{4.576}\frac{1}{T_A} \tag{13.30}$$

which may be written in the form

$$\log N_A = \frac{\Delta H_A}{4.576}\left(\frac{1}{T_A} - \frac{1}{T}\right) = \frac{\Delta H_A}{4.576}\left(\frac{T - T_A}{TT_A}\right) \tag{13.31}$$

Equation (13.31) is obtained directly when we integrate (13.26) between the limits $N_A = 1$, $T = T_A$ and $N_A = N_A$, $T = T$. At the temperature T' where N_A has the value N'_A, equation (13.28) becomes

$$\log N'_A = -\frac{\Delta H_A}{4.576}\frac{1}{T'} + I \tag{13.32}$$

which may be combined with equation (13.28) to give

$$\begin{aligned}\log \frac{N_A}{N'_A} &= -\frac{\Delta H_A}{4.576}\left(\frac{1}{T} - \frac{1}{T'}\right) \\ &= \frac{\Delta H_A}{4.576}\left(\frac{1}{T'} - \frac{1}{T}\right) = \frac{\Delta H_A}{4.576}\left(\frac{T - T'}{TT'}\right)\end{aligned} \tag{13.33}$$

All the above equations contain only functions of the substance A. There are no terms for the "solvent" or "solute" B. In an ideal solution at constant pressure the solubility of A is a function of the temperature, the heat of melting of A, and the melting point of A. In the ideal solution, it is, therefore, possible to obtain the solubility curve for A without reference to any particular solvent. In the substance C, A will have the same solubility curve as in B. Because the $\log N$ *vs.* $1/T$ graph is linear, only two experimental points or one experimental point and the slope are required to establish the solubility curve. Thus, the solubility curve can be established with (*a*) a solubility determination at each of two temperatures, (*b*) a solubility determination and the melting point, (*c*) the heat of melting (solution) and the melting point, or (*d*) the heat of melting and one solubility value.

The above equations were called "solubility equations." When the constants of the equations are evaluated or when the equation is plotted, the solubility (in mole fractions) can be obtained at any temperature. However, the equations are also freezing point equations. When pure A freezes to the pure solid, $N_A = 1$ and $T = T_A$; but when it freezes from a solution, $N_A < 1$ and $T < T_A$. The addition of B to the solution lowers the value of N_A; hence, the freezing of A from the solution occurs at a lower temperature. The freezing point lowering may be obtained from equation (13.31) by solving for $T_A - T$. Thus,

$$T_A - T = -\frac{4.576TT_A}{\Delta H_A}\log N_A \tag{13.34}$$

An approximate expression for the freezing point lowering is derived in a following section.

Exact Solubility-temperature Curve.—In the integration of equation (13.26) to give equation (13.27) and subsequent equations, the approximation was made that the heat of melting (heat of solution) of the solid does not change with temperature. As we know, the heat capacities of solid and liquid are not identical so that the heat of melting changes somewhat, though not rapidly, with temperature. When the molar heat of melting is represented by the equation

$$\Delta H = \Delta H_0 + \alpha T + \tfrac{1}{2}\beta T^2 \tag{13.35}$$

the constants α and β being obtained from the heat capacity equations of solid and liquid, equation (13.26) becomes

$$d \ln N_A = \left(\frac{\Delta H_0}{RT^2} + \frac{\alpha}{RT} + \frac{\beta}{2R}\right) dT \tag{13.36}$$

If this equation is integrated between the limits $N_A = N_A$, $T = T$ and the melting point where $N_A = 1$, $T = T_A$, we obtain

$$-\ln N_A = -\frac{\Delta H_0}{R}\left(\frac{1}{T_A} - \frac{1}{T}\right) + \frac{\alpha}{R}\ln\frac{T_A}{T} + \frac{\beta}{2R}(T_A - T)$$

On change of sign and conversion to common logarithms with R in calories per degree, this equation becomes

$$\log N_A = \frac{\Delta H_0}{4.576}\left(\frac{1}{T_A} - \frac{1}{T}\right) - \frac{\alpha}{1.987}\log\frac{T_A}{T} \qquad \frac{\beta}{2 \times 4.576}(T_A - T) \tag{13.37}$$

Because α and β are relatively small, the second and third terms introduce small or negligible corrections, so that instead of being straight the log N *vs.* $1/T$ graph may be slightly curved. When accurate data are available, the plotted experimental data fall on a solubility graph that is slightly curved; if the data are not so precise, the accidental errors tend to hide any curvature of the line because the plotted experimental points scatter on both sides of the "best straight line" drawn through the data.

Freezing Point Lowering.—The familiar expression for the freezing point lowering may be derived directly from equation (13.26). If A is the solvent and is present in great excess, the solution is dilute with respect to the solute, B, N_A approaches the value of unity, and T approaches T_A. Under these conditions,

$$\mathrm{d}\ln N_A = \frac{\mathrm{d}N_A}{N_A} \doteq \mathrm{d}N_A \tag{13.38}$$

But, in a binary solution,

$$\mathrm{d}N_A = -\mathrm{d}N_B \tag{13.39}$$

If these equations are combined with (13.26), we have

$$\frac{\mathrm{d}N_A}{\mathrm{d}T} = -\frac{\mathrm{d}N_B}{\mathrm{d}T} \doteq \frac{\Delta \mathrm{H}_A}{RT_A^2} \tag{13.40}$$

When the concentration of B is low, the freezing point lowering defined as $T_A - T \equiv -\Delta T_f$ is directly proportional to the mole fraction of B, as indicated in the equation

$$\frac{\mathrm{d}N_A}{\mathrm{d}T} = -\frac{\mathrm{d}N_B}{\mathrm{d}T} \doteq -\frac{N_B}{T - T_A} = \frac{N_B}{-\Delta T_f} \tag{13.41}$$

The freezing point lowering $-\Delta T_f$ produced on A when B is added to A in sufficient quantity to make its mole fraction equal to N_B is, from equations (13.40) and (13.41),

$$-\Delta T_f \doteq \frac{RT_A^2}{\Delta \mathrm{H}_A} N_B = \frac{RT_A^2}{\Delta \mathrm{H}_A}(1 - N_A) \tag{13.42}$$

This value for the freezing point lowering of the solvent derived with approximations from the differential solubility equation may be compared with that obtained from the integral solubility equation in equation (13.34).

The freezing point lowering depends on the heat of melting of A, on its freezing temperature, and on the concentration of A (or B) in the solution. When the freezing point lowering of different solvents is compared, therefore, it seems reasonable to compare them at equal concentrations. In the last column of Table 13.2 the freezing point lowering $-\Delta T_f = k'$ of different solvents containing 5 mole per cent of solute are compared. In all these solutions the concentration of the solvent is 95 mole per cent. Observe that, with few exceptions, the freezing point lowerings of the solvents are between 2 and 4°c at this concentration.

The "freezing point constant" k_f usually listed for solvents compares the different solvents not at *equal mole fractions* but at *equal molalities of solute.* On this basis the constants for the different solvents differ widely as indicated in column (6) of Table 13.2. This constant involves the following further approximation: When $N_B \doteq n_B/n_A$, that is, when $n_A + n_B \doteq n_A$, equation (13.42) becomes

TABLE 13.2.—A COMPARISON OF FREEZING POINT CONSTANTS FOR EQUAL MOLALITIES AND FOR EQUAL MOLE FRACTIONS OF SOLUTE

Solvent	Formula	Molar weight	Melting point, °C	Heat of melting, kjoules	Freezing point constants	
					k_f, for molality of solute = 1	k', for mole fraction of solute = 0.05
(1)	(2)	(3)	(4)	(5)	(6)	(7)
Water	H_2O	18.02	0	6.01	1.86	5.26
Benzene	C_6H_6	78.05	5.5	9.91	4.90 – 5.23	3.38 – 3.61
Cyclohexane	C_6H_{12}	84.09	6.5	......	20.0 –20.3	12.8 –13.1
p-Xylene	C_8H_{10}	106.08	13.2	17.45	4.30	2.24
Naphthalene	$C_{10}H_8$	128.06	80.1	19.07	6.899– 7.10	3.04 – 3.13
Diphenyl	$C_{12}H_{10}$	154.08	69.0	16.84	8.00 – 8.35	3.0 – 3.13
Anthracene	$C_{14}H_{10}$	178.08	218	28.85	11.65	3.86
Phenanthrene	$C_{14}H_{10}$	178.08	99.6	18.1	12.00	3.97
Dibenzyl	$C_{14}H_{14}$	182.11	52.5	23.645	7.20 – 7.23	2.34 – 2.35
Triphenylmethane	$C_{19}H_{16}$	244.12	92.5	18.2	12.45	3.18
Carbon tetrachloride	CCl_4	153.83	−23.0	2.68	29.8 –34.8	11.2 –13.1
Chloroform	$CHCl_3$	119.38	−63.5	......	4.67 – 4.90	2.37 – 2.49
Bromoform	$CHBr_3$	252.76	7.7	......	14.25 - 14.44	3.52 – 3.57
Ethylene dibromide	$C_2H_4Br_2$	187.86	10.0	10.637	12.50 –11.80	3.96 – 3.74
Formic acid	CH_2O_2	46.015	8.4	11.34	2.77 – 2.80	3.15 – 3.18
Acetic acid	$C_2H_4O_2$	60.03	16.6	11.23	3.90	3.45
Benzoic acid	$C_7H_6O_2$	122.05	121.7	17.3	7.85 – 8.788	3.61 – 4.04
Phenylacetic acid	$C_8H_8O_2$	136.06	76.7	......	9.00	3.75
Palmitic acid	$C_{16}H_{32}O_2$	256.25	64	42.05	4.40	1.08
Stearic acid	$C_{18}H_{36}O_2$	284.28	69.3	56.5	4.40 – 4.50	0.991–1.01
Cyclohexanol	$C_6H_{12}O$	100.09	23.9	1.756	38.28	20.95
Phenol	C_6H_6O	94.05	41	11.4	7.20 – 7.50	4.18 – 4.26
o-Cresol	C_7H_8O	108.06	30.1	......	5.62	2.88
p-Cresol	C_7H_8O	108.06	34.8	11.9	7.55	3.88
β-Naphthol	$C_{10}H_8O$	144.06	122	18.8	11.25	4.47
Thymol	$C_{10}H_{14}O$	150.11	51.5	17.3	8.30 – 8.32	3.16 – 3.17
Camphor	$C_{10}H_{16}O$	152.12	179	......	49.80	19.15
Salol	$C_{13}H_{10}O_3$	214.08	43	......	12.30	3.49
Benzil	$C_{14}H_{10}O_2$	210.08	95.2	19.45	10.50	3.02

$$-\Delta T_f \doteq \frac{RT_A^2}{\Delta H_A} \frac{n_B}{n_A} \tag{13.43}$$

When the *molality constant* k_f is defined as the value of $-\Delta T_f$ when 1 mole of B is dissolved in 1,000 grams of A, equation (13.43) becomes, for a one molal solution,

$$k_f = -\Delta T_f = \frac{RT_{\mathrm{A}}^2}{\Delta \mathrm{H}_{\mathrm{A}}} \frac{1}{1{,}000/M_{\mathrm{A}}} = \frac{RT_{\mathrm{A}}^2}{\Delta \mathrm{H}_{\mathrm{A}}} \frac{M_{\mathrm{A}}}{1{,}000} \tag{13.44}$$

where M_{A} is the molar weight of A.

Equation (13.44) indicates that, if two solvents have equal values of $T_{\mathrm{A}}^2/\Delta \mathrm{H}_{\mathrm{A}}$, their values of k_f are directly proportional to their molecular weights. This relation has been misinterpreted by some chemists who have used freezing point lowering experiments to determine the molecular weights of organic molecules. For example, some have used ethylene dibromide as a solvent "because it has a high constant." The reasoning is erroneous; as column (7) of Table 13.2 shows its mole fraction constant k' is normal. Ethylene dibromide has a high molality constant primarily because it has two heavy bromine atoms in the molecule which give it a relatively high density but do not necessarily make it a better solvent for molecular weight determinations. Because deviations from the laws of ideal solution increase with increasing concentration of solute, we should judge two solvents at comparable concentrations. Generally speaking, we prefer a solvent that is nearly enough like the solute to form an ideal solution with it; to favor ideality, we desire the largest freezing point lowering for a given concentration of solute in the solution. It is obvious from Table 13.2 that the method of expressing concentration is important when we undertake to compare "equal concentrations" of different solvents (or solutes).

Let us compare benzene (m.p. = 5.5°c) and ethylene dibromide (m.p. = 10.0°c) as solvents for molecular weight determinations. We see from column (6) of Table 13.2 that the freezing point lowering produced by 1 mole of solute on 1,000 grams of ethylene dibromide is 11.8 to 12.5°, whereas that produced on 1,000 grams of benzene by the same amount of solute is 4.90 to 5.23°c. As a result of this difference in "constants," some have preferred ethylene dibromide as a solvent for molecular weight determinations. But the 1,000 grams of ethylene dibromide occupy only 0.454 liter at 10°c, whereas the 1,000 grams of benzene occupy 1.118 liters at 5.5°c. The freezing point lowering produced when the mole of solute is dissolved in 1 liter of ethylene dibromide at 10°c ranges between 5.4 to 5.7°c, whereas that produced when the mole of solute is dissolved in 1 liter of benzene at 5.5° ranges from 5.5 to 5.9°c. On a volume basis, the two solvents appear nearly equal. On a basis of equal mole fractions (0.05 of solute) the last column of Table 13.2 shows that ethylene dibromide has a slightly higher constant, 3.96 to 3.74°c as compared with 3.38 to 3.61°c for benzene. We may, therefore, conclude that solvents for molecular weight determinations should be chosen primarily on the basis of their similarity to the solute and not on the basis of misinterpreted "molality" freezing point constants.

Boiling Point Rise.—The boiling point rise law may be derived in a similar manner. Because $\mathrm{d}\ln P^\circ = \mathrm{d}P^\circ/P^\circ$, we have from equation (13.12)

$$\frac{\mathrm{d}P^\circ}{P^\circ} = \frac{\Delta\mathrm{H}_A}{RT^2}\,\mathrm{d}T \tag{13.45}$$

If we write $P_A^\circ - P_A$ for $\mathrm{d}P^\circ$ and combine with equation (13.1), we have

$$\mathrm{d}P^\circ \doteq P^\circ - P_A = P^\circ - P^\circ N_A \tag{13.46}$$

from which we obtain

$$\mathrm{d}P^\circ \doteq P^\circ(1 - N_A) = P^\circ N_B \tag{13.47}$$

because $N_A + N_B = 1$. As a further approximation, we may substitute the boiling point rise $\Delta T_b = T - T_A$ for $\mathrm{d}T$. Equation (13.45), then becomes

$$\Delta T_b = \frac{RT_A{}^2}{\Delta\mathrm{H}_A} N_B \tag{13.48}$$

which has the same form as the freezing point lowering equation. Here $\Delta\mathrm{H}_A$ is the molar heat of evaporation of the solvent. Values of the boiling point rise for different organic solvents calculated for equal mole fractions show agreement corresponding to that found for freezing point lowering. When the boiling point rise is calculated for different molalities, the "constants" differ widely for the same reasons as do those for the freezing point lowering under similar conditions.

Solubility in a Binary System.—We have seen [equation (13.30)] that all the constants in the ideal solubility relation

$$\log N_A = -\frac{\Delta\mathrm{H}_A}{4.576}\frac{1}{T} + \frac{\Delta\mathrm{H}_A}{4.576}\frac{1}{T_A} \tag{13.49}$$

are functions of the component A, so that the solubility of A will be the same in all ideal solvents. Values of N_A at various temperatures can be derived from this equation and plotted with temperature as ordinate and mole fraction as abscissa, as in Fig. 13.2. The curve begins at T_A and $N_A = 1$ and continues toward lower values of N at lower temperatures. Similarly the equation for the solubility of B in A, which is

$$\log N_B = -\frac{\Delta\mathrm{H}_B}{4.576}\frac{1}{T} + \frac{\Delta\mathrm{H}_B}{4.576}\frac{1}{T_B} \tag{13.50}$$

may be evaluated with the data on the heat of melting of B and the melting point T_B. The values of N_B at various temperatures can be calculated for this substance and plotted on the same diagram beginning at T_B and $N_A = 0$, $N_B = 1$.

At the point E where the solubility curves intersect, both solid A and solid B are in equilibrium with the solution. This point of intersection is called the "eutectic point." At this eutectic temperature, the values of N_A and N_B are such that

$$N_A + N_B = 1$$

If we substitute the substance B′ for B, the solubility curve for A, as in Fig. 13.2, is unaltered; it extends from T_A through E and E'. The solid B′, with its own heat of melting $\Delta H'_B$ and its own melting point T'_B, has a solubility curve different from B, as indicated in Fig. 13.2. The curve for B′ intersects that for A at E'; this is the eutectic for this binary system. If B and B′ form an ideal solution, the complete solubility diagram for a system containing these substances may be plotted in a similar manner.

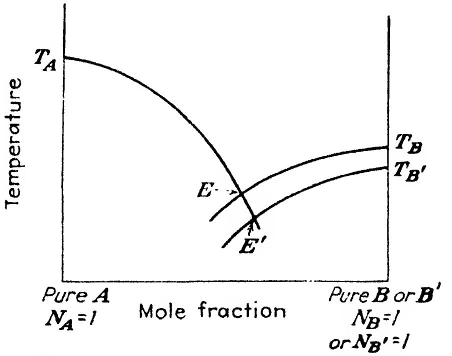


FIG. 13.2.—Solubility diagrams for binary systems.

The factors in the solubility equation that change from substance to substance are the heat of melting and the melting point. Figure 13.2 shows that B′ is more soluble than B; at any temperature the value of N'_B is greater than that of N_B. Where the heats of melting do not differ too widely, the substance with the lower melting point is the more soluble; it "melts" more easily into the solution just as it melts more readily to form the pure liquid.

Ideal Ternary Systems.—The above considerations can be applied to ideal ternary systems. If the solids A, B, and C dissolve mutually to form a set of ideal binary systems, they form an ideal ternary system. These relationships were discussed by Johnston,[1] Andrew, and Kohman in a series of papers. They found for the systems, the three dinitrobenzenes, the three nitroanilines, and the three nitrochlorobenzenes,

---

[1] JOHNSTON, J., D. H. ANDREWS, and G. T. KOHMAN, *J. Phys. Chem.*, **29**, 882, 914, 1041, 1048, 1317 (1925).

that the pairs of compounds *ortho* + *meta*, *ortho* + *para*, and *meta* + *para* and the ternary system *ortho* + *meta* + *para* all fulfil the above requirements for ideal solutions. Table 13.3 gives data obtained by the cooling curve method for the binary systems *ortho* + *meta*, *ortho* + *para*, and *meta* + *para*-dinitrobenzene. The temperatures marked "ideal" are those calculated from observed heats of melting and the melting temperature according to equation (13.30). When the mole fraction of the *o*-dinitrobenzene is 0.90 in the solution, it begins to crystallize from the solution at 110°c, regardless of whether the other component is the *meta*- or *para*-compound. A mixture of the *meta*- and *para*-compounds does not change the solubility of the *ortho*-compound so long as the mole fraction of the latter remains unchanged. However, when a third component, C, is added to a binary system of A and B, more moles are added and the mole fraction of A in the solution is reduced. The temperature at which A crystallizes from the solution is therefore lowered. If both A and B are crystallizing from the solution at the binary eutectic point where

TABLE 13.3.—THE MUTUAL SOLUBILITIES* OF *ortho*-, *meta*-, AND *para*-DINITROBENZENE

[Temperatures at which one of the dinitrobenzenes (called A) crystallizes from solutions of each of the others (called B)]

Mole per cent of A in the solution (= 100N_A)	Crystallization temperatures, °c								
	Ortho = A			*Meta* = A			*Para* = A		
	Ideal	Observed when		Ideal	Observed when		Ideal	Observed when	
		Meta = B	*Para* = B		*Ortho* = B	*Para* = B		*Meta* = B	*Ortho* = B
100	116.9	.....	.....	89.8	....	....	173.5		
90	110.0	110.0	110.6	83.2	83.2	83.2	167.1	167.1	167.7
80	104.5	104.8	104.0	75.5	75.5	....	160.4	160.4	161.2
70	97.2	97.2	.....	67.6	67.6	....	152.3	152.3	154.5
60	89.6	88.7	.....	....	....	....	144.3	144.3	146.1
50	80.7	79.5	.....	....	....	....	134.3	134.3	136.6
40	70.4	68.7	.....	....	....	....	122.1	122.0	125.2
30	.....	.....	.....	....	....	....	107.1	107.0	111.7
20	.....	.....	.....	....	....	....	87.1	87.5	93.7

$$N_A + N_B = 1$$

---

* ANDREWS D. H., *J. Phys. Chem.*, **29**, 1041 (1925).

addition of C decreases both N_A and N_B so that the solution is no longer saturated. It becomes saturated again only when the temperature is lowered. Thus, a third substance present, even as an impurity, may lower the eutectic temperature for a binary system. In general the eutectic point of A-B is lowered by C, that of A-C by B, and that of B-C by A, so that the ternary eutectic point is lower than the binary eutectic points. This principle is used in the production of low-melting alloys.

At the ternary eutectic point, we have

$$\log N_A = -\frac{\Delta H_A}{4.576}\frac{1}{T} + \frac{\Delta H_A}{4.576}\frac{1}{T_A}$$

$$\log N_B = -\frac{\Delta H_B}{4.576}\frac{1}{T} + \frac{\Delta H_B}{4.576}\frac{1}{T_B}$$

$$\log N_C = -\frac{\Delta H_C}{4.576}\frac{1}{T} + \frac{\Delta H_C}{4.576}\frac{1}{T_C}$$

and

$$N_A + N_B + N_C = 1$$

The temperature that satisfies these equations is the ternary eutectic temperature. It can be calculated by the methods outlined by Andrews and Kohman.[1]

Free Energy of an Ideal Solution.—At constant temperature the change of free energy of a simple substance with pressure is given in equation (10.43); it may be expressed as

$$dF = V\,dP$$

which for 1 mole of ideal gas becomes

$$F_2 - F_1 = RT \ln \frac{P_2}{P_1} \tag{13.51}$$

Let us select the pure liquid A as the standard state with $F_1 = F_A^\circ$ and $P_1 = P_A^\circ$, where P_A° is the saturated vapor pressure of A. When the liquid A enters a solution where its molar free energy at the mole fraction N_A is $F_2 = F_A$ and the vapor pressure is $P_2 = P_A$, the change of free energy for the solution process is

$$F_A - F_A^\circ = RT \ln \frac{P_A}{P_A^\circ} \tag{13.52}$$

The assumption that the vapors in equilibrium with the solution behave as ideal gases is implicit in this equation. If they do not, we must use

---

[1] *J. Phys. Chem.*, **29**, 1317 (1925).

the form

$$\text{F}_\text{A} - \text{F}_\text{A}^\circ = RT \ln \frac{f_\text{A}}{f_\text{A}^\circ} \tag{13.53}$$

But, if the solution obeys Raoult's law, $P_\text{A}/P_\text{A}^\circ = N_\text{A}$ and equation (13.52) becomes

$$\text{F}_\text{A} - \text{F}_\text{A}^\circ = RT \ln N_\text{A} \tag{13.54}$$

where $\text{F}_\text{A} - \text{F}_\text{A}^\circ$ is the change in free energy when 1 mole of pure liquid A dissolves in the solution. Equation (13.54) was derived for an ideal liquid solution, but it can be shown that the free energy of solution of ideal solids and of ideal gases may also be represented by this equation.

Equation (13.54) gives the free energy of solution of 1 mole of A. For 1 mole of solution containing N_A moles of A and N_B moles of B, the free energy of formation of the solution from pure A and pure B is

$$\begin{aligned} N_\text{A}(\text{F}_\text{A} - \text{F}_\text{A}^\circ) &= N_\text{A}RT \ln N_\text{A} \\ N_\text{B}(\text{F}_\text{B} - \text{F}_\text{B}^\circ) &= N_\text{B}RT \ln N_\text{B} \\ \hline \Delta F(\text{solution}) &= N_\text{A}RT \ln N_\text{A} + N_\text{B}RT \ln N_\text{B} \end{aligned} \tag{13.55}$$

Entropy of Solution.—We found earlier that, for ideal solutions, the heat of solution of a gas or a solid is identical with the heat of condensation of the gas or heat of melting of the solid. When there is no phase change, as in the mixing of liquids, there is no heat effect. In ideal solutions, there is no heat of mixing and $\text{H}_\text{A} = \text{H}_\text{A}^\circ$, as indicated in equation (13.14). The solution process is spontaneous, however, and there is, therefore, a free energy of mixing as indicated in equation (13.54). From equation (10.51), for this constant-temperature process,

$$\Delta F = \Delta H - T\,\Delta S \tag{13.56}$$

and because $\Delta H = 0$, we have for the solution of 1 mole of A

$$\text{F}_\text{A} - \text{F}_\text{A}^\circ = 0 - T(\text{S}_\text{A} - \text{S}_\text{A}^\circ) \tag{13.57}$$

which combined with equation (13.54) becomes

$$\text{S}_\text{A} - \text{S}_\text{A}^\circ = -\frac{RT \ln N_\text{A}}{T} = -R \ln N_\text{A} \tag{13.58}$$

From the point of view of probability, there must be an entropy change for the mixing of two liquids just as for the mixing of gases. The entropy change results because the liquids or gases are diluting each other so that the molar volume of each is increased. In this and in all other spontaneous processes at constant energy, there is an increase in entropy. Observe that $\text{S}_\text{A} - \text{S}_\text{A}^\circ$ is positive, for $\ln N_\text{A}$ is negative. Although equation (13.58) was derived for liquid solutions, it applies to ideal gaseous and solid solutions as well; for it is derived from the rules of ideal solution that can be applied to gaseous, liquid, and solid phases.

Regular Solutions.—In Chap. 7, the relation between entropy and probability was derived for and applied to ideal gases. We discovered there that the probability of a given state of the gas is related to the volume of the gas in that state. For this reason, the probability of a gas in a mixture is related to the volume of the gas in the mixture, and this volume of the mixture in turn depends on the extent of the dilution of the gases. At constant pressure, this dilution is measured by the mole fraction of the gas. The mole fraction of the gas, therefore, becomes a measure of the probability and of the entropy. This is the relation expressed in equation (13.58).

The probability of a given state can be expressed in terms of the concentration of a substance only if complete randomness exists. If the molecules combine or associate, the complete randomness is destroyed and the mole fraction can no longer be a measure of the probability of a state. We have stated as a requirement of ideal solution that the molecules of A shall not behave differently in an environment of molecules of B than they do in an environment of pure A. If the molecules of A and B tend to associate or combine with each other, the randomness of distribution is obviously destroyed.

The thermal motion of the molecules will, if pronounced enough, ensure complete mixing of A and B if the attractive forces between them are not too great. Under these conditions, it may be entirely possible for the molecules of a solution to be thoroughly mixed even though the attractive forces between the molecules do not permit adherence to Raoult's law. The number of solutions having a complete randomness of distribution is greater than the number that are ideal over the complete concentration range. Hildebrand has suggested that solutions in which this randomness exists shall be called *regular solutions*. The entropy of the component A in a regular solution may therefore be represented by equation (13.58). In such a solution there may, of course, be a heat of mixing and a nonideal free energy of mixing, as indicated in equation (13.56). Under these conditions, the difference between the free energy of mixing for the ideal and the regular solutions is measured by the observed heat of mixing. In the regular solution, the free energy may not be measured by the mole fraction in accordance with equation (13.54), so that it will be necessary here to use the partial molal free energy, that is, the free energy per mole at the given concentration. For the regular solution, we have, therefore, from equation (13.56),

$$\overline{\mathrm{F}_{\mathrm{A}}{}^{r}} - \mathrm{F}_{\mathrm{A}}^{\circ} = \overline{\mathrm{H}_{\mathrm{A}}{}^{r}} - \mathrm{H}_{\mathrm{A}}^{\circ} - T(\overline{\mathrm{S}_{\mathrm{A}}{}^{r}} - \mathrm{S}_{\mathrm{A}}^{\circ}) \qquad (13.59)$$

and, for the ideal solution,

$$\mathrm{F_A}^i - \mathrm{F}_\mathrm{A}^\circ = \mathrm{H_A}^i - \mathrm{H}_\mathrm{A}^\circ - T(\mathrm{S_A}^i - \mathrm{S}_\mathrm{A}^\circ) \tag{13.60}$$

But because, for the regular and ideal solutions,

$$\mathrm{S_A}^i - \mathrm{S}_\mathrm{A}^\circ = \overline{\mathrm{S_A}^r} - \mathrm{S}_\mathrm{A}^\circ \tag{13.61}$$

and because, for the ideal solution,

$$\mathrm{H_A}^i - \mathrm{H}_\mathrm{A}^\circ = 0 \tag{13.62}$$

we have, on subtracting equation (13.60) from (13.59),

$$\overline{\mathrm{F_A}^r} - \mathrm{F_A}^i = \overline{\mathrm{H_A}^r} - \mathrm{H}_\mathrm{A}^\circ \tag{13.63}$$

For a solution process at constant temperature and pressure, $\overline{\mathrm{H_A}^r} - \mathrm{H}_\mathrm{A}^\circ$ is the partial heat of solution of liquid A in the regular solution at the given concentration.

Ideal Solutions of Isotopes.—In recent years, many substances formerly considered pure have been shown to be composed of molecules that are not identical in mass. Water, for example, is composed of molecules of $H^1{}_2O^{16}$, $H^2{}_2O^{16}$, $H^1{}_2O^{18}$, and the other possible combinations of these isotopes of hydrogen and oxygen. These molecules are so similar in properties that they fulfill all the requirements we have set up for ideal solutions. It is customary in chemistry to consider the naturally occurring isotopic mixtures as "pure" substances and to define the standard state for the substance in terms of these naturally occurring mixtures. As a result, the thermodynamic functions are evaluated in terms of these mixtures.

If we wish to determine the values of these functions for each of the isotopic forms present in the naturally occurring mixture, we must know how the thermodynamic functions change on formation of the mixture from the simple isotopes. These changes can be readily evaluated with the aid of the laws of ideal solution. Thus the vapor pressures and the free energies of mixtures of $H^1{}_2O^{16}$ and $H^2{}_2O^{16}$ can be calculated from corresponding functions of the simple molecules with the aid of Raoult's law.

As usually carried out, chemical reactions do not distinguish between the isotopes of an element so that the relative proportion of the isotopes remains unchanged throughout a series of reactions. Under these conditions, the isotopic mixture acts as a pure substance and the values of the free energy and entropy, which are a measure of the distance from equilibrium at constant temperature and pressure and constant energy and volume, respectively, may be treated like those of a corresponding pure substance. This practice is entirely legitimate because the values of our thermodynamic functions are relative rather than absolute.

If reactions are found that can distinguish between two isotopes so that a separation is made, the isotopic mixture can no longer be assigned the value of the free energy for a pure substance. Under these conditions, the free energy of the isotopic mixture differs from that of the simple isotopes by the free energy of mixing.

Our ability to distinguish among the isotopes is an important factor here. When we connect two liter vessels of oxygen, there is no tendency toward a new equilibrium and, therefore, no change in free energy and entropy as the contents of the two vessels mix. When we connect a liter of $Cl^{35}{}_2$ and one of $Cl^{37}{}_2$, the two isotopes will interdiffuse until each is distributed uniformly throughout the system. If we cannot distinguish between the two isotopes of chlorine, this process will not seem different from the mixing of the oxygen from the two vessels. It appears, therefore, that, for practical purposes, entropy increases in processes which we can detect and measure. Many *practical values* of entropy based on this principle are in use. This point of view must be used in correlating entropies measured from thermal data with those calculated by statistical methods. In the statistical methods, isotopes that cannot be distinguished from each other in a process are treated as a single species. However, the energy levels of isotopes can be distinguished in the band spectra and these levels can be used to calculate the thermodynamic functions. When the value of the entropy of a gas, for example, calculated in this way, is compared with the entropy obtained from thermal data, it should not contain a term for the entropy of mixing of the isotopes because the isotopic mixture is not resolved in the thermal measurements.

Problems

In making systematic calculations, put the equations in a convenient explicit form and *tabulate* the calculations. See your instructor for suggestions. Hand in the tabulated calculations with the diagrams.

13.1. A solution of benzene contains 10 per cent of toluene by weight. Calculate the temperature at which benzene first crystallizes from the solution, using the van't Hoff equation. Obtain the necessary data from the "International Critical Tables." From the same tables, obtain data for the actual freezing temperature of this solution, and compare with your calculated value.

13.2. A mole of solute when added to 1,000 grams of benzene forms an ideal solution. Secure the necessary data and calculate the freezing point lowering produced by 1 mole of solute in 1,000 grams of benzene with the aid of (*a*) one of the integral solubility equations (*b*) the mole fraction formula [equation (13.42)], and (*c*) the molality formula [equation 13.44)]. Explain any discrepancy between the lowerings calculated by the three methods. Which of these represents the molal "freezing point constant"? Compare with the value commonly recorded in textbooks. In a molal ideal benzene solution, what is the percentage deviation between the freezing point lowering calculated by the three methods above and the observed lowering?

13.3. Repeat the calculations in Prob. 13.2 for 0.1 and 0.01 molal solutions of benzene. [Note that the integral solubility equation in the form of equation (13.30) cannot be applied with accuracy at low concentrations unless six- or seven-place logarithms are available. Why?] On a single diagram, plot the values you obtained for the freezing point lowering in this problem and Prob. 13.2 against molality and mole fraction of solute, respectively. What are the limiting ratios of $-\Delta T/m_B$ and $-\Delta T/N_B$?

13.4. Over what range of concentration is the approximation in equation (13.38) valid to 1 per cent? 5 per cent?

13.5. Calculate the vapor pressure of benzene at 50°C from the observed boiling point, 80.10°C, and the heat of evaporation of benzene.

13.6. The vapor pressure of benzene is represented by the equation

$$\log P_{\text{mm}} = 6.89745 - \frac{1206.350}{220.237 + t}$$

Calculate the value for the vapor pressure at 50°C and compare with the value obtained in Prob. 13.5.

13.7. At 25°C, ethyl alcohol and *n*-propyl alcohol form ideal solutions. Obtain from the "International Critical Tables" values for the vapor pressure of these liquids at 25°. Calculate the partial pressures of the two alcohols and the composition of the vapor in equilibrium with solutions containing, respectively, 0.2, 0.4, 0.6, and 0.8 mole fractions of ethyl alcohol. Construct graphs, with mole fraction as abscissa and vapor pressure as ordinate, showing

(*a*) The variation of the total pressure of the solution with change in composition of the solution.

(*b*) The variation of the partial pressures with change in composition.

(*c*) The variation of the vapor pressure of the solution with change in composition (mole fraction) of the vapor.

13.8. Calculate the free energy of formation in calories for the formation of 1 mole of air from 0.21 mole of oxygen, 0.78 mole of nitrogen, and 0.01 mole of argon at 27°C.

13.9. Calculate the entropy of formation for the process in Prob. 13.8.

13.10. Plot the solubility data for the dinitrobenzenes in Table 13.3 on a log N *vs.* $1/T$ graph. Calculate the three binary eutectic temperatures and compositions and the ternary eutectic temperature and composition.

13.11. Prove that equation (13.55) when applied to the formation of 1 mole of gaseous mixture from N_A moles of A and N_B moles of B at constant pressure and temperature gives the same free energy change as that calculated with the aid of the equation

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

13.12. Assuming that ethanol and *n*-propanol form ideal solutions, calculate the entropy of formation of 1 mole of solution containing ethanol and propanol in the mole ratios of 1:4, 1:3, 1:2, 1:1, 2:1, 3:1, and 4:1, respectively.

13.13. Assuming that ethanol and *n*-propanol form ideal solutions, calculate the entropies of solution of 1 mole of ethanol in 1, 2, 3, and 4 moles of *n*-propanol, respectively.

13.14. According to J. Smittenberg, H. Hoog, and R. A. Henkes [*J. Am. Chem. Soc.*, **60,** 17 (1938)], *n*-heptane, freezing at −90.6°c, and 2,2,4-trimethylpentane, freezing at −107.8°c, form ideal solutions. The eutectic point obtained from the intersection of the solubility curves is at −114.4°c where the composition is 24 mole per cent *n*-heptane. Calculate the heat of fusion of *n*-heptane and of 2,2,4-trimethylpentane.

13.15. Secure for benzene and naphthalene the best data on their melting point and heat of melting. Calculate with the aid of these data the mutual solubilities of these substances. Plot these solubilities on a *T-N* diagram (temperature as ordinate, and mole fraction as abscissa).

13.16. On the same diagram, plot the solubilities from the values given in the "International Critical Tables," Vol. 4. Compare the experimental values of the eutectic composition and temperature with those read from the curves in Prob. 13.15.

CHAPTER 14

THE THIRD LAW OF THERMODYNAMICS

The relative energies of the products and reactants of a reaction may be obtained in accordance with the first law of thermodynamics. We have observed, however, that the direction of a reaction is not defined by the heat of the reaction. The first law, therefore, cannot be used to predict equilibrium conditions. When the second law of thermodynamics is combined with the first, we obtain entropy and free energy functions that are related to the equilibrium conditions. Thermal data may be used to establish the change of these functions with temperature, but they cannot establish the value of the integration constant that appears in the equations. The first and second laws, therefore, cannot be used with thermal data alone to predict the conditions of chemical equilibrium. The functions based on thermal data give the change in equilibrium with temperature, as in equation (12.98); but *one* equilibrium value must be measured in order to fix the value of the integration constant. The search for a principle that will enable us to predict the equilibrium conditions from the thermal data alone led to the statements frequently called the "third law of thermodynamics."

Limitations of the First and Second Laws.—For a chemical reaction in which the change of heat capacity ΔC_P (heat capacity of the products minus heat capacity of reactants) is given by the equation

$$\Delta C_P = \alpha + \beta T + \gamma T^2 \tag{14.1}$$

we found from the first law equation that the heat of reaction at constant pressure is given by the equation

$$\Delta H = \Delta H_0 + \alpha T + \tfrac{1}{2}\beta T^2 + \tfrac{1}{3}\gamma T^3 \tag{14.2}$$

The only data required to evaluate all the constants in this equation are thermal data—the heat capacities, and the heat of reaction at one temperature. A combination of the first and second law equations gave us the free energy equation for an isothermal reaction,

$$\Delta F = -w_r + \Delta(PV) = \Delta E + \Delta(PV) - T\,\Delta S \tag{14.3}$$

and, therefore,

$$\Delta F = \Delta H - T\,\Delta S \tag{14.4}$$

For the change of free energy with temperature at constant pressure, we found in equation (10.57) that

$$\left(\frac{\mathrm{d}\,\Delta F}{\mathrm{d}T}\right)_P = -\Delta S = \frac{\Delta F - \Delta H}{T} \tag{14.5}$$

whence we obtained equation (11.31)

$$\mathrm{d}\left(\frac{\Delta F}{T}\right)_P = -\frac{\Delta H}{T^2}\,\mathrm{d}T \tag{14.6}$$

which, with equation (14.2), gives

$$\Delta F = \Delta H_0 - \alpha T \ln T - \tfrac{1}{2}\beta T^2 - \tfrac{1}{6}\gamma T^3 + IT \tag{14.7}$$

derived earlier as equation (11.34). When the products and reactants are at standard conditions, equation (14.7) represents the standard free energy change; it is related to the equilibrium constant by the equation

$$\Delta F^\circ = -RT \ln K_P \tag{14.8}$$

When equations (14.7) and (14.8) are combined, we have

$$-RT \ln K_P = \Delta H_0^\circ - \alpha T \ln T - \tfrac{1}{2}\beta T^2 - \tfrac{1}{6}\gamma T^3 + IT \tag{14.9}$$

which is equivalent to equation (12.97).

The values of α, β, γ, and ΔH_0 are obtained from heat capacity data within a limited temperature range and from the heat of reaction at one temperature. For this reason, equations (14.7) and (14.9), which are based on these values, cannot be applied at temperatures outside of the range for which the constants were obtained. Even the form of equation (14.1) is not suitable for expressing observed heat capacities at low temperatures. Because the constants are empirical, the integration constant I in equations (14.7) and (14.9) is also empirical. If we employ a free energy expression in which the constants express the actual behavior of the heat of reaction function, we see by comparison with equation (14.4) that the integration constant must be related to the entropy change for the reaction. Hence, if we can calculate the integration constant from entropy values, we can determine equilibrium conditions from purely thermal data without any equilibrium constant or free energy measurements.

In 1888, Le Châtelier showed, from a study of the free energy equation, that the integration constants of additive equations are additive. He predicted that we should be able to calculate the integration constants of a reaction from the constants relating to the evaporation or dissociation of the reactants and products. Because dissociations and evaporations are equilibrium reactions, Le Châtelier's proposal is essentially the calculation of an equilibrium condition from other equilibrium data in addition to the thermal data. Others (Lewis, Richards, van't Hoff, and Haber) worked on this problem. In 1906, Nernst, chiefly on the basis of Le Châtelier's and Richards's work, proposed his *heat theorem.*

Entropy and the Integration Constant.—Before we state Nernst's heat theorem, we shall discuss briefly the relation between entropy and the integration constant. From equation (14.5), it is evident that ΔS may be obtained either by differentiating equation (14.7) with respect to T or by subtracting (14.7) from (14.2) and dividing by T. In either case, we find that

$$\Delta S = \alpha + \alpha \ln T + \beta T + \tfrac{1}{2}\gamma T^2 - I \tag{14.10}$$

This equation is not important practically; for the equation on which it rests, namely, equation (14.1), does not represent the experimental facts at low temperatures. Equations (14.2) and (14.7) are valid only within restricted temperature limits, which do not extend into low temperatures. Near the absolute zero of temperature, we shall find there is no α term; hence, the integration constant is numerically equal to the entropy change at absolute zero, ΔS_0. Whenever equations (14.7) and (14.9) are used within the range for which the heat capacities equations are valid, they give the correct value of the changes in free energy and heat content. Under these conditions, equation (14.10) is an accurate expression of the entropy change. At low temperatures, however, I has a value different from ΔS; for the coefficients α, β, γ have values that do not fit the heat capacity curve at the lower temperatures.

The relation between the entropy change and the true integration constant may be derived as follows: For a reaction at constant pressure, represented by the chemical equation

$$\mathrm{A + B = D + E} \tag{14.11}$$

the entropy of reaction at the temperature T is represented by

$$\Delta S = (\mathrm{s_D} + \mathrm{s_E}) - (\mathrm{s_A} + \mathrm{s_B}) \tag{14.12}$$

We can evaluate the change of entropy of reaction with temperature if we know how the entropies of the substances A, B, D, and E change with temperature. From the relation between the heat capacity and entropy for simple substances at constant pressure given in equation (8.9), we have, from equation (14.12),

$$\frac{d\,\Delta S}{dT} = \left(\frac{\mathrm{c_D}}{T} + \frac{\mathrm{c_E}}{T}\right) - \left(\frac{\mathrm{c_A}}{T} + \frac{\mathrm{c_B}}{T}\right) = \frac{\Delta C_P}{T} \tag{14.13}$$

which may be written in the form

$$\mathrm{d}\,\Delta S = \frac{\Delta C_P\,\mathrm{d}T}{T} \tag{14.14}$$

When equation (14.14) is integrated between the temperature limits $T = 0$ and $T = T$ where ΔS has the values ΔS_0 and ΔS, respectively, we obtain

$$\Delta S = \int_0^T \frac{\Delta C_P\,\mathrm{d}T}{T} + \Delta S_0 \tag{14.15}$$

It appears, therefore, that we can obtain the value of ΔS_0, the entropy of reaction at zero temperature, from the measured value of ΔS at the temperature T, if we can evaluate the integral in equation (14.15).

When equation (14.15) is substituted in (14.4), we obtain

$$\Delta F = \Delta H - T\int_0^T \frac{\Delta C_P\,\mathrm{d}T}{T} - T\,\Delta S_0 \tag{14.16}$$

Equation (14.4), which relates free energy change to change in heat content and entropy change for an isothermal reaction, will, for the isothermal reaction at zero temperature, become

$$\Delta F_0 = \Delta H_0 - T\,\Delta S_0 \tag{14.17}$$

It appears from equation (14.17) that the free energy of reaction at zero temperature equals the heat of reaction for the constant pressure process if

$$T\,\Delta S_0 = 0 \tag{14.18}$$

At zero absolute where $T = 0$, equation (14.18) can be valid if ΔS_0 is zero or finite. It is clear, therefore, that the first and second laws leave ΔS undefined. Even if, in equation (14.16), we know the value of the integral $\int \frac{\Delta C_P\,\mathrm{d}T}{T}$, the free energy of reaction cannot be calculated from known values of ΔH so long as ΔS_0 is unknown.

Nernst Heat Theorem.—The relation between ΔF and ΔH for an isothermal reaction may be expressed in still another form obtained from equation (10.57),

$$\Delta F - \Delta H = T\left(\frac{\partial\,\Delta F}{\partial T}\right)_P \tag{14.19}$$

A comparison with equation (14.4) shows that at constant pressure

$$\frac{\partial\,\Delta F}{\partial T} = -\Delta S \tag{14.20}$$

which is equation (10.56).

In 1902, Richards found that the values of ΔF and ΔH for a number of cell reactions of condensed systems approach each other as the temperature is lowered. If ΔF and ΔH become equal at $T = 0$, we have, from equation (14.19),

$$\lim_{T=0} (\Delta F - \Delta H) = \lim_{T=0} T\left(\frac{\partial\,\Delta F}{\partial T}\right) = 0 \tag{14.21}$$

On the basis of these results, Nernst in 1906 proposed that not only do ΔF and ΔH approach the same value at $T = 0$ so that $T\,\partial\,\Delta F/\partial T$ approaches zero but that $\partial\,\Delta F/\partial T$ also approaches zero. It might be possible for $\partial\,\Delta F/\partial T$ to have a finite value as in Fig. 14.1*b*, in which case $T\,\partial\,\Delta F/\partial T$ at the absolute zero would still have zero value when $T = 0$. According to Nernst's proposal, ΔF approaches its limiting value at the absolute zero of temperature with zero slope as in Fig. 14.1*a*.

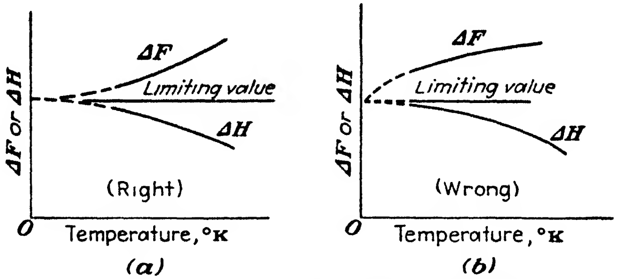


FIG. 14.1.—The limiting values of ΔF and ΔH.

The consequences of this proposal are clear; from equation (14.20), we see it is equivalent to saying that, at the zero absolute of temperature,

$$-\Delta S_0 = \lim_{T=0}\left(\frac{\partial\,\Delta F}{\partial T}\right)_P = 0 \tag{14.22}$$

This statement, that the entropy change for an isothermal reaction at the absolute zero of temperature is zero, is the Nernst heat theorem. It is a partial statement of what many call the third law of thermodynamics. Although the experimental data on which Nernst based his heat theorem were obtained for condensed systems, the restriction need not prove troublesome, for all known systems in the neighborhood of zero absolute are condensed at finite pressure.

Let us now see how ΔH must change with temperature in the neighborhood of $T = 0$. Equation (14.19) may be written in the form

$$\left(\frac{\partial\,\Delta F}{\partial T}\right)_P = \frac{\Delta F - \Delta H}{T} \tag{14.23}$$

When T approaches zero and $\Delta F - \Delta H$ approaches zero, the right side of equation (14.23) assumes the indeterminate value 0/0, which would be satisfied by $(\partial\,\Delta F/\partial T)_P$ having either a finite or a zero value. The indeterminate value may be resolved mathematically by differentiation of numerator and denominator of the right-hand term of equation (14.23). Then, at the limit $T = 0$,

$$\lim_{T=0}\left(\frac{\partial\,\Delta F}{\partial T}\right)_P = \lim_{T=0}\frac{\Delta F - \Delta H}{T} = \frac{0}{0} = \lim_{T=0}\left(\frac{\dfrac{\partial\,\Delta F}{\partial T} - \dfrac{\partial\,\Delta H}{\partial T}}{1}\right)$$

so that

$$\lim_{T=0}\left(\frac{\partial\,\Delta F}{\partial T}\right)_P = \lim_{T=0}\left(\frac{\partial\,\Delta F}{\partial T}\right)_P - \lim_{T=0}\left(\frac{\partial\,\Delta H}{\partial T}\right)_P \tag{14.24}$$

But, from equation (14.22), $(\partial\,\Delta F/\partial T)_P = -\Delta S_0$ at $T = 0$, and from equation (5.24), $(\partial\,\Delta H/\partial T)_P = \Delta C_P$. Therefore, equation (14.24) may be written in the form

$$\Delta S_0 = \Delta S_0 + \lim_{T=0}\Delta C_P \tag{14.25}$$

If ΔS_0 has zero value or a finite value, equation (14.25) shows that

$$\lim_{T=0}\Delta C_P = 0 \tag{14.26}$$

The consequence of ΔC_P being greater than zero would be that ΔS_0 must be infinitely large. On the other hand, as equation (14.25) shows, experimental proof that the limiting value of ΔC_P is zero cannot tell us whether ΔS_0 is zero or whether it is finite. Observation on the heat capacities alone cannot give us the Nernst theorem; the heat theorem cannot be deduced from the first and second law equations. The same conclusion follows from equations (14.16) and (14.17). If ΔC_P approaches zero at $T = 0$, the integral approaches zero, and equation (14.16) becomes equation (14.17). However, equation (14.17) is satisfied either by $\Delta S_0 = 0$ or by ΔS_0 equal to a finite number.

We stated earlier that a heat capacity equation of the type of (14.1) cannot represent heat capacities at low temperatures for it is in conflict with the deductions of the heat theorem. Thus, if ΔC_P is to equal zero at $T = 0$, α must be zero. To repeat our previous statements, if there is an α term in the heat capacity equation, the integration constant in equations (14.7) and (14.9) cannot equal zero, and I, therefore, represents an extrapolation value of an empirical equation and not the value of the entropy. This relation is clearly shown in equation (14.10).

Third Law of Thermodynamics.—The Nernst heat theorem, which bans entropy changes during reactions at the absolute zero, requires accordingly that *all condensed systems at the absolute zero have the same entropy value.* Nothing is implied by the theorem as to the numerical value of this common entropy.

According to statistical theory, entropy is related to probability by equation (7.46), which is

$$S = k \ln W$$

As a result of cessation of translational molecular motion at the absolute zero of temperature, the positions of the atoms may be fixed uniquely so that the probability of this state becomes unity. But if $W = 1$ at absolute zero, $\ln W = 0$ and $S_0 = 0$. Planck, therefore, proposed that zero is the natural value of this entropy value common to all substances at the absolute zero of temperature. Any other value of S_0 is consistent with the Nernst heat theorem so long as this value represents the entropy of each condensed substance at zero temperature. The Planck proposal, therefore, goes beyond the Nernst heat theorem. If Planck's proposal is valid, the Nernst heat theorem must follow; in addition, there are consequences of the Planck formulation that cannot be deduced from the heat theorem.

The assignment of zero entropy to each substance may be accepted as the *third law of thermodynamics.* It may be expressed provisionally in the following words:

At the absolute zero of temperature, the entropy of every substance is zero. The law is also represented by the equation

$$S_0 = 0 \tag{14.27}$$

Planck limited his assignment of zero entropy to pure crystalline solids; he exempted glasses and solid solutions from adherence to the third law. If the entropy of a solid solution at zero temperature has a value different from that of a pure crystalline solid, the Nernst heat theorem is not valid for the formation of the solution. But, as we pointed out in the preceding section, if ΔS_0 has a finite value, ΔC_P must still be zero.

The limits of applicability of the third law must be determined from the experimental evidence. Before we discuss this evidence, we shall derive some of the consequences of equation (14.27) that cannot be derived from the heat theorem. Chemical reactions do not permit a direct proof of equation (14.27), for they give only changes in entropy; that is, they fix the values of ΔS and not absolute values of entropy. For that matter, we have seen that the first and second laws enable us to calculate only relative values of energy, heat content, and free energy. However, the values of ΔE, ΔH, and ΔF, which we require, may be calculated from relative values as readily as from absolute values.

Heat Capacity at the Absolute Zero of Temperature.—We were able to show from the Nernst heat theorem that, at the absolute zero of temperature, $\Delta C_P = 0$. This condition is fully met in the transition of a solid from one crystalline form to another, if both forms have the same heat capacity at zero absolute. The latter condition is fulfilled if the numerical value of the heat capacity is a finite number and not zero. If equation (14.27) is valid, however, this common heat capacity value must be zero and not some finite number, as is evident from the following:

When a simple substance is heated at constant pressure, the increase in entropy per mole, from equation (8.6) or (8.10), is

$$\mathrm{ds} = \frac{\mathrm{c}_P}{T}\,\mathrm{d}T \tag{14.28}$$

If this equation is integrated between the absolute zero of temperature where $\mathrm{s} = \mathrm{s}_0$ and the temperature T where $\mathrm{s} = \mathrm{s}$, we have

$$\mathrm{s} - \mathrm{s}_0 = \int_0^T \frac{\mathrm{c}_P}{T}\,\mathrm{d}T \tag{14.29}$$

If c_P remained finite and not zero as T approached zero, the integral would become equal to ∞. Therefore, if entropy is to be positive at all temperatures above zero, c_P for each substance must approach zero. This prediction of the third law has been amply verified. A similar derivation at constant volume shows that c_V must also approach zero. We may, therefore, write

$$\lim_{T=0} \mathrm{c}_P = \mathrm{c}_V = \mathrm{c} = 0 \tag{14.30}$$

Other Properties at the Absolute Zero of Temperature.—For a process near 0°K in which the only entropy change results from an infinitesimal pressure change, we have

$$S_2 - S_1 = \int \left(\frac{\partial S}{\partial P}\right)_T \mathrm{d}P \tag{14.31}$$

From the heat theorem, $\Delta S = 0$, so that

$$\lim_{T=0} \left(\frac{\partial S}{\partial P}\right)_T = 0 \tag{14.32}$$

But, from equation (8.25),

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

whence,

$$\lim_{T=0}\left(\frac{\partial V}{\partial T}\right)_P = 0 \tag{14.33}$$

According to equation (14.33) the coefficient of thermal expansion vanishes near $T = 0$. Thus, when the pressure remains constant near $T = 0$, the volume also remains constant and the heat capacities at constant pressure and at constant volume assume a constant value c, as indicated in equation (14.30).

Similarly, it can be shown that

$$\lim_{T=0}\left(\frac{\partial S}{\partial V}\right)_T = 0 \tag{14.34}$$

so that

$$\lim_{T=0}\left(\frac{\partial P}{\partial T}\right)_V = 0 \tag{14.35}$$

Just as pressure and volume become independent of the temperature at $T = 0$, so must surface tension, also. At constant temperature and pressure, the increase of free energy with increase in surface area is expressed by the equation

$$\Delta F = \gamma\,\Delta A \tag{14.36}$$

where γ is the surface tension and ΔA the increase in surface area. If the heat theorem is valid, we have from equations (14.22) and (14.36), because surface area is not a function of temperature,

$$\lim_{T=0}\frac{\mathrm{d}\,\Delta F}{\mathrm{d}T} = \lim_{T=0}\frac{\mathrm{d}\gamma}{\mathrm{d}T} = 0 \tag{14.37}$$

This equation may be tested with helium, which remains liquid under its own vapor pressure at the lowest temperatures (less than 1°K). For liquid helium, the surface tension becomes independent of temperature, as required.

Liquid helium may be frozen at pressures higher than its vapor pressure. When the system containing solid and liquid helium is subjected to pressure, the change with temperature of this equilibrium pressure tends toward zero at low temperatures so that the equilibrium pressure at very low temperatures approaches a constant value that is independent of the temperature, as required by equation (14.35).

Equation (14.33) requires that the coefficient of thermal expansion shall become zero at low temperatures. Buffington and Latimer[1] found in confirmation that the coefficients of expansion of a number of crystal-

---

[1] BUFFINGTON, R. M., and W. M. LATIMER, *J. Am. Chem. Soc.*, **48**, 2305 (1926).

line solids approach zero, changing slightly more rapidly with temperatures than do the heat capacities. These agreements with predictions made from the third law of thermodynamics may be taken as evidence for the validity of the law.

Heat Capacities at Low Temperatures.—The predicted radical influence of low temperatures on heat capacity stimulated research to verify the conclusions. Nernst and his coworkers carried out extensive heat capacity measurements which showed that heat capacities decrease rapidly at low temperatures in such a way as to indicate that the heat capacity vanishes at zero temperature.

In Chap. 3, we showed that on the basis of the classical mechanics the gram-atomic heat capacity of a solid at constant volume is $3R = 5.96$ cal/deg. Many of the lighter elements, however, have heat capacities smaller than $3R$ at room temperatures; their heat capacities approach the upper limit of $c_V = 5.96$ cal, only at relatively high temperatures. In 1907, Einstein[1] derived an equation for heat capacity based on the quantum theory that gives the upper limit $c_V = 3R$ at high temperatures and $c_V = 0$ at $T = 0$. This was the first theoretical explanation of the general sigmoidal form observed for the heat capacity curves. Although the Einstein equation gives the general trend of heat capacity curves, it does not give close numerical agreement with the experimental results. In 1912, Debye[2] outlined a theory for the heat capacity c_V of isotropic solids that reproduces the observed heat capacities well. We shall not discuss the theory in detail. One of the terms in the equation is $(T/\theta)^3$ where θ is a constant for each substance called the *characteristic temperature* of the substance. It is defined by

$$\theta = \frac{h\nu_0}{k} \qquad (14.38)$$

where ν_0 is the upper limit of the spectrum of frequencies of vibration, h is Planck's constant, and k, Boltzmann's molecular gas constant. This constant, θ, contains the individual characteristics of a substance in the ν_0 term so that if c_V is plotted against T/θ the curves for all the different substances that obey the Debye equation fall on a single universal curve. For very low temperatures, the Debye equation becomes

$$c_V = \frac{12\pi^4}{5} R \left(\frac{T}{\theta}\right)^3 = 464.5 \left(\frac{T}{\theta}\right)^3 \text{ cal/deg}$$

which is of the form

$$c_V = aT^3 \qquad (14.39)$$

---

[1] EINSTEIN, A., *Ann. Physik*, **22**, 180, 800 (1907).

[2] DEBYE, P., *Ann. Physik*, **39**, 789 (1912).

The prediction that in the neighborhood of zero temperatures the heat capacity varies as the cube of the temperature has been confirmed for a great many substances, including glassy solids. Equation (14.39) is, therefore, widely used in the extrapolation of experimental heat capacity curves. The lower temperature limit for many data is that of the triple point of hydrogen at about 14°K. For solids that obey the Debye formula and do not have transitions in this range, equation (14.39) may be employed in the extrapolation from 14 to 0°K. Observe that the heat capacity here is that at constant volume. Near 0°K, however, c_P and c_V become identical within the limits of experimental error, as required by equation (14.30).

As stated above, c_V may be plotted against (T/θ) to give a single curve for all substances following the Debye equation. A single curve will, therefore, be obtained when c_V is plotted against $\log (T/\theta)$. But

$$\log\left(\frac{T}{\theta}\right) = \log T - \log \theta \tag{14.40}$$

It appears, therefore, that when c_V is plotted against $\log T$, curves for all these substances coincide if they are displaced along the log-T-axis by the distance $-\log \theta$, which is characteristic of each substance. This method was used by Lewis and Gibson[1] to correlate the heat capacities of different substances. For substances that do not follow the Debye equation, they[2] plotted c_V against $n \log (T/\theta)$ where n is also characteristic of each substance. These substances they classify as Class II.

We should point out that Lewis and Gibson used $\theta = \frac{1}{2}(3R)$ instead of θ as defined in equation (14.38) so that $\theta_{\text{Debye}} = 4.02\theta_{\text{Lewis}}$.

Calculation of Entropy from Heat Capacity Data.—Relative values of both heat content and entropy may be obtained from heat capacity data down to low temperatures. Thus, for the increase in heat content, at constant pressure,

$$dH = c_P\, dT$$

$$H - H_0 = \int_0^T c_P\, dT \tag{14.41}$$

Because $S_0 = 0$, from the third law, the increase in entropy, from equation (14.29), is

$$S = \int_0^T \frac{c_P}{T}\, dT = \int_0^T c_P\, d\ln T \tag{14.42}$$

---

[1] LEWIS, G. N., and G. E. GIBSON, *J. Am. Chem. Soc.*, **39**, 2554 (1917).

[2] The method is described by G. N. Lewis and M. Randall, in "Thermodynamics and the Free Energy of Chemical Substances," p. 76, McGraw-Hill Book Company, Inc., New York, 1923.

These relations are indicated in Figs. 14.2 to 14.4. The shaded area under the C_P *vs.* T curve in Fig. 14.2 represents $H - H_0$; that under the C_P *vs.* log T curve in Fig. 14.3 or under the C_P/T *vs.* T curve in Fig. 14.4 represents S. Observe that, at log $T = 0$, $T = 1$°K and that, at temperatures below 1°K log T approaches $-\infty$; but in this range the contribution to the total entropy appears to be small for all elements except hydrogen.

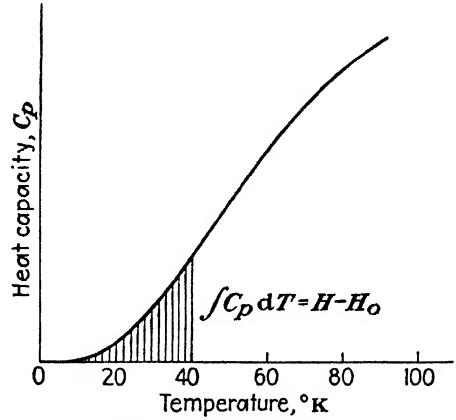


FIG. 14.2.—Graphical computation of heat content.

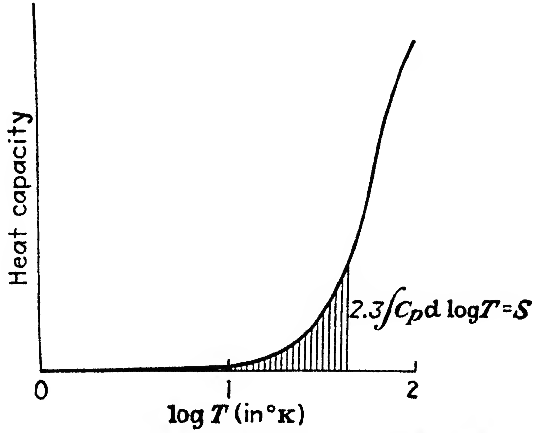


FIG. 14.3.—Graphical computation of entropy.

We stated earlier that small errors in heat capacity measurements at low temperatures are not particularly important in evaluating H, but that they do cause significant errors in entropy. This is evident from equations (14.41) and (14.42). Thus, a small error in C_P at low temperatures produces no greater error in H than a similar absolute error at high temperatures, but an error of 0.1 calorie at 10°K produces as large an error in S as an error of 1 calorie at 100°K or 3 calories at 300°K.

The numerical evaluation of entropy of a substance at room temperature is usually carried out in several steps. If the heat capacity data are available only between room temperature and liquid air or liquid hydrogen temperatures, a graphical integration of $\int c_P \, d \ln T$ between these temperature limits gives the entropy increase in this interval. If there are any phase transitions, solid-solid, solid-liquid, or liquid-gas, the entropy of the transitions is obtained either from the apparent heat capacities over the transition interval or from the measured heat of transition at the transition temperature. Between liquid hydrogen or liquid air temperatures and zero temperature an extrapolation of the observed heat capacity curves is required. Table 14.1 illustrates the types of calculation used to obtain the entropy of chlorine.

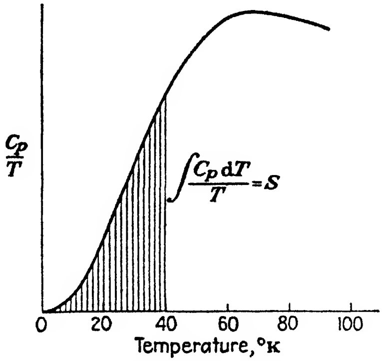


FIG. 14.4.—Graphical computation of entropy.

In many systems, significant heat effects are found below liquid air temperatures so that extrapolation below these temperatures does not reproduce the experimental results in this range. Extrapolation below liquid hydrogen temperatures is usually permissible. The entropy change in this low temperature range may then be obtained analytically from equations such as (14.39) or (14.42) or graphically from the area under the C_P/T *vs.* T curve, as in Fig. 14.4.

The value of the entropy of the substance at room temperature is then obtained from the summation of all these entropies between 0°K and room temperature, S_0 being assumed to be zero. As we have indicated, the entropies of gases may also be calculated from spectroscopic data. These spectroscopic values offer an independent check on the validity of the third law.

Some Experimental Tests of the Third Law.—We have already indicated some of the evidence for the validity of the third law of thermodynamics. Thus, its predictions concerning the behavior of heat capacity, surface tension, and coefficient of expansion in the neighborhood of zero temperature have all been confirmed by experiment. A further test of the law is furnished by the comparative values of $s - s_0$ for substances with known entropy difference at room temperature. Different crystalline modifications of an element are suitable for this type of measurement because few experimental measurements are required.

TABLE 14.1.—THE ENTROPY OF CHLORINE[*] GAS AT THE BOILING POINT FROM THERMAL DATA

(In calories per degree, 1 cal = 4.1832 int joules, 0°C = 273.10°K)

Temperature range or transition temperature, °K	Type of calculation	Entropy/mole
0–15	From Debye function, $hc\nu/k = 115$	0.331
15–172.12	Graphical calculation from c_P for solid	16.573
172.12	Fusion $\Delta H_{172.12} = 1{,}531$ cal	8.895
172.12–239.05	Graphical calculation from c_P for liquid	5.231
239.05	Vaporization $\Delta H_{239.05} = 4{,}878$ cal	20.406
	Entropy of actual gas at boiling point	51.44
	Correction for gas imperfection	0.12
	Entropy of ideal gas at boiling point	51.56

Let us take two crystalline forms A and B of an element. At the transition temperature, A and B are in equilibrium with each other, ΔF for the transition is zero, and the heat of transition becomes the reversible heat. For a constant-pressure process, the change in entropy for the transition A to B is

$$s_B - s_A = \frac{q_P}{T} = \frac{\Delta H_P}{T} \tag{14.43}$$

so that we obtain directly the difference between the entropy of A and of B at the transition temperature.

If the third law is valid, both A and B have the same value of entropy, $s_0 = 0$, at zero temperature; hence, s_A and s_B at the transition temperature can be evaluated from the respective heat capacity data for these crystals. We have, therefore, from equation (14.42),

$$s_B - s_A = \int_0^T \frac{c_B - c_A}{T}\, dT = \int_0^T \Delta c \, d \ln T \tag{14.44}$$

---

[*] GIAUQUE, W. F., and F. M. POWELL, *J. Am. Chem. Soc.*, **61**, 1970 (1939).

The value of $s_B - s_A$ calculated from equation (14.44) can be compared with that from equation (14.43). If these two methods give the same value of ΔS, the equality of s_0 for A and B is confirmed.

Early measurements on the transitions rhombic-monoclinic sulfur, white tin–gray tin, quartz-cristobalite, and calcite-aragonite furnished agreement with the heat theorem, within the limits of the experimental accuracy. The experiments on tin were the most accurate and were in agreement with the theorem. Discussion of this system is reserved for the following chapter. More recently, accurate heat capacities have been obtained for a number of systems. With exceptions of the type discussed later, they support the heat theorem.

Entropy of Sulfur.—Crystalline sulfur occurs in two crystalline forms, rhombic, stable below 95.5°C, and monoclinic, stable between 95.5°C and the melting point. The heat capacities of these forms were measured by Eastman and McGavock.[1] They used 273.1°K as the ice point temperature; hence, we shall here adopt the temperature scale, $T = 273.1 + t$. The heat values are in defined calories. If 95 ± 10 calories is accepted as the atomic heat of transition at 95.5°C, we have

$$\text{S(rhombic)} = \text{S(monoclinic)}; \qquad \Delta H_{368.6} = 95 \pm 10 \text{ cal}$$

$$\Delta s = \frac{95 \pm 10}{368.6} = 0.258 \pm 0.027 \text{ cal/deg}$$

The heat capacity data for this system are listed in Table 14.2. The entropy difference for rhombic sulfur between 0 and 15°K, obtained graphically from an extrapolated curve of c_P/T *vs.* T or by calculation from a Debye function fitted to the experimental points up to 40°K, is 0.12 ± 0.02 calorie per degree. The entropy between 15 and 298.1 or 368.6°K is obtained graphically from the data in Table 14.2. The total entropy of rhombic sulfur is found to be 7.624 ± 0.05 calories per degree at 298.1°K, and 8.827 ± 0.06 calories per degree at 368.6°K.

In Table 14.2 the difference Δc_P between the heat capacities of monoclinic and rhombic sulfur is tabulated. At 298.1°K the resulting entropy difference is 0.157 ± 0.04 calorie per degree; at 368.6°K, it is 0.215 ± 0.05 calorie per degree. If both rhombic and monoclinic sulfur have zero entropy (or the same value) at 0°K, this difference of 0.215 calorie per degree represents the difference in their entropies at the transition point. This value agrees with the entropy value calculated from the measured heat of transition. The third law, therefore, applies to crystalline sulfur.

Glasses and Solutions and the Third Law.—In proposing that a value of s_0 be assigned to the entropy of solids at zero temperature, Planck held that solid solutions should be assigned a positive entropy. If so, the

---

[1] EASTMAN, E. D., and W. C. MCGAVOCK, *J. Am. Chem. Soc.*, **59**, 145 (1937).

TABLE 14.2.—ATOMIC HEAT CAPACITY OF SULFUR*
(In calories per degree)

T, °K	c_P rhombic	$\Delta c_P =$ c(m) − c(r)	c_P mono-clinic	T, °K	c_P rhombic	$\Delta c_P =$ c(m) − c(r)	c_P mono-clinic
15	0.311			210	4.743		
20	0.605			220	4.841	0.180	5.021
25	0.858			230	4.927		
30	1.075			240	5.010	0.199	5.209
40	1.452			250	5.083		
50	1.772			260	5.154	0.217	5.371
60	2.084	0.007	2.091	270	5.220		
70	2.352			280	5.286	0.234	5.520
80	2.604	0.020	2.624	290	5.350		
90	2.838			298.1	5.401	0.248	5.649
100	3.060	0.040	3.100	300	5.412	0.250	5.662
110	3.254			310	5.474		
120	3.445	0.063	3.508	320	5.535	0.264	5.799
130	3.624			330	5.598		
140	3.795	0.087	3.882	340	5.660	0.276	5.936
150	3.964			350	5.721		
160	4.123	0.112	4.235	360	5.783	0.286	6.069
170	4.269			368.6	(5.837)	0.289	6.126
180	4.404	0.136	4.540				
190	4.526						
200	4.639	0.159	4.798				

* EASTMAN, E. D., and W. C. MCGAVOCK, *J. Am. Chem. Soc.*, **59**, 145 (1937).

formation of solid solutions from the pure solid should result at zero temperature in an entropy increase, and this process would form an exception to the heat theorem. Nernst believed that undercooled liquids (glasses) and solid solutions have an entropy value at zero temperature which is identical with that of crystalline solids. There is, accordingly, a conflict between the Nernst heat theorem in this form and the Planck inference that the common entropy value of zero should be restricted to pure crystalline solids.

In equation (13.58), the molar entropy of A in an ideal solution was given. If 1 mole of solid solution containing N_A moles of A and N_B moles of B is formed, the entropy change for the solution process is

$$\begin{aligned} N_A(s_A - s_A^\circ) &= -N_A R \ln N_A \\ N_B(s_B - s_B^\circ) &= -N_B R \ln N_B \\ \hline s(\text{solution}) - (N_A s_A^\circ + N_B s_B^\circ) &= -R(N_A \ln N_A + N_B \ln N_B) \qquad (14.45) \end{aligned}$$

The entropy of formation of 1 mole of solution containing 0.5 mole of A and 0.5 mole of B is, therefore, given by

$$\begin{aligned}\Delta s(\text{solution}) &= -4.576(0.5 \log 0.5 + 0.5 \log 0.5)\\ &= -4.576 \log 0.5\\ &= +4.576 \log 2\\ &= 1.38 \text{ cal/deg} \qquad (14.46)\end{aligned}$$

This is in agreement with the conclusion from the statistical theory, for the number of available positions for the molecule of A is doubled and the number for the molecule of B is doubled so that a factor of 2 appears in the probability expression, and the entropy for the mole of solution is increased by $R \ln 2$ as in equation (7.49).

However, if the positions of the individual atoms at zero temperature are fixed in the glass or solid solution as well as for the pure solid, both may be expected to give the same entropy expression and hence to have equal entropies. To settle this point, the measured entropies of glasses and solutions were compared with those of the corresponding pure substances. In all the experiments, the glasses and solid solutions were found to have greater entropy than the corresponding pure crystalline solids. The entropies for these substances were obtained from the heat capacity data by the methods outlined above.

Thus, the entropy of glycerol glass at 0°K appears to have a value higher by 4.6 calories per degree than crystalline glycerol at the same temperature. Similarly, for a glassy solution of glycerol and water, the entropy increase found from the heat capacity data was 1.30 ± 0.36 calories per degree at 0°K as compared with an increase calculated from equation (14.45) of 1.14 calories per degree. These values agree within the experimental error. The entropy of mixing of 0.728 mole of AgBr with 0.272 mole of AgCl to form 1 mole of solid solution is calculated from equation (14.45) to be 1.16 calories per degree. Eastman and Milner[1] found the entropy of mixing at 298°K to be 1.12 ± 0.1 calories per degree and that at absolute zero as calculated from the heat capacity data to be 1.03. These three values agree within the experimental error. We must, therefore, conclude that, if the entropies of pure crystalline solids at the absolute zero of temperature are zero, the entropies of glasses and solutions are positive.

Entropy of Gases.—The entropy of gases can be checked in still another way; it can be calculated from the energy levels obtained from band spectrum data by the methods of statistical mechanics. Table 14.3 lists some entropies of gases obtained by calorimetric and by spectroscopic methods. There is agreement between the two methods within

---

[1] EASTMAN, E. D., and R. T. MILNER, *J. Chem. Physics*, **1**, 444 (1933).

the experimental error for all the listed gases except hydrogen, carbon monoxide, nitric oxide, water and nitrous oxide. For these the discrepancies are, respectively, 1.5, 1.1, 0.75, 0.78, and 1.14 calories per degree. The discrepancy for hydrogen is explained by the fact that solid hydrogen is a solution of *ortho* and *para* forms. The discrepancy for the others is explained in terms of an indefiniteness of position of the atoms or bonds in the crystal.

TABLE 14.3.—MOLAR ENTROPIES OF SOME GASES AT 25°C FROM CALORIMETRIC AND SPECTROSCOPIC DATA
(In calories per degree)

Substance	Entropy (calorimetric)	Entropy (spectroscopic)
H_2	29.7	31.211
N_2	45.9	45.767
O_2	49.1	49.003
HCl	44.5	44.66
HBr	47.6	47.48
HI	49.5	49.36
CO	46.22	47.301
CO_2	51.11	51.061
NO	43.0*	43.75*
H_2O	44.33	45.106
N_2O	51.44	52.58

*At 121.36°K.

For example, in a perfectly oriented crystal of nitric oxide, the molecules are aligned in a regular manner such as NO-NO. However, if the two ends of the molecule may be interchanged in the crystal, the arrangement might be NO-ON. If there is no preferred orientation, the number of available arrangements for each molecule is doubled and the molar entropy is increased by $\boldsymbol{R} \ln 2$ which equals 4.576 log 2, or 1.38 calories per degree. Since the calorimetric value for nitric oxide differs from the spectroscopic value, based on perfect orientation, by less than this value, we conclude that the orientation of the nitric oxide molecules, though not unique, is not a perfectly random one. If the number of ways of realizing a system is g, we found in equation (7.50) that the entropy is increased by $\boldsymbol{R} \ln g$. This equation, based on probabilities, is applicable at the absolute zero of temperature. If the molar entropy of the perfect crystal of a pure substance is $s_0 = 0$, the entropy of the imperfect crystal is

$$s_0 = 0 + \boldsymbol{R} \ln g \qquad (14.47)$$

The imperfect crystal, therefore, has a finite but not a zero entropy value at zero temperature.

Because there is an entropy of mixing, it appears also that the entropy of a substance which is an isotopic mixture cannot be zero at zero temperature. Chlorine, for example, with the isotopes Cl^{35} and Cl^{37}, is a mixture of the molecules $Cl^{35}Cl^{35}$, $Cl^{37}Cl^{37}$, and $Cl^{35}Cl^{37}$. But chemical reactions do not separate this mixture, the chlorine acting as a single molecular species throughout a series of reactions. Consequently, the entropy of mixing cancels out in all the calculations. Entropy values for chlorine that do not include the entropy of mixing are, therefore, as useful as those which do, if they are used consistently throughout the calculations. For the same reason the tabulated "absolute" entropy values for the elements and compounds do not include the entropy of nuclear spin. This term cancels out of the calculations for chemical reactions.

A Final Statement of the Third Law.—Because not all crystalline solids have zero entropy at 0°K, the statement of Planck should be revised. The following statement fits the facts, although it is less definite than Planck's or Nernst's proposals:

The entropy of a solid or liquid at the absolute zero of temperature is never infinite; it may be finite and may be zero. It is zero when the solid is in a single pure quantum mechanical state.

Problems

14.1. Plot the heat capacity data of rhombic sulfur on the following types of graphs: (*a*) c *vs.* log T; (*b*) c/T *vs.* T. From these graphs, calculate the entropy increase between 15 and 368.6°K. Compare.

14.2. Calculate the entropy of formation of 1 mole of solid solution containing 0.728 mole of AgBr and 0.272 mole of AgCl. How does this value of the entropy of solution change with temperature?

14.3. Suppose that ΔF and ΔH approach the common limiting value at low temperatures not as we find experimentally (Fig. 14.1*a*) but as in Fig. 14.1*b*. Start with the fundamental equations, and show which of the following quantities have a zero value, finite value, or infinite value under these hypothetical conditions at constant pressure and $T = 0$:

$$\Delta S,\ \Delta C_P,\ \Delta F - \Delta H,\ \frac{\Delta F - \Delta H}{T},\ \frac{\partial\,\Delta H}{\partial T},\ \frac{\partial\,\Delta F}{\partial T},\ T\,\Delta S,\ \Delta F,\ \Delta H$$

14.4. The difference in heat capacity between white tin and gray tin between 79.8 and 298.1°K as determined by Brønsted [*Z. physik. Chem.*, **88**, 479 (1914)] may be represented by the equation

$$\Delta C = 1.365 - 8.75 \times 10^{-3}T + 29.2 \times 10^{-6}T^2 - 32.5 \times 10^{-9}T^3$$

For reasons indicated in the text, this equation is not valid near zero absolute. If this equation *were* extrapolated to 0°K, what would be the value of ΔC at 0, 20, 40°K? Compare with the values calculated with the Debye equation as listed in column (8) of Table 15.1.

14.5. Extend the heat capacity equation for the transition

$$\text{Sn(gray)} = \text{Sn(white)}$$

given in Prob. 14.4, to the temperature range 0 to 80°K; and find by integration between the indicated temperature limits the values of $\Delta S_{80} - \Delta S_{40}$, $\Delta S_{40} - \Delta S_{30}$, $\Delta S_{30} - \Delta S_0$. Why is this extrapolation invalid? Compare with the values obtained from column (7) of Table 15.2.

14.6. From the values of $(\partial s/\partial P)_T$ for the Berthelot gas and for the ideal gas derived in Prob. 10.16 calculate, for chlorine, whose critical constants are $T_c = 417$°K, $P_c = 76.1$, the value of $s_{\text{ideal}} - S_{\text{Berthelot}}$ at the boiling point 239°K and at 298.1°K, for 1 atmosphere pressure. (Slide rule.) Compare with the value in Table 14.1.

14.7. Calculate the values for the heat capacities of gray tin and white tin at the temperatures 1, 5, 10, 15, and 20°K, using for the characteristic temperatures $\theta = 253$ and $\theta = 198$, respectively, for gray tin and white tin. Tin follows the Debye equation; the simple T^3 relation holds below 20°K.

14.8. Plot the heat capacity data for tin obtained in Prob. 14.7:

(*a*) On a c *vs.* log T plot.

(*b*) On a c/T *vs.* T plot.

From one of these graphs calculate the value of s for gray tin and for white tin at 20°K.

(*c*) Calculate the entropies of gray tin and white tin at 20°K from their heat capacity equations obtained in Prob. 14.7. Compare with the entropy values that you obtained graphically.

CHAPTER 15

SOME APPLICATIONS OF THERMODYNAMICS

The data for any chemical system come from a variety of sources. They vary in completeness and in accuracy and may be inconsistent among themselves. Because the principles of thermodynamics enable us to combine data from different types of experiment in such a way as to derive values that can be compared with those obtained directly by experiment, thermodynamics is a powerful tool. Correlation and criticism of data require a systematic examination of the available data. We shall discuss several relatively simple systems as illustrations of some of the methods that may be used.

THE SYSTEM WHITE TIN–GRAY TIN

The observation that white tin at temperatures below room temperature changes to a gray powder is a relatively old one. Cohen[1] and his coworkers investigated the tin system and found a transition at 18°c, white tin being stable above and gray tin below this temperature. Brønsted[2] measured the heat capacities of these forms down to 79.8°K and the heat of transition at 0°c. This heat of transition was obtained by the following method: White tin at 0°c is transferred to a calorimeter held at 45 or 58°c. The heat absorbed by the tin in the calorimeter is a measure of its heat capacity. Similarly, gray tin at 0° is added to the same calorimeter. At the calorimeter temperature of 45 or 58° the transition of gray tin to white tin proceeds rapidly, the final material being white tin. Subtracting the observed heat absorbed by the white tin over the entire temperature interval from the heat absorbed by the gray tin, we obtain the difference in heat content of the two forms at 0°c. Thus, we have for the transition, the ice point being assumed to be 273°c,

$$\mathrm{Sn(gray)} = \mathrm{Sn(white)}; \qquad \Delta H_{273} = 532 \text{ cal} \tag{15.1}$$

Brønsted found 19°c (292°K) as the transition temperature; at this temperature, gray and white tin are in equilibrium so that

$$\Delta \mathrm{F}_{292} = \mathrm{F(white)} - \mathrm{F(gray)} = 0 \tag{15.2}$$

---

[1] Cohen, E., *Z. physik. Chem.*, **30**, 601 (1899); **33**, 59 (1900); **35**, 588 (1900); **36**, 513 (1901); **50**, 225 (1904); **63**, 625 (1908).

[2] **Brønsted**, J. N., *Z. physik. Chem.*, **88**, 479 (1914).

The entropy of transition at 0°C cannot be calculated directly from the heat of transition given in equation (15.1) because the transition at this temperature is not reversible. However, we may obtain the values of ΔH and ΔF as functions of temperature with the aid of the heat capacity data. On application of the general equation,

$$\Delta F = \Delta H - T\,\Delta S$$

we may then calculate the value of ΔS for the transition at any temperature in the experimental range. Observe, however, that these relations give only the change in entropy. If we wish to obtain the entropy of transition at 0°K or the absolute values of the entropy of white tin and gray tin, we need heat capacity curves down to 0°K. Because the heat capacities were not measured below 80°K, they must be extrapolated to 0°K. If the Debye formula, when fitted to the data in the observed range, represents the heat capacities in the extrapolated range, Brønsted found that the third law of thermodynamics is confirmed. These calculations of Brønsted are given in some detail as an illustration of the application of thermodynamics to a concrete chemical system.

Heat Capacities, Heats of Transition, and Free Energies of Transition between 80 and 288°K.—Brønsted's data on the atomic heat capacity of white tin, C_w, and of gray tin, C_g, at constant pressure and in the temperature range 79.8 to 288.1°K are given in columns (2) and (4) of Table 15.1, and the values of $\Delta C = C_w - C_g$ are given in column (6). The experimental values of ΔC are fitted by the empirical equation

$$\Delta C = 0.49 + 3.25 \times 10^{-8}(300 - T)^3 \tag{15.3}$$

The agreement between the experimental values and those calculated from equation (15.3) becomes evident when columns (6) and (7) of Table 15.1 are compared. When equation (15.3) is expanded with some slight rounding off of numerical values, it becomes

$$\Delta C = 1.365 - 8.75 \times 10^{-3}T + 29.2 \times 10^{-6}T^2 - 32.5 \times 10^{-9}T^3$$

This equation has the form of equation (5.27) so that by the methods previously described [compare equation (5.31)] the general heat of reaction is obtained for this transition. Thus,

$$\Delta H = \Delta H_0 + 1.365T - 4.37 \times 10^{-3}T^2 + 9.72 \times 10^{-6}T^3 - 8.1 \times 10^{-9}T^4 \tag{15.4}$$

ΔH_0 may be evaluated by the substitution of the values $\Delta H = 532$ cal and $T = 273$°K* from equation (15.1) in equation (15.4). We find

$$\Delta H_0 = 332.4 \tag{15.5}$$

---

* In the older data, 273°K was usually selected as the temperature of the ice point.

Observe that this value of ΔH_0 is obtained by extrapolation of the equation (15.4), valid between the temperatures 80 and 288°K down to 0°K. Therefore, ΔH_0 is not the real value of the heat of this transition at 0°K, but merely the integration constant.

TABLE 15.1.—THE ATOMIC HEAT CAPACITIES OF WHITE AND OF GRAY TIN
(In calories per degree)

T, °K (1)	c_w,* obs (2)	c_w, from the Debye formula ($\theta = 198$) (3)	c_g,† obs (4)	c_g, from the Debye formula ($\theta = 253$) (5)	Δc,‡ obs (6)	Δc, from equation (15.3) (7)	Δc, from the Debye formula (8)
20	....	0.469	....	0.228	....	....	0.241
30	....	1.30	....	0.744	....	....	0.556
40	....	2.235	....	1.42	....	....	0.815
60	....	3.65	....	2.82	....	....	0.83
79.8	4.64	.....	3.80	3.80	0.84	0.84	
87.3	4.87	.....	4.07	4.07	0.80	0.80	
94.8	5.07	.....	4.30	4.31	0.77	0.77	
194.9	6.20	.....	5.66	5.60	0.54	0.53	
197.2	6.23	.....	5.71	5.64	0.52	0.52	
205.2	6.25	.....	5.75	5.69	0.50	0.52	
248.4	6.36	.....	5.87	5.86	0.49	0.49	
256.4	6.37	.....	5.88	5.88	0.49	0.49	
264.3	6.38	.....	5.89	5.90	0.49	0.49	
273.0	6.39	.... .	5.90	5.93	0.49	0.49	
288.1	6.40	.....	5.91	5.97	0.49	0.49	

* c_w = atomic heat capacity of white tin.
† c_g = atomic heat capacity of gray tin.
‡ $\Delta c = c_w - c_g$.

By the methods previously described [compare equation (11.34)] the equation for the free energy of transition, obtained from equation (15.4) is

$$\Delta F = 332.4 - 1.365(2.3026)T \log T + 4.37 \times 10^{-3}T^2 - 4.86 \times 10^{-6}T^3 + 2.7 \times 10^{-9}T^4 + IT \quad (15.6)$$

When the integration constant I is evaluated at the transition temperature where $T = 292$°K and $\Delta F = 0$, Brønsted found I to be 5.677 so that equation (15.6) becomes

$$\Delta F = 332.4 - 3.143T \log T + 4.37 \times 10^{-3}T^2 - 4.86 \times 10^{-6}T^3 + 2.7 \times 10^{-9}T^4 + 5.677T \quad (15.7)$$

The values of ΔH and ΔF calculated from equations (15.4) and (15.7) are tabulated in columns (2) and (3), Table 15.2, and their difference in column (6). Observe that, as the temperature decreases, $\Delta H - \Delta F$ approaches zero, as required by the third law.

Table 15.2.—The Heat, Free Energy, and Entropy of Transition of Gray Tin to White Tin between 0 and 298°K
(In calories, or calories per degree, per mole)

T, °K (1)	ΔH, from equation (15.4) (2)	ΔF, from equation (15.7) (3)	ΔH, calculated (4)	ΔF, calculated (5)	$\Delta H - \Delta F$ (6)	ΔS (7)
0	...	...	371	371	0	0
30	...	...	376	369	7	0.23
40	...	...	383	365	18	0.45
60	...	...	401	353	48	0.80
80	418	334	...	...	84	1.05
100	434	311	...		123	1.23
200	495	162	...	...	333	1.67
273	532	34	...	...	498	1.82
292	541	0	...	...	541	1.85
298	545	−13	...	...	558	1.87

Temperature Range 60 to 80°K.—In order to extrapolate the data to absolute zero, we must know the form of equation followed by the data. If the Debye equation is valid, it can be fitted to the experimental data over the range 80 to 288°K and then used to give values[1] of C_P below 80°. A comparison between the observed heat capacities of gray tin in column (4) and the corresponding values calculated from the Debye equation, which are listed in column (5), Table 15.1, shows excellent agreement. We, therefore, feel confident in the extrapolated values derived from the Debye formula. A similar extrapolation for the heat capacity of white tin is tabulated in column (3), and the calculated values of ΔC are listed in column (8). These values of ΔC may now be used in setting up equations for ΔH and ΔF in this range.

It appears from columns (7) and (8) that ΔC increases from the value $\Delta C = 0$ at $T = 0$ to $\Delta C = 0.83$ at $T = 60°$, remains constant at $\Delta C = 0.84$ between 60 and 80°, and then decreases again. In the temperature range 60 to 80°

$$\Delta C = 0.84 \tag{15.8}$$

---

[1] Brønsted assumed that, below 60°, $c_V = c_P$. At higher temperatures, he used the Nernst and Lindemann formula [*Z. Elektrochem.*, **17**, 817 (1911)], $c_P - c_V = k c_P^2 T$, where $k = 2.3 \times 10^{-5}$ for gray tin.

Hence,

$$\Delta H = \Delta H_0 + 0.84T \tag{15.9}$$

and

$$\Delta F = \Delta H_0 - 2.303 \times 0.84\, T \log T + IT \tag{15.10}$$

But the value of ΔH_{80} as calculated from equations (15.4) and (15.5) and listed in Table 15.2 is $\Delta H_{80} = 418$ cal. When this value is substituted in equation (15.9), ΔH_0 is found equal to 350.8 calories. This value and the value $\Delta F_{80} = 334$ cal obtained from equation (15.7) may now be substituted in equation (15.10) so that I is evaluated. We find that $I = 3.47$.

When these values of ΔH_0 and I are substituted in equations (15.9) and (15.10), we obtain

$$\Delta H_{60} = 401 \text{ cal}; \qquad \Delta F_{60} = 353 \text{ cal} \tag{15.11}$$

These values are listed in Table 15.2. Observe that the value of ΔH_0 obtained from equation (15.9) differs from that obtained from equation (15.4). In neither case are these the heats of transition at 0°K.

Temperature Range, 0 to 60°K.—Because the heat of transition changes with temperature according to the equation

$$d\,\Delta H = \Delta c\, dT$$

we have

$$\Delta H - \Delta H_0 = \int_0^T \Delta c_P\, dT \tag{15.12}$$

At 60°K, the integral is found equal to 30 calories, so that from equations (15.11) and (15.12)

$$\Delta H_0 = 401 - 30 = 371 \text{ cal} \tag{15.13}$$

Similar evaluations of the integral at the temperatures 30 and 40°K give us the values

$$\Delta H_{30} = 376 \text{ cal}; \qquad \Delta H_{40} = 383 \text{ cal} \tag{15.14}$$

Compare the true value of the heat of transition at 0°K, 371 calories, with the values of the integration constant ΔH_0 obtained when equations (15.4) and (15.9) were extrapolated to 0°K.

From the equation

$$\Delta F = \Delta H - T\,\Delta S \tag{15.15}$$

which applies to an isothermal process, we obtain the equation

$$\Delta F = \Delta H - T \int_0^T \frac{\Delta c_P}{T}\, dT \tag{15.16}$$

From the value of the integral at the temperatures 0, 30, 40, and 60°K and the calculated value of ΔH at these temperatures, Brønsted obtained the values

$$\Delta F_0 = 371 \text{ cal}; \qquad \Delta F_{30} = 369 \text{ cal}; \qquad \Delta F_{40} = 365 \text{ cal}; \qquad \Delta F_{60} = 353 \text{ cal} \qquad (15.17)$$

But the value $\Delta F_{60} = 353$ is identical with that obtained by extrapolation of the experimental data to 60°, on the assumption that, from 60 to 80°, $\Delta c = 0.84$. In other words, on the assumption that the Debye equation is valid between 0 and 60° and that, from 60 to 80°, Δc is constant, the ΔH and ΔF values confirm the Nernst heat theorem. In the neighborhood of zero temperature, as Table 15.2 indicates,

$$\Delta H_0 = \Delta F_0; \qquad \frac{d\,\Delta H}{dT} = \frac{d\,\Delta F}{dT} = \Delta c_P = -\Delta S = 0 \qquad (15.18)$$

From these data, it appears that white tin and gray tin have the same entropy value at 0°K.

Entropy of Tin.—From Brønsted's heat capacity data, Lewis and Randall[1] derived the entropies of white tin and gray tin at 298°. Assuming that the common entropy value for these forms is $S_0 = 0$ as stated by Planck, they found entropies equal to 11.17 and 9.23 calories per degree, respectively. The entropy of transition gray tin = white tin calculated from the heat capacity data is, therefore, 1.94 calories per degree.

At 298°, the free energy of the transition as listed in Table 15.2 is $\Delta F_{298} = -13$ cal. As stated earlier, the negative free energy change means that the forward reaction in equation (15.1) is spontaneous, gray tin being converted to white tin at this temperature. From equation (15.15) and Table 15.2, we have

$$\Delta S_{298} = \frac{\Delta H - \Delta F}{T} = \frac{558}{298} = 1.87 \text{ cal/deg} \qquad (15.19)$$

This value for the entropy difference, based on the experimental heat of transition and free energy of transition at room temperature, is in excellent agreement with that calculated from the observed heat capacity data. This system furnished one of the best early confirmations of the third law of thermodynamics.

THE SYSTEM CALCIUM CARBONATE + CALCIUM OXIDE + CARBON DIOXIDE

Heat of Dissociation at Room Temperature.—The heat of dissociation of calcium carbonate may be evaluated at room temperature from

---

[1] LEWIS, G. N., and M. RANDALL, "Thermodynamics and the Free Energy of Chemical Substances," p. 450, McGraw-Hill Book Company, Inc., New York, 1923.

measurements of the heat of solution of calcium carbonate and of calcium oxide in hydrochloric acid. This heat was measured by Bäckström[1] from the following reactions:

$$CaO(c) + 2HCl(aq) = CaCl_2(aq) + H_2O; \qquad \Delta H = -46{,}200 \text{ cal} \tag{15.20}$$

$$CaCO_3(\text{calcite}) + 2HCl(aq) = CaCl_2(aq) + H_2O + CO_2(g); \quad \Delta H = -3{,}260 - 330 \text{ cal} \tag{15.21}$$

In equation (15.21) the observed heat (−3,260 calories) must be corrected for the heat (330 calories) used in evaporating water to saturate the escaping CO_2 gas. When equation (15.20) is subtracted from (15.21) the result is

$$CaCO_3(\text{calcite}) = CaO(c) + CO_2(g); \qquad \Delta H = 42{,}600 \pm 200 \text{ cal} \tag{15.22}$$

The earlier values are Thomsen's value of 42,520 calories and Berthelot's value of 43,300 calories. It is possible to calculate the heat of reaction at the higher temperatures at which dissociation occurs, from the corresponding heat at room temperature if the heat capacities of the substances involved in the equation are known to these higher temperatures. However, the heat capacities have not been accurately determined up to these temperatures. It is also possible to calculate the heat of reaction from the vapor pressure data.

Dissociation Pressure of $CaCO_3$.—If CO_2 behaves as a perfect gas at the low temperatures where its partial pressure is low and at the high temperatures necessary for high partial pressures, the equilibrium constant for reaction (15.22) may be written in the form

$$K_P = P_{CO_2} \tag{15.23}$$

The activities of solid $CaCO_3$ and solid CaO remain at unity during the dissociation, for it has been shown to proceed without a solution of the CaO in the undissociated $CaCO_3$ to form a solid solution. On comparison with equation (12.98), we see that the equilibrium constant may be represented by the equation

$$\log P = -\frac{A}{T} + B \log T + CT + DT^2 + E \tag{15.24}$$

This equation is identical with that obtained by integration of the approximate form of the Clausius-Clapeyron equation (9.24). If the approximations made in the development of this equation (what approximations?) are adequate for CO_2 in this temperature range, the constants

---

[1] BÄCKSTRÖM, H. L. J., *J. Am. Chem. Soc.*, **47**, 2446 (1925).

for the equation are fixed by the constants H_0, α, β, and γ, obtained solely from thermal data. It would be possible in this case to use the heat capacities, a heat of reaction at room temperature, and one point on the vapor pressure curve to determine the whole vapor pressure curve for this system. In practice, the thermal data are not known with sufficient accuracy; they are used solely as guides in determining the constants in an empirical equation set up in the form of equation (15.24). The vapor pressure equation so set up may then be used to give values of $d \ln P/dT$ or dP/dT that may be substituted in the Clausius-Clapeyron equation to give values of the heat of dissociation.

Vapor pressures of carbon dioxide for the dissociation of calcite have been obtained by a number of investigators among whom are Le Châtelier,[1] Johnston,[2] Smyth and Adams,[3] Andrussow,[4] Tamaru, Siomi, and Adati,[5] and Southard and Royster.[6]

Johnston expressed his pressures in terms of the equation

$$\log P_{\text{mm}} = -\frac{9{,}340}{T} + 1.1 \log T - 0.0012T + 8.882 \qquad (15.25)$$

for temperatures up to 900°C. Smyth and Adams extended their measurements beyond the eutectic point for crystalline $CaCO_3$ and CaO, which is 1240°C and 30,000 mm pressure, to a temperature of 1390°C where the pressure is 779,000 mm. They give an equation applicable through the experimental points of Johnston up to their value of the eutectic temperature and pressure, namely,

$$\log P_{\text{mm}} = \frac{-11{,}355}{T} - 5.388 \log T + 29.119 \qquad (15.26)$$

Tamaru, Siomi, and Adati, between 614 and 891°C, obtained pressures represented by the equation

$$\log P_{\text{mm}} = \frac{-9{,}220}{T} + 1.70 \log T - 0.00149T + 1.443 \times 10^{-7}T^2 + 7.181 \qquad (15.27)$$

Their pressures are distinctly higher than the corresponding pressures of Johnston and of Smyth and Adams, but the curves have similar slopes, so that they lie parallel and give similar heats of dissociation. Various

---

[1] LE CHÂTELIER, H., *Compt. rend.*, **102**, 1243 (1886).

[2] JOHNSTON, J., *J. Am. Chem. Soc.*, **32**, 938 (1910).

[3] SMYTH, F. H., and L. H. ADAMS, *J. Am. Chem. Soc.*, **45**, 1167 (1923).

[4] ANDRUSSOW, L., *Z. physik. Chem.*, **116**, 81 (1925).

[5] TAMARU, S., K. SIOMI, and M. ADATI, *Z. physik. Chem.*, **157A**, 447 (1931).

[6] SOUTHARD, J. C., and P. H. ROYSTER, *J. Phys. Chem.*, **40**, 435 (1936).

values reported for the dissociation temperature at 1 atmosphere are Johnston, 898; Smyth and Adams, 897; Andrussow, 882; and Tamaru, Siomi, and Adati, 882°c—a spread of 16°. More recent work by Southard and Royster (1936) suggests that the preceding discrepancies are caused by systematic errors in temperature measurement. By use of precautions that enabled them to hold their reaction system and thermocouple at 900°c with a maximum variation of 0.04°c for 30 hours, they obtained the equation

$$\log P_{\text{cm}} = \frac{-9{,}140}{T} + 0.382 \log T - 0.668 \times 10^{-3}T + 9.3171 \qquad (15.28)$$

The coefficients 0.382 and 0.668 were obtained from the relation

$$\Delta C_P = 0.76 - 0.0061T$$

which is assumed to hold for the range 900 to 1200°K. The other coefficients are chosen to give agreement with the experimental data. The atmospheric dissociation temperature calculated from equation (15.28) is 894.4°c (1167.6°K); it is assumed to be correct to less than 0.3°. When pressure is expressed in atmospheres instead of in centimeters of mercury,

TABLE 15.3.—HEAT CAPACITIES IN THE CALCIUM CARBONATE SYSTEM

Temperature, t°C	Molar heat capacity, cal/deg			$-\Delta C_P$
	$CaCO_3$	CaO	CO_2	
200	23.83	11.56	9.94	2.33
400	27.06	12.00	10.94	4.12
600	29.45	12.20	11.78	5.47
800	31.35	12.26	12.48	6.61
1000	32.92	12.30	13.03	7.59

$$\log P_{\text{atm}} = \log \frac{P_{\text{cm}}}{76} = \log P_{\text{cm}} - 1.8808$$

so that the integration constant in equation (15.28) becomes 7.4363.

In the meantime, Bäckström had set up a vapor pressure equation, based on the data of Johnston and Smyth and Adams, by the use of his own value of the heat of reaction at 25° and of assembled heat capacity data, some of which are given in the Table 15.3. An equation set up to express ΔC_P for these data in degrees centigrade is

$$-\Delta C_P = 0.12 + 1.1525 \times 10^{-2}t - 4.13 \times 10^{-6}t^2$$

which, when expressed in degrees Kelvin, becomes

$$\Delta C_P = 3.34 - 1.378 \times 10^{-2}T + 4.13 \times 10^{-6}T^2 \qquad (15.29)$$

From this formula, the equation for ΔH as a function of temperature is derived in the usual manner, the observed heat of dissociation at 25°c, namely, $\Delta H_{298} = 42{,}600$ cal, being used to evaluate ΔH_0. Because $K_P = P$ from equation (15.23), the van't Hoff relation may be used with this value for ΔH to give the general expression[1] of P as a function of temperature, namely,

$$\log P = \frac{-9{,}212.4}{T} + 1.6797 \log T - 1.5048 \times 10^{-3}T + 0.1503 \times 10^{-6}T^2 + I \quad (15.30)$$

It should be emphasized that all the constants in equation (15.30), with the exception of the integration constant I, were obtained from thermal data alone. All the other constants being selected from the thermal data, the observed vapor pressures may be used to evaluate I. Bäckström substituted Johnston's vapor pressures and the corresponding temperatures in the range 860 to 1167°K in equation (15.30) and obtained an average value of $I = 7.161$, P being in millimeters. The data of Smyth and Adams between 1115 and 1514°K yielded an average value of $I = 7.1635$. This value places the curve for the Smyth and Adams data slightly above that for the Johnston data. The mean value $I = 7.162$ was selected. The corresponding value, when P is expressed in atmospheres, becomes $I = 4.281$.

A comparison of the dissociation pressures calculated from equations (15.25) to (15.30) is made in Table 15.4, the temperatures in degrees Kelvin being 900, 1000, 1100, 1167.6, which is the atmospheric dissociation temperature according to Southard and Royster, 1200, and 1513, which is the eutectic temperature for calcium carbonate and calcium oxide according to Smyth and Adams.

The Tamaru equation (15.27) gives pressures that appear to be 20 per cent too high over the entire temperature range. The Johnston equation (15.25) derived from older, less accurate thermal data may evidently not be extrapolated far above the experimental range for which it was derived. The Smyth and Adams equation (15.26), which was derived on the basis that ΔC_P is constant, fits the data at the higher temperatures well but gives values that are too low at the lower pressures. There is substantial agreement between the pressures predicted by the Southard and Royster equation (15.28) and the Bäckström equation (15.30). The calculations show that, if empirical equations are to be extrapolated with confidence beyond an experimental range, they should have the proper form dictated by theory. Additional information, such

---

[1] In the derivation, Bäckström used the values 25°c = 298°K, $R = 1.9885$ cal/deg, and $2.3026\,R = 4.5786$ cal/deg.

as thermal data, is desirable to indicate the appropriate value of the constants in the equation.

TABLE 15.4.—DISSOCIATION PRESSURES OF CALCIUM CARBONATE
(Calculated from various vapor pressure equations. Pressures in atmospheres)

Temperature, °K Vapor pressure formulas	900	1000	1100	1167.6 (894.4°c)	1200	1513 (eutectic temperature)
(15.25) Johnston	0.00621	0.0577	0.344	0.944	1.46	(32.4)*
(15.26) Smyth and Adams	0.00506	0.0524	0.337	0.966	1.53	39.9
(15.27) Tamaru, Siomi, and Adati	0.00715	0.0682	0.421	1.19	1.87	(48.8)*
(15.28) Southard and Royster	0.006428	0.05947	0.3583	1.000	1.565	39.7
(15.30) Bäckström	0.00596	0.0566	0.348	0.979	1.53	39.9

* Values in parentheses represent values obtained above the stated range of the formula.

Heat of Dissociation from Dissociation Pressure Data.—From the van't Hoff equation (or the approximate Clausius-Clapeyron equation), we have

$$RT^2\frac{d\ln K}{dT} = RT^2\frac{d\ln P}{dT} = \Delta H = \Delta H_0 + \alpha T + \frac{1}{2}\beta T^2 + \frac{1}{3}\gamma T^3 \quad (15.31)$$

When an experimental pressure equation in the form of equation (15.24) is converted to one in natural logarithms, it becomes

$$\ln P = -\frac{2.303A}{T} + B\ln T + 2.303CT + 2.303DT^2 + 2.303E \quad (15.32)$$

which may be differentiated with respect to temperature to give

$$\frac{d\ln P}{dT} = \frac{2.303A}{T^2} + \frac{B}{T} + 2.303C + 2(2.303)DT$$

R being 1.9872 calories per degree, the heat of dissociation in calories is

$$\Delta H = RT^2\frac{d\ln P}{dT} = 4.5757A + 1.9872BT + 4.5757CT^2 + 2(4.5757)DT^3 \quad (15.33)$$

Within the limits of the approximate Clausius-Clapeyron equation, then, the heat of dissociation may be calculated from the constants in the dissociation pressure equation. When the constants A, B, C, and D were evaluated originally from thermal data, the calculation based on equation (15.33) is obviously merely a process to recover the originally assumed value for the heat of dissociation equation.

There is much better agreement between the heats of dissociation calculated from the various equations, that is, between the slopes of the log P *vs.* $1/T$ curves, than between the actual value of the vapor pressures. At 800°C the values for the heat of dissociation of calcium carbonate calculated from the vapor pressures equations (15.25) to (15.28) and (15.30) are, respectively, 38,750, 40,460, 39,330, 39,020, and 39,160 calories.

Heat of Dissociation from the Exact Clausius-Clapeyron Equation.—The error introduced by the approximations inherent in the approximate Clausius-Clapeyron equation can be evaluated for this system from available data. The exact equation

$$\frac{dP}{dT} = \frac{\Delta H}{T\,\Delta V} \tag{15.34}$$

may be used to calculate ΔH if values for the rate of change of pressure with temperature and the change of molar volume are known for the dissociation. Smyth and Adams obtain dP/dT from equation (15.26) by the following steps:

$$\ln P = \frac{-2.303 \times 11{,}355}{T} - 5.388 \ln T + I'$$

$$\frac{dP}{dT} = \frac{d \ln P}{dT} \times P = P\left(\frac{2.303 \times 11{,}355}{T^2} - \frac{5.388}{T}\right)$$

At the eutectic point of $CaCO_3$ and CaO, $T = 1513°\text{K}$,

$$P = 30{,}000 \text{ mm}$$

and $dP/dT = 237.02$ mm/deg. At this temperature, the molar volumes of $CaCO_3$, CaO, and CO_2 are calculated to be 36.89 cc, 18.15 cc, and 3,208.33 cc, respectively, so that $\Delta V = +3{,}190$ cc. The volume of carbon dioxide under these conditions of temperature and pressure is obtained from the Keyes equation[1] of state. When these values are substituted in equation (15.34), the value of $\Delta H_{1513} = 36{,}440$ cal is obtained, as compared with the value of 35,790 calories obtained by the use of equation (15.33). The values of ΔH at 897°C, where the dissociation pressure was 760 mm, are 39,420 and 39,440 calories for the exact and the approximate equations, respectively. It is evident that here the approximations used in the integration of the Clausius-Clapeyron equation tend to cancel each other and that the values obtained by the use of the approximate form are surprisingly good.

---

[1] KEYES and KENNEY, *J. Am. Soc. Refrig. Eng.*, **3**, 1 (1917).

Free Energy of Dissociation of Calcium Carbonate.—From the general relation between the standard free energy change and the equilibrium constant, it follows that the standard free energy change for the dissociation of calcium carbonate is represented by the equation

$$\Delta F^\circ = -RT \ln P = -4.5757T \log P \qquad (15.35)$$

If this equation is combined with equation (15.24) for the value of log P in terms of the empirical constants A, B, C, D, and E, we obtain the equation

$$\Delta F^\circ = 4.5757\left(A - \frac{BT}{2.303}\ln T - CT^2 - DT^3 - ET\right) \qquad (15.36)$$

Any of the dissociation pressure equations (15.25) to (15.30) could be combined with equation (15.36) to give the standard free energy of dissociation for the temperature range in which the equations are valid. However, observe that, if the selected standard state of carbon dioxide is at 1 atmosphere pressure, the dissociation pressure equations must be in the form to give pressures in atmospheres. If the equations give pressures in millimeters or centimeters of mercury, the values of log 760 and log 76, respectively, must be subtracted from the reported integration constants to give the new constants for the pressure in atmospheres.

If the dissociation pressure equations can be safely extrapolated to 25°C, equation (15.35) may be used to give the standard free energy of dissociation at this temperature. As may be suspected from the trends of the various equations at the higher temperatures, they diverge at 25°C. At this temperature, the values of log P derived from equations (15.25) to (15.28) and (15.30) are -22.959, -25.178, -22.847, -22.473, and -22.896, respectively. It is evident that the values of $\Delta F^\circ_{298.16}$ calculated from these values are not in complete agreement, the values for the last three equations being 31,170, 30,660, and 31,240 calories, respectively. Using $R = 1.9885$ cal/deg Bäckström obtained $\Delta F^\circ_{298} = 31{,}258$.

Entropy of Dissociation.—The entropy of dissociation of calcite can be calculated from the measured entropies of $CaCO_3$ (calcite), CaO, and CO_2. From Table 11.2, they are, respectively, 22.2, 9.5, and 51.06 calories per degree. Hence,

$$\begin{aligned}\Delta S_{298.16} &= s_{CO_2} + s_{CaO} - s_{CaCO_3}\\ &= 38.4 \text{ cal/deg}\end{aligned}$$

This value may be compared with the entropy change calculated from the general equation (15.15) whence, at 298.16°K,

$$\Delta S = \frac{\Delta H - \Delta F}{298.16} \text{ cal/deg} \qquad (15.37)$$

Taking $\Delta H_{298.16} = 42{,}600$, after Bäckström, and using the values o $\Delta F^{\circ}_{298.16}$ calculated from the dissociation pressure equations, we have, from equation (15.27),

$$\Delta S = \frac{11{,}430}{298.16} = 38.34 \text{ cal/deg}$$

from equation (15.28),

$$\Delta S = \frac{11{,}940}{298.16} = 40.05 \text{ cal/deg}$$

and, from equation (15.30),

$$\Delta S = \frac{11{,}360}{298.16} = 38.10 \text{ cal/deg}$$

It is clear that the uncertainty in the value of $\Delta F_{298.16}$ results in a corresponding uncertainty in the calculated value of ΔS, an uncertainty of 100 calories in ΔF corresponding to an uncertainty in $\Delta S_{298.16}$ of 0.34 calorie per degree. From the general relation in equation (15.37), it follows that an uncertainty of 100 calories in $\Delta H_{298.16}$ results in the same uncertainty in $\Delta S_{298.16}$. According to equation (15.22), the uncertainty of ΔH is 200 calories. Consequently, the uncertainty in $\Delta S_{298.16}$, attributable to the experimental uncertainty of ΔH alone, is 0.7 calorie per degree. The uncertainty in ΔS arising from that of ΔF is even greater.

For many reactions, the value of ΔS is more accurately known than the measured or estimated values of ΔH and ΔF. If the value of either ΔH or ΔF is accurately known, this value may be combined with that of ΔS to give the value of the other function. Thus, if we accept the values

$$\Delta H_{298.16} = 42{,}600 \text{ cal} \qquad \text{and} \qquad \Delta S_{298.16} = 38.4 \text{ cal/deg}$$

we calculate, for the dissociation of calcite at 25°C,

$$\begin{aligned}\Delta F_{298.16} &= 42{,}600 - 298.16 \times 38.4 = 42{,}600 - 11{,}400 \\ &= 31{,}200 \text{ cal}\end{aligned}$$

With this value, we obtain from equation (15.35)

$$\log P = \frac{-31{,}200}{4.5757(298.16)} = -22.87$$

whence we find, for the equilibrium pressure of CO_2 at 25°C,

$$P = 1.3 \times 10^{-23} \text{ atm}$$

Similarly, for a reaction for which ΔF and ΔS are accurately known, the value of ΔH calculated from these values is frequently more accurate than the measured values.

Problems

15.1. From the vapor pressure equations (15.25) to (15.28), and (15.30), derive the equations for ΔC_P used in setting up these formulas. Tabulate the values of ΔC_P obtained from these equations for the temperatures 1000, 1200, and 1500°K.

15.2. From equation (15.28), calculate the equilibrium partial pressure of carbon dioxide over calcium carbonate at 25°C. Would it be possible to cause calcium carbonate to dissociate at room temperature with a diffusion pump that maintains a vacuum in which the pressure is 10^{-6} mm Hg?

15.3. At what temperature will calcium carbonate begin to dissociate in air that contains 0.03 per cent of carbon dioxide by volume?

15.4. Plot the heat capacity data given in Table 15.1 for gray tin and white tin against log T. From these diagrams, calculate the entropies of these forms of tin at 292 and 298°K relative to their values at 20°K. (The graphical integration is conveniently done by measuring ordinates at frequent but even intervals or by cutting out the graphs and weighing.) Combine the results with the entropies calculated at 20°K in Prob. 14.8 to find the entropies of these forms of tin at 19 and 25°C.

15.5. From the entropy values obtained in Prob. 15.4 for gray tin and white tin at the equilibrium temperature 19°C, calculate the heat of transition. Compare with the value 541 calories found by Brønsted.

15.6. The free energy of formation of HCl may be calculated from the free energies of the following reactions:

$$\tfrac{1}{2}H_2(g,\ 1\ \text{atm}) + AgCl(c) = HCl(aq,\ a = 1) + Ag(c) \qquad (15.38)$$
$$Ag(c) + \tfrac{1}{2}Cl_2(g,\ 1\ \text{atm}) = AgCl(c) \qquad (15.39)$$
$$HCl(aq,\ a = 1) = HCl(g,\ 1\ \text{atm}) \qquad (15.40)$$

From the standard electrode potentials, we have, for the emf of reaction (15.38), $E^{\circ}_{298.1} = 0.2225$ int volt. For reaction (15.39), the emf is $E^{\circ}_{298.1} = 1.1362$ int volts. For equation (15.40), the equilibrium constant as determined by M. Randall and L. E. Young [*J. Am. Chem. Soc.*, **50,** 989 (1928)] is

$$K = \frac{P_2}{a_2} = 4.97 \times 10^{-7}$$

where P_2 is the partial pressure of HCl over the solution and a_2 the activity of the HCl in the solution. From these data, calculate the standard free energy change for each of the above reactions, and derive the standard free energy of reaction for

$$\tfrac{1}{2}H_2(g,\ 1\ \text{atm}) + \tfrac{1}{2}Cl_2(g,\ 1\ \text{atm}) = HCl(g,\ 1\ \text{atm}) \qquad (15.41)$$

15.7. From the values for the entropies of H_2, Cl_2, and HCl in Table 11.2, calculate the entropy of formation of gaseous HCl. Combine this datum with the free energy of formation obtained in Prob. 15.6, and calculate the heat of formation of HCl at 25°C. F. D. Rossini [*Bur. Standards J. Research*, **9,** 679 (1932)] obtained −22,063 ± 12 calories for this heat of formation in a calorimeter. (Compare with the results in Prob. 11.6.)

15.8. R. H. Gerke [*J. Am. Chem. Soc.*, **44,** 1684 (1922)] found the temperature coefficient of the emf of the cell representing equation (15.39) in Prob. 15.6 to be

$$\frac{dE}{dT} = -0.000595 \pm 0.000006 \text{ int volt/deg at } 25^{\circ}\text{C}$$

From this value, calculate the entropy change for the reaction in equation (15.39) at 25°c.

15.9. Combine Rossini's value of ΔH and the values of ΔS calculated in Prob. 15.7 to give an independent value of the standard free energy of formation for reaction (15.41) in Prob. 15.6. Compare the two free energy values.

15.10. From the value of ΔF° calculated in Prob. 15.9 for reaction (15.41) in Prob. 15.6, calculate the equilibrium constant for the reaction at 25°c. What is the equilibrium pressure of H_2 (and Cl_2) obtained from the dissociation of HCl at 25°c?

15.11. Derive equation (15.30) from (15.29) and the datum $\Delta H_{298} = 42{,}600$ cal. In the derivation of (15.30) the value $R = 1.9885$ cal/deg was assumed. Use this value here. What is the value of ΔH_0?

15.12. From the data given in this chapter, calculate the entropy of dissociation of calcite at the temperature at which the dissociation pressure equals 1 atmosphere.

15.13. Assuming that the dissociation pressure of sodium sulfate decahydrate is 19.19 mm at 25°c, calculate the standard free energy change for the reaction

$$Na_2SO_4(c) + 10H_2O(g) = Na_2SO_4 \cdot 10H_2O(c)$$

Indicate clearly the standard states chosen for the reactants and products.

15.14. The heats of solution of Na_2SO_4 and of $Na_2SO_4 \cdot 10H_2O$ in water are

$$\Delta H^\circ = -560 \pm 10 \text{ cal/mole}$$

and $\Delta H^\circ = 18{,}840 \pm 20$ cal/mole, respectively, at 25°c, according to Pitzer and Coulter [*J. Am. Chem. Soc.*, **60**, 1310 (1938)]. The heat of evaporation of water at 25° to form water vapor at 1 atmosphere is 10,520 calories per mole. Calculate the change in heat content for the reaction,

$$Na_2SO_4(c) + 10H_2O(g) = Na_2SO_4 \cdot 10H_2O(c)$$

15.15. From the change in heat content calculated in Prob. 15.14 and the free energy change calculated in Prob. 15.13, calculate the change in entropy for the reaction

$$Na_2SO_4(c) + 10H_2O(g) = Na_2SO_4 \cdot 10H_2O(c)$$

15.16. Accepting 45.11 calories per degree as the molar entropy of water vapor at 25°c = 298.16°K and the value $\overset{\circ}{s}_{298.16} - \overset{\circ}{s}_0 = 35.7$ cal/deg as the molar entropy of solid Na_2SO_4, combine these values with the entropy of dissociation of $Na_2SO_4 \cdot 10H_2O$ obtained in Prob. 15.15 to derive a value for the entropy of formation of $Na_2SO_4 \cdot 10H_2O$. The calorimetric value of the entropy obtained by Pitzer and Coulter (*loc. cit.*) as calculated from the integral $\int_0^{298.16} C_P \, d \ln T$ is $\overset{\circ}{s}_{298.16} - \overset{\circ}{s}_0 = 140.5$ cal/deg. Compare the two results. How do Pitzer and Coulter explain the difference?

CHAPTER 16

THERMODYNAMIC FUNCTIONS FROM STATISTICAL METHODS

Values of the thermodynamic functions for many elements and the simpler compounds in the gaseous phase have been calculated from the energy levels of the molecules which in turn are derived from spectroscopic data as interpreted in terms of the quantum mechanical models for the molecules. Statistical methods are then used to find the distribution of the molecules among the various possible energy states for the gas. For not too complicated molecules, the assignment of energy levels from the spectroscopic data is fairly certain and the calculated results for the thermodynamic functions agree well with the best experimental values. Indeed, for these molecules, the calculated values are more precise than the values determined from heat capacity measurements. For more complicated molecules, the assignment of energy levels is not so certain and approximations are used in the calculations. However, the derived results are extremely valuable; for many molecules, they appear to be more reliable than the scattered and inconclusive experimental values. Since we shall use the results of the calculations in the form of various tabulated functions, we shall examine the basic assumptions and methods and shall then be able to apply the results of the calculations more intelligently.

In the preceding chapters, the variation of the thermodynamic functions with temperature was expressed in the form of algebraic equations. Thus, heat content and free energy were expressed as functions of temperature in terms of coefficients obtained from the heat capacity equations. Algebraic equations are convenient for deriving the values of the functions at any specific temperature but they are, in general, valid only over restricted temperature ranges because the heat capacities are expressed in equations of a form not suitable for too wide ranges of temperature. On the other hand, tabulated values at even temperature intervals permit a ready and precise calculation of the thermodynamic functions at these temperatures, and yet calculations for temperatures other than those appearing in the tables necessitate interpolation of the published values. The relative merits and demerits of the two methods for evaluating the thermodynamic functions for specific systems will appear as the methods are used in practice.

Equilibrium among Molecules in Different States.—In a gas with molecules so widely separated from neighboring molecules that they do not interact, the energy of the gas may be described completely in terms of the energies of the individual molecules. Consider a sample of such a gas A at constant energy and volume and at the same time at constant temperature and pressure. In accordance with the quantum theory, each molecule has a definite amount of energy and it gains or loses energy in quanta as it exchanges energy with other molecules. The total energy of the gas being constant, the molecules exchange energy until the numbers of molecules in the different energy states are the equilibrium numbers. Let the equilibrium number of molecules of A in the lowest energy or ground state be n_0 and the energy of each molecule in this state be ϵ_0. This energy is called the *zero point energy.* Let the number of molecules in the next energy state be n_1 and the energy be ϵ_1'.

We shall, however, be interested not in the absolute energy of the molecules in this state but in the excess in energy over that in the ground state. This energy difference, designated as ϵ_1, is defined by the equation

$$\epsilon_1 \equiv \epsilon_1' - \epsilon_0 \tag{16.1}$$

It is the value of ϵ_1 rather than the absolute values ϵ_1' and ϵ_0 that determines the equilibrium distribution of the molecules between the two states. The relative numbers of molecules in the two energy states are given by the equation

$$\frac{n_1}{n_0} = e^{-\epsilon_1/kT} \tag{16.2}$$

where $\mathbf{k}$ is the Boltzmann constant[1] and T the absolute temperature. This equation was derived by Maxwell and Boltzmann from the statistical mechanics and is called the *Boltzmann factor.* It has been verified experimentally in a number of different ways. For example, when it is used to calculate heat capacities of gases, it yields values reproducing the experimental heat capacities of different gases at different temperatures. In a later section, we shall show how equation (16.2) may be used to calculate heat capacities and other thermodynamic functions.

It may be instructive to see how equation (16.2) is related to our thermodynamic functions which were derived for macroscopic systems and, therefore, represent the average behavior of large numbers of molecules in different energy states. If the number of molecules passing from the ground state to the first energy state is the Avogadro number N, we have

$$\Delta E_1 = N\epsilon_1$$

---

[1] In this chapter the gas constants $\mathbf{R}$ and $\mathbf{k}$ will appear as light-faced italics in exponents. Otherwise they will appear in their usual bold-faced form.

where ΔE_1 is the energy difference per mole. Then, we have from equation (16.2), Nk being equal to R

$$\frac{n_1}{n_0} = e^{-\epsilon_1/kT} = e^{-\Delta\text{E}_1/RT} \tag{16.3}$$

which may be written in the forms

$$-\frac{\Delta\text{E}_1}{RT} = \ln\frac{n_1}{n_0}$$

$$\Delta\text{E}_1 = -RT\ln\frac{n_1}{n_0} \tag{16.4}$$

But the ratio n_1/n_0 represents the equilibrium constant K for the transition

$$\text{A}_0 = \text{A}_1; \qquad K = \frac{n_1}{n_0} \tag{16.5}$$

where A_0 represents the gas in the ground state and A_1 the gas in the first energy state. It appears, therefore, that ΔE_1 in this transition corresponds to ΔF°, the standard free energy of reaction which is related to the equilibrium constant by equation (12.21).

$$\Delta F^\circ = -RT\ln K \tag{16.6}$$

Furthermore, from equation (10.51), we have

$$\Delta F^\circ = \Delta H^\circ - T\,\Delta S^\circ \tag{16.7}$$

For the transition under consideration, $P\text{v}$ for the gas remains constant so that

$$\Delta\text{H} = \Delta\text{E} + \Delta(P\text{v}) = \Delta\text{E} \tag{16.8}$$

Consequently, equation (16.7) becomes

$$\Delta F^\circ = \Delta\text{E} - T\,\Delta\text{s}^\circ$$

But if, from equations (16.4) to (16.6), $\Delta F^\circ = \Delta\text{E}$, it follows that Δs° is zero for the transition.

When two configurations or energy states have practically the same energies, the difference in energy becomes approximately zero. If n is the number of molecules in the one state and n' the number in the second state, we have from equation (16.2)

$$\epsilon = 0; \qquad \frac{n'}{n} = e^{-0/kT} = 1; \qquad n = n' \tag{16.9}$$

Thus, at equilibrium there are equal numbers of molecules in two states with equal energies. Accordingly, if there are two states with equal energies, the number of molecules in the two states is $2n$; if there are g states, the total number of molecules in these states is gn. The factor g is called the *statistical weight*, the *quantum weight*, or the *a priori probability*. It appeared in equations (7.50) and (14.47).

Partition Function.—The sum of the numbers of molecules of the gas in all possible energy states equals the total number of molecules N. Thus,

$$N = n_0 + n_1 + n_2 + \cdot \cdot \cdot + n_i \tag{16.10}$$

From the equilibrium ratio of the number of molecules in different states expressed in equation (16.2), it appears that the total number of molecules can be represented in terms of the number of molecules in the ground state and the energy of each state in excess of the zero point energy. Thus, from equation (16.2) the number of molecules in state 2 is given by $n_2 = n_0 e^{-\epsilon_2/kT}$. On making the appropriate substitutions in equation (16.10), we have

$$N = n_0 + n_0 e^{-\epsilon_1/kT} + n_0 e^{-\epsilon_2/kT} + \cdot \cdot \cdot \tag{16.11}$$

the sum including all possible energy states. This sum may be simplified somewhat if all terms with approximately the same energies are combined. Thus, if there are g_0 states with zero point energy, g_1 states with approximately the same additional energy ϵ_1, etc., the total number of molecules may be expressed as

$$N = n_0 g_0 + n_0 g_1 e^{-\epsilon_1/kT} + n_0 g_2 e^{-\epsilon_2/kT} + \cdot \cdot \cdot \tag{16.12}$$

or as

$$N = n_0 \sum^{i} g_i e^{-\epsilon_i/kT} \tag{16.13}$$

where the summation is over all values of ϵ, including the value $\epsilon = 0$. At this point, we remind ourselves that the ϵ's represent the energy in excess of that of the ground state. Hence, a value of $\epsilon = 0$ applies to the molecules with only the zero point energy. The sum in equation (16.13) occurs frequently in calculations of energy and the other thermodynamic quantities from the energy levels of molecules. It is called the *partition function* or *state sum* and designated by the symbol Q. Thus,

$$Q = \sum_{0}^{i} g_i e^{-\epsilon_i/kT} \tag{16.14}$$

In terms of the partition function Q, equation (16.13) becomes

$$N = n_0 Q \tag{16.15}$$

The preceding equations were derived for the condition of constant temperature. As equation (16.14) shows, the partition function is a function of temperature. Consequently, from equation (16.15) the relative number n_0/N of molecules in the ground state is also a function of temperature. At higher temperatures, relatively more molecules are in higher energy states and the number in the ground state decreases. On the other hand as T becomes small, approaching zero, all values of $e^{-\epsilon/kT}$ except the $e^{-0/kT}$ term approach zero, Q approaches unity, and practically all the molecules are in the ground state.

For future use, we shall derive the general equation for the change of Q with temperature. In the differentiation of equation (16.14) with respect to temperature, g, ϵ, and k are constant. The energy differences and quantum weights for the various states of the molecule are not functions of the temperature though the relative numbers of molecules in the various energy states are. Therefore, from equation (16.14),

$$\frac{dQ}{dT} = \frac{d}{dT}\left(\sum g_i e^{-\epsilon_i/kT}\right) = \sum g_i e^{-\epsilon_i/kT}\left(\frac{\epsilon_i}{kT^2}\right) = \frac{1}{kT^2}\sum \epsilon_i g_i e^{-\epsilon_i/kT} \qquad (16.16)$$

Energy of the Molecules.—Since we are here concerned with the internal equilibrium of the gas among the different energy states, we shall for the present consider all energy dependent on temperature except the translational energy of the molecules. The energy to be considered includes the energy of rotation of molecules or of parts of molecules with respect to the rest of the molecule, the energy of vibration of the atoms within the molecule, and the energy of electron excitation. All molecules have zero point energy; at the absolute zero of temperature, the molecules are in the ground state with this minimum energy. As additional energy is added to the system, the temperature rises in a way required by the heat capacity of the system. In previous chapters, we considered the translational part of this added energy. Any energy absorbed in addition to that required by the increased translational motion of the molecules will raise some of the molecules to rotational, vibrational, or electronic levels higher than those of the ground state. This energy is the part we shall now consider.

Since all the molecules have zero point energy, and some have energy in addition, we may represent the zero point energy of all the molecules as in equations (2.43) and (2.44) by E_0. If E is all the energy of the molecules (except translational energy), that part of the energy in excess of the zero point energy will be $E - E_0$. This energy may be expressed as the sum of *excess* energies of all the molecules, as defined in equation (16.1). There being gn_0 molecules with excess energy, $\epsilon = 0$, g_1n_1 molecules with excess energy ϵ_1, etc., we have for the energy of all the molecules

$$E - E_0 = n_0g_00 + n_1g_1\epsilon_1 + n_2g_2\epsilon_2 + \cdots \tag{16.17}$$

But, from equation (16.2) it appears that the numbers n_1, n_2, etc., can be expressed in terms of n_0, the energies, and the temperature. Thus,

$$E - E_0 = n_0g_00 + n_0\epsilon_1g_1\mathrm{e}^{-\epsilon_1/kT} + n_0\epsilon_2g_2\mathrm{e}^{-\epsilon_2/kT} + \cdots \tag{16.18}$$

This equation may also be written as

$$E - E_0 = n_0 \sum_0^i \epsilon_i g_i \mathrm{e}^{-\epsilon_i/kT} \tag{16.19}$$

where, as before, the summation is over all values of ϵ. When the value for n_0 from equation (16.13) is substituted in equation (16.19), it becomes

$$E - E_0 = N\frac{\Sigma\epsilon g\mathrm{e}^{-\epsilon/kT}}{\Sigma g\mathrm{e}^{-\epsilon/kT}} \tag{16.20}$$

Thus, the energy of the gas can be calculated from the number of molecules, N, the energy levels obtained from spectroscopic data, and the statistical weights of the levels obtained from the quantum mechanical theory. As was stated earlier, the number of molecules in the higher levels depends on the temperature. If ϵ is large enough, $\mathrm{e}^{-\epsilon/kT}$ becomes negligible in the summation, and there are few molecules in that energy state.

Comparison of equation (16.20) with (16.14) shows that the denominator is the partition function Q. Comparison with equation (16.16) shows that the sum in the numerator equals $kT^2(\mathrm{d}Q/\mathrm{d}T)$. Consequently, the energy may be expressed in terms of the partition function as

$$E - E_0 = \frac{NkT^2}{Q}\frac{\mathrm{d}Q}{\mathrm{d}T} = NkT^2\frac{\mathrm{d}\ln Q}{\mathrm{d}T} \tag{16.21}$$

The preceding equations are for N molecules of gas. For 1 mole of gas, the number N becomes equal to the Avogadro number and Nk becomes R. Then, for 1 mole

$$\mathrm{E} - \mathrm{E}_0 = RT^2\frac{\mathrm{d}\ln Q}{\mathrm{d}T} \tag{16.22}$$

From this relation between the energy of the gas, the partition function of the gas at the temperature T, and the change of the partition function with temperature, we shall be able, through known thermodynamic relations, to calculate the equations for the other thermodynamic functions in terms of the partition function.

Heat Capacity.—From equation (16.22), we may calculate the contributions of the rotational, vibrational, and electronic energies of the molecules to the heat capacity of the gas. The heat capacity measures only the part of the energy that varies with temperature. Thus, the heat capacity for 1 mole of gas, exclusive of the translational heat capacity, is, for this constant-volume system,

$$\mathrm{C} = \mathrm{C}_V = \frac{\mathrm{d}(\mathrm{E} - \mathrm{E}_0)}{\mathrm{d}T} = \frac{\mathrm{dE}}{\mathrm{d}T}$$

for the zero point energy E_0 is not a function of temperature. Consequently, on differentiating equation (16.22) with respect to temperature, we have

$$\mathrm{C}_V = \frac{\mathrm{d}}{\mathrm{d}T}\left(RT^2\frac{\mathrm{d}\ln Q}{\mathrm{d}T}\right) = -R\left\{\frac{\mathrm{d}}{\mathrm{d}T}\left[\frac{\mathrm{d}\ln Q}{\mathrm{d}(1/T)}\right]\right\} \qquad (16.23)$$

since $\mathrm{d}(1/T) = -(\mathrm{d}T/T^2)$.

Entropy.—The entropy of a gas is related to the heat capacity by equation (8.6), from which, between the temperatures $T = 0$ and $T = T$

$$\mathrm{S} - \mathrm{S}_0 = \int_0^T \frac{\mathrm{C}_V}{T}\,\mathrm{d}T = -R\int_0^T \left(\frac{1}{T}\right)\frac{\mathrm{d}}{\mathrm{d}T}\left[\frac{\mathrm{d}\ln Q}{\mathrm{d}(1/T)}\right]\mathrm{d}T$$

This equation may be simplified to

$$\mathrm{S} - \mathrm{S}_0 = -R\int_0^T \left(\frac{1}{T}\right)\mathrm{d}\left[\frac{\mathrm{d}\ln Q}{\mathrm{d}(1/T)}\right] \qquad (16.24)$$

Equation (16.24) may be integrated by parts. Thus, in the general formula

$$\int u\,\mathrm{d}v = uv - \int v\,\mathrm{d}u$$

we have

$$u = \frac{1}{T}; \qquad \mathrm{d}u = \mathrm{d}\left(\frac{1}{T}\right)$$

$$\mathrm{d}v = \mathrm{d}\left[\frac{\mathrm{d}\ln Q}{\mathrm{d}(1/T)}\right]; \qquad v = \frac{\mathrm{d}\ln Q}{\mathrm{d}(1/T)}$$

From equation (16.24) we have, therefore,

$$\mathrm{S} - \mathrm{S}_0 = -R\left[\left(\frac{1}{T}\right)\frac{\mathrm{d}\ln Q}{\mathrm{d}(1/T)} - \int_0^T \frac{\mathrm{d}\ln Q}{\mathrm{d}(1/T)}\,\mathrm{d}\left(\frac{1}{T}\right)\right] \qquad (16.25)$$

But, $\mathrm{d}(1/T) = -(\mathrm{d}T/T^2)$ so that the first term in the brackets becomes

$$-\left(\frac{1}{T}\right)\frac{\mathrm{d}\ln Q}{\mathrm{d}T}T^2 = -T\frac{\mathrm{d}\ln Q}{\mathrm{d}T}$$

For the second term in the brackets, Q being Q_0 at $T = 0$ and Q at $T = T$, we obtain on integration, $\ln Q - \ln Q_0$. When these are substituted in equation (16.25), it becomes

$$\mathrm{S} - \mathrm{S}_0 = RT \frac{\mathrm{d} \ln Q}{\mathrm{d}T} + R \ln Q - R \ln Q_0 \tag{16.26}$$

At zero temperature, equation (16.26) becomes

$$-\mathrm{S}_0 = -R \ln Q_0 \tag{16.27}$$

If there is a single state with zero point energy and all the molecules are in this state, $N = n_0$ and, from equation (16.15), $Q = 1$. Then $\ln Q_0 = 0$ and $\mathrm{S}_0 = 0$. This is a statement of the third law of thermodynamics. On the other hand, if there are g ways of realizing states with zero point energy, we have from equations (16.12) and (16.15) at $T = 0$, $N = n_0 g_0$, $Q_0 = g_0$, and $\mathrm{S}_0 = R \ln g_0$. This is equation (7.50). From equations (16.26) and (16.27) the equation for the rotational, vibrational, and electronic entropy of the gas is

$$\mathrm{S} = RT \frac{\mathrm{d} \ln Q}{\mathrm{d}T} + R \ln Q \tag{16.28}$$

Comparison with equation (16.22) shows that this equation may also be written in the form

$$\mathrm{S} = \frac{\mathrm{E} - \mathrm{E}_0}{T} + R \ln Q \tag{16.29}$$

In calculations of the thermodynamic functions from the logarithm of Q and its change with temperature, the rotational, vibrational, and electronic contributions are usually evaluated separately. When the energy of a given level can be separated into the rotational, vibrational, and electronic components, we may write

$$\epsilon = \epsilon_r + \epsilon_v + \epsilon_e \tag{16.30}$$

From the exponential character of the partition function Q, it appears that it is the product of the component functions so that

$$Q = Q_r \times Q_v \times Q_e \tag{16.31}$$

Thus, equation (16.22) may be put in the form

$$\begin{aligned} \mathrm{E} - \mathrm{E}_0 &= (\mathrm{E} - \mathrm{E}_0)_r + (\mathrm{E} - \mathrm{E}_0)_v + (\mathrm{E} - \mathrm{E}_0)_e \\ &= RT^2 \frac{\mathrm{d} \ln (Q_r Q_v Q_e)}{\mathrm{d}T} \\ &= RT^2 \left(\frac{\mathrm{d} \ln Q_r}{\mathrm{d}T} + \frac{\mathrm{d} \ln Q_v}{\mathrm{d}T} + \frac{\mathrm{d} \ln Q_e}{\mathrm{d}T} \right) \end{aligned} \tag{16.32}$$

Corresponding relations hold for the other thermodynamic functions. For many of the gases, the electronic levels are so high that at moderate temperatures the electronic contributions are negligible. The rotational contributions may be closely approximated by analytical functions of the moments of inertia of the molecule. The vibrational contributions usually require summation, which is a tedious process. However, when the exact energy levels and the statistical weights are known, the final results are accurate. The translational contributions are considered separately.

Thermodynamic Functions for Translation.—The thermodynamic functions just discussed represent energy contributions exclusive of translational energies. The translational contributions are considered separately for most of them do not differ for different kinds of molecules so long as the gases remain ideal. We have already derived the equations for the ideal monatomic gas. But, the translational energies of ideal polyatomic gases are identical with those of ideal monatomic gases, and the translational entropies differ from gas to gas only in the term for the molecular weight in the Sackur-Tetrode equation. The thermodynamic functions already derived for translation will be collected here.

Energy and Heat Content of Translation.—From the kinetic theory we derived equation (4.63) for the translational energy of 1 mole of ideal gas. Thus,

$$\text{E} = \tfrac{3}{2}RT \tag{16.33}$$

For the molar heat content of the gas, we have from equation (2.35) and from the ideal gas equation, $P\text{v} = RT$,

$$\text{H} = \text{E} + P\text{v} = \text{E} + RT \tag{16.34}$$

Consequently, the translational heat content becomes

$$\text{H} = \tfrac{3}{2}RT + RT = \tfrac{5}{2}RT \tag{16.35}$$

Heat Capacity of Translation.—From equation (16.33), we have directly for the translational heat capacity at constant volume

$$\text{C}_V = \left(\frac{dE}{dT}\right)_V = \frac{3}{2}R \tag{16.36}$$

which is equation (4.64); from equation (16.35) we have, for the translational heat capacity at constant pressure,

$$\text{C}_P = \left(\frac{d\text{H}}{dT}\right)_P = \frac{5}{2}R \tag{16.37}$$

which is equation (4.65).

Entropy of Translation.—The entropy of translation is given by the Sackur-Tetrode equation (8.57). Thus,

$$\text{s} = \tfrac{3}{2}R \ln M + \tfrac{5}{2}R \ln T - R \ln P + \tfrac{5}{2}R - 7.282 \qquad (16.38)$$

At 1 atmosphere, the translational contribution to the entropy becomes

$$\text{s} = 6.864 \log M + 11.439 \log T - 2.314 \qquad (16.39)$$

Relative Energy of a Gas.—When the translational energy of a gas in equation (16.33) is added to the rotational, vibrational, and electronic energies represented by equation (16.22), we have an expression for the total energy of the gas dependent on the temperature. Thus,

$$\text{E} - \text{E}_0 = RT^2 \frac{d \ln Q}{dT} + \frac{3}{2} RT \qquad (16.40)$$

Observe that $\text{E} - \text{E}_0$ represents only the energy in excess of the zero point energy as in equation (2.44). Included in the zero point energy are the minimum rotational and vibrational energies characteristic of the molecules in their ground state and the energies of nuclear and electronic spin. However, in every chemical reaction the atoms in products of the reaction are those initially present in the reactants so that the energies associated with atoms in their ground states remain unaltered by the reaction. On the other hand, molecules in their ground states have also the energies associated with bonds between the atoms in the molecules. These bond energies, whose differences represent the energies of chemical reaction, are of special interest to chemists. At temperatures above the absolute zero, the measured energies of reaction include the differences in rotational, vibrational, and electronic energies of the reacting substances as well as the differences in bond energies and are, therefore, not a direct measure of the chemical forces.

In accordance with the usual chemical practice, we may assign a zero value to E_0 for the molecules of the elements. Thus, we may assign a value of E_0 equals zero for hydrogen gas H_2 and a value E_0 equals zero for oxygen gas O_2. Then the value of E_0 for water vapor cannot be zero for, in the formation of 1 mole of water from 1 mole of hydrogen and $\frac{1}{2}$ mole of oxygen at zero temperature, 57,104 calories are evolved. Hence, on this standard, the value of E_0 for gaseous water would be $-57{,}104$ calories. Similarly, if the value of E_0 for molecular hydrogen is zero, the value of E_0 for atomic hydrogen cannot be zero for the energy of formation of atomic hydrogen from molecular hydrogen at zero temperature is 51,620 calories. Thus, the value of E_0 for H is 51,620 calories if the value of E_0 for H_2 is zero. It appears, therefore, that in calculations attention must be paid to the reference state of the element chosen as the standard state.

Relative Heat Content.—For use in constant-pressure reactions, we shall need relative values for heat content corresponding to the relative energy equation (16.40). It appears from equation (16.34) that the heat content of 1 mole of the gas differs from the energy by RT. But, at zero temperature RT equals zero, so that at this temperature we have

$$\text{H}_0 = \text{E}_0 \tag{16.41}$$

where H_0 is the heat content at zero temperature. Since the zero point heat content of the gas is identical with the zero point energy, we may subtract equation (16.41) from equation (16.34) and obtain

$$\text{H} - \text{H}_0 = \text{H} - \text{E}_0 = \text{E} - \text{E}_0 + RT \tag{16.42}$$

Then, from equations (16.40) and (16.42),

$$\text{H} - \text{H}_0 = RT^2 \frac{d \ln Q}{dT} + \frac{5}{2} RT \tag{16.43}$$

$\text{H} - \text{H}_0$, like $\text{E} - \text{E}_0$, is a measure of the energies that are dependent on the temperature. At zero temperature, the terms on the right-hand side of equation (16.43) vanish and H becomes equal to H_0.

Because of the equality between H_0 and E_0, what has been said concerning the relative values of E_0 for different elements and compounds and for elements in different reference states applies also to the values for H_0. All the tables of heat content that we have used hitherto have shown relative values. Thus, heat of formation tables usually list the heat contents of the compounds relative to the heat contents of the constituent elements in their standard states. The proof in Chap. 2 that the particular reference state chosen does not influence the heat content values calculated for a specific reaction may be reviewed at this point.

Values of $\text{H} - \text{H}_0$ are usually listed for a standard pressure of 1 atmosphere. Where the superscript ° refers as before to the substance in its standard state, and the subscript $_0$ to a temperature of 0°K, we may express the relative heat content of a substance in terms of the difference $\text{H}^\circ - \text{H}^\circ_0$. Values of this standard relative heat content are given in Table 16.1 for a number of gases as well as for crystalline carbon, both with graphite and with diamond as the standard phase. The values of $\text{H}^\circ - \text{H}^\circ_0$ at different temperatures are related to the heat capacity of the substances. Thus, $\text{H}^\circ - \text{H}^\circ_0$ for hydrogen has a value of 2,731.0 at 400°K and a value 2,036.47 at 300°K, the difference, 694.5, representing the integral of $C_P\,dT$ for hydrogen between these two temperatures. The tabulated values enable us to avoid integration of the heat capacity equation over the temperature interval but they do not give the heat content at intermediate temperatures. If such a value is desired, however, one may interpolate between the values given in the table.

TABLE 16.1.—RELATIVE HEAT CONTENT ($\text{H}^\circ - \text{H}_0^\circ$) OF SOME SUBSTANCES*
(In calories per mole)

Substance (formula)	Temperature, °K							
	298.16	400	600	800	1000	1500	2000	3000
O_2(g)	2069.78	2792.4	4279.2	5854.1	7,497.0	11,776.4	16,219	25,500
H_2(g)	2023.81	2731.0	4128.6	5537.4	6,965.8	10,694.2	14,672	23,186
OH(g)	2106.2	2829.6	4240.8	5658.4	7,106.0	10,910	14,960	23,562
H_2O(g)	2365.1	3190.0	4873.2	6666.4	8,580.0	13,876	19,760	32,580
N_2(g)	2072.27	2782.4	4198.0	5668.6	7,202.5	11,253.6	15,499	24,245
NO(g)	2194.2	2920.8	4381.2	5909.6	7,506.0	11,694	16,030	24,921
C(graphite)	251.56	502.6	1198.1	2081.7	3,074.6	5,814		
C(diamond)	128.13	325	950	1804	2,782			
CO(g)	2072.63	2783.8	4209.5	5699.8	7,256.5	11,358.8	15,636	24,434
CO_2(g)	2238.11	3194.8	5322.4	7689.4	10,222	17,004	24,144	38,950
CH_4(g)	2397	3323	5549	8321	11,560	21,130		
O(g)	1607.4	2134.9	3151.7	4157.6	5,158.8	7,653.3	10,143	15,129
H(g)	1481.2	1987.2	2980.8	3974.4	4,968.0	7,451.9	9,935.9	14,904
N(g)	1481.2	1987.2	2980.8	3974.4	4,968.0	7,451.9	9,936.2	14,918

* WAGMAN, D. D., J. E. KILPATRICK, W. J. TAYLOR, K. S. PITZER, and F. D. ROSSINI, *J. Research Natl. Bur. Standards*, **34,** 143 (1945).

American Petroleum Institute Research Project 44 at the National Bureau of Standards. Selected Values of Properties of Hydrocarbons. Table Ou, Heat Content ($H^\circ - H_0^\circ$) at 0° to 4000°K, July 31, 1944; Aug. 31, 1946; Table OOu, *ibid.*, June 30, 1946.

In certain calculations, the value of $(\text{H}^\circ - \text{H}_0^\circ)/T$ is required. This function is called the *heat content function.* Values of this function for some substances are listed in Table 16.2. Observe that the values have the order of magnitude and the dimensions of heat capacity though they are not the values of the true heat capacity, $\mathrm{d}H/\mathrm{d}T$. They correspond to the mean heat capacity for the substance over the range 0 to T°K, as may be seen by comparison with equation (3.9). From equation (16.43), we have, for the heat content function,

$$\frac{\text{H}^\circ - \text{H}_0^\circ}{T} = RT\frac{\mathrm{d}\ln Q}{\mathrm{d}T} + \frac{5}{2}R \qquad (16.44)$$

Heat Capacity.—The heat capacity of the gas may be obtained by adding the value for the translational heat capacity in equation (16.37) to the rotational, vibrational, and electronic heat capacity as given in equation (16.23). For calculations on the change of heat of reaction with temperature, we desire the values for the change in heat contents with temperature and not the true heat capacities. Tabulated values of $\text{H}_0 - \text{H}_0$ for different temperatures permit us to calculate this change directly, so that the heat capacities are not required.

TABLE 16.2.—HEAT CONTENT FUNCTION $\frac{H^\circ - H_0^\circ}{T}$ OF SOME SUBSTANCES*

(In calories per degree mole)

Substance (formula)	Temperature in °K							
	298.16	400	600	800	1000	1500	2000	3000
O_2(g)	6.9418	6.9811	7.1320	7.3176	7.4970	7.8509	8.1094	8.5000
H_2(g)	6.7877	6.8275	6.8810	6.9218	6.9658	7.1295	7.3358	7.7286
OH(g)	7.064	7.074	7.068	7.073	7.106	7.273	7.480	7.854
H_2O(g)	7.934	7.975	8.122	8.333	8.580	9.251	9.88	10.86
N_2(g)	6.9502	6.9559	6.9967	7.0857	7.2025	7.5024	7.7497	8.0816
NO(g)	7.359	7.302	7.302	7.387	7.506	7.796	8.015	8.307
C(graphite)	0.84369	1.2565	1.9968	2.0621	3.0746	3.876		
C(diamond)	0.4297	0.8125	1.583	2.255	2.782			
CO(g)	6.9514	6.9594	7.0159	7.1247	7.2565	7.5725	7.8182	8.1448
CO_2(g)	7.5064	7.9870	8.8707	9.6117	10.222	11.336	12.072	12.98
CH_4(g)	8.039	8.307	9.249	10.401	11.56	14.09		
O(g)	5.391	5.337	5.253	5.197	5.159	5.102	5.071	5.043
H(g)	4.968	4.968	4.968	4.968	4.968	4.968	4.968	4.968
N(g)	4.968	4.968	4.968	4.968	4.968	4.968	4.968	4.973

* WAGMAN, D. D., J. E. KILPATRICK, W. J. TAYLOR, K. S. PITZER, and F. D. ROSSINI, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

American Petroleum Institute Research Project 44 at the National Bureau of Standards. Selected Values of Properties of Hydrocarbons. Table Or, Heat Content Function $(H^\circ - H_0^\circ)/T$ at 0° to 4000°K, July 31, 1944; Aug. 31, 1946; Table OOr, *ibid.*, June 30, 1946.

Entropy.—The total entropy for 1 mole of gas may be obtained by adding equation (16.38) for the translational entropy to equation (16.28). Thus, for the standard state of 1 atmosphere,

$$S^\circ = RT\frac{d\ln Q}{dT} + R\ln Q + \frac{3}{2}R\ln M + \frac{5}{2}R\ln T + \frac{5}{2}R - 7.282 \tag{16.45}$$

A comparison with equation (16.44) for the heat content function shows that the entropy may also be expressed as

$$S^\circ = \frac{H^\circ - H_0^\circ}{T} + R\ln Q + \frac{3}{2}R\ln M + \frac{5}{2}R\ln T - 7.282 \tag{16.46}$$

As was stated earlier, the nuclear spin energies are usually not included in the partition function. Consequently, the equations for the entropy do not include the entropy of nuclear spin. Similarly, equations (16.45) and (16.46) do not include a term for the entropy of mixing of isotopic forms of the gas. Hence, the entropies calculated from the equation are relative rather than absolute entropies. They may be used in calculations for all reactions that do not result in a separation of isotopes. This limitation is not usually of practical importance for nuclear spins and the ratios of isotopes remain unchanged in most chemical reactions.

Free Energy.—In the preceding sections, relations were found between the partition function of a gas and the entropy and relative heat content. But the free energy is related to these functions as is evident from the defining equation

$$F \equiv H - TS$$

from which

$$F - H_0 = H - H_0 - TS$$

and

$$\frac{F - H_0}{T} = \frac{H - H_0}{T} - S \tag{16.47}$$

The function $(F - H_0)/T$ defined by equation (16.47) is called the *free energy function.* For 1 mole of the gas in its standard state, we have from equations (16.46) and (16.47)

$$\frac{F^\circ - H_0^\circ}{T} = -R \ln Q - \frac{3}{2} R \ln M - \frac{5}{2} R \ln T + 7.282 \tag{16.48}$$

TABLE 16.3.—FREE ENERGY FUNCTION $\frac{F^\circ - H_0^\circ}{T}$ FOR SOME SUBSTANCES*

(In calories per degree mole)

Substance (formula)	Temperature, °K							
	298.16	400	600	800	1000	1500	2000	3000
O_2(g)	−42.061	−44.112	−46.968	−49.044	−50.697	−53.808	−56.103	−59.468
H_2(g)	−24.423	−26.422	−29.203	−31.186	−32.738	−35.590	−37.669	−40.719
OH(g)	−36.824	−38.904	−41.772	−43.804	−45.385	−48.295	−50.415	−53.521
H_2O(g)	−37.172	−39.508	−43.768	−45.131	−47.018	−50.622	−53.38	−57.59
N_2(g)	−38.817	−40.861	−43.688	−45.711	−47.306	−50.284	−52.478	−55.687
NO	−42.980	−45.134	−48.090	−50.202	−51.864	−54.964	−57.239	−60.549
C(graphite)	− 0.5172	− 0.8245	− 1.477	− 2.138	− 2.771	− 4.181		
C(diamond)	− 0.1532	− 0.331	− 0.808	− 1.358	− 1.920			
CO(g)	−40.350	−42.393	−45.222	−47.254	−48.860	−51.884	−54.078	−57.314
CO_2(g)	−43.555	−45.828	−49.238	−51.895	−54.109	−58.461	−61.85	−67.11
CH_4(g)	−36.46	−38.86	−42.39	−45.21	−47.65	−52.84		
O(g)	−33.078	−34.654	−36.801	−38.304	−39.460	−41.539	−43.002	−45.052
H(g)	−22.425	−23.884	−25.899	−27.328	−28.436	−30.451	−31.880	−33.894
N(g)	−31.646	−33.106	−35.120	−36.550	−37.658	−39.673	−41.102	−43.117

* WAGMAN, D. D., J. E. KILPATRICK, W. J. TAYLOR, K. S. PITZER, and F. D. ROSSINI, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

American Petroleum Institute Research Project 44 at the National Bureau of Standards. Selected Values of Properties of Hydrocarbons. Table Os, Free Energy Function $(F^\circ - H_0^\circ)/T$ at 0° to 4000°K, July 31, 1944; Aug. 31, 1946; Table OOs, *ibid.*, June 30, 1946.

Values of this function for several substances are listed in Table 16.3. Values for F°/T may be obtained from the free energy function, since

$$\frac{\mathrm{F}^\circ}{T} = \frac{\mathrm{F}^\circ - \mathrm{H}_0^\circ}{T} + \frac{\mathrm{H}_0^\circ}{T} \tag{16.49}$$

It appears that absolute values of F° and of F°/T may be obtained from the free energy function only if absolute values of H_0° are known. However, for calculations on chemical reactions, we desire the difference in free energy between that of the products and that of the reactants. This difference can be obtained from relative values as well as from absolute values. If, then, we use proper relative values for the standard heat content of the reacting substances at zero temperature, we may obtain the value for the free energy change in the reaction. Thus, from the heat of formation of a compound from its elements at zero temperature, we may obtain the value for the free energy of formation of the compound at this temperature, for, from the third law, $\mathrm{S}_0 = 0$ and $\mathrm{F}_0 = \mathrm{H}_0$.

Heat of Reaction at Zero Temperature.—The heat of reaction at zero temperature may be obtained from the measured heat of reaction at room temperature and the values of $\mathrm{H}^\circ - \mathrm{H}_0^\circ$ for the reacting substances. The heat of reaction at zero temperature and the $\mathrm{H}^\circ - \mathrm{H}_0^\circ$ values may then be used to calculate the heat of reaction at other temperatures. In Chap. 5 we showed how heats of reaction may be derived from heats of formation of compounds from the elements. The formation of gaseous water from hydrogen and oxygen will serve as an example. At 25°C for the substances in their standard states, we have

$$\mathrm{H_2(g)} + \tfrac{1}{2}\mathrm{O_2(g)} = \mathrm{H_2O(g)}; \qquad \Delta H^\circ_{298.16} = -57{,}798 \text{ cal}$$

At this temperature, as in equation (5.3),

$$\Delta H^\circ = \mathrm{H}^\circ(\mathrm{H_2O}) - \mathrm{H}^\circ(\mathrm{H_2}) - \tfrac{1}{2}\mathrm{H}^\circ(\mathrm{O_2}) = -57{,}798 \tag{16.50}$$

At zero temperature for the same reaction

$$\Delta H_0^\circ = \mathrm{H}_0^\circ(\mathrm{H_2O}) - \mathrm{H}_0^\circ(\mathrm{H_2}) - \tfrac{1}{2}\mathrm{H}_0^\circ(\mathrm{O_2}) \tag{16.51}$$

But the heat of reaction at zero temperature is

$$\Delta H_0^\circ = \Delta H^\circ - \Delta(H^\circ - H_0^\circ) \tag{16.52}$$

The values of $\Delta(H^\circ - H_0^\circ)$ may be obtained from the data for water, hydrogen, and oxygen in Table 16.1. Thus,

$$\begin{aligned}\Delta(H^\circ - H_0^\circ) &= (\mathrm{H}^\circ - \mathrm{H}_0^\circ)(\mathrm{H_2O}) - (\mathrm{H}^\circ - \mathrm{H}_0^\circ)(\mathrm{H_2}) - \tfrac{1}{2}(\mathrm{H}^\circ - \mathrm{H}_0^\circ)(\mathrm{O_2}) \\ &= 2{,}365.1 - 2{,}023.81 - 1{,}034.89 = -693.6 \text{ cal}\end{aligned} \tag{16.53}$$

Hence, from equations (16.50) to (16.53),

$$\Delta H^\circ_0 = H^\circ_0(H_2O) - H^\circ_0(H_2) - \tfrac{1}{2}H^\circ_0(O_2) = -57{,}798 + 694 = -57{,}104 \text{ cal} \tag{16.54}$$

Thus, it appears that the zero point heat content of 1 mole of gaseous water, which from equation (16.41) is identical with the zero point energy, is smaller by 57,104 calories than that of 1 mole of hydrogen and $\frac{1}{2}$ mole of oxygen. If the zero point energies of the molecular hydrogen and oxygen are arbitrarily placed at zero, the zero point heat content of water on this scale becomes $-57{,}104$ calories. This value being fixed, we may now calculate the heat of reaction at any temperature, for, from equation (16.52),

$$\Delta H^\circ = \Delta H^\circ_0 + \Delta(H^\circ - H^\circ_0) \tag{16.55}$$

Values for the heat of formation ΔH°_f of various substances are given in Table 16.4. From these data and the values in Table 16.1, we may calculate the heat of formation of atomic hydrogen at 1000°K, the zero point energy of molecular hydrogen being arbitrarily set at zero. Thus, for the reaction

$$H_2 = 2H$$

we have, from Table 16.4,

$$\Delta H^\circ_0 = 2H^\circ_0(H) - H^\circ_0(H_2) = 2 \times 51{,}620 = 103{,}240 \text{ cal}$$

and from Table 16.1,

$$\begin{aligned}\Delta(H^\circ - H^\circ_0) &= 2(H^\circ - H^\circ_0)(H) - (H^\circ - H^\circ_0)(H_2)\\ &= 2 \times 4968.0 - 6{,}965.8 = 2{,}970 \text{ cal}\end{aligned}$$

TABLE 16.4.—HEAT OF FORMATION ΔH°_f OF SOME SUBSTANCES FROM THE ELEMENTS IN THEIR STANDARD STATES*
(In kilocalories per mole)

Substance (formula)	ΔH°_f		Substance (formula)	ΔH°_f	
	At 0°K	At 298.16°K		At 0°K	At 298.16°K
O_2(g)	0	0	C(graphite)	0	0
H_2(g)	0	0	CO(g)	−27.2019	−26.4157
OH(g)	10.0	10.061	CO_2(g)	−93.9686	−94.0518
H_2O(g)	−57.1043	−57.7979	CH_4(g)	−15.987	−17.889
N_2(g)	0	0	O(g)	58.586	59.159
NO(g)	21.477	21.600	H(g)	51.620	52.089
			N(g)	85.120	85.566

---

* WAGMAN, D. D., J. E. KILPATRICK, W. J. TAYLOR, K. S. PITZER, and F. D. ROSSINI, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

American Petroleum Institute Research Project 44 at the National Bureau of Standards. Selected Values of Properties of Hydrocarbons. Table 0w, Heat of Formation ΔH_f° at 0 to 4000°K, July 31, 1944; Aug. 31, 1946; Table 00w, *ibid.*, June 30, 1946.

Therefore, the heat of formation of 2 moles of atomic hydrogen at 1000°K is

$$\Delta H^\circ = \Delta H_0^\circ + \Delta(H^\circ - H_0^\circ) = 103{,}240 + 2{,}970 = 106{,}210 \text{ cal}$$

Entropy of Reaction.—From equation (16.47) it appears that the entropy of a substance at any temperature may be calculated from the values for the heat content function and the free energy function at that temperature. Thus, for the substance in its standard state,

$$S^\circ = \frac{H^\circ - H_0^\circ}{T} - \frac{F^\circ - H_0^\circ}{T} \tag{16.56}$$

For a chemical reaction, the corresponding change in entropy is

$$\Delta S^\circ = \Delta\left(\frac{H^\circ - H_0^\circ}{T}\right) - \Delta\left(\frac{F^\circ - H_0^\circ}{T}\right) \tag{16.57}$$

Free Energy of Reaction.—The free energy of reaction at any temperature T may be derived from the value of the free energy function for that temperature and the heat of reaction at zero temperature divided by the temperature T. Thus, from equation (16.49), we have

$$\frac{\Delta F^\circ}{T} = \frac{\Delta H_0^\circ}{T} + \Delta\left(\frac{F^\circ - H_0^\circ}{T}\right) \tag{16.58}$$

which may be used directly in the calculation of the equilibrium constant. However, if free energy values are desired explicitly, equation (16.58) may be multiplied by T.

Equilibrium Constant.—The equilibrium constant for reactions may be obtained from the tabulated functions. Equation (12.21), which is

$$\Delta F^\circ = -RT \ln K$$

may be rearranged to

$$\frac{\Delta F^\circ}{T} = -R \ln K = -4.5757 \log K \tag{16.59}$$

Hence, from equation (16.58),

$$-R \ln K = -4.5757 \log K = \frac{\Delta H_0^\circ}{T} + \Delta\left(\frac{F^\circ - H_0^\circ}{T}\right) \tag{16.60}$$

This equation may be applied to the reaction

$$H_2 + CO_2 = CO + H_2O(g); \qquad K = \frac{P_{CO}P_{H_2O}}{P_{H_2}P_{CO_2}}$$

From the data in Tables 16.3 and 16.4, we have for the reaction at 1000°K

$$\frac{\Delta F^\circ}{T} = -4.5757 \log K = \frac{(-27{,}202 - 57{,}104 + 0 + 93{,}969)}{1000}$$
$$+ (-47.018 - 48.860 + 32.738 + 54.109)$$
$$= 9.663 - 9.031 = 0.632 \text{ cal/deg}$$

whence,

$$\Delta F^\circ = 0.632 \times 1{,}000 = 632 \text{ cal}$$

and

$$\log K = \frac{0.632}{4.5757} = -0.138_1$$

so that

$$K = 0.728$$

The value for ΔF° at 1000°K may be compared with that obtained from the algebraic functions in Prob. 11.4.

Problems

16.1. Calculate the values for the heat of formation of gaseous water at the temperatures, 298.16, 400, 600, 800, 1000, 1500, 2000, and 3000°K. Carry out the calculations in tabular form and show your complete calculations.

16.2. From the tabulated data, calculate the values of the equilibrium constant for the reaction

$$H_2 + CO_2 = CO + H_2O(g)$$

at the temperatures, 298.16, 400, 600, 800, 1000, 1500, and 2000°K. Report your calculations in tabular form and compare the results with those obtained in Prob. 12.8.

16.3. (*a*) Plot the values of the equilibrium constant for the reaction in Prob. 16.2 against temperature and find the temperature at which $K = 1$.

(*b*) For the same reaction, plot the values of log K and of ΔF° against temperature. Find the temperatures at which $\log K = 0$ and $\Delta F^\circ = 0$, reading the values from a large scale plot. Which of the functions in (*a*) and (*b*) permits the more accurate interpolation?

16.4. From the tabulated data, calculate the values for the entropy of hydrogen gas at the temperatures, 298.16, 1000, 2000, and 3000°K.

16.5. A gas containing approximately 77 mole per cent of nitrogen, 21 of oxygen, and 2 of water vapor is heated at 1 atmosphere pressure to 1500°K. Which of the following reactions can occur to an appreciable extent at this temperature?

$$N_2 + O_2 = 2\ NO$$
$$H_2O = H_2 + \tfrac{1}{2}O_2$$
$$H_2 + O_2 = 2\ OH$$

Estimate the quantities of H_2, OH, and NO at equilibrium.

16.6. Calculate the values for the dissociation of water into hydrogen and oxygen at 1 atmosphere pressure and the temperatures 1000, 2000, and 3000°K.

16.7. Steam is heated with excess carbon (graphite) at 1000°K and 1 atmosphere pressure until complete equilibrium is established. Consider the following reactions and their equilibrium constants:

(1) $C(c) + H_2O = CO + H_2$; $K_P = 2.609$
(2) $C(c) + CO_2 = 2\,CO$; $K_P = 1.900$
(3) $C(c) + 2H_2 = CH_4$; $K_P = 9.829 \times 10^{-2}$
(4) $CO + \frac{1}{2}O_2 = CO_2$; $K_P = 1.582 \times 10^{10}$
(5) $CO + H_2O = CO_2 + H_2$; $K_P = 1.374$
(6) $\frac{1}{2}H_2 + \frac{1}{2}O_2 = OH$; $K_P = 4.130 \times 10^{-2}$
(7) $H_2 + \frac{1}{2}O_2 = H_2O$; $K_P = 1.151 \times 10^{10}$

Make preliminary calculations to see which of the possible gases, H_2O, H_2, O_2, OH, CO, CO_2, and CH_4 will be present at equilibrium at a concentration of more than 1 mole per cent and find the equilibrium mole fractions of these gases. Remember that mole fractions may be used to represent partial pressures when the total pressure is unity, that not all the above reactions are independent, and that the total number of moles of substances containing hydrogen is related to the total number of moles of substances containing oxygen. The equilibrium mole fractions may be read from suitable plots showing the change of mole fraction of one substance with change in another substance.

16.8. The heats of formation and the entropies of ethane, ethylene, and acetylene at the temperatures 298.16, 1000, and 1500°K are

Gas	$\Delta H°$ (formation) in kilocalories at			s° in calories per degree at		
	298.16°K	1000°K	1500°K	298.16°K	1000°K	1500°K
C_2H_6	−20.236	−25.28	−25.73	54.85	79.39	92.46
C_2H_4	12.496	9.205	8.61	52.45	72.06	82.01
C_2H_2	54.194	53.304	52.548	47.997	64.095	70.925

With the aid of the data in this chapter, determine for each of the temperatures

(*a*) Which of these hydrocarbons are stable with respect to the elements in their standard states.

(*b*) The equilibrium constants for the dehydrogenation reactions

$$C_2H_6 = C_2H_4 + H_2$$
$$C_2H_4 = C_2H_2 + H_2$$
$$C_2H_6 = C_2H_2 + 2H_2$$

(*c*) The relative numbers of moles of the hydrocarbons at equilibrium with each other when the hydrogen pressure is 1 atmosphere.

CHAPTER 17

GENERAL EQUILIBRIUM CONDITIONS

In a system in which an entropy change results from a reversible transfer of heat, no external work being done, we found that the increase in entropy of the system equals, numerically, the decrease in entropy of the surroundings. For such a process, the total energy of system and surroundings remains constant, and

$$(\Sigma\, dS)_E = 0 \tag{17.1}$$

It is possible, however, for the entropy of the system to increase because of a change in volume, even though the internal energy remains unchanged, as in the reversible expansion of an ideal gas at constant temperature. Under these conditions, the gain in entropy of the system is equal numerically to the loss in entropy of the surroundings, so that for both system and surroundings, the total volume being constant, we have

$$(\Sigma\, dS)_V = 0 \tag{17.2}$$

Equations (17.1) and (17.2) may be combined to give the general equation

$$(\Sigma\, dS)_{E,V} = 0 \tag{17.3}$$

which applies to every reversible process.

If the system is so isolated that all changes in energy and volume and the other properties occur within the system itself, the total energy and volume of the system remain constant. According to equation (17.3), any reversible changes in this system must occur without any change in the entropy of the system. But reversible processes are processes at equilibrium; the system is at equilibrium at constant energy and volume when any changes within the system take place without a change in the entropy of the system. Then, for the system itself,

$$dS_{E,V} = 0 \tag{17.4}$$

Equation (17.4) is a general criterion of equilibrium applicable to any system at constant energy and volume. It is but one of the many criteria that may be set up.

Free Energy as a Criterion of Equilibrium.—In the chemical laboratory, systems are rarely observed under the conditions of constant energy and constant volume. As has been stated repeatedly, the common experimental conditions are those of constant temperature and constant pressure. In Chap. 10, we showed that under these conditions the function that remains constant in a system at equilibrium is the free energy F and not the entropy. Thus, in equation (10.32), we found that

$$\mathrm{d}F_{T,P} = 0 \tag{17.5}$$

is the criterion for equilibrium under these conditions.

Similarly, when the volume of the system remains constant, the temperature still being constant, the function A, called the maximum or total work or the Helmholtz free energy, is the function that remains constant. For these conditions, equation (10.27) expresses still another criterion of equilibrium, namely,

$$\mathrm{d}A_{T,V} = 0 \tag{17.6}$$

Because pressure and not volume remains constant under the usual experimental conditions, we have developed the function F to the neglect of the function A. Although we shall discuss the F function and its relation to equilibrium most completely, we shall return later to a brief discussion of the criteria of equilibrium that may be applied under different sets of experimental restrictions.

Some Free Energy Equations.—In Chap. 10, we derived the free energy equations for simple systems and for systems in which chemical reaction occurs. The differential free energy equation for a simple system was given in (10.41) as

$$\mathrm{d}F = -S\,\mathrm{d}T + V\,\mathrm{d}P \tag{17.7}$$

Here F, S, and V are the extensive properties that refer to a fixed amount of substance in the system. There is no term for the free energy change that may occur when material is added to or removed from the system, and there is no term for any net external work done by the system. If temperature and pressure are uniform throughout the system and if no substance is transferred into or out of the system, the system is at equilibrium. Under these conditions, temperature and pressure remain constant, $\mathrm{d}T$ and $\mathrm{d}P$ are zero, and $\mathrm{d}F$ becomes zero in agreement with equation (17.5). Equation (17.7) then becomes identical with equation (17.5).

When a chemical reaction occurs within a system not at equilibrium, there is a resulting change in free energy and the system is capable of doing external work in addition to work of expansion. For such a system, we obtained in equation (10.39) the more general free energy expression

$$\mathrm{d}F = -S\,\mathrm{d}T + V\,\mathrm{d}P - \mathrm{D}w' \tag{17.8}$$

$\mathrm{D}w'$ being the net useful reversible work previously defined in equation (7.32). Under the experimental conditions of constant temperature and pressure, equation (17.8) indicates that the system may still do net work if it is not at equilibrium, the decrease in free energy being a measure of this work, as in the equation

$$\mathrm{d}F_{T,P} = -\mathrm{D}w' \tag{17.9}$$

If the system is at equilibrium, $\mathrm{D}w' = 0$ and equation (17.9) becomes equal to equation (17.5), which is our criterion of equilibrium.

We shall now discuss in more detail the nature of the terms for the various substances in a reaction, represented by the $\mathrm{D}w'$ term in the free energy equation. A system is capable of doing external useful work when material is added to or removed from the system and when a chemical reaction occurs that produces new substances with a free energy different from that of the substances that were consumed in the reaction. In the latter instance, there is a free energy change and, therefore, a value of $\mathrm{D}w'$ even though there is no movement of material into or out of the system. This type of free energy change resulting from chemical reaction is of special interest to the chemist.

General Free Energy Equations.—Because the free energy of a system is a function of the composition of the system as well as of the temperature and pressure, we may include in the free energy expression terms for the change of the free energy with composition. If the composition is expressed in terms of the number of moles n_1, n_2, and so forth, of the various substances present, this relation may be expressed as

$$F = \phi_1(T, P, n_1, n_2, \cdots) \tag{17.10}$$

or, by the differential equation,

$$\mathrm{d}F = \left(\frac{\partial F}{\partial T}\right)_{P,n_1,n_2,\ldots} \mathrm{d}T + \left(\frac{\partial F}{\partial P}\right)_{T,n_1,n_2,\ldots} \mathrm{d}P + \left(\frac{\partial F}{\partial n_1}\right)_{T,P,n_2,\ldots} \mathrm{d}n_1 + \left(\frac{\partial F}{\partial n_2}\right)_{T,P,n_1,\ldots} \mathrm{d}n_2 + \cdots \tag{17.11}$$

We have already discussed the $\partial F/\partial T$ and $\partial F/\partial P$ terms. For a system of constant composition where $n_1, n_2, \ldots$ remain constant, equations (10.43) and (10.47) tell us that

$$\left(\frac{\partial F}{\partial T}\right)_P = -S \quad \text{and} \quad \left(\frac{\partial F}{\partial P}\right)_T = V \tag{17.12}$$

When these values are substituted in equation (17.11), we have the general free energy equation in the form

$$dF = -S\,dT + V\,dP + \left(\frac{\partial F}{\partial n_1}\right)_{T,P,n_2,\ldots} dn_1 + \left(\frac{\partial F}{\partial n_2}\right)_{T,P,n_1,\ldots} dn_2 + \cdots \tag{17.13}$$

The change in free energy with number of moles of one constituent, when temperature, pressure, and composition remain constant, has been named by Lewis the *partial molal free energy* (symbol $\overline{\mathrm{F}}$). By definition, therefore,

$$\overline{\mathrm{F}}_1 \equiv \left(\frac{\partial F}{\partial n_1}\right)_{T,P,n_2,\ldots}; \qquad \overline{\mathrm{F}}_2 \equiv \left(\frac{\partial F}{\partial n_2}\right)_{T,P,n_1,\ldots} \tag{17.14}$$

so that equation (17.13) may be written

$$dF = -S\,dT + V\,dP + \overline{\mathrm{F}}_1\,dn_1 + \overline{\mathrm{F}}_2\,dn_2 + \cdots \tag{17.15}$$

These general equations must obviously reduce to the simpler free energy equations previously given. For example, when the composition remains unchanged, dn_1, dn_2, and so forth, are zero, and equation (17.15) becomes identical with (17.7). Similarly, a comparison with equation (17.8) shows that

$$\overline{\mathrm{F}}_1\,dn_1 + \overline{\mathrm{F}}_2\,dn_2 + \cdots = -Dw' \tag{17.16}$$

At constant temperature and pressure a system can do net useful work only when dn_1, dn_2, *and so forth, are not all zero.* This is in agreement with our previous statement that a system can do net useful work at constant temperature and pressure only if there is a change in composition of the system.

Equation (17.16) is a fundamental equation of chemical thermodynamics because it establishes the conditions of chemical equilibrium. At equilibrium, under which condition no net work may be done by the system, equation (17.16) becomes

$$\overline{\mathrm{F}}_1\,dn_1 + \overline{\mathrm{F}}_2\,dn_2 + \cdots = 0 \tag{17.17}$$

Although we have specifically indicated only two constituents, represented by the quantities n_1 and n_2 moles, respectively, the above equations are applicable to any number of constituents. For example, with four constituents whose quantities are, respectively, n_1, n_2, n_3, and n_4 moles, equation (17.17) becomes

$$\overline{\mathrm{F}}_1\,dn_1 + \overline{\mathrm{F}}_2\,dn_2 + \overline{\mathrm{F}}_3\,dn_3 + \overline{\mathrm{F}}_4\,dn_4 = 0 \tag{17.18}$$

These general equations may be applied to all equilibrium processes in which there is a transfer of material from one phase to another within a system, or in which a chemical reaction is proceeding at constant temperature and pressure. With their aid, we can derive the phase rule of

Gibbs. We shall apply them to different types of equilibrium involving several phases and several components.

In many of the general equations that follow, we shall express the composition in terms of only two components. However, we do not thereby sacrifice the general applicability of the equations, for they can be extended to more than two components just as equation (17.17) was extended to include four components as in equation (17.18). When we write $(\partial F/\partial n_1)_{n_2}$, we shall remember that, in the partial differentiation of F with respect to n_1, temperature, pressure, and the quantities of *all other components* remain constant. In a four-component system, the above partial derivative becomes

$$\left(\frac{\partial F}{\partial n_1}\right)_{T,P,n_2,n_3,n_4}$$

n_3 and n_4 remaining constant as well as n_2.

General Conditions for Equilibrium.—Several criteria of equilibrium were indicated in the previous sections. Thus, if a system is to be at equilibrium at constant temperature and pressure, any changes within the system may not produce a change in the free energy function F. Similarly, for equilibrium in a system at constant temperature and volume, any changes within the system may not produce changes in the A function. When the temperature is permitted to change but the internal energy and volume remain constant, the entropy of the system may not change if equilibrium is maintained in the system. But, these are not the only functions that may be used as criteria of equilibrium in a chemical system, nor are they independent of each other. From the statement made above on the existence of equilibrium in a system at constant energy, volume, and entropy, we deduce that when entropy and volume remain constant a criterion of equilibrium is that there shall be no change in energy and that, when entropy and energy remain constant, there shall be no change in volume.

The various equations that determine completely the state of any particular system, including the equilibrium state, were named by Gibbs the *fundamental equations*. All these equations are equally valid; each may be derived from any of the others. Accordingly, we base our decision on which of these equations to use primarily on the ease with which the various sets of restricting conditions can be applied and maintained in practice. Thus, in chemistry the common experimental condition of constant temperature and pressure dictates the use of the free energy function as the simplest criterion of equilibrium.

A few of the many conditions for equilibrium that may be expressed are the following:

$$\left.\begin{aligned} dF_{T,P} &= 0 \\ dA_{T,V} &= 0 \\ dS_{E,V} &= 0 \\ dE_{S,V} &= 0 \\ dH_{S,P} &= 0 \end{aligned}\right\} \tag{17.19}$$

As we stated above, these criteria are all related to each other and may, therefore, be derived from each other.

Fundamental Equations of Gibbs.—We have expressed in equations (17.10) and (17.11) and the subsequent free energy equations the relation between the free energy and the temperature, pressure, and composition of a system that enables us to set up the requirements for equilibrium. Equations (17.10) and (17.11) are two forms of what Gibbs[1] in his famous papers "On the Equilibrium of Heterogeneous Substances" called the "fundamental equation" for this function.[2] As the criterion of chemical equilibrium at constant temperature and pressure, we obtain, from equations (17.13) and (17.19), the equation

$$\left(\frac{\partial F}{\partial n_1}\right)_{T,P,n_2} dn_1 + \left(\frac{\partial F}{\partial n_2}\right)_{T,P,n_1} dn_2 = 0 \tag{17.20}$$

Similar equations for the other thermodynamic functions may be derived. Thus, the total work function A is a function of composition as well as of the temperature and volume so that we may write

$$A = \phi_2(T,V,n_1,n_2) \tag{17.21}$$

This is another "fundamental equation" from which the equilibrium conditions may be obtained. The equation may be written in differential form as

$$dA = \left(\frac{\partial A}{\partial T}\right)_{V,n_1,n_2} dT + \left(\frac{\partial A}{\partial V}\right)_{T,n_1,n_2} dV + \left(\frac{\partial A}{\partial n_1}\right)_{T,V,n_2} dn_1 + \left(\frac{\partial A}{\partial n_2}\right)_{T,V,n_1} dn_2 \tag{17.22}$$

But the values of $\partial A/\partial T$ and $\partial A/\partial V$ are given in equations (10.44) and (10.42) as $-S$ and $-P$, respectively, so that equation (17.22) may be written,

$$dA = -S\,dT - P\,dV + \left(\frac{\partial A}{\partial n_1}\right) dn_1 + \left(\frac{\partial A}{\partial n_2}\right) dn_2 \tag{17.23}$$

The qualifying subscripts are omitted here for the sake of simplicity.

---

[1] "The Collected Works of J. Willard Gibbs," Vol. 1, "Thermodynamics," Longmans, Green & Company, New York, 1928.

[2] Our free energy function F corresponds to the ζ function of Gibbs. He used the symbols ϵ, η, χ, ψ, and ζ for the functions we call E, S, H, A, and F, respectively.

Combining equation (17.23) and our general condition for equilibrium in equation (17.19), we have

$$dA_{T,V} = \left(\frac{\partial A}{\partial n_1}\right)_{T,V,n_2} dn_1 + \left(\frac{\partial A}{\partial n_2}\right)_{T,V,n_1} dn_2 = 0 \qquad (17.24)$$

which gives the condition for equilibrium for an isothermal constant-volume process.

This general process may be repeated for the other functions that measure chemical equilibrium or the distance from chemical equilibrium. The corresponding equations for these various functions are listed in Table 17.1. Because it is characteristic of all these "fundamental" equations that each may be derived from the others, any of them may be used to establish criteria for chemical equilibrium.

TABLE 17.1

A. The Fundamental Equations for Some Thermodynamic Functions:

(1) $F = \phi_1(T, P, n_1, n_2, \cdots n_i)$
(2) $A = \phi_2(T, V, n_1, n_2, \cdots n_i)$
(3) $S = \phi_3(E, V, n_1, n_2, \cdots n_i)$
(4) $E = \phi_4(S, V, n_1, n_2, \cdots n_i)$
(5) $H = \phi_5(S, P, n_1, n_2, \cdots n_i)$

B. The Fundamental Equations in Differential Form:

(1) $dF = -S\,dT + V\,dP + \left(\frac{\partial F}{\partial n_1}\right) dn_1 + \left(\frac{\partial F}{\partial n_2}\right) dn_2 + \cdots$
(2) $dA = -S\,dT - P\,dV + \left(\frac{\partial A}{\partial n_1}\right) dn_1 + \left(\frac{\partial A}{\partial n_2}\right) dn_2 + \cdots$
(3) $T\,dS = dE + P\,dV - T\left(\frac{\partial S}{\partial n_1}\right) dn_1 - T\left(\frac{\partial S}{\partial n_2}\right) dn_2 + \cdots$
(4) $dE = T\,dS - P\,dV + \left(\frac{\partial E}{\partial n_1}\right) dn_1 + \left(\frac{\partial E}{\partial n_2}\right) dn_2 + \cdots$
(5) $dH = T\,dS + V\,dP + \left(\frac{\partial H}{\partial n_1}\right) dn_1 + \left(\frac{\partial H}{\partial n_2}\right) dn_2 + \cdots$

C. The Criteria of Equilibrium:

(1) $dF_{T,P} = \left(\frac{\partial F}{\partial n_1}\right)_{T,P} dn_1 + \left(\frac{\partial F}{\partial n_2}\right)_{T,P} dn_2 + \cdots = 0$
(2) $dA_{T,V} = \left(\frac{\partial A}{\partial n_1}\right)_{T,V} dn_1 + \left(\frac{\partial A}{\partial n_2}\right)_{T,V} dn_2 + \cdots = 0$
(3) $T\,dS_{E,V} = -T\left(\frac{\partial S}{\partial n_1}\right)_{E,V} dn_1 - T\left(\frac{\partial S}{\partial n_2}\right)_{E,V} dn_2 + \cdots = 0$
(4) $dE_{S,V} = \left(\frac{\partial E}{\partial n_1}\right)_{S,V} dn_1 + \left(\frac{\partial E}{\partial n_2}\right)_{S,V} dn_2 + \cdots = 0$
(5) $dH_{S,P} = \left(\frac{\partial H}{\partial n_1}\right)_{S,P} dn_1 + \left(\frac{\partial H}{\partial n_2}\right)_{S,P} dn_2 + \cdots = 0$
(6) In general, $\mu_1\,dn_1 + \mu_2\,dn_2 + \cdots = 0$

Chemical Potentials of Gibbs.—From the various equations in Table 17.1*C*, it is evident that

$$\begin{aligned}\left(\frac{\partial F}{\partial n_1}\right)_{T,P,n_2} dn_1 + \left(\frac{\partial F}{\partial n_2}\right)_{T,P,n_1} dn_2 \\ &= \left(\frac{\partial A}{\partial n_1}\right)_{T,V,n_2} dn_1 + \left(\frac{\partial A}{\partial n_2}\right)_{T,V,n_1} dn_2 \\ &= -T\left(\frac{\partial S}{\partial n_1}\right)_{E,V,n_2} dn_1 - T\left(\frac{\partial S}{\partial n_2}\right)_{E,V,n_1} dn_2 \\ &= \left(\frac{\partial E}{\partial n_1}\right)_{S,V,n_2} dn_1 + \left(\frac{\partial E}{\partial n_2}\right)_{S,V,n_1} dn_2 \\ &= \left(\frac{\partial H}{\partial n_1}\right)_{S,P,n_2} dn_1 + \left(\frac{\partial H}{\partial n_2}\right)_{S,P,n_1} dn_2 \qquad (17.25)\end{aligned}$$

But, all the coefficients of dn_1 are independent of the mass of material being considered, and all must have the same value. This common coefficient Gibbs[1] called the *potential* μ. It is frequently called the *thermodynamic potential* or the *chemical potential.*

The chemical potential μ_1 of the first constituent of the system is identical with the partial molal free energy $\overline{F_1}$ of this constituent. Thus we have, from equation (17.14),

$$\mu_1 = \overline{F_1} \qquad (17.26)$$

From the relations in equation (17.25), it appears that μ_1 is also expressed by the equations

$$\mu_1 = \left(\frac{\partial A}{\partial n_1}\right)_{T,V,n_2} = -T\left(\frac{\partial S}{\partial n_1}\right)_{E,V,n_2} = \left(\frac{\partial E}{\partial n_1}\right)_{S,V,n_2} = \left(\frac{\partial H}{\partial n_1}\right)_{S,P,n_2} \qquad (17.27)$$

In all these differentiations with respect to the first constituent, the quantities of any other constituents, n_2, n_3, n_4, and so forth, remain unchanged.

The chemical potential μ_2 of the second constituent is identical with the partial molal free energy $\overline{F_2}$ for this constituent, so that

$$\mu_2 = \overline{F_2} \qquad (17.28)$$

The potential for the second constituent may also be represented by the equations

---

[1] Gibbs expressed the composition in terms of the mass m of the several constituents. We are expressing the composition in terms of the number of moles n of these constituents. The molar mass of each substance may obviously be used instead of the mass in grams. Under these conditions the masses m_1, m_2, and so forth, of Gibbs correspond to our n_1, n_2, and so forth.

$$\mu_2 = \left(\frac{\partial A}{\partial n_2}\right)_{T,V,n_1} = -T\left(\frac{\partial S}{\partial n_2}\right)_{E,V,n_1} = \left(\frac{\partial E}{\partial n_2}\right)_{S,V,n_1} = \left(\frac{\partial H}{\partial n_2}\right)_{S,P,n_1} \qquad (17.29)$$

In these differentiations with respect to the second constituent, the quantities of all other constituents, n_1, n_3, n_4, and so forth, remain unchanged.

In the above sections, we have shown how the conditions for chemical equilibrium can be obtained from a number of different functions. Because of our interest in equilibrium at constant temperature and pressure, we shall discuss at length only the free energy function and the partial molal free energies. Under different experimental conditions, other functions would be utilized, for the statements we make in applying the partial molal free energy to equilibrium conditions apply to any of the other partial derivatives that equal the chemical potential μ.

Equilibrium in One-component Systems.—The general usefulness of our general criteria for equilibrium appears when we apply them to a variety of types of equilibrium. We shall first apply the free energy equations to the problem of equilibrium in a one-component system at constant temperature and constant pressure. In such a system the composition of the system may be expressed in terms of the number of moles n of the substance in the system, n_2, n_3, and so forth, being zero.

1. *Free Energy of Transfer.*—From the general equation (17.15), we have, at constant temperature and pressure,

$$dF_{T,P} = \frac{\partial F}{\partial n}\,dn = \bar{\mathrm{F}}\,dn \qquad (17.30)$$

But, in a pure substance, the partial molal free energy $\bar{\mathrm{F}}$ is identical with the molar free energy F/n, for it is independent of the amount of substance already present. Accordingly, equation (17.30) may be integrated to give the equation

$$F = n\bar{\mathrm{F}} = n\mathrm{F} \qquad (17.31)$$

which states that the free energy of a pure substance is directly proportional to the number of moles of the substance that are present. If n moles of the substance are added to a system, the free energy is increased by n times the molar free energy. According to equation (17.16), this increase in free energy is equal to the maximum useful work done on the system in the reversible transfer of n moles into the system. Thus,

$$n\bar{\mathrm{F}} = -w' \qquad (17.32)$$

2. *Transfer of Substance from One Phase to Another.*—In a system containing a pure substance, the substance may be present in more than one phase. It may be present as one or more solid phases, one and occasionally two liquid phases, and a gas phase, although all these phases

may not be able to coexist. If there are n moles of substance in the system, they may be distributed among the various phases, n' being in the first phase, n'' in the second phase, n''' in the third, and so forth. Where n' and n'' now take the place of n_1 and n_2, respectively, in the general free energy equation, we have, from equation (17.17), for equilibrium between the two phases at constant temperature and pressure,

$$\overline{\mathrm{F}'}\,dn' = -\overline{\mathrm{F}''}\,dn'' \qquad (17.33)$$

But when n' moles enter the first phase, n'' moles must leave the second phase so that

$$dn' = -dn'' \qquad (17.34)$$

At equilibrium, therefore,

$$\overline{\mathrm{F}'} = \overline{\mathrm{F}''} \qquad (17.35)$$

Equation (17.35) expresses a fundamental requirement for the equilibrium of a substance distributed among several phases. *The partial molal free energy of a substance in one phase is equal to the partial molal free energy of the substance in any other phase in equilibrium with the first phase.* If the partial molal free energy is greater in one phase than it is in the other, it tends to decrease spontaneously until it reaches the equilibrium value. In this process, work may be done at constant temperature and pressure, for

$$-d\mathrm{F} = Dw' \qquad (17.36)$$

If no work is to be done, that is, if Dw' is zero, equation (17.35) must represent the relation between the partial molal free energies.

When a third phase is placed in contact with the first phase, the partial molal free energy of a substance in the third phase must equal that of the substance in the first phase if the substance is not to be transported from the one phase to the other. The condition for equilibrium, as in equation (17.35), is, therefore,

$$\overline{\mathrm{F}'} = \overline{\mathrm{F}'''} \qquad (17.37)$$

When three phases are to be in equilibrium simultaneously, the partial molal free energy of the substance must evidently have the same value in all three phases and

$$\overline{\mathrm{F}'} = \overline{\mathrm{F}''} = \overline{\mathrm{F}'''} \qquad (17.38)$$

3. ***Equilibrium between Several Phases.***—We have stated earlier the general requirements of thermodynamic equilibrium. They are

(*a*) There must be no thermal gradients in the system; that is, the temperature must be uniform throughout the system. If thermal gradients exist, they may be utilized to perform useful work, as in the Carnot cycle.

(*b*) There must be mechanical equilibrium in the system. This means that there must be no uncompensated pressure differences in the system. In a system in which the parts are free to move from one part to another, pressure gradients can be used to perform useful work.

(*c*) There must be chemical equilibrium. This means, in a one-component system, that the partial molal free energy of the component must have the same value in each phase. Otherwise, the transfer of material from one part of the system to another could be used to do useful work.

Between two phases designated, respectively, by ′ and ″, these requirements may be summarized by the equations

$$\left.\begin{aligned} T' &= T'' \\ P' &= P'' \\ \bar{F}' &= \bar{F}'' \end{aligned}\right\} \tag{17.39}$$

4. *Maximum Number of Phases in Equilibrium.* *a.* THE RESTRICTIONS FOR A ONE-PHASE SYSTEM.—Let us consider an equilibrium condition in a single phase. If the phase is to remain stable, any change in pressure, temperature, or composition of the phase cannot result in useful work. In such a system, $dF = 0$. If the composition remains constant, we have, from equation (10.41) for the relation between the temperature and the pressure,

$$-S\,dT + V\,dP = 0 \tag{17.40}$$

where S and V have values proportional to the number of moles n in the system. In equation (17.40), which is based on a fixed value for n, we may still vary T or P independently without causing the disappearance of the phase or the appearance of a new one, but we cannot vary both independently. When n and T have fixed values, the pressure must have the value that corresponds to the chosen values of n and T. Similarly, n and P may be fixed, in which case T may not be varied independently but must have the value fixed by the chosen values of n and P. In a system for which these relations are valid, the "variance" or "number of degrees of freedom" is said to be two. Two variables may be arbitrarily chosen without the disappearance of a phase or the formation of a new one.

These relations are better illustrated with the more general equation for the one-component system, which, from equation (17.15), is

$$dF = -S\,dT + V\,dP + \bar{F}\,dn \tag{17.41}$$

For equilibrium, at which changes in temperature, pressure, or number of moles will not result in useful work, we have $\mathrm{d}F = 0$, so that equation (17.41) becomes

$$-S\,\mathrm{d}T + V\,\mathrm{d}P + \bar{F}\,\mathrm{d}n = 0 \tag{17.42}$$

If the number of moles n is fixed, $\mathrm{d}n = 0$ and equation (17.42) becomes

$$S\,\mathrm{d}T = V\,\mathrm{d}P \tag{17.43}$$

which corresponds to the relation in equation (17.40). Either T or P may be varied independently, but not both; for, from equation (17.43), $\mathrm{d}P/\mathrm{d}T = S/V$. Both S and V are properties of the substance that are not subject to independent variation under these conditions, their values being defined by the partial derivatives in equations (17.12). The molar free energy is also a property defined by equations (17.30) and (17.31).

On the other hand, we may arbitrarily fix the values for $\mathrm{d}T$ and $\mathrm{d}P$, in which instance $\mathrm{d}n$ cannot vary independently if no work is to be done as a result of the process. Regardless of the particular variables designated as the independent variables, the maximum number is two. There are, therefore, 2 degrees of freedom in this system.

b. THE RESTRICTIONS FOR A TWO-PHASE SYSTEM.—When a substance is present in two phases not in contact, a separate equilibrium equation corresponding to equation (17.42) may be written for each of the phases. Where the terms for the first phase are designated by the single primes ′ and those of the second phase by the double primes ″, we have, for the two separate equations,

$$\left.\begin{aligned} -S'\,\mathrm{d}T' + V'\,\mathrm{d}P' + \bar{F}'\,\mathrm{d}n' &= 0 \\ -S''\,\mathrm{d}T'' + V''\,\mathrm{d}P'' + \bar{F}''\,\mathrm{d}n'' &= 0 \end{aligned}\right\} \tag{17.44}$$

When the two phases are separate, each has 2 degrees of freedom as in the single-phase system. When the two phases are placed in contact, one might therefore expect 4 degrees of freedom among the two phases. However, restrictions are placed on the equilibrium states of the two phases as soon as they come in contact. If equilibrium is to exist, there can be no temperature or pressure gradients between the two phases nor can there be differences in the partial molal free energies of a substance present in both phases. If there were a difference in partial molal free energies, there would be a tendency for material to be transported from one phase to the other phase. Such a process could be used to do useful work, and the phases could not be in equilibrium. These conditions for thermodynamic equilibrium, previously given in equations (17.39), which act as restrictions on the number of independent variables, are

$$\left.\begin{aligned} T' &= T'' \\ P' &= P'' \\ \overline{F}' &= \overline{F}'' \end{aligned}\right\} \tag{17.45}$$

Because $\overline{F}' = \overline{F}''$ when the phases are at equilibrium and because $\mathrm{d}n' = -\mathrm{d}n''$, the separate equations in (17.44) may be combined to give

$$-S'\,\mathrm{d}T' + V'\,\mathrm{d}P' = -S''\,\mathrm{d}T'' + V''\,\mathrm{d}P'' \tag{17.46}$$

But, because, from equations (17.45), $T' = T''$ and $P' = P''$

$$\mathrm{d}T' = \mathrm{d}T'' = \mathrm{d}T$$

and

$$\mathrm{d}P' = \mathrm{d}P'' = \mathrm{d}P$$

so that equation (17.46) becomes

$$\mathrm{d}T = \frac{V' - V''}{S' - S''}\,\mathrm{d}P \tag{17.47}$$

This equation is equivalent to equation (9.7) and to the Clausius-Clapeyron equation (9.8).

The above restrictions have been imposed by the condition of equilibrium so that of the four independent variables in the separate equations in (17.44) only one remains. If pressure is arbitrarily fixed, temperature must have a unique, corresponding value. If we arbitrarily fix both temperature and pressure, one of the phases must disappear so that we may have the 2 degrees of freedom. If two phases are present, there is only 1 degree of freedom.

c. RESTRICTIONS FOR A THREE-PHASE SYSTEM.—When three phases are to be at equilibrium, there must be equilibrium between the first and second phases and equilibrium between the first and third phases. As a result, there will be equilibrium between the second and third phases. The requirement of equilibrium between the first and third phases introduces another set of restrictive equations similar to those in equation (17.45), namely,

$$\left.\begin{aligned} T' &= T''' \\ P' &= P''' \\ \overline{F}' &= \overline{F}''' \end{aligned}\right\} \tag{17.48}$$

By use of the restrictions on a pair of equations corresponding to (17.44) we may derive an equation similar to equation (17.47), which must express the equilibrium conditions between the first and third phases. Thus, we obtain the equation

$$\mathrm{d}T = \frac{V' - V'''}{S' - S'''}\,\mathrm{d}P \tag{17.49}$$

When the first phase is in equilibrium with the second and third phases simultaneously, dT in exuations (17.47) and (17.49) has the same value so that the two equations may be combined to give

$$\frac{V' - V''}{S' - S''}\,\mathrm{d}P = \frac{V' - V'''}{S' - S'''}\,\mathrm{d}P \qquad (17.50)$$

In general, the two coefficients of dP in (17.50) are not equal, because dP/dT has a different value for each of the pairs of phases. Consequently, equation (17.50) can be generally valid only if dP = 0, that is, if P has a single value. If three phases of a one-component system are in equilibrium and none of the phases tends to disappear, P and T must have single values. Accordingly, there are no degrees of freedom in this system. This result is confirmed by experiment.

We have not specified, here, the kinds of phases that are in equilibrium. The general equilibrium expression limits to three the number of phases of a one-component system that may be in equilibrium, but it does not specify the particular ones that shall be in equilibrium. The three phases that are in equilibrium may include several solid and liquid phases and a gas phase, but the total number is limited to three in a one-component system. The number of phases is here limited to three because for this number of phases the number of restrictive equations among the various variables becomes equal to the number of independent variables among the three phases. If there are more restrictive equations, one of the phases must disappear.

Phase Rule of Gibbs.—The line of reasoning followed in finding the maximum variance in a one-component system may be extended to a system of more than one component. For a system of c components the general differential equation for the free energy in any one phase as stated in equation (17.15) is

$$\mathrm{d}F' = -S'\,\mathrm{d}T' + V'\,\mathrm{d}P' + \overline{\mathrm{F}}'_1\,\mathrm{d}n'_1 + \overline{\mathrm{F}}'_2\,\mathrm{d}n'_2 + \cdots + \overline{\mathrm{F}}'_c\,\mathrm{d}n'_c \qquad (17.51)$$

For equilibrium within this phase, the value of dF' = 0, so that equation (17.51) becomes

$$-S'\,\mathrm{d}T' + V'\,\mathrm{d}P' + \overline{\mathrm{F}}'_1\,\mathrm{d}n'_1 + \overline{\mathrm{F}}'_2\,\mathrm{d}n'_2 + \cdots + \overline{\mathrm{F}}'_c\,\mathrm{d}n'_c = 0 \qquad (17.52)$$

In this equation, there are $(c + 2)$ variables, one corresponding to each of the components, and T and P in addition. But only $(c + 1)$ of the variables are independent, as equation (17.52) shows.

Let there be p phases, designated by the primes $'$, $''$, $'''$, and so forth. For each of the p phases, we shall have an equation corresponding to equation (17.52). Thus for the second and third phases, and so forth, we have the equations

$$\left.\begin{aligned} -S''\,dT'' + V''\,dP'' + \overline{F}_1''\,dn_1'' + \overline{F}_2''\,dn_2'' & \\ + \cdots + \overline{F}_c''\,dn_c'' &= 0 \\ -S'''\,dT''' + V'''\,dP''' + \overline{F}_1'''\,dn_1''' + \overline{F}_2'''\,dn_2''' + \cdots & \\ + \overline{F}_c'''\,dn_c''' &= 0 \end{aligned}\right\} \qquad (17.53)$$

and so forth, to p equations.

If there are p phases, there are $p(c + 1)$ independent variables when the phases are separate. However, when the phases are brought into contact, a number of restrictive equations are obtained. Thus, the temperatures, pressures, and partial free energies of each component must be identical in each of the phases. These requirements are expressed in the restrictive equations

$$\left.\begin{array}{lllll} T' &= T'' &= T''' & \cdots & \text{to } p \text{ phases} \\ P' &= P'' &= P''' & \cdots & \text{to } p \text{ phases} \\ \overline{F}_1' &= \overline{F}_1'' &= \overline{F}_1''' & \cdots & \text{to } p \text{ phases} \\ \overline{F}_2' &= \overline{F}_2'' &= \overline{F}_2''' & \cdots & \text{to } p \text{ phases} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \overline{F}_c' &= \overline{F}_c'' &= \overline{F}_c''' & \cdots & \text{to } p \text{ phases} \end{array}\right\} \qquad (17.54)$$

The number of necessary equations between the T's is one less than the number of phases, or $(p - 1)$. But the number of variables in equations (17.54) having $(p - 1)$ relations is the number of components plus 2, or $(c + 2)$, so that there are $(p - 1)(c + 2)$ restrictive equations in all. We found in the one-component system that the variance, or number of degrees of freedom, equals the excess of number of independent variables for the separate phases over the number of restrictive equations. The same statement applies to a system of c components. Thus, if v is the *variance*, or *number of degrees of freedom*, its value is represented by the equation

$$v = p(c + 1) - (p - 1)(c + 2)$$

or

$$\left.\begin{aligned} v &= c - p + 2 \\ v + p &= c + 2 \end{aligned}\right\} \qquad (17.55)$$

This equation represents the phase rule of Gibbs. The number of degrees of freedom in a heterogeneous system is 2 greater than the excess of number of components over the number of phases. Thus, in a system of 2 components, the maximum number of phases, the number that will produce zero variance, is 4, because

$$v = 2 - 4 + 2 = 0$$

In such a system, there may be two solid phases, a liquid phase and a gas phase all in equilibrium at a unique pressure and temperature. If there are three solid phases, however, either the gas phase or the liquid phase must disappear.

In the above derivation, terms were included for each component in each phase. However, the number of degrees of freedom remains unchanged if not all the components are present in each phase. For example, when the first component is present in only the first phase, the terms $\overline{F}_1'' \, dn_1''$, $\overline{F}_1''' \, dn_1'''$, and so forth, in equations (17.53) are absent and the number of independent variables is reduced by $(p - 1)$. At the same time, however, an equal number of restrictive equations in (17.54) also disappear, for we no longer have the $(p - 1)$ equations represented by the equations

$$\overline{F}_1' = \overline{F}_1'' = \overline{F}_1''' \cdots \text{ to } p \text{ phases}$$

The total number of degrees of freedom in the system, therefore, remains unchanged.

We have indicated several definitions for the number of degrees of freedom that may be used interchangeably. The number of degrees of freedom v may be defined (1) as the number of variables that must be specified in order to define the system completely or (2) as the number of variables that may be arbitrarily fixed without the disappearance of one of the phases at equilibrium. In accordance with our previous definition of a phase as representing a homogeneous system, the number of phases in a system is the number of different homogeneous systems in the heterogeneous system.

The number of components in a system is more troublesome to define. It is not necessarily identical with the number of different substances present in the system. Suppose that two substances A and B are in chemical equilibrium in the system. If so, the number of moles of B in the system cannot be varied independently from that of A. If the number of moles of A is fixed arbitrarily, the number of moles of B must also have the value dictated by the chemical equilibrium. If we wish to include terms for B among equations (17.53), we are compelled to introduce an equal number of additional restrictive equations dictated by the equilibrium between A and B. As a result, the total number of degrees of freedom for the system remains unchanged. The number of components c may be defined in either of the two following ways: (1) as the smallest number of chemical constituents needed to express the composition of every phase; (2) as the total number of chemical constituents C less the number of reversible chemical reactions r occurring in the system.[1] Thus, c may be defined as equal to $C - r$, so that the

---

[1] For example, see S. T. Bowden, *Nature*, **141**, 331 (1938).

phase rule may be expressed in the form

$$v = (C - r) - p + 2 \tag{17.56}$$

Problems

17.1. In a system at equilibrium at constant temperature and pressure the partial molal free energy of a substance distributed between two phases has the value $\overline{\text{F}}' = \overline{\text{F}}''$ as in equation (17.35). How is $\overline{\text{A}}'$ related to $\overline{\text{A}}''$ under these conditions?

17.2. At the triple point for water at approximately +0.0075°C, liquid water is in equilibrium with ice and vapor. At this temperature, the heat of fusion of ice is 79.72 calories per gram, the heat of evaporation of water is 2500.17 int joules per gram, the specific volume of water vapor is 206,288 cm³ per gram, that of liquid water is 1.00021 cm³ per gram, and that of ice is 1.0908 cm³ per gram. From these data, calculate the change of equilibrium pressure with temperature for each of the pairs of phases ice, vapor; ice, liquid; and liquid, vapor in the neighborhood of the triple point. Indicate your conclusions on a pressure-temperature diagram for the water system.

17.3. Calcium carbonate and calcium oxide do not form a solid solution. At the eutectic point for the system calcium carbonate plus calcium oxide plus carbon dioxide, at 1240°C and 30,000 mm pressure, how many phases can be at equilibrium? What are they?

17.4. Two salts AB and CD when melted together may form AD and CB. If the solids do not form solid solutions, what is the maximum number of the possible solids AB, AD, CB, and CD that can be in equilibrium with the fused mixture at a given temperature and pressure?

17.5. Does the system water plus sodium sulfate plus sodium sulfate decahydrate have any degrees of freedom? Under what conditions can this system be used as a "fixed point" in the calibrating of a thermometer?

17.6. What is the maximum number of compounds or complexes such as AB, A_2B_3, AB_2, and so forth, that can exist together at equilibrium in a homogeneous system?

17.7. Is the "melting point" of a pure solid an invariant point? Under what conditions can a melting point be used as a fixed point in thermometry? Is the "boiling point" of a liquid a fixed point? When may it be used as a calibrating point in thermometry?

17.8. Copper sulfate forms a series of hydrates, $CuSO_4 \cdot H_2O$, $CuSO_2 \cdot 3H_2O$, and $CuSO_4 \cdot 5H_2O$. What is the maximum number of these solid hydrates that can coexist in a closed system in equilibrium with a limited amount of water vapor?

17.9. Derive the relations

$$\left(\frac{\partial S}{\partial E}\right)_{V,n} = \frac{1}{T}; \quad \left(\frac{\partial S}{\partial V}\right)_{E,n} = \frac{P}{T}; \quad \left(\frac{\partial E}{\partial S}\right)_{V,n} = T;$$

$$\left(\frac{\partial E}{\partial V}\right)_{S,n} = -P; \quad \left(\frac{\partial H}{\partial S}\right)_{P,n} = T; \quad \left(\frac{\partial H}{\partial P}\right)_{S,n} = V$$

which are applied in the equations in Table 17.1*B*.

CHAPTER 18

PARTIAL MOLAL QUANTITIES

The partial molal free energy of a simple substance has a constant value that is independent of the quantity of the substance already present; it is identical with the molar free energy of the substance. Thus, the change in free energy when a mole of oxygen is added to another mole is identical with that observed when the mole of oxygen is added to 10 moles under the same conditions of temperature and pressure. The concept of the partial molal free energy makes no new useful contribution to the description of the behavior of simple systems. We have been able to avoid the formal use of the function hitherto because the systems we have discussed are of limited types. When the different substances remain pure, their molar free energy can be used directly; when they are present in ideal solutions of gases, liquids, or solids, the free energy of each substance can be calculated directly from a simple function of the concentrations.

However, the majority of chemical systems are not so simple. In many solutions, the free energy and the other thermodynamic functions of each substance are influenced significantly by the presence of each of the other constituents. Under these circumstances, the partial molal free energy and the other partial molal quantities in the solution are not identical with the corresponding molar values for the pure substances at the same temperature, pressure, and concentration.

Notation in Solutions.—Hitherto, we have used the subscripts 1 and 2 chiefly to designate the initial and final states of a system. In the equations of the previous chapter, however, the subscripts were used to denote the different substances in a system. This latter practice is continued.

In many solutions, there is no fundamental difference between the behavior of the different constituents. If both components of a binary solution are liquids, for example, both may be represented by equations of the same type. In such instances, either component may be designated by the subscript $_1$ or $_2$ and either may be designated the solvent or solute. However, if one of the components is a solid and the other a liquid, it is traditional to call the liquid the "solvent" and the solid the "solute." For systems of this type, it is conventional, following the precedent established by Lewis and Randall, to designate the "solvent" as component 1 and the "solute" as component 2. This distinction is important chiefly when corresponding functions of the two components are represented by equations of dissimilar types.

In the usual treatment of solutions, attention is directed to a single phase. When a second phase is present, it is usually of pure 1 or pure 2. When a pure phase is selected as the standard state of component 2, its free energy per mole may be designated either as the molar free energy F_2°, or as the partial molal free energy $\overline{\text{F}_2^\circ}$, since for a pure substance $\partial F/\partial n = F/n = \text{F}$. In the solution, the partial molal free energy is no longer identical with the molar free energy of the pure substance, since $\bar{\text{F}} = \partial F/\partial n$ has varying values in solutions of varying composition.

Other Partial Molal Quantities.—In Chap. 17, we found that the chemical potential μ, which is generally useful in the calculation of equilibrium conditions in a chemical system, is identical with the partial molal free energy $\bar{\text{F}}$. The partial molal free energy, in turn, is defined as the partial derivative of F with respect to n at constant temperature, pressure, and composition. Now the free energy, which depends on the composition of the solution, is related to other functions such as heat content, entropy, volume, and so forth. It follows that these other functions must also depend on the composition of the solution. Thus, for the solutions discussed in Chap. 6, we found that the heat of solution at constant temperature and pressure is very definitely a function of the composition of the solutions.

The partial molal heat contents, entropies, volumes, and so forth, bear the same relation to the partial molal free energy as their total quantities bear to the total free energy. For example, the free energy equation

$$F = H - TS$$

which serves as a definition of free energy, may be differentiated with respect to n_1, the number of moles of constituent 1. At constant temperature, pressure, and composition, we obtain, by this partial differentiation, the equation

$$\frac{\partial F}{\partial n_1} = \frac{\partial H}{\partial n_1} - T\frac{\partial S}{\partial n_1} \tag{18.1}$$

which may be written in the form

$$\overline{\text{F}_1} = \overline{\text{H}_1} - T\overline{\text{S}_1} \tag{18.2}$$

Similarly, because

$$\frac{\partial F}{\partial P} = V$$

we find, on differentiating with respect to n_1, when T, P, and n_2 remain constant, that

$$\frac{\partial}{\partial n_1}\left(\frac{\partial F}{\partial P}\right) = \frac{\partial}{\partial P}\left(\frac{\partial F}{\partial n_1}\right) = \frac{\partial V}{\partial n_1}$$

In the partial molal notation, this relation is written in the form

$$\frac{\partial \overline{\mathrm{F}_1}}{\partial P} = \overline{\mathrm{V}_1} \tag{18.3}$$

As indicated in Chap. 6, the partial molal quantities for all functions are defined by the partial differentiations with respect to n for one constituent, P, T, and all other n's remaining constant. Thus, the partial molal quantities for volume, heat content, heat capacity, and entropy are defined for constituent 1 by the equations

$$\overline{\mathrm{V}_1} = \left(\frac{\partial V}{\partial n_1}\right)_{P,T,n_2}; \qquad \overline{\mathrm{H}_1} = \left(\frac{\partial H}{\partial n_1}\right)_{P,T,n_2}; \qquad \overline{\mathrm{C}_{P_1}} = \left(\frac{\partial C_P}{\partial n_1}\right)_{P,T,n_2};$$
$$\overline{\mathrm{S}_1} = \left(\frac{\partial S}{\partial n_1}\right)_{P,T,n_2} \tag{18.4}$$

The corresponding partial molal quantities for the second constituent 2 are

$$\overline{\mathrm{V}_2} = \frac{\partial V}{\partial n_2}; \qquad \overline{\mathrm{H}_2} = \frac{\partial H}{\partial n_2}, \qquad \overline{\mathrm{C}_{P_2}} = \frac{\partial C_P}{\partial n_2}; \qquad \overline{\mathrm{S}_2} = \frac{\partial S}{\partial n_2} \tag{18.5}$$

it being understood from the definition of partial molal quantities that pressure, temperature, and the amount of all other constituents remain constant in the partial differentiation.

From these definitions and the rules of differentiation, we may write, in a formal way,

$$\frac{\partial \overline{\mathrm{H}}}{\partial T} = \overline{\mathrm{C}_P} \tag{18.6}$$

$$\frac{\partial \overline{\mathrm{F}}}{\partial T} = -\overline{\mathrm{S}} \tag{18.7}$$

$$\overline{\mathrm{F}} - \overline{\mathrm{H}} = T\frac{\partial \overline{\mathrm{F}}}{\partial T} \tag{18.8}$$

The student should derive these relations from the more general equations previously given.

Partial Molal Quantities and the Chemical Potential.—We must emphasize the fact that the partial molal quantity of a thermodynamic function and the chemical potential for the same function are not identical, except in the instance of the free energy function. Both partial molal quantities and chemical potentials represent the change of the functions with change in number of moles of a constituent at constant composition, but the other restrictive conditions are different. For example, the partial molal energy $\bar{\mathrm{E}}$ is defined by the partial derivative of E with respect to n at constant temperature and constant pressure, but the chemical potential μ is defined by the partial derivative of E with respect to n at constant entropy and constant volume as in equation (17.27). Thus,

$$\bar{\mathrm{E}} = \left(\frac{\partial E}{\partial n}\right)_{T,P} \quad \text{but} \quad \mu = \left(\frac{\partial E}{\partial n}\right)_{S,V} \tag{18.9}$$

Only for the free energy may we write

$$\bar{\mathrm{F}} = \left(\frac{\partial F}{\partial n}\right)_{T,P} = \mu \tag{18.10}$$

In systems under restrictions other than those of constant temperature and pressure, we may, of course, define functions that are analogous to the partial molal quantities. Thus, in a system at constant entropy and volume, only the partial derivative of E with respect to n is equal to the chemical potential μ. In such a system, the partial derivative of A with respect to n would be useful, but it is equal neither to the chemical potential nor to the partial molal Helmholtz free energy. Because we are concerned in practice with systems at constant temperature and pressure, we have discussed only the partial molal free energy as a measure of the chemical potential. For the same reason, we shall use only the partial derivatives of the other functions with respect to the number of moles n under these same experimental conditions. These partial derivatives, and these only, are called the partial molal quantities.

Generalized Treatment of Partial Molal Quantities.—A number of general relations between the partial molal quantities for the various constituents of solutions are applicable to all partial molal quantities. These common relations arise from the fact that the number of moles of the several constituents in systems at equilibrium cannot all be independent of each other. For example, when a substance is transferred from one phase to another or when it is converted to another substance in a chemical reaction, the number of moles of a substance that are removed from one phase is related to the number that appear in the new phase or in the solution.

Let any extensive property of a system at constant temperature and pressure be represented by the symbol G in accordance with the nomenclature of Lewis and Randall. If this extensive property is a function of the number of moles of the constituents, 1, 2, and so forth, the partial derivatives of G with respect to the number of moles of each constituent may be obtained in the usual manner. These partial molal quantities for the various constituents, always under the conditions of constant temperature and pressure, are defined by the equations

$$\overline{G}_1 = \frac{\partial G}{\partial n_1}; \qquad \overline{G}_2 = \frac{\partial G}{\partial n_2}; \qquad \overline{G}_3 = \frac{\partial G}{\partial n_3} \tag{18.11}$$

In each of the above derivatives the concentrations of the remaining constituents remain unchanged. For a change in G at constant temperature, pressure, and composition, we may, therefore, write

$$dG = \frac{\partial G}{\partial n_1} dn_1 + \frac{\partial G}{\partial n_2} dn_2 + \frac{\partial G}{\partial n_3} dn_3 + \cdots \tag{18.12}$$

When the partial molal notation is used, this equation becomes

$$dG = \overline{G}_1\, dn_1 + \overline{G}_2\, dn_2 + \overline{G}_3\, dn_3 + \cdots \tag{18.13}$$

Equation (18.13) is readily integrated for any system in which $\overline{G}_1$ and $\overline{G}_2$ remain constant while n_1 and n_2 are varied. An example of such a system is a mixture of ice and liquid water. The partial molal property $\overline{G}_1$ of the ice remains constant, regardless of the relative or absolute amounts of ice. The same statement applies to the corresponding partial molal property for liquid water, so that $\overline{G}_2$ remains constant. The partial molal quantities, like other specific quantities, are intensive properties whose values do not depend on the total quantity of material.

When equation (18.13) is integrated between the limit $n_1 = n_2 = 0$, where $G = 0$, and the limit $n_1 = n_1$, $n_2 = n_2$, $G = G$, we have, $\overline{G}_1$ and $\overline{G}_2$ remaining constant,

$$G = \overline{G}_1 n_1 + \overline{G}_2 n_2 + \cdots \tag{18.14}$$

Thus, if $\overline{V}_1$ for ice is 19.6 ml and $\overline{V}_2$ for water is 18 ml. the volume of a system containing 1 mole of ice and 2 of water is

$$V = 1 \times 19.6 + 2 \times 18 = 55.6 \text{ ml}$$

Partial Molal Equations for Solutions.—Equation (18.14) has a more general applicability than the above example implies. In solutions where the $\overline{G}$'s vary greatly with change in composition, equation (18.14) may still be applied to any solution in which the *relative* proportions of the various constituents remain unchanged. The $\overline{G}$'s are intensive properties that depend not on the total amount of solution but on the composition in terms of the proportions in which the various constituents are present. For example, the partial molal heat of solution of a salt in 1 liter of 2 molal solution is the same as in 100 liters of the 2 molal solution. So long as the relative proportion of the different constituents in a solution remain unaltered by the addition or withdrawal of material, as they do when the change in n is very small and can be represented by dn, the values of $\overline{G_1}$, $\overline{G_2}$ and so forth, remain constant. Therefore, equation (18.14) applies to solutions of definite composition as well as to systems composed of pure substances. It is one of the fundamental partial molal equations.

Equation (18.14) enables us to calculate the value of any extensive property G of a system if the composition and the partial molal values of G are known. Similarly, in a binary solution, if the values of G, $\overline{G_1}$, n_1, and n_2 are known, $\overline{G_2}$ can be calculated. This principle is widely used in the application of partial molal quantities to solutions.

For example, equation (18.14) may be applied to the aqueous solution of potassium chloride studied in Chap. 6. In Table 6.1 are listed, not the partial molal heats of solution of potassium chloride and of water, but the corresponding average values $\Delta Q/\Delta n_1$ and $\Delta Q/\Delta n_2$. Let us take these values, averaged for the concentration interval of 12 to 15 moles of water per mole of potassium chloride and assume the average value of n_1 to be 13.5 moles. From equation (18.14), we have

$$Q = 13.5 \times 30.7 + 1 \times 3{,}420 = 3{,}834 \text{ cal}$$

The observed values of Q at $n_1 = 12$ and $n_1 = 15$ moles of water are 3,786 and 3,878 calories, respectively, and the average value is 3,832 calories, in good agreement with the value calculated above.

Although $\overline{G_1}$ and $\overline{G_2}$ are constant in a solution having any given proportion of components, they change when this proportion is varied. For any infinitesimal change in composition, whether produced by change in n_1, n_2, or both, we obtain, from equation (18.14),

$$dG = n_1\,\partial\overline{G_1} + \overline{G_1}\,\partial n_1 + n_2\,\partial\overline{G_2} + \overline{G_2}\,\partial n_2 + \cdots \qquad (18.15)$$

When equation (18.13) is subtracted from this equation, we obtain

$$n_1\,\partial\overline{G_1} + n_2\,\partial\overline{G_2} + \cdots = 0 \qquad (18.16)$$

It is, therefore, possible in an infinitesimal change in composition to find $d\overline{G_2}$ from a given value of $d\overline{G_1}$. Equations (18.11) to (18.16), though indicating directly only two components, are not limited to any specified number of components. They are general for any process at constant temperature and pressure, the conditions we specified at the beginning.

We may wish to know the change of $\overline{G_1}$, $\overline{G_2}$, and so forth, when n_1 is varied, n_2 remaining constant. On dividing equation (18.16) by ∂n_1, we obtain the relation between $\partial\overline{G_1}/\partial n_1$ and $\partial\overline{G_2}/\partial n_1$, and so forth, which is

$$n_1\frac{\partial\overline{G_1}}{\partial n_1} + n_2\frac{\partial\overline{G_2}}{\partial n_1} + \cdots = 0 \qquad (18.17)$$

Partial molal equations of the type of (18.14), (18.16), and (18.17) are particularly useful in expressing the change of G or $\overline{G_1}$, $\overline{G_2}$, and so forth, with composition, when composition is expressed in terms of molalities. In the molal solution containing 1 mole of solute in 1,000 grams of solvent, n_2 equals the molality m and $n_1 = 1{,}000/M_1$, where M_1 is the molar weight of the solvent.

Partial Molal Equations for One Mole of Solution.—As we discovered in the chapter on ideal solutions, the concentrations of binary solutions that obey Raoult's law are best expressed in terms of mole fractions or mole per cents rather than in molalities. One advantage of the mole fraction graph is that the value of a property for any composition of the solution ranging from pure component 1 to pure component 2 can be represented on a single diagram. For this reason, the properties of many nonideal solutions that do not depart too widely from ideality are also plotted on this type of diagram. One further advantage of the mole fraction method of expressing concentration rests on the fact that the total quantity of solution under consideration may be kept constant at 1 mole while the proportions of the two components vary. As we shall discover, the partial molal equations assume particularly useful forms when they are applied to 1 mole of solution.

The mole of solution is defined as that quantity of solution in which the total number of moles of the constituents is unity. Thus, for 1 mole of solution,

$$n_1 + n_2 + \cdots = 1 \tag{18.18}$$

and the number of moles of each constituent is equal to its mole fraction. For the mole fraction, we have by definition

$$N_1 + N_2 + \cdots \equiv 1 \tag{18.19}$$

Because the numerical value of any extensive property depends on the quantity of material under consideration, the value of G is evidently a function of the number of moles of the constituents as well as of the temperature and pressure. We shall designate the value of G for 1 mole of solution by the symbol G_i. Thus, in a solution containing $n_1 + n_2 + \cdots$ moles, G_i is related to G by the equation

$$\mathrm{G}_i = \frac{G}{n_1 + n_2 + \cdots} \tag{18.20}$$

From the relations in equations (18.18) and (18.19), it is clear that, for 1 mole of solution, equation (18.14) becomes

$$\mathrm{G}_i = \overline{\mathrm{G}}_1 N_1 + \overline{\mathrm{G}}_2 N_2 + \cdots \tag{18.21}$$

Similarly, when equation (18.16) is divided by $n_1 + n_2 + \cdots$, it becomes

$$N_1\, \partial\overline{\mathrm{G}}_1 + N_2\, \partial\overline{\mathrm{G}}_2 + \cdots = 0 \tag{18.22}$$

When equation (18.22) is divided by ∂N_1, we obtain an equation analogous to equation (18.17), namely,

$$N_1 \frac{\partial \overline{\mathrm{G}}_1}{\partial N_1} + N_2 \frac{\partial \overline{\mathrm{G}}_2}{\partial N_1} + \cdots = 0 \tag{18.23}$$

The relations among the partial molal quantities in a solution in equations (18.21) to (18.23) are particularly useful when composition is expressed in mole fractions just as equations (18.14), (18.16), and (18.17) are readily applied to solutions whose composition is expressed in molalities.

One important advantage in the mole fraction notation is that the entire range of composition can be plotted in a single diagram. When G (or G_i), $\overline{\mathrm{G}}_1$, and $\overline{\mathrm{G}}_2$ are plotted against the mole fraction of component 1 of a binary solution, the tangents to the resulting curves at the composition N_1 have the values $\partial G/\partial N_1$, $\partial \overline{\mathrm{G}}_1/\partial N_1$, and $\partial \overline{\mathrm{G}}_2/\partial N_1$, respectively. These values can be substituted in the above equations. Because of the relation between dN_1 and dN_2 in a binary solution, which is $dN_1 = -dN_2$, we can also evaluate the corresponding partial derivatives with respect to N_2, the mole fraction of the second component of the solution. However, the partial derivatives with respect to the mole fraction are not equal to the partial derivatives with respect to the number of moles n_1, namely, $\partial G/\partial n_1$, $\partial \overline{\mathrm{G}}_1/\partial n_1$, and $\partial \overline{\mathrm{G}}_2/\partial n_1$. The two sets of partial derivatives must differ, for $dN \neq dn_1$, as we found in Chap. 6. If we wish to calculate the partial molal quantities from mole fraction diagrams, we are required to find the relation between the measured slopes $\partial G/\partial N_1$, and so forth, and the desired partial molal quantities $\partial G/\partial n_1$, and so forth.

When the calculated values of the partial molal quantities $\overline{\mathrm{G}}_1$ and $\overline{\mathrm{G}}_2$ are plotted against mole fraction, the slopes of the curves give us the values $\partial \overline{\mathrm{G}}_1/\partial N_1$ and $\partial \overline{\mathrm{G}}_2/\partial N_1$, which may be substituted in equation (18.23). Useful relations are derived from this equation.

Calculation of Partial Molal Quantities from Mole Fraction Diagrams.—When the value of an extensive property G for an isothermal, isobaric process is plotted as ordinate against N_1 as abscissa, the tangent to the curve at N_1 is $(\partial G/\partial N_1)_{T,P}$. From this value of $\partial G/\partial N_1$, we may derive the value of G_1 and also that of $\overline{\mathrm{G}}_2$ because of the interdependence between these two functions. We remember that $\partial G/\partial N_1$ is not the partial molal quantity $\overline{\mathrm{G}}_1$; for, in the change in mole fraction represented by dN_1 both n_1 and n_2 vary, whereas, in the change in n_1 represented by dn_1, n_2 remains constant.

Because the value of G depends on the quantity of material under consideration, the numerical value of $\partial G/\partial N_1$ also depends on this quantity of material. If G_i is plotted instead of G, the corresponding slope $\partial\mathrm{G}_i/\partial N$ represents the change in G_i per mole of solution. As we shall see, the partial molal quantities $\overline{\mathrm{G}_1}$ and $\overline{\mathrm{G}_2}$ are obtained more simply from the slopes of the G_i curve than from the more general G curve. For this reason, we shall derive the relations between the partial molal quantities and the values of $\partial\mathrm{G}_i/\partial N_1$ and $\partial\mathrm{G}_i/\partial N_2$. We shall expand here some of the discussion we applied in Chap. 6 to heats of solution.

The relation between $\partial G/\partial N_1$ and $\overline{\mathrm{G}_1} = \partial G/\partial n_1$ depends on the relation between dN_1 and dn_1, which was found in equations (6.21) and (6.22) to be for a binary solution

$$dN_1 = \frac{n_2}{(n_1 + n_2)^2}\,dn_1 = \frac{N_2}{(n_1 + n_2)}\,dn_1 \tag{18.24}$$

Because we are plotting G_i as ordinate, we shall also wish to know the relation between $\partial\mathrm{G}_i/\partial n_1$ and $\overline{\mathrm{G}_1}$, which is $\partial G/\partial n_1$. On differentiating equation (18.20) with respect to n_1, we have

$$\overline{\mathrm{G}_1} = \frac{\partial}{\partial n_1}\left[(n_1 + n_2)\mathrm{G}_i\right] = (n_1 + n_2)\frac{\partial\mathrm{G}_i}{\partial n_1} + \mathrm{G}_i \tag{18.25}$$

because $\partial n_2/\partial n_1 = 0$. (Why?)

Because of the relation between dn_1 and dN_1 in equation (18.24), we may transform equation (18.25) to

$$\overline{\mathrm{G}_1} = N_2\frac{\partial\mathrm{G}_i}{\partial N_1} + \mathrm{G}_i \tag{18.26}$$

By methods analogous to the above, we find for $\overline{\mathrm{G}_2}$, n_1 now remaining constant, that

$$\overline{\mathrm{G}_2} = N_1\frac{\partial\mathrm{G}_i}{\partial N_2} + \mathrm{G}_i \tag{18.27}$$

By the definition of mole fraction, we have, for the binary solution,

$$N_1 = 1 - N_2 \tag{18.28}$$

and, therefore,

$$dN_1 = -dN_2 \tag{18.29}$$

Consequently, equation (18.27) may be expressed in the equivalent form

$$\overline{\mathrm{G}_2} = (N_2 - 1)\frac{\partial\mathrm{G}_i}{\partial N_1} + \mathrm{G}_i \tag{18.30}$$

which may be subtracted from equation (18.26) to give the relation

$$\overline{\mathrm{G}_1} - \overline{\mathrm{G}_2} = \frac{\partial\mathrm{G}_i}{\partial N_1} = -\frac{\partial\mathrm{G}_i}{\partial N_2} \tag{18.31}$$

and the corresponding relation

$$\overline{\mathrm{G}}_2 - \overline{\mathrm{G}}_1 = \frac{\partial \mathrm{G}_i}{\partial N_2} = -\frac{\partial \mathrm{G}_i}{\partial N_1} \tag{18.32}$$

The relation between $\partial G/\partial n_1$ and $\partial \mathrm{G}_i/\partial n_1$ was expressed in equation (18.25). The relation between $\partial G/\partial N_1$ and $\partial \mathrm{G}_i/\partial N_1$ is simpler. On differentiating equation (18.20) with respect to N_1, we have

$$\frac{\partial \mathrm{G}_i}{\partial N_1} = \frac{1}{n_1 + n_2}\frac{\partial G}{\partial N_1} \tag{18.33}$$

$n_1 + n_2$ remaining constant during the differentiation. (Why?) Therefore, when G, the value of the extensive property for $n_1 + n_2$ moles of solution, is plotted against mole fraction, the values of $\overline{\mathrm{G}}_1$ and $\overline{\mathrm{G}}_2$ may be calculated from the following equations:

$$(n_1 + n_2)\overline{\mathrm{G}}_1 = N_2 \frac{\partial G}{\partial N_1} + G \tag{18.34}$$

$$(n_1 + n_2)\overline{\mathrm{G}}_2 = N_1 \frac{\partial G}{\partial N_2} + G \tag{18.35}$$

$$(n_1 + n_2)(\overline{\mathrm{G}}_1 - \overline{\mathrm{G}}_2) = \frac{\partial G}{\partial N_1} \tag{18.36}$$

$$(n_1 + n_2)(\overline{\mathrm{G}}_2 - \overline{\mathrm{G}}_1) = \frac{\partial G}{\partial N_2} \tag{18.37}$$

These equations reduce to equations (18.26), (18.27), (18.31), and (18.32), respectively, when $n_1 + n_2 = 1$, that is, for 1 mole of solution.

Special Forms of the Partial Molal Equations. 1. *At Maximum or Minimum Values of G.*—The partial molal equations derived for the extensive property G have been derived without special reference to the form of the curve obtained when G is plotted against n_1, n_2, or N. Accordingly, the equations have general applicability to all quantities such as heat of reaction, heat capacity, volume, entropy, and free energy, that are functions of the pressure, temperature, and composition of the system. In all the partial molal equations, we have considered only the change of G with composition; these changes of composition were assumed to take place at constant temperature and pressure.

Whenever the plotted curve of G, or G_i, *vs.* mole fraction passes through a maximum or minimum, $\partial \mathrm{G}_i/\partial N = 0$. Under these conditions, it appears from equations (18.26) and (18.27) that

$$\overline{\mathrm{G}}_1 = \overline{\mathrm{G}}_2 = \mathrm{G}_i \tag{18.38}$$

This relation was observed for the heat of solution curves in Fig. 6.2, where values of $\overline{\mathrm{Q}}_1$, $\overline{\mathrm{Q}}_2$, and Q_i were plotted on the same graph. The curves intersect at the maximum of the heat of solution curve, the partial molal heat of solution of the two components here being identical with heat of solution for 1 mole of solution, which is, by definition, the integral heat. Similarly, from the relation between G and G_i in equation (18.20) we find at this point that

$$\overline{\mathrm{G}_1} = \overline{\mathrm{G}_2} = \frac{G}{n_1 + n_2} \tag{18.39}$$

where G is the value for $n_1 + n_2$ moles of solution.

2. *At the Limit* $N = 1$.—When a solution becomes infinitely dilute or infinitely concentrated, the partial molal equations again assume simpler forms. As the solute, component 2, becomes more and more dilute, its concentration in the solution approaches the limiting value $N_2 = 0$. At the same time, the solvent becomes more and more concentrated until its concentration approaches the limiting value $N_1 = 1$. The "solution" then consists of pure solvent. From equation (18.26), we obtain as the limiting value

$$\overline{\mathrm{G}_1} = \mathrm{G}_i \tag{18.40}$$

which tells us what we already knew: the partial molal quantity for a pure substance is identical with the corresponding molar value. This limiting partial molal quantity $\overline{\mathrm{G}_1}$, therefore, has zero value or a finite value, depending on the corresponding molar value of the pure substance.

3. *At the Limit* $N = 0$.—In the previous section, we found the limiting value of $\overline{\mathrm{G}}$ of the first component as its mole fraction approaches unity. We are here concerned with the limiting value of $\overline{\mathrm{G}_1}$ as N_1 approaches zero and N_2 approaches unity. Under these conditions, equation (18.26) becomes

$$\overline{\mathrm{G}_1} = \frac{\partial \mathrm{G}_i}{\partial N_1} + \mathrm{G}_i \tag{18.41}$$

Therefore, it appears that we cannot evaluate the partial molal quantity for component 1 at the limit $N_1 = 0$ unless we know the value of $\partial \mathrm{G}_i/\partial N_1$ as well as the value of G_i, which by analogy with equation (18.40) is here equal to $\overline{\mathrm{G}_2}$, the molar value of G for component 2.

From equations (18.40) and (18.41), we can set up the following pairs of limiting values:

At $N_1 = 1$, $N_2 = 0$,

$$\left.\begin{aligned} \overline{\mathrm{G}_1} &= \mathrm{G}_i \\ \overline{\mathrm{G}_2} &= \frac{\partial \mathrm{G}_i}{\partial N_2} + \mathrm{G}_i = \frac{\partial \mathrm{G}_i}{\partial N_2} + \overline{\mathrm{G}_1} \end{aligned}\right\} \tag{18.42}$$

At $N_1 = 0$, $N_2 = 1$

$$\left.\begin{aligned} \overline{\mathrm{G}_1} &= \frac{\partial \mathrm{G}_i}{\partial N_1} + \mathrm{G}_i = \frac{\partial \mathrm{G}_i}{\partial N_1} + \overline{\mathrm{G}_2} \\ \overline{\mathrm{G}_2} &= \mathrm{G}_i \end{aligned}\right\} \tag{18.43}$$

Change of Partial Molal Quantities with Composition.—We have been discussing primarily the change of the extensive property G with number of moles of either component 1 or 2, and we have shown how this value may be obtained from a graph of G or G_i *vs.* mole fraction. By use of equations (18.26) and (18.27) the values of $\overline{\mathrm{G}}_1$ and $\overline{\mathrm{G}}_2$ are obtained from the family of tangents to the curve and the corresponding values of G_i.

The values of $\overline{\mathrm{G}}_1$ and $\overline{\mathrm{G}}_2$ calculated in this way can be plotted against the mole fraction of their respective substances in the solution. From the slopes of these curves, values of $\partial\overline{\mathrm{G}}_1/\partial N_1$ and $\partial\overline{\mathrm{G}}_2/\partial N_1$ are obtained, for $\partial N_2 = -\partial N_1$. The ratio between these slopes for any value of N_1 may be obtained with the aid of equation (18.23), whence we have

$$\frac{\partial\overline{\mathrm{G}}_1/\partial N_1}{\partial\overline{\mathrm{G}}_2/\partial N_1} = -\frac{\partial\overline{\mathrm{G}}_1/\partial N_1}{\partial\overline{\mathrm{G}}_2/\partial N_2} = -\frac{N_2}{N_1} \tag{18.44}$$

It is at once evident that the ratio between the two slopes at any concentration is equal to the mole ratio $N_2/N_1 = n_2/n_1$ at that concentration. When $N_1 = N_2$, the mole fraction of each being 0.5, it is evident that

$$\frac{\partial\overline{\mathrm{G}}_1}{\partial N_1} = -\frac{\partial\overline{\mathrm{G}}_2}{\partial N_1} = \frac{\partial\overline{\mathrm{G}}_2}{\partial N_2} \tag{18.45}$$

At this concentration the slopes of the two curves are equal but opposite in sign. At all other values of N_1, the signs of the slopes must also be opposite, for N_2/N_1 is always positive. If $\overline{\mathrm{G}}_1$ passes through a maximum,

TABLE 18.1.—SOME GENERAL PARTIAL MOLAL EQUATIONS FOR THE EXTENSIVE PROPERTY G

(At constant pressure and temperature)

(18.13)	$dG = \overline{\mathrm{G}}_1\,dn_1 + \overline{\mathrm{G}}_2\,dn_2 + \overline{\mathrm{G}}_3\,dn_3 + \cdots$
	At constant composition
(18.14)	$G = n_1\overline{\mathrm{G}}_1 + n_2\overline{\mathrm{G}}_2 + n_3\overline{\mathrm{G}}_3 + \cdots$
(18.16)	$n_1\,\partial\overline{\mathrm{G}}_1 + n_2\,\partial\overline{\mathrm{G}}_2 + \cdots = 0$
(18.17)	$n_1\frac{\partial\overline{\mathrm{G}}_1}{\partial n_1} + n_2\frac{\partial\overline{\mathrm{G}}_2}{\partial n_1} + \cdots = 0$
	For 1 *mole of solution* $(n_1 + n_2 + \cdots = 1; G = \mathrm{G}_i)$
(18.21)	$\mathrm{G}_i = N_1\overline{\mathrm{G}}_1 + N_2\overline{\mathrm{G}}_2 + \cdots$
(18.22)	$N_1\,\partial\overline{\mathrm{G}}_1 + N_2\,\partial\overline{\mathrm{G}}_2 + \cdots = 0$
(18.23)	$N_1\frac{\partial\overline{\mathrm{G}}_1}{\partial N_1} + N_2\frac{\partial\overline{\mathrm{G}}_2}{\partial N_1} + \cdots = 0$
(18.26)	$\overline{\mathrm{G}}_1 = N_2\frac{\partial\mathrm{G}_i}{\partial N_1} + \mathrm{G}_i$
(18.27), (18.30)	$\overline{\mathrm{G}}_2 = N_1\frac{\partial\mathrm{G}_i}{\partial N_2} + \mathrm{G}_i = (N_2 - 1)\frac{\partial\mathrm{G}_i}{\partial N_1} + \mathrm{G}_i$
(18.31)	$\overline{\mathrm{G}}_1 - \overline{\mathrm{G}}_2 = \frac{\partial\mathrm{G}_i}{\partial N_1} = -\frac{\partial\mathrm{G}_i}{\partial N_2}$
(18.44)	$\frac{\partial\overline{\mathrm{G}}_1/\partial N_1}{\partial\overline{\mathrm{G}}_2/\partial N_1} = -\frac{N_2}{N_1}$

$\partial\overline{G}_1/\partial N_1$ being zero, $\overline{G}_2$ must pass through a minimum, the indeterminate number 0/0 having the value $-N_2/N_1$.

Some of the partial molal equations are summarized in Table 18.1.

Limiting Values of the Partial Molal Quantities.—Equations (18.42) and (18.43) represent the limiting values of $\overline{G}_1$ and $\overline{G}_2$, both in infinitely concentrated and in infinitely dilute solutions of the two components. We are now in a position to say more about these limiting values, for we are able to discover how they must be approached if equation (18.44) is to be satisfied.

From equation (18.44), it appears that the ratio N_2/N_1 approaches zero in a solution where N_1 approaches unity and N_2 approaches zero. We have, therefore,

$$\lim_{N_1=1,N_2=0} \frac{\partial\overline{G}_1/\partial N_1}{\partial\overline{G}_2/\partial N_1} = 0 \tag{18.46}$$

This limiting ratio is satisfied by two pairs of values for the slopes of the curves obtained when the $\overline{G}_1$ and $\overline{G}_2$ curves are plotted against the mole fraction. Thus, when

$$\left.\begin{aligned} \frac{\partial\overline{G}_1}{\partial N_1} &= 0 \\ \frac{\partial\overline{G}_2}{\partial N_1} &= \text{a finite value} \end{aligned}\right\} \tag{18.47}$$

Or, when

$$\left.\begin{aligned} \frac{\partial\overline{G}_1}{\partial N_1} &= \text{a finite value} \\ \frac{\partial\overline{G}_2}{\partial N_1} &= \infty \end{aligned}\right\} \tag{18.48}$$

The form of the $\overline{G}_1$ and $\overline{G}_2$ curves in the neighborhood of $N_1 = 1$ is illustrated in Fig. 18.1 for the pair of values that follow the relations in equations (18.47). As is evident from the heat of solution data in Chap. 6, heats of solution furnish an example of this type of system. The partial molal volumes also follow the relations in Fig. 18.1 and equations (18.47). In the neighborhood of $N_1 = 1$, the partial molal heat content or volume of component 1 is essentially that of pure 1 and the partial molal heat content or volume of the solute, component 2, must remain finite.

The forms of the $\overline{G}_1$ and $\overline{G}_2$ curves in the neighborhood of $N_1 = 1$ that satisfy the requirements in equations (18.48) are illustrated in Fig. 18.2. The free energy and entropy functions are of this type. Thus, in the neighborhood of $N_1 = 1$, the free energy of component 1 in solution differs from that of pure 1, for the change of free energy with N_1 is finite. But, because the partial molal free energy curve of the solute, component

2, has an infinite slope, the free energy of the solute at infinite dilution must be infinite (negative in this case). An infinite amount of work is required to compress a mole of solute at infinite dilution to the pure solute where by analogy $\overline{F}_2 = F_2$, a finite value.

Limiting Free Energies and Entropies of Ideal Solution.—The above conclusions on the limiting values of the partial molal functions may be compared with those which are obtained from the equations for the free energy and entropy of ideal solution. These equations previously derived for these functions are (13.54) and (13.58), respectively. If component A in these equations is now designated as component 1, we have for the change in free energy of this component when 1 mole dissolves in a solution having the composition N_1,

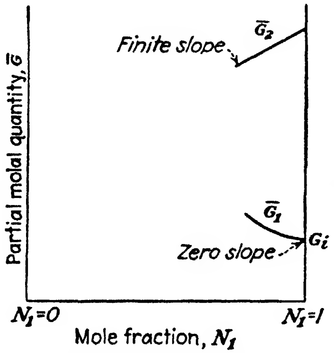


FIG. 18.1.—Limiting values of the partial molal quantities according to equations (18.47).

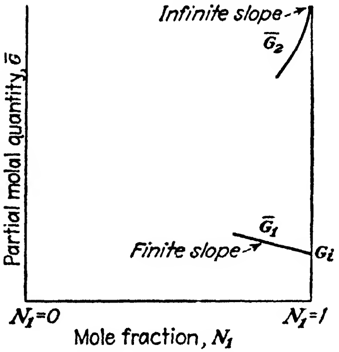


FIG. 18.2.—Limiting values of the partial molal quantities according to equations (18.48).

$$F_1 - F_1^\circ = RT \ln N_1 \tag{18.49}$$

Here F_1, the free energy of 1 mole of component 1 in the ideal solution, is identical with what we have since called the partial molal free energy of this component, $\overline{F}_1$. Similarly, the molar free energy in the standard state, F_1° is identical with the partial molal free energy of pure 1, namely, $\overline{F}_1^\circ$. Equation (18.49) may, therefore, be written

$$\overline{F}_1 - \overline{F}_1^\circ = RT \ln N_1 \tag{18.50}$$

In the neighborhood of pure 1 where N_1 approaches unity, ln N_1 approaches zero and $\overline{F}_1$ approaches the value $\overline{F}^\circ$ as required by equation (18.40). Because $\overline{F}_1^\circ$ has a finite value, $\overline{F}_1$ approaches this finite value. But we are interested also in discovering how $\overline{F}_1$ approaches this finite value, that is, in the slope of the $\overline{F}_1$ *vs.* N_1 curve at this concentration. On differentiating equation (18.50) with respect to N_1, we obtain the equation

$$\frac{\partial \overline{\mathrm{F}}_1}{\partial N_1} = RT\frac{\partial \ln N_1}{\partial N_1} = RT\frac{1}{N_1} \tag{18.51}$$

Equation (18.51) indicates that, as N_1 approaches unity, $\partial \overline{\mathrm{F}}_1/\partial N_1$ approaches the finite value RT. This, except for sign, is the relation shown in Fig. 18.2.

Similarly, for extremely dilute solutions of component 1, we have N_1 approaching zero and $\ln N_1$ approaching the value $-\infty$. It follows from equations (18.50) and (18.51), therefore, that, at the limit $N_1 = 0$,

$$\left.\begin{aligned} \overline{\mathrm{F}}_1 &= -\infty \\ \frac{\partial \overline{\mathrm{F}}_1}{\partial N_1} &= \infty \end{aligned}\right\} \tag{18.52}$$

The above equations obviously may be applied also to the second component for its limits $N_2 = 0$ and $N_2 = 1$, so that we obtain the following pairs of values:

At $N_1 = 1$, $N_2 = 0$,

$$\left.\begin{aligned} \overline{\mathrm{F}}_1 &= \mathrm{F}_1^\circ \\ \overline{\mathrm{F}}_2 &= -\infty \end{aligned}\right\} \tag{18.53}$$

$$\left.\begin{aligned} \frac{\partial \overline{\mathrm{F}}_1}{\partial N_1} &= RT \\ \frac{\partial \overline{\mathrm{F}}_2}{\partial N_1} &= -\frac{\partial \overline{\mathrm{F}}_2}{\partial N_2} = -\infty \end{aligned}\right\} \tag{18.54}$$

The relations in equations (18.54) correspond to the limiting values in (18.48).

The entropy in the ideal solution, by comparison with equation (13.58), may be expressed by the equation

$$\overline{\mathrm{S}}_1 - \mathrm{S}_1^\circ = -R\ln N_1 \tag{18.55}$$

We find, therefore,

$$\frac{\partial \overline{\mathrm{S}}_1}{\partial N_1} = -R\frac{\partial \ln N_1}{\partial N_1} = -\frac{R}{N_1} \tag{18.56}$$

Similarly, the pairs of limiting values have the relations shown in the following equations:

At $N_1 = 1$, $N_2 = 0$,

$$\left.\begin{aligned} \overline{\mathrm{S}}_1 &= \mathrm{S}_1^\circ \\ \overline{\mathrm{S}}_2 &= \infty \end{aligned}\right\} \tag{18.57}$$

$$\left.\begin{aligned} \frac{\partial \overline{\mathrm{S}}_1}{\partial N_1} &= -R \\ \frac{\partial \overline{\mathrm{S}}_2}{\partial N_1} &= -\frac{\partial \overline{\mathrm{S}}_2}{\partial N_2} = \infty \end{aligned}\right\} \tag{18.58}$$

Problems

18.1. Let the molar heat content of pure component 1 be H_1°, that of pure component 2 be H_2°, and that of a mole of solution containing $N_1 = x$ moles of 1 and $N_2 = 1 - x$ moles of 2 be H_i. If these heat contents have the values indicated in Fig. 18.3 where the lower curve represents the values of H_i for values of N_1 ranging from $N_1 = 0$ to $N_1 = 1$, show graphically from Fig. 18.3 and the partial molal equations that the intercepts of the tangent to the curve at $N_1 = x$ give the values of $\overline{H}_1$ and $\overline{H}_2$ for these components in the solution.

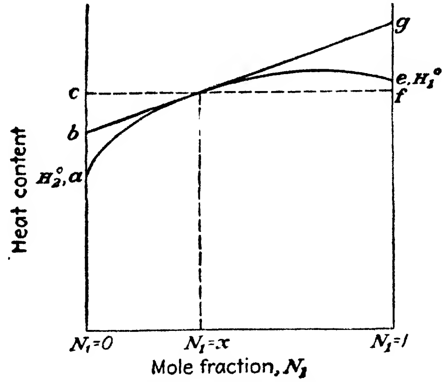


FIG. 18.3.—Calculation of partial molal heat content by the method of intercepts.

18.2. Show that, for the same conditions as those stated in Prob. 18.1, Q_i in Fig. 18.4 represents the integral heat of solution measured experimentally and that

$$Q_i = H_i - (N_1H_1^\circ + N_2H_2^\circ)$$

What is the physical meaning of $N_1H_1^\circ + N_2H_2^\circ$?

18.3. Where the various terms have the values indicated in Probs. 18.1 and 18.2 and in Figs. 18.3 and 18.4, show that

$$\overline{Q}_1 = \overline{H}_1 - H_1^\circ$$
$$\overline{Q}_2 = \overline{H}_2 - H_2^\circ$$

If H_1° and H_2° are arbitrarily assigned the values of zero as in Fig. 18.5, where Q_i is plotted directly against N_1, show that the same values of $\overline{Q}_1$ and $\overline{Q}_2$ are obtained at $N_1 = x$ from Fig. 18.5 as from Fig. 18.4.

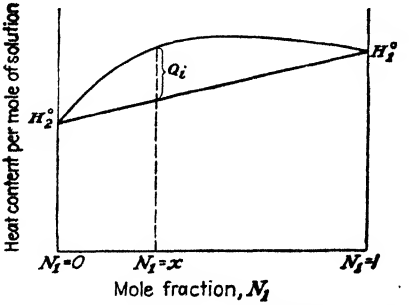


FIG. 18.4.—Relation of integral heat of solution to heat content.

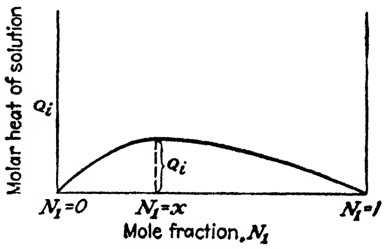


FIG. 18.5.—Integral heat of solution.

18.4. If the relative partial molal heat content $\overline{L_1}$ of the solvent is defined by

$$\overline{L_1} = \overline{Q_1} = \overline{H_1} - H_1^\circ$$

show that

$$\frac{\partial \overline{L_1}}{\partial T} = (\overline{c_P})_1 - (c_P^\circ)_1$$

What is the physical meaning of $(\overline{c_P})_1$ and $(c_P^\circ)_1$?

18.5. What is the physical meaning of $\overline{H_1} - H_1^\circ$? Under what conditions and in what equations is this function useful?

CHAPTER 19

NONIDEAL SOLUTIONS

The free energy equations that we have applied to the various components of solutions were derived from the ideal gas laws and the laws of ideal solution. Their application is, therefore, limited to systems in which the vapors behave as ideal gases and the solutions obey the laws of ideal solution. In these equations, the free energy of a substance is expressed as a logarithmic function of the pressure, mole fraction, or some other corresponding measure of the concentration of the substance in the gas phase or in the solution. Equation (13.51) for the expansion of 1 mole of ideal gas at constant temperature may be expressed in the differential form as

$$d\text{F} = RT \, d \ln P \tag{19.1}$$

Similarly, for the ideal gas, liquid, or solid solution, temperature and pressure both remaining constant, the relation between the free energy of 1 mole of substance and its mole fraction given in equation (13.54) may be expressed in the differential form as

$$d\text{F} = RT \, d \ln N \tag{19.2}$$

Fugacity and Activity.—In nonideal gases and in nonideal solutions the free energy of a substance cannot be represented by equations (19.1) and (19.2). However, when empirical functions are substituted for pressure and mole fraction, equations having the form of (19.1) and (19.2) can be made to represent the free energy of a substance regardless of the extent or nature of the departure from the laws of ideal gases or of ideal solution. The empirical functions in common use are the *fugacity* f and *activity* a, which were introduced in Chap. 12. Fugacity was defined in part in equation (12.75) by the relation

$$d\text{F} = RT \, d \ln f \tag{19.3}$$

From the relation between activity and fugacity expressed in equation (12.78), it follows that the corresponding function for activity is

$$d\text{F} = RT \, d \ln a \tag{19.4}$$

Observe that in both these equations the ideal gas constant R is retained, all deviations from ideality being grouped in the empirical functions f and a.

Although there is no theoretical restriction on the application of either fugacity or activity to systems of any particular type, in common practice the fugacity function is expressed almost exclusively in absolute values. It is applied to gases and to liquids or solids in equilibrium with their vapors as an empirical substitute for pressure in the free energy equations. Its numerical values are, therefore, expressed in pressure units, usually in atmospheres. On the other hand, activity is almost always expressed in relative values. It is applied chiefly to solutions as an empirical substitute for concentration, and its numerical values are, therefore, expressed in concentration units. In practice, equation (19.3) is paired with (19.1), f becoming identical with P for the ideal gas; and equation (19.4) is paired with (19.2), a becoming identical with N for the ideal solution or the molality m, or molarity C in the ideal "dilute" solution.

Because a factor n for the number of moles of substance is absent from equations (19.3) and (19.4), it is evident that these equations refer to 1 mole of substance, F being the molar (or partial molal) free energy. The ideal equations (19.1) and (19.2) also refer to 1 mole of substance.

The differential equations (19.3) and (19.4) define only changes in the functions f and a; therefore, they express only the relative values of these functions. When we integrate equation (19.3), keeping temperature constant, we obtain the equation

$$\mathrm{F} = RT \ln f + A \tag{19.5}$$

The value A is a constant of integration that may be, and is, a function of the temperature. It can be evaluated for some standard state where the free energy has the value F° and the fugacity the value f°. Under these conditions, equation (19.5) becomes

$$\mathrm{F} - \mathrm{F}^\circ = RT \ln \frac{f}{f^\circ} \tag{19.6}$$

$\mathrm{F} - \mathrm{F}^\circ$ representing the difference between the free energy of the experimental state and that of the standard state and f/f° the relative fugacity of these two states. When the standard state is so selected that $f^\circ = 1$, the integration constant A becomes equal to the free energy F° of this standard state, and equations (19.5) and (19.6) become

$$\mathrm{F} - \mathrm{F}^\circ = RT \ln f \tag{19.7}$$

but this value of $\mathrm{F}^\circ = A$ is not identical with F° in equation (19.6) unless both represent the same standard state.

Inspection of equation (19.6) shows that, even though the numerical values of F and F° are known, only the relative values of f and f° can be obtained from the equation. Absolute values of fugacity must be established with the aid of some independent relation. The requirement, expressed in Chap. 12, that the fugacity of a gas must equal its pressure as the gas approaches ideal behavior, gives the additional relation. The pressure of a mole of gas is a function of the temperature; and the fugacity, which is related to this pressure, must also be a function of the temperature. Because the standard fugacity f° is a function of the temperature, it follows that A, in equation (19.5), is also. When the standard state selected for a gas is at $P = 1$, a real gas has a standard fugacity value f° not equal to unity. The fugacity of this gas at any other state at the same temperature is expressed by equation (19.6).

In practice, the activity function is applied to the various components of a solution rather than to the solution as a whole. Under these conditions, the general activity equations represented by equations (19.4) and (12.79) become the corresponding partial molal equations for the various components. However, we here use the more general form to indicate the similarities between the activity and fugacity functions. Their differences are analyzed in more detail later.

From the general integration of equation (19.4) at constant temperature, we have

$$\mathrm{F} = RT \ln a + B \tag{19.8}$$

where B is the integration constant.

Because activity is used only in the relative sense, the activity of the standard state invariably being assigned the value of unity, we have, for the defining equation of activity,

$$a = \frac{a}{a^\circ} = \frac{f}{f^\circ} \tag{19.9}$$

Equation (19.9) leaves undefined the units in which a is to be expressed. A number of different units have been used in practice. The constant B can be evaluated for any arbitrary standard state for which a is placed equal to unity; for, by definition, $f = f^\circ$ for this state. When $a = 1$, F becomes equal to F° and, therefore, $B = \mathrm{F}^\circ$. As a result, equation (19.8) may be expressed in the form

$$\mathrm{F} - \mathrm{F}^\circ = RT \ln a \tag{19.10}$$

If the activity is to become identical with the mole fraction for the ideal solution, it may be assigned the value $a = 1$ at $N = 1$, so that the pure component at the experimental temperature and pressure has unit activity. When a is expressed in concentration units of this type, we find that F° and, therefore, B are functions of pressure and temperature. This question of the standard state is discussed in more detail below.

Free Energies and Standard States in Ideal Solutions.—The meaning of the "standard state" as applied to the fugacity and activity functions becomes clearer when we review the relations between the standard states for ideal solutions.

1. *Solutions of Ideal Gases.*—For the isothermal expansion of a definite amount of a pure substance the change in free energy with pressure is given by the equation $(\partial F/\partial P)_T = V$. If the gas is ideal, we have, for a mole of the gas, $\mathrm{v} = RT/P$, whence we obtain the isothermal relation

$$d\mathrm{F} = RT\frac{dP}{P} = RT\,d\ln P$$

which is equation (19.1).

When the gas, here called component 1, expands into a mixture of ideal gases at constant temperature, the change in free energy for a mole of component 1 is the change in the partial molal free energy $\overline{\mathrm{F}}_1$. For this process, expressed in the partial molal notation

$$d\overline{\mathrm{F}}_1 = \overline{\mathrm{V}}_1\,dP_1 \tag{19.11}$$

For the ideal gas, the partial molal volume $\overline{\mathrm{V}}_1$ is related to the partial pressure P_1 by the equation

$$\overline{\mathrm{V}}_1 = \frac{RT}{P_1} \tag{19.12}$$

When equations (19.11) and (19.12) are combined, we have, for component 1,

$$d\overline{\mathrm{F}}_1 = RT\,d\ln P_1 \tag{19.13}$$

This equation, when integrated at constant temperature, becomes

$$\overline{\mathrm{F}}_1 = RT\ln P_1 + C_1 \tag{19.14}$$

where C_1 is the integration constant. If the standard state is chosen at $P_1 = 1$ where $\overline{\mathrm{F}}_1 = \overline{\mathrm{F}}^\circ$, we find that

$$C_1 = \overline{\mathrm{F}}_1^\circ \tag{19.15}$$

We observe here that, although C_1 remains constant as the pressure varies at constant temperature, its value must change as the free energy of the gas at 1 atmosphere pressure, that is, the gas in its standard state, changes with temperature. Therefore, C_1 is a function of temperature.

When equation (19.15) is combined with (19.14), we obtain the familiar equation

$$\overline{\mathrm{F}}_1 - \overline{\mathrm{F}}_1^\circ = RT\ln P_1 \tag{19.16}$$

In a gaseous solution that obeys Dalton's law of partial pressures, the partial pressure P_1 of the gas is related to the mole fraction N_1 and the total pressure P by the equation

$$P_1 = N_1 P \tag{19.17}$$

It is, therefore, apparent that equation (19.14) may be expressed in the form

$$\begin{aligned} \overline{F}_1 &= RT \ln (N_1 P) + C_1 \\ &= RT \ln N_1 + RT \ln P + C_1 \end{aligned} \tag{19.18}$$

If, for this isothermal solution process, the total pressure P remains constant, the term $RT \ln P$ may be combined with the term C_1 to give the equation

$$\overline{F}_1 = RT \ln N_1 + D_1 \tag{19.19}$$

where

$$D_1 = C_1 + RT \ln P \tag{19.20}$$

Because C_1 is a function of the temperature, it is evident from equation (19.20) that D_1 is a function of both temperature and pressure.

When the standard state is defined in terms of pure substance at P and T where $N_1 = 1$, the free energy of this standard state being $\overline{F}_1^\circ$, we obtain, from equation (19.19),

$$D_1 = \overline{F}_1^\circ \tag{19.21}$$

Therefore, at constant temperature and pressure, we have

$$\overline{F}_1 - \overline{F}_1^\circ = RT \ln N_1 \tag{19.22}$$

Observe that, in equation (19.22), $\overline{F}_1^\circ$ is constant only under the restriction of constant temperature and pressure. Observe also that the numerical value of $\overline{F}_1^\circ$ in equation (19.22) is not equal to that of $\overline{F}_1^\circ$ in (19.16), for the standard states are differently chosen. When a gas is pure, $N_1 = 1$, but its pressure may or may not equal 1 atmosphere.

Equation (19.22) may be differentiated at constant temperature and pressure. Under these conditions, $\overline{F}_1^\circ$ remains constant and we obtain the differential equation corresponding to equation (19.2). Equation (19.2) is, therefore, valid under these restrictions.

2. *Ideal Liquid Solutions.*—In Chap. 13, we defined an ideal liquid solution as one that obeys Raoult's law at all pressures and temperatures. When the vapor pressure of pure component 1 is P_1°, the partial pressure P_1 of this component in the vapor above the ideal solution is

$$P_1 = N_1 P_1^\circ \tag{19.23}$$

N_1 being the mole fraction of component 1 in the solution. At this partial pressure, we see from equations (19.14) and (19.23) that the free energy of the vapor is represented by the equations

$$\begin{aligned} F_1 &= RT \ln P_1 + C_1 \\ &= RT \ln N_1 + RT \ln P_1^\circ + C_1 \end{aligned} \tag{19.24}$$

But component 1 in the solution is in equilibrium with component 1 in the vapor, so that

$$\overline{\mathrm{F}}_1(\text{in vapor}) = \mathrm{F}(\text{in soln}) \tag{19.25}$$

The partial molal free energy of component 1 in the solution is, therefore, given by the equation

$$\overline{\mathrm{F}}_1 = RT \ln N_1 + E_1 \tag{19.26}$$

where

$$E_1 = C_1 + RT \ln P_1^\circ \tag{19.27}$$

Again, if the standard state of component 1 is that of the pure liquid whose mole fraction is unity, we have

$$E_1 = \overline{\mathrm{F}}_1^\circ \tag{19.28}$$

so that equation (19.26) may be expressed in the form

$$\overline{\mathrm{F}}_1 - \overline{\mathrm{F}}_1^\circ = RT \ln N_1 \tag{19.29}$$

This equation agrees in form with the partial molal equation for the ideal gas in a gaseous solution; but the standard state and therefore the value of the standard free energy differ numerically in the two cases, as indicated by equations (19.20) and (19.27).

FUGACITY

The empirical function fugacity, which is to play the role of the pressure or partial pressure in the free energy equations, was defined in part in equations (19.3) and (19.6). Because these equations establish only the ratio between two values of the fugacity, another relation is required to determine the absolute values of fugacity. The fugacity is further defined as being identical with the pressure for a perfect gas. Because all gases approach ideal behavior as their pressures approach zero, $f = P$ for real gases at sufficiently low pressures. We have, therefore, the further definition

$$\lim_{P=0} \frac{f}{P} = 1 \tag{19.30}$$

Equations (19.6) and (19.30) define fugacity completely. When pressure and fugacity functions can be extrapolated to zero pressure where pressures and fugacities become identical, the absolute values of fugacity at higher pressures can be readily calculated.

Change of Fugacity with Pressure.—For a system in which no net useful work is done, that is, a simple system or a system at equilibrium, the change of free energy with pressure at constant temperature is represented by equation (10.43), which becomes, for 1 mole of substance,

$$\left(\frac{\partial \mathrm{F}}{\partial P}\right)_T = \mathrm{V} \tag{19.31}$$

When equation (19.5) is differentiated with respect to pressure at constant temperature, we obtain an expression for the change of fugacity with pressure. Because the integration constant A in this equation is a function of the temperature only, we have

$$\left(\frac{\partial \mathrm{F}}{\partial P}\right)_T = RT\left(\frac{\partial \ln f}{\partial P}\right)_T \tag{19.32}$$

On combining equations (19.31) and (19.32), we obtain the equation

$$\left(\frac{\partial \ln f}{\partial P}\right)_T = \frac{\mathrm{v}}{RT} \tag{19.33}$$

This equation may be expressed in the form

$$RT \,\mathrm{d} \ln f = \mathrm{v}\, \mathrm{d}P \tag{19.34}$$

it being distinctly understood, however, that this represents the relation for the isothermal process.

Equation (19.34) follows directly from (19.3) and (10.43) applied to 1 mole of substance. It applies to liquids and solids as well as to gases.

Fugacity of a Pure Nonideal Gas.—The fugacity of a real gas may be calculated from the above equations if the necessary data on the molar volumes of the gas at various pressures are available. When v can be expressed as a known function of P, as in the van der Waals equation, for example, equation (19.34) can be integrated. If the numerical values of v are available, they may be plotted against the pressure and the integration carried out graphically. Thus, from equation (19.34), we have,

$$\int_1^2 \mathrm{v}\, \mathrm{d}P = RT \ln \frac{f_2}{f_1} \tag{19.35}$$

Observe, however, that the integral $\int_1^2 \mathrm{v}\, \mathrm{d}P$ evaluates only $\ln (f_2/f_1)$ and not the absolute value of either f_1 or f_2. If absolute values of fugacity are required, it is necessary to carry the integration to low pressures where the fugacity becomes equal to the pressure.

The calculation is simplified if a term α is introduced into equation (19.34) to represent the deviation of the ideal molar volume v_i from the real molar volume v, v_i being defined by the ideal gas law relation $\mathrm{v}_i = RT/P$. Thus,

$$\begin{aligned}\mathrm{v} &= \mathrm{v}_i - \alpha \\ &= \frac{RT}{P} - \alpha\end{aligned} \tag{19.36}$$

When equation (19.36) is introduced into (19.34), we have

$$RT\,\mathrm{d}\ln f = \frac{RT}{P}\,\mathrm{d}P - \alpha\,\mathrm{d}P \tag{19.37}$$

which may be written in the form

$$RT\,\mathrm{d}\ln f = RT\,\mathrm{d}\ln P - \alpha\,\mathrm{d}P \tag{19.38}$$

This equation, when integrated between zero pressure where $f = P = 0$ and the pressure P where f differs from P, becomes

$$RT\ln f = RT\ln P - \int_0^P \alpha\,\mathrm{d}P \tag{19.39}$$

Hence, when the difference, at constant temperature, between the ideal volume and the real volume is plotted against pressure, we can obtain the difference between fugacity and pressure at this temperature by graphical integration.

At low pressures, the value of α approaches a constant value, $-B$, defined in equation (4.14). This fact permits accurate extrapolation of molar volumes to zero pressure where all real gases behave as ideal gases. In the low pressure range where α equals $-B$, the integral in equation (19.39) becomes equal to $-BP$ and the equation itself may be written in the forms

$$\left.\begin{aligned} RT\ln f - RT\ln P &= -\alpha P = BP \\ \text{and}\qquad RT\ln\frac{f}{P} &= -\alpha P = BP \end{aligned}\right\} \tag{19.40}$$

which are valid at low pressures for all gases. A plot of α against P at low pressures evaluates B and enables us to evaluate f for any value of P.

Equation (19.40) may be applied to oxygen at 1 atmosphere for which, from Table 4.1, we have $B = -0.0213$ liter/mole at 0°c. Consequently, P being unity and RT being 22.41 liter-atmospheres,

$$\ln f = \frac{-0.0213}{22.41} = -9.51 \times 10^{-4}$$

$$f = 0.99905 \text{ atm}$$

It appears that, for a gas as nearly ideal as oxygen, the difference between the fugacity and pressure may be neglected except for the most exact work.

Following the suggestion of Lewis and Randall, a further approximation can be made. Thus, equation (19.40) may be written in the alternative forms

$$\left.\begin{aligned} \ln\frac{f}{P} &= -\frac{\alpha P}{RT} \\ \frac{f}{P} &= e^{-\frac{\alpha P}{RT}} \end{aligned}\right\} \tag{19.41}$$

But, when $x = \alpha P/RT$ is small, $e^{-x} = 1 - x$, and equation (19.41) becomes

$$\frac{f}{P} = 1 - \frac{\alpha P}{RT} \tag{19.42}$$

We have expressed v_i as equal to RT/P. Similarly, the ideal pressure P_i may be defined as $P_i = RT/\text{v}$. If these values are substituted in equation (19.36), we have

$$\alpha = \text{v}_i - \text{v} = \frac{RT}{P} - \frac{RT}{P_i}$$

which, when substituted in equation (19.42), gives the simple relation

$$\frac{f}{P} = \frac{P}{P_i} \tag{19.43}$$

This equation holds at low values of α. Observe, however, that values of the real molar volume v are still needed to calculate P_i.

Fugacity of Liquids and Solids.—For liquids and solids in equilibrium with vapors, $\overline{\text{F}}$ being the partial molal free energy of the gas and $\overline{\text{F}}'$ that of the liquid or solid, we have the general condition of equilibrium, namely,

$$\overline{\text{F}} = \overline{\text{F}}' \tag{19.44}$$

Because the integration constant A in equation (19.5) is fixed by the chosen standard state at a definite temperature, it has the same value for all phases at that temperature. Accordingly, from equations (19.5) and (19.44), we have for equilibrium

$$f = f' \tag{19.45}$$

where f is the fugacity of the gas and f' that of the liquid or solid. *The fugacities of a substance in all phases at equilibrium must be equal.* The fugacity, therefore, serves as a measure of the escaping tendency from any phase. Because the activities of gases and liquids or solids are usually not referred to the same standard state, the activity of a substance at equilibrium between two phases may have different numerical values in the different phases. The fugacities, at equilibrium, always have the same numerical value because they are referred to the same standard state.

Equation (19.34) may be applied to liquids and solids as well as to gases. In general, the molar volume of liquids and solids is small compared with that of gases, and it is essentially constant for pressure differences that are not too great. When v remains essentially constant, as for liquids and solids at pressure differences that are not too great, equation (19.34) may be integrated to give the simple equation

$$RT \ln \frac{f_2}{f_1} = \mathrm{v}(P_2 - P_1) \tag{19.46}$$

This equation may be used to calculate the change of fugacity of a liquid or solid with pressure. It indicates, however, only relative values of the fugacity; to obtain absolute values, we must know the absolute value for the liquid or solid for some one pressure. This absolute value is obtained from the fugacity of the gas in equilibrium with the liquid or solid.

Change of Fugacity with Temperature.—When the standard state is selected at $f^\circ = 1$, equation (19.6) becomes

$$\mathrm{F} - \mathrm{F}^\circ = RT \ln f \tag{19.47}$$

This equation may be differentiated with respect to temperature. Although F°, the free energy of the standard state, is not a function of the pressure, it is a function of temperature. On differentiation of equation (19.47), therefore, we have

$$\frac{d\mathrm{F}}{dT} - \frac{d\mathrm{F}^\circ}{dT} = RT\frac{d \ln f}{dT} + R \ln f \tag{19.48}$$

But, from equation (19.47),

$$\frac{\mathrm{F} - \mathrm{F}^\circ}{T} = R \ln f \tag{19.49}$$

and, from equation (10.49), we have, at constant pressure,

$$\left.\begin{aligned} \left(\frac{\partial \mathrm{F}}{\partial T}\right)_P &= \frac{\mathrm{F} - \mathrm{H}}{T} \\ \left(\frac{\partial \mathrm{F}^\circ}{\partial T}\right)_P &= \frac{\mathrm{F}^\circ - \mathrm{H}^\circ}{T} \end{aligned}\right\} \tag{19.50}$$

On combining equations (19.49) and (19.50) with (19.48), we obtain the equation for the change of fugacity with temperature at constant pressure, namely,

$$\left(\frac{\partial \ln f}{\partial T}\right)_P = \frac{\mathrm{H}^\circ - \mathrm{H}}{RT^2} \tag{19.51}$$

Here H° is the molar heat content of the substance in its standard state of unit fugacity at the temperature T and H is that of the substance at the experimental pressure and temperature. Equation (19.51) may be applied to liquids and solids as well as to gases, for in the derivation we made no special restrictions. In each case, however, the proper value of H must be used. In the application of equation (19.51) to different phases at equilibrium, we remember that under these conditions

$$\bar{\mathrm{F}}(\mathrm{g}) = \bar{\mathrm{F}}(\mathrm{liq}) = \bar{\mathrm{F}}(\mathrm{solid})$$

and

$$f(\text{g}) = f(\text{liq}) = f(\text{solid}) \qquad (19.52)$$

When the substance is not pure, the above relations apply to the fugacity f_1 of the substance in the mixture and to the corresponding partial molal heat content $\overline{\text{H}}_1$.

Heat Content of a Gas at Unit Fugacity.—Because the fugacity of a gas approaches the pressure as the gas approaches ideality, $\ln f$ approaches $\ln P$. But, for a constant-pressure process, $d \ln P$ equals zero, so that $d \ln f$ approaches zero. It follows from equation (19.51) that H approaches H°, the heat content at unit fugacity. Thus, for a gas behaving as an ideal gas, $\text{H} = \text{H}^\circ$. As we found in Chap. 4, the heat content of a perfect gas at constant temperature is independent of the volume, and hence of the pressure. Consequently, H° is independent of the pressure and may be regarded as the heat content of the gas at unit fugacity, as the heat content of an ideal gas, or as the heat content of the real gas at $P = 0$ where $f = P$. Because the heat content of a gas at the standard state of unit fugacity is identical with that of an ideal gas, the state of unit fugacity is selected as the standard state of gases for many calorimetric determinations (see Chap. 5).

Evaporation of Liquids and Solids.—When f in equation (19.51) represents the fugacity of a liquid or solid, H represents the molar heat content of the same substance, and H° represents the heat content of the ideal gas, as indicated in the preceding section. Under these conditions, equation (19.51) expresses the change in escaping tendency of liquid or solid at constant pressure. The pressure may be maintained at the constant value P by some inert gas while the partial pressure P_1 of the evaporated liquid or solid changes with temperature. According to equation (19.51), therefore, the change with temperature of the fugacity of a liquid or solid in equilibrium with its vapor is measured by the heat of evaporation of the liquid or solid to the ideal gas state where its heat content is H°. If the vapor behaves as an ideal gas,the fugacity equals the vapor pressure P_1; when P_1 is substituted for fugacity in equation (19.51), we have the familiar Clausius-Clapeyron equation for the vapor pressure of a liquid or solid.

Mass Action Law in Terms in Fugacities.—The law of mass action, derived in Chap. 12 for perfect gases, may be derived for nonideal substances by a simple application of the general partial molal equations. Whenever a substance is present in a system with other substances, the fugacity of the substance is defined, not in terms of the free energy of the system as a whole, but in terms of the partial molal free energy of the substance. For component 1 in the system, the fugacity f_1 is defined by the equation

$$\overline{F}_1 - F_1^\circ = RT \ln f_1 \tag{19.53}$$

which corresponds to equation (19.7) for the pure substance. Similar equations may be written for the other components of the system. Observe that the free energy of the standard state need not be written in the partial molal form because it has a value fixed for each substance in its standard state of unit fugacity at constant temperature.

According to equation (18.13), the change of free energy for any process at constant temperature and pressure may be expressed in the form

$$dF = \overline{F}_1\, dn_1 + \overline{F}_2\, dn_2 + \overline{F}_3\, dn_3 + \overline{F}_4\, dn_4 + \cdots \tag{19.54}$$

But, for a system at equilibrium, there is no change in free energy so that $dF = 0$, and equation (19.54) becomes

$$\overline{F}_1\, dn_1 + \overline{F}_2\, dn_2 + \overline{F}_3\, dn_3 + \overline{F}_4\, dn_4 + \cdots = 0 \tag{19.55}$$

At equilibrium, therefore, not all these terms can be independent variables.

Let us apply this equation to the chemical reaction expressed in equation (12.1) as

$$aA + bB + \cdots = dD + eE + \cdots$$

At equilibrium, a moles of A and b moles of B may react to form d moles of D and e moles of E without the performance of any useful work. Similarly, the reverse reaction may occur without any change in free energy of the reacting system. If the chemical substances A, B, D, and E are identified with the components 1, 2, 3, and 4, we have, for the forward reaction at equilibrium,

$$\left.\begin{aligned} a &= -dn_1 \\ b &= -dn_2 \\ d &= dn_3 \\ e &= dn_4 \end{aligned}\right\} \tag{19.56}$$

On comparison with equation (19.53), we see also that the partial molal free energies of the various substances are

$$\left.\begin{aligned} \overline{F}_A &= RT \ln f_A + F_A^\circ \\ \overline{F}_B &= RT \ln f_B + F_B^\circ \\ \overline{F}_D &= RT \ln f_D + F_D^\circ \\ \overline{F}_E &= RT \ln f_E + F_E^\circ \end{aligned}\right\} \tag{19.57}$$

When equations (19.56) and (19.57) are substituted in equation (19.55), we have

$$\begin{aligned} -aRT \ln f_A - bRT \ln f_B + dRT \ln f_D + eRT \ln f_E& \\ - aF_A^\circ - bF_B^\circ + dF_D^\circ + eF_E^\circ &= 0 \end{aligned} \tag{19.58}$$

which may be written in the form

$$d\text{F}_\text{D}^\circ + c\text{F}_\text{E}^\circ - a\text{F}_\text{A}^\circ - b\text{F}_\text{B}^\circ = -RT \ln \frac{f_\text{D}{}^d f_\text{E}{}^e}{f_\text{A}{}^a f_\text{B}{}^b} \tag{19.59}$$

But the left-hand terms of equation (19.59) represent the standard free energy change for the reaction, ΔF°, and the right-hand term equals $-RT \ln K_f$ where K_f is the equilibrium constant in terms of fugacities defined by equation (12.82). Equation (19.59) is, therefore, identical with equation (12.81), which is

$$\Delta F^\circ = -RT \ln K_f$$

Fugacity of Substances in Solution.—When a substance is present in solution, its fugacity depends on the composition as well as on the temperature and pressure of the solution. At constant temperature and pressure, it is, therefore, necessary to express the fugacity of a component as a function of the partial molal free energy of this component in solution. Similarly, the change of fugacity of a component with pressure or with temperature at constant composition is measured by the change of the partial molal free energy of this component with these variables. These relations for the component 1 may be obtained from equations (19.33) and (19.51). They are

$$\left(\frac{\partial \ln f_1}{\partial P}\right)_{T,N} = \frac{\overline{\text{V}}_1}{RT} \tag{19.60}$$

and

$$\left(\frac{\partial \ln f_1}{\partial T}\right)_{P,N} = \frac{\overline{\text{H}}_1^\circ - \overline{\text{H}}_1}{RT^2} \tag{19.61}$$

These equations show why we need experimental data on the partial molal volumes and heat contents instead of the corresponding molar values when we desire to calculate the change of fugacity of a component of a solution with temperature or with pressure.

The relations between the various partial molal properties and the values for 1 mole of the solution may be obtained by application of some of the equations derived in Chap. 18 for partial molal quantities in general. Thus, from equation (18.21), we have, for 1 mole of solution,

$$\text{V}_i = N_1\overline{\text{V}}_1 + N_2\overline{\text{V}}_2 + \cdots \tag{19.62}$$

$$\text{H}_i = N_1\overline{\text{H}}_1 + N_2\overline{\text{H}}_2 + \cdots \tag{19.63}$$

Therefore, we may add equations (19.60) and (19.61), respectively, for all the components in the solution to obtain the corresponding equations for 1 mole of solution, namely,

$$N_1\left(\frac{\partial \ln f_1}{\partial P}\right)_{T,N} + N_2\left(\frac{\partial \ln f_2}{\partial P}\right)_{T,N} + \cdots = \frac{\text{V}_i}{RT} \tag{19.64}$$

and

$$N_1\left(\frac{\partial \ln f_1}{\partial T}\right)_{P,N} + N_2\left(\frac{\partial \ln f_2}{\partial T}\right)_{P,N} + \cdots = \frac{\mathrm{H}_i^\circ - \mathrm{H}_i}{RT^2} \qquad (19.65)$$

Gibbs-Duhem Equation.—From equation (18.23), which was derived under the conditions of constant temperature and pressure for 1 mole of solution, we have, in terms of the partial molal free energies,

$$N_1 \frac{\partial \overline{\mathrm{F}_1}}{\partial N_1} + N_2 \frac{\partial \overline{\mathrm{F}_2}}{\partial N_1} + \cdots = 0 \qquad (19.66)$$

This fundamental relation was derived by Gibbs in terms of his thermodynamic functions. When the partial molal free energy equations, such as equations (19.53), are differentiated with respect to N_1, since F_1° and F_2°, and so forth, are not functions of composition, we have

$$\left.\begin{aligned}\frac{\partial \overline{\mathrm{F}_1}}{\partial N_1} &= RT\frac{\partial \ln f_1}{\partial N_1}\\ \frac{\partial \overline{\mathrm{F}_2}}{\partial N_1} &= RT\frac{\partial \ln f_2}{\partial N_1}\end{aligned}\right\} \qquad (19.67)$$

It is apparent that equation (19.66) may, therefore, be expressed in the form

$$N_1 \frac{\partial \ln f_1}{\partial N_1} + N_2 \frac{\partial \ln f_2}{\partial N_1} + \cdots = 0 \qquad (19.68)$$

For vapors that obey the gas laws, $f = P$, and we have the corresponding equation for the partial pressures of vapors

$$N_1 \frac{\partial \ln P_1}{\partial N_1} + N_2 \frac{\partial \ln P_2}{\partial N_1} + \cdots = 0 \qquad (19.69)$$

This equation is called the *Duhem*[1] *equation.*

For a binary solution, we have, from equation (19.68), the relation between the fugacities of the two components

$$\frac{\partial \ln f_1}{\partial \ln f_2} = -\frac{N_2}{N_1} = \frac{N_1 - 1}{N_1} \qquad (19.70)$$

The corresponding relation for the vapor pressures, where they do not differ too widely from the fugacities, is

$$\frac{\partial \ln P_1}{\partial \ln P_2} = -\frac{N_2}{N_1} = \frac{N_1 - 1}{N_1} \qquad (19.71)$$

These equations have been verified for the vapor pressures of binary

---

[1] DUHEM, *Compt. rend.*, **102,** 1449 (1886).

systems. Consequently, they may be used to test the experimental vapor pressure data for solutions.

ACTIVITY

The function activity is applied chiefly to the components of solutions whose absolute fugacity values are difficult to determine. The activity of pure substances is seldom calculated from the fugacity through the relations in equation (19.9). For solutions, however, the activity is the function almost exclusively used. Thus, for component 1 in a solution, we have

$$a_1 = \frac{f_1}{f_1^0}$$

Similarly, in terms of component 1, the general activity equation (19.8) is expressed as

$$\overline{F_1} = RT \ln a_1 + B_1 \qquad (19.72)$$

The standard state of component 1 may be selected as any state for which its activity a_1 is assigned the value of unity. The integration constant B_1 is evidently equal to the free energy of this component in this selected state, and its numerical value must, therefore, be altered by any change that results in an altered value of the standard free energy. As we stated earlier, the activity is used in a relative sense so that the state selected for this standard state varies according to the convenience of the experimenter. Illustrations of such change in standard state are given in the latter part of the chapter. Since the activity is used as an empirical function to play the role of concentration in the free energy equations, a comparison with equations (19.14) and (19.18) suggests that the standard free energy B_1 is a function of both temperature and pressure.

Standard States of Unit Activity.—Because the activity function a is a relative empirical function, it need not be, and is not, always referred to a single standard state of a substance. The fugacity of a substance in several phases in equilibrium has a single value for this substance in every phase in which it is present but activities are defined in relative units, and the standard states chosen for a component may vary from phase to phase. Then the activity of the component may have a different value in each of the phases at equilibrium. Although the selection of arbitrary standard states facilitates the calculation of activity from the experimental data in any one problem, it makes less convenient the comparison of systems whose activities are based on different standard states.

At constant temperature and pressure, we may select any state of the solvent or solute, whether that of the pure component or that of the component in a solution of a given composition, as the standard state for which the activity of the component is designated as unity. In this standard state, the partial molal free energy has the value $\overline{F}_1^\circ$. It is evident from equation (19.72) that, when $a_1 = 1$, $B_1 = \overline{F}_1^\circ$ and equation (19.72) may be written in the form

$$\overline{F}_1 - \overline{F}_1^\circ = RT \ln a_1 \qquad (19.73)$$

where $RT \ln a_1$ represents the difference between the partial molal free energy in any state and that of the standard state where $a = 1$. It is evident also that there are as many different values of $\overline{F}_1^\circ$ as there are different states designated as standard. Some of the different methods in common use for expressing activity, each of which results in a different standard state, are given below:

1. *For a Gas, $a = f$. Standard State, the Gas at Unit Fugacity Where $a = f = 1$.*—When the activity of a gas is defined in terms of its fugacity, it is defined in the absolute units such as atmospheres. Under these conditions, B_1 in equation (19.72) is identical with the standard free energy F_1° in equation (19.53). Because we have already discussed some of the fugacity equations, we shall not discuss this standard state further.

2. *For a Solvent or Solute, a Becomes Equal to N When $N = 1$. Standard State, Pure Solid or Pure Liquid.*—When the standard state of a component is so selected that the activity is unity when the mole fraction is unity, the substance in this state is the pure substance. Under these conditions, B_1 in equation (19.72) has a value equal to the molar free energy of the pure liquid or solid. Because the free energy of the pure substance is a function of the temperature and pressure in accordance with equation (10.41), the standard free energy for this state will be such a function. The standard state may, of course, be defined at unit pressure, in which case the free energy of the standard state is not a function of the pressure.

In completely miscible systems such as those of gaseous solutions, of liquids in liquids, and of solids in solids, the pure components of the solutions represent convenient reference states, especially for solutions that do not deviate too widely from ideal behavior. In solutions of this kind, there is no fundamental difference between the behavior of the two components and no theoretical reason for classifying one component as the solvent and the other as solute. Accordingly, both components are represented by similar functions. In many solutions, however, the solute does not approximate the behavior of ideal solutions even though it obeys the dilute solution laws based on Henry's law and even though the solvent in these "dilute" solutions is approximately ideal. In these solutions the standard state chosen for the solvent is commonly that of the pure solvent whereas the standard state selected for the solute is not the pure solute but that of the solute in an infinitely dilute solution.

3. *For a Solute, a Becomes Equal to N When N = 0. Standard State, the Solute in Solution When a = 1 Mole Fraction Unit.*—When the solution is formed from components not miscible in all proportions, it is convenient to select a standard state for the solute other than that of the pure solute. For example, when the solute is a solid with a limited solubility, its maximum concentration in the solution is limited by its solubility. If the solvent, component 1, is a liquid, the pure liquid may still be used as its standard state, the activity of the solvent approaching the mole fraction as the mole fraction approaches unity as in Method 2. However, the mole fraction of a partly miscible solute, usually designated as component 2, cannot approach unity in the solution.

For this reason, the activity of the solute may be defined as approaching the mole fraction of the solute when the solution becomes more and more dilute. Then a becomes equal to N at the limit $N = 0$ so that

$$\lim_{N=0} \frac{a}{N} = \frac{0}{0} = 1$$

In a solution that is ideal over the whole concentration range, $a/N = 1$ for all values of N including both $N = 1$ (Method 2) and $N = 0$ (Method 3). For a solute so dilute that Henry's law is obeyed, the ratio of a/N is constant over the Henry's law range, but the solute need not have the same Henry's law constant in the different solvents.

If the activity is placed equal to the mole fraction at $N = 0$, the standard state of unity activity may be a hypothetical state even for completely miscible components. Thus, the activity of a solute may still be less than unity in a nonideal solution when N_2 approaches unity. And, in a solution in which the solute is a gas or a solid and has a limited solubility, the mole fraction of the solute in the solution cannot equal unity even if the dissolved solute forms an ideal solution. Then the activity of unity represents an extrapolation to a pure liquid solute. In either case, the state of unit activity represents merely an extrapolation of the activity function to a hypothetical state.

4. *For a Solute, a Becomes Equal to m When m = 0. Standard State, the Solute in Solution When a = 1 in Molal Units.*—In aqueous solution, the concentration of the solute is usually expressed in moles per liter of solution (molarity) or moles per 1,000 grams of solvent (molality). Because the latter method expresses concentration in weight units that are independent of the temperature, it is chosen for most physicochemical work. When concentration is expressed in molality m, the standard state chosen is that in which activity has the value of unit molality. In very dilute solutions, the molality of a solute is proportional though not equal to the mole fraction of solute. At the higher concentrations, however, the two are no longer proportional. In the ideal solution, the

molality of the solute cannot be proportional to the mole fraction beyond the very dilute range for mathematical reasons, since molality represents *mole ratios* rather than *mole fractions.* For completely miscible solutions that do not depart too widely from ideality, the expression of activity in terms of molality is not suitable, in part because the entire concentration range cannot be plotted on one diagram. The "molal" activity is used principally for aqueous solutions of electrolytes that are not completely soluble and that do not follow the laws of ideal solution at all. For such systems, this method of expressing concentrations is convenient. At the same time, the deviation from the form of the ideal solution equation causes no concern, for this equation is not followed by the solute regardless of the particular selected standard state.

5. *For a Solute, a Becomes Equal to C When C = 0. Standard State, the Solute in Solution at a = 1 Molar.*—The expression of solute concentrations in volume concentration units is traditional. Although the quantity of solvent in a molar solution is undetermined and although the number of moles of solute in a liter of solution varies with temperature because of the thermal expansion of solutions, volume concentrations are still used in certain types of problems. With the exceptions indicated above, the activity function of a solute in a molar system behaves like the activity in a molal system. Both systems give values that diverge widely from those of the mole fraction system. In dilute aqueous solutions, the volume of a liter of solution is approximately equal to that of 1,000 grams of water, and the activities in the molar and molal systems are essentially equal.

Change of Activity with Temperature and Pressure.—The change of fugacity with temperature and pressure could be expressed in relatively simple terms, for the standard state is so defined that it can be expressed as a known function of temperature. As defined, it is not a function of the pressure at all. In general, the standard state of unit activity is a function of both temperature and pressure. This statement applies to pure solvent or pure solute as standard states. If the standard state of the solute is defined in terms of the infinitely dilute solute in a solution, as in Methods 3 and 4, the state for which activity is unity may depend on the composition of the solution as well as on temperature and pressure.

It is clear from equation (19.73) that we cannot express the change of activity with temperature or pressure unless we know how both $\bar{F}$ and $\overline{F^0}$ change with these variables. The change of the standard partial molal free energy with temperature or pressure depends in turn on the way in which the standard state is defined.

It is possible, of course, so to define the standard state that it does not change with temperature and pressure. This practice does not eliminate the problem, however; for, in an experiment carried on under the usual conditions of constant temperature and pressure, there is no direct comparison between the activity of a component in the solution and at the standard state if the experimental temperature and pressure differ from the temperature and pressure chosen for the standard state. Under these conditions, data are still needed to determine the relation between the activity chosen at a reference state under the experimental conditions and the activity at the standard state. Because there is no general agreement on the methods of defining standard states, we shall not give here equations for the change of activity with temperature and pressure.[1] For Method 1, the equations derived for fugacity obviously apply. For the other methods, any specific definition establishes the variance of the standard free energy of a component with temperature and pressure.

Activity Coefficient.—The composition of solutions is expressed in units that indicate the relative proportions of the various components present. It is for many purposes convenient to tabulate not the actual activities of the components in these solutions but the ratios of the activities to the concentrations as expressed in the customary units. These ratios are called the *activity coefficients.* In general, there are as many different sets of activity coefficients as there are standard states. Between all the sets of activity coefficients based on activities in mole fraction units, there exist definite ratios that permit the ready calculation of one set from another. However, because activities expressed in molalities or molarities are not proportional to those expressed in mole fractions (for mathematical reasons), the corresponding activity coefficients must also diverge from each other. The symbol γ is widely used for the activity coefficient when the activity is expressed in molalities. The symbol f is also widely used. We shall reserve this symbol for the activity coefficient when activities are expressed in molarities. To distinguish between these coefficients and that for the activity expressed in mole fraction units, we shall denote the latter coefficient by α.

Mole Fraction Activity Coefficient.—Let the mole fraction activity coefficient be defined by the ratio

$$\alpha = \frac{a}{N} \tag{19.74}$$

It is evident that α expresses the ratio between the *effective* mole fraction and the *actual* mole fraction of a component in a solution. When the activity coefficient is introduced into equation (19.73), we have

$$\begin{aligned} \overline{F}_1 - \overline{F}_1^\circ &= RT \ln \alpha_1 N_1 \\ &= RT \ln \alpha_1 + RT \ln N_1 \end{aligned} \tag{19.75}$$

---

[1] Some of the possibilities and inconsistencies are discussed by R. W. Goranson, *J. Chem. Phys.*, **5**, 107 (1937), and L. H. Adams, *Chem. Rev.*, **19**, 1 (1936).

For the ideal solution, α obviously equals unity. For the nonideal solution, α is used as a convenient term for expressing the deviation of the component from the laws of ideal solution.

When the standard state is defined as in Method 2 where $a = 1$ when $N = 1$, the activity coefficient is evidently unity at the standard state. For any other composition, α may be greater than, less than, or equal to unity. The Gibbs-Duhem equation applies here, however, so that the behavior of the activity coefficient for one component is related to those of the other components. This relation enables us to calculate activity coefficients for both or all components from limited sets of data.

When the standard state is defined as in Method 3 above, it appears that the activity coefficient α equals unity at $a = N = 0$, that is, in the infinitely dilute solution and not necessarily at $N_2 = 1$ where a_2 may differ widely from N_2. For the ideal solution, α is unity at both concentration limits. But when α is greater than unity over the entire concentration range, it appears from equation (19.74) that the solute reaches its standard state $a_2 = 1$ at a concentration in which the mole fraction is less than unity. Similarly, when α is less than unity, the solute reaches its standard state $a_2 = 1$ in the hypothetical state where the mole fraction of the solute is greater than unity.

Molal Activity Coefficient.—In a solution in which the activity is expressed in terms of molalities, the molal activity coefficient is defined by the ratio

$$\gamma = \frac{a}{m} \tag{19.76}$$

This activity coefficient expresses the ratio between the *effective* molality and the *actual* molality of a component in a solution. When, as in Method 4, a is so defined that it becomes equal to m in the infinitely dilute solution, $\gamma = 1$ in such a solution. When this activity coefficient is introduced into equation (19.73), we obtain, for the solute,

$$\begin{aligned} \overline{F}_2 - \overline{F}_2^0 &= RT \ln \gamma_2 m \\ &= RT \ln \gamma_2 + RT \ln m \end{aligned} \tag{19.77}$$

We use here the subscript 2 because this method of expressing concentration is reserved for the solute. As we stated earlier, equation (19.77) is not suitable for expressing the activities of concentrated solutions that are nearly ideal, for m is not proportional to N except in very dilute solutions. Thus, an ideal solution has a value of α equal to unity at all concentrations but γ cannot be unity for mathematical reasons.

Molar Activity Coefficient.—When the activity is expressed in molarities, as in Method 5, C being the concentration in this volume concentration unit, the molar activity coefficient is defined by the ratio

$$f = \frac{a}{C} \tag{19.78}$$

In infinitely dilute aqueous solutions, C approaches m and f approaches γ as the density of the solution approaches unity. Because C diverges from m for more concentrated solutions, f also diverges from γ. In nonaqueous solutions, C and m do not approach the same limit. When equation (19.78) is combined with (19.73), we have

$$\begin{aligned} \overline{F}_2 - \overline{F}_2^\circ &= RT \ln f_2C \\ &= RT \ln f_2 + RT \ln C \end{aligned} \tag{19.79}$$

Because the standard states, where the activity is unity, are different when the activity is expressed in mole fraction, molal, or molar units as previously stated, it follows that $\overline{F}_2^\circ$ has a different value in each of equations (19.75), (19.77), and (19.79).

Relations between the Different Concentration Units.—In discussing the relations between the various concentration units, we shall use the following symbols. They are assembled here for convenient reference.

n_1 = number of moles of solvent.
n_2 = number of moles of solute.
M_1 = molar weight of solvent.
M_2 = molar weight of solute.
d = density of solution.
d° = density of solvent.
N_1 = mole fraction of solvent.
N_2 = mole fraction of solute.
C = molarity of solute.
m = molality of solute.
w_1 = weight of solvent per liter of solution.

Because the weight of solvent in a liter of solution is

$$w_1 = 1{,}000d - CM_2$$

we have

$$n_1 = \frac{w_1}{M_1} = \frac{1{,}000d - CM_2}{M_1} \tag{19.80}$$

Let us now consider a solution with a single solute and a composition defined by the mole ratio n_2/n_1, the solute having the partial molal free energy $\overline{F}_2$. The composition of this solution may be expressed in molar, molal, and mole fraction units as follows:

In 1 liter of solution where $n_2 = C$ and n_1 has the value in equation (19.80), we have

$$\frac{n_2}{n_1} = \frac{CM_1}{1{,}000d - CM_2} \tag{19.81}$$

This relation may also be expressed in the form

$$C = \frac{1{,}000dn_2}{M_1n_1 + M_2n_2} \tag{19.82}$$

Similarly, for the molal concentration of this solution,

$$\frac{n_2}{n_1} = \frac{m}{1{,}000/M_1} = 0.001\ mM_1 \tag{19.83}$$

whence,

$$m = \frac{1{,}000n_2}{M_1n_1} \tag{19.84}$$

In mole fraction units, where

$$N_2 = \frac{n_2}{n_1 + n_2} \tag{19.85}$$

we have, similarly,

$$\frac{n_2}{n_1} = \frac{N_2}{N_1} = \frac{N_2}{1 - N_2} \tag{19.86}$$

For this solution, therefore, the relation between these different concentration units is

$$\frac{CM_1}{1{,}000d - CM_2} = \frac{mM_1}{1{,}000} = \frac{N_2}{1 - N_2} \tag{19.87}$$

The relations in equation (19.87) may be applied to any solvent. When more than one solute or an ionizing solute is present, equation (19.85) and the subsequent equations must obviously be modified. (Why?) For very dilute aqueous solutions, d approaches $d°$, CM_2 becomes small compared with 1,000, N_2 becomes small compared with unity, and $1{,}000/M_1 = 55.51$, so that equation (19.87) takes the limiting value

$$\lim_{\frac{n_2}{n_1}=0} \frac{C^*}{55.51d°} = \frac{m^*}{55.51} = N_2^* \tag{19.88}$$

where the starred concentrations refer to concentrations of the solute at infinite dilution.

Relations between the Different Activity Coefficients.—Because the molar and molal concentration units and their corresponding activity coefficients are used mostly for aqueous solutions, we shall derive the relationships between these coefficients for such solutions. Let us consider a solution so dilute that the activity of the solute becomes equal to the concentration, as for Methods 3, 4, and 5, the concentration of solute in mole ratio being n_2^*/n_1 and its partial molal free energy being

$\overline{F}_2^*$. For this dilute solution, the various activities and corresponding coefficients become

$$\left.\begin{array}{lll} a_C^* = C^*; & a_m^* = m^*; & a_N^* = N^* \\ f = \gamma = \alpha = 1 & & \end{array}\right\} \qquad (19.89)$$

where the starred symbols as in the previous section refer to the solute at infinite dilution.

On combining equations (19.88) and (19.89), we have

$$\frac{a_C^*}{d^\circ} = a_m^* = 55.51 a_N^* \qquad (19.90)$$

These activities are related to the corresponding activities of the solute in the solution with concentration n_2/n_1 by the defining equation

$$\overline{F}_2 - \overline{F}_2^* = RT \ln \frac{a}{a^*} \qquad (19.91)$$

so that the activities of the solute in these two solutions in any concentration unit are expressed by the ratios

$$\frac{a_C}{a_C^*} = \frac{a_m}{a_m^*} = \frac{a_N}{a_N^*} \qquad (19.92)$$

When equation (19.90) is combined with (19.92) we have, therefore,

$$\frac{a_C}{d^\circ} = a_m = 55.51 a_N \qquad (19.93)$$

This equation shows the relation between the activities of a solute in terms of the various concentration units when the activities in infinitely dilute solution approach the concentrations as required by equation (19.89).

Now, from equation (19.93) and the definition of activity coefficients in equations (19.74), (19.76), and (19.78), we obtain the equation

$$\frac{fC}{d^\circ} = \gamma m = 55.51 \alpha N_2 \qquad (19.94)$$

which expresses the relations between the activity coefficients and concentrations. Equation (19.94) may be combined with equation (19.87) to yield other relations among f, γ, and α. It is clear that, in a solution, f, γ, and α have different values and that, for the molal standard state when $\gamma m = 1$, fC and αN_2 will not be unity. When the concentration of the solute is expressed in molarity or mole fraction, the solute is at its standard state in a solution having a different concentration.

Activity of Cadmium in Cadmium Amalgam. 1. *The Saturated Amalgam as the Standard State.*—We have indicated that any state of a substance may be selected as the standard state and that when the necessary free energy data are available the activities relative to this state may be derived. Some of the principles involved in the calculation of activities and activity coefficients and in a change in standard state will be illustrated for solutions of cadmium in mercury.

When cadmium is added to mercury, it dissolves in the liquid until a saturated solution is reached. According to Hulett and De Lury,[1] this saturated liquid amalgam at 25°C contains 5.573 per cent cadmium or 0.05902 gram of cadmium per gram of mercury. When more cadmium is added, a solid phase rich in cadmium is formed, which is in equilibrium with the mercury-rich liquid phase. Hulett and De Lury measured the difference in potential between a saturated amalgam and a series of dilute amalgams of cadmium down to concentrations of 1 part by weight of cadmium per 100 million of mercury. The very dilute amalgams showed a drifting potential, however, probably because the cadmium was slowly oxidized. Here a small amount of oxidation produces a large relative change in the amount of cadmium remaining in the dilute amalgam. Accordingly, we shall consider only the amalgams with the concentrations listed in column (2) of Table 19.1. Values for the emf of the cells formed with the saturated amalgam as one electrode and the dilute amalgams in turn as the other electrode, a solution of cadmium sulfate being the electrolyte, are listed in column (1).

The cell may be indicated as follows:

$$\text{Cd(satd amalgam); CdSO}_4\text{(solution); Cd(dil amalgam)}$$

the reaction being the transference of cadmium from the saturated to the dilute amalgam as expressed by the equation

$$\text{Cd(satd amalgam)} = \text{Cd(dil amalgam)} \tag{19.95}$$

From equation (19.4) or (19.91), we have, for the relation between the activity of cadmium and the change in free energy,

$$\Delta F = \bar{F}_{\text{Cd(dil)}} - \bar{F}_{\text{Cd(satd)}} = RT \ln \frac{a_{\text{(dil)}}}{a_{\text{(satd)}}} \tag{19.96}$$

It is evidently convenient to select the saturated amalgam as the standard state with $a_{\text{(satd)}} = 1$, so that equation (19.96) becomes

$$\Delta F = \bar{F}_{\text{Cd(dil)}} - \bar{F}^0_{\text{Cd(satd)}} = RT \ln a' \tag{19.97}$$

where a' is the activity of the cadmium referred to the cadmium in the saturated amalgam as the standard state.

Because the change in free energy is related to the equilibrium emf

---

[1] HULETT, G. A., and R. E. DE LURY, *J. Am. Chem. Soc.*, **30**, 1805 (1908).

TABLE 19.1.—THE ACTIVITY OF DILUTE CADMIUM AMALGAMS AT 25°C

Measured emf, $E_{(dil)} - E_{(satd)}$, volts	Concentration		Standard state, $a'_{(satd)} = 1$		Standard state, $a'' = N$ at $N = 0$		Standard state, $a''' = N$ at $N = 1$	
	Grams of cadmium/gram of mercury	Mole fraction of cadmium	Activity, a'	Activity coefficient, $\alpha' = a'/N$	Activity, a''	Activity coefficient, $\alpha'' = a''/N$	Activity, a'''	Activity coefficient, $\alpha''' = a'''/N$
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
0.000000	0.05902	0.09529	1	10.49	0.11005	1.155	0.01968	
0.005366	0.040000	0.06663	0.6585	9.883	0.07247	1.088	0.01296	
0.014445	0.020000	0.03446	0.3247	9.423	0.03573	1.037	0.0_26390	
0.023375	0.010000	0.01753	0.1620	9.241	0.01783	1.017	0.0_23188	
0.05294	0.001000	0.0_21781	0.01621	9.102	0.0_21784	1.002	0.0_33190	
0.08254	0.000100	0.0_31784	0.0_21617	9.064	0.0_31780	0.998	0.0_43182	
0.1121	0.000010	0.0_41785	0.0_31619	9.070	0.0_41782	0.998	0.0_53186	
0.1416	0.000001	0.0_51785	0.0_41628	9.120	0.0_51792	1.004	0.0_63204	
∞	0	0	0	9.087	0	1	0	

by equation (11.12), we have for these amalgams

$$-nFE = \Delta F = RT \ln a' \tag{19.98}$$

On substituting the proper numerical values in equation (19.98), we find the relation between log a' and E, which is

$$\log a' = -\frac{2 \times 96{,}501}{2.3026 \times 8.3130 \times 298.16} E = -33.816E \tag{19.99}$$

From these values of log a', we obtain the values of a' listed in column (4) of Table 19.1. These values may be compared with the corresponding values of the mole fraction in column (3). Observe that in the more dilute solutions the change in activity of cadmium is proportional to the change in mole fraction as required by Henry's law. The ratio a'/N, which is the activity coefficient α', is tabulated in column (5). The irregularities in the value of α' for the more dilute solutions indicate the presence of some experimental error.

2. *Cadmium in Mercury at $N = 0$ as the Standard State.*—The selection of the saturated amalgam as a standard state was arbitrary; it was justified on the grounds of convenience. However, the activities and the activity coefficients calculated on this basis have no theoretical significance. Because the activity parallels the concentration in the more dilute solutions, it is instructive to identify the activity with the mole fraction in these solutions. This procedure is equivalent to Method 3 for which $a = N$ at $N = 0$.

Because of the experimental errors in the dilute amalgams reflected in the fluctuations of α' in this "ideal dilute solution" range, we must find some way of obtaining a reasonable limiting value for α'. We might arbitrarily select the solution containing 1 gram of cadmium per 1,000 grams of mercury as representing the ideal dilute solution with $a_1 = N_1$. If this is done, we may obtain the activities on the new scale from the general relation in equation (19.92) for the relations between activities on different scales. Thus, we have for the activity ratio for a second state, here the saturated amalgam, and a first state, here a dilute amalgam,

$$\frac{a_2'}{a_1'} = \frac{a_2}{a_1} \tag{19.100}$$

But a_2' was defined as unity, so that on the new scale the activity of the saturated amalgam is

$$a_2 = \frac{a_1}{a_1'} = \frac{0.001781}{0.01621} = 0.1099$$

Observe, however, that the above method establishes a new activity scale on a single experimental point in the dilute range. We shall, therefore, discard this method and shall set up a scale of activity $a = a''$ that considers all the points given for the dilute range.

Because $a' \doteq 0$ and $a'' = N \doteq 0$ at infinite dilution, we cannot substitute these values for a_1' and a_1 in equation (19.100). However, if this equation is placed in the form

$$\frac{a_2'}{a_2''} = \frac{a_1'}{a_1''} \tag{19.101}$$

we see that the ratio of the activities of the saturated amalgam on the two scales is equal to the indeterminate 0/0, which can be evaluated.

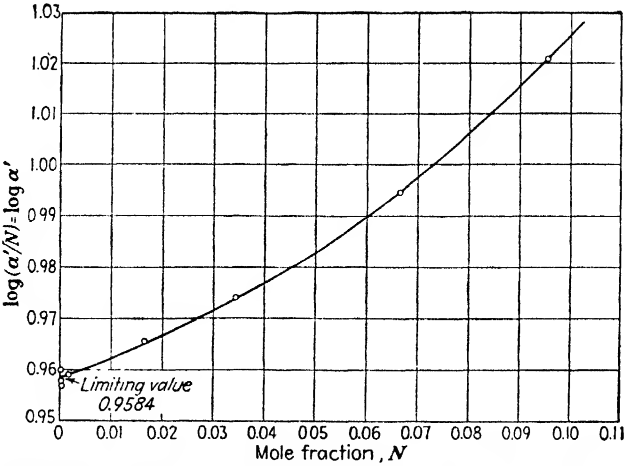


FIG. 19.1.—Graphical computation of the limiting value of an activity ratio for cadmium in mercury.

Because we define a'' as equal to N at low concentrations, we have, from equation (19.101),

$$\lim_{a''=N=0} \frac{a'}{a''} = \frac{a'}{N} = \alpha = \frac{0}{0} \tag{19.102}$$

It appears from column (5) of Table 19.1 that 0/0 has a value of approximately 9.1.

When all the values of $\log (a'/N) = \log \alpha'$ are plotted against N as in Fig. 19.1, a smooth curve may be drawn through all the points except those for the lowest concentrations, and these scatter about the curve that is extended to $N = 0$. From this graph the limiting value of log (a'/N) appears to be 0.9584, whence we have $0/0 = a'/N = 9.087$. From equation (19.101), it follows that, because

$$\frac{a_2'}{a_2''} = 9.087$$

for the saturated amalgam,

$$a_2'' = \frac{a_2'}{9.087} = \frac{1}{9.087} = 0.11005$$

Compare this value with that obtained when the 1/1,000 amalgam was selected as having an activity coefficient equal to unity.

The ratio 0.11005 between the a'' and the a' activity scales may now be used to calculate the activities for the other concentrations. These values are tabulated in column (6) of Table 19.1. The corresponding values of the activity coefficient α'' are listed in column (7). The fluctuations of the values of α'' about a mean value of unity at the lower concentrations are an indication of the experimental errors in this range.

3. *Pure Cadmium as the Standard State.*—In order to refer the activity of the cadmium in the amalgams to the activity of cadmium in the pure state where $N = 1$, we must know the difference in free energy, or some related function, between pure cadmium and the cadmium in one of the amalgams listed in Table 19.1. This free energy change and the corresponding activity ratio may be calculated from the measured emf of a cell at 25°C containing pure cadmium as one electrode and the saturated amalgam at the other. For this cell,[1]

$$\text{Cd(c)} = \text{Cd(in satd amalgam)}; \qquad E = 0.05045 \text{ int volt} \quad (19.103)$$

Because pure cadmium is selected as the new standard state, its molar free energy is $F^\circ_{\text{Cd(c)}}$ and its activity is unity. If the activities on this scale are indicated as a''', we have, as before,

$$\Delta F = \bar{F}_{\text{Cd(satd)}} - F^\circ_{\text{Cd(c)}} = RT \ln a'''_{\text{(satd)}}$$

From the relations in equations (19.96) to (19.99), this equation becomes

$$\log a'''_{\text{(satd)}} = -33.816E = -33.816(0.05045)$$
$$= -1.7060$$

whence

$$a'''_{\text{(satd)}} = 0.01968$$

From this value, the activities in column (4), and equation (19.100), it is evident that the activities on this scale may be calculated for all the concentrations. These values of a''' are listed in column (8). Observe that the activities of the cadmium in the amalgams are smaller than the corresponding mole fractions over the entire concentration range. Column (9) for the activity coefficients on this activity scale is left blank. The student should calculate these coefficients.

The free energy change for the transference of cadmium between any two states can be obtained from the activity ratio on any scale.

---

[1] PARKS, W. G., and V. K. LA MER, *J. Am. Chem. Soc.*, **56**, 90 (1934).

Thus, for the transference of a mole of cadmium from the saturated amalgam to the $1/10^5$ amalgam we have, for these three scales,

$$\frac{a_2'}{a_1'} = \frac{a_2''}{a_1''} = \frac{a_2'''}{a_1'''}$$

so that, with the proper numerical substitutions,

$$\frac{a_2}{a_1} = \frac{0.0_3 1619}{1} = \frac{0.0_4 1782}{0.11005} = \frac{0.0_5 3186}{0.01968} = 0.0001619$$

from which we have

$$\log \frac{a_2}{a_1} = \bar{4}.2092 = -3.7908$$

Because

$$\Delta F = -nFE = RT \ln \frac{a_2}{a_1}$$

the emf corresponding to this activity ratio at 25°c is

$$\begin{aligned} E &= -0.02957 \log \frac{a_2}{a_1} = 0.02957(3.791) \\ &= 0.1121 \text{ volt} \end{aligned}$$

which is the observed value listed in column (1).

Gibbs-Duhem Equation.—Because the Gibbs-Duhem equation expresses a relation between the partial molal free energies of the different components in a solution, it enables us to calculate certain relations from limited data. Thus, for a binary solution at constant temperature and pressure, we have, from equation (18.22),

$$N_1\, \partial \overline{\mathrm{F}}_1 = -N_2\, \partial \overline{\mathrm{F}}_2$$

From equation (19.4), therefore,

$$N_1 \, d \ln a_1 = -N_2 \, d \ln a_2 \tag{19.104}$$

At constant composition, we obtain, from this equation and equations (19.74), (19.76), and (19.78), the corresponding equations in terms of the activity coefficients

$$N_1 \, d \ln \alpha_1 = -N_2 \, d \ln \alpha_2 \tag{19.105}$$

$$N_1 \, d \ln \gamma_1 = -N_2 \, d \ln \gamma_2 \tag{19.106}$$

$$N_1 \, d \ln f_1 = -N_2 \, d \ln f_2 \tag{19.107}$$

These equations permit us to calculate the activities and activity coefficients for one component from those of the other component.

We shall here emphasize the fact that, because $N_2 = (1 - N_1)$ for a binary solution, $(1 - N_1)$ may be substituted for N_2 in any equation for the solution. Thus, for the ideal solution, the free energy of both solvent and solute may be expressed in terms of the mole fraction of either component.

$$\left.\begin{aligned} dF_1 &= RT\,d\ln N_1 \\ dF_2 &= RT\,d\ln N_2 = RT\,d\ln(1 - N_1) \end{aligned}\right\} \qquad (19.108)$$

However, we cannot write the corresponding relations for a_1 and a_2; for, in general, $a_2 \neq 1 - a_1$. For this reason, we find equations such as the Gibbs-Duhem equation useful. Only with its aid can the free energies of one component be calculated from those of the other.

Problems

19.1. Calculate the activity coefficient α''' for cadmium dissolved in mercury at 25°c from the recorded values of the activity in Table 19.1, pure cadmium being the standard state. What is the value of this activity coefficient at infinite dilution?

19.2. With the aid of the Gibbs-Duhem equation, calculate the activity of the mercury in the amalgams listed in Table 19.1. Consider pure mercury at 25°c as the standard state for mercury. What is the free energy change when 1 mole of pure mercury dissolves in the saturated amalgam?

19.3. Show that for a solution having a single solute and a composition n_2/n_1 the various concentration units are related by the equations

$$\log N_2 = \log m - \log(1 + 0.001mM_1) + \log(0.001\,M_1) \qquad (19.109)$$

$$\log N_2 = \log C - \log[1{,}000d + C(M_1 - M_2)] + \log M_1 \qquad (19.110)$$

19.4. For a solute that dissociates into ν ions, show that the mole fraction N_i of an ion is defined by

$$N_i = \frac{n_i}{n_1 + \nu n_i} \qquad (19.111)$$

If the molality of this ion is m_i, show that

$$\log N_i = \log m_i - \log(1 + 0.001\nu mM_1) + \log(0.001M_1) \qquad (19.112)$$

19.5. For a solute that dissociates into ν ions, derive the relations between C_i, m_i, and N_i for one of the ions corresponding to the relations given in equation (19.87) for a single solute.

19.6. For a solute that dissociates into ν ions, show that the values of α_i, γ_i, and f_i for one of the ions are related by the equations

$$\frac{\alpha_i}{\gamma_i} = 1 + 0.001\nu mM_1 \qquad (19.113)$$

$$\frac{\alpha_i}{f_i} = \frac{d + 0.001C(\nu M_1 - M_2)}{d^\circ} \qquad (19.114)$$

$$\frac{f_i}{\gamma_i} = \frac{d^\circ m}{C} \qquad (19.115)$$

19.7. At 25°c the pressure of hydrogen is represented by the equation

$$Pv = RT(1 + 0.000537P + 3.5 \times 10^{-8}P^2)$$

Calculate the fugacity of hydrogen at 1, 100, and 1,000 atmospheres when the temperature is 25°c.

19.8. Calculate a value for the fugacity of oxygen at 0°C and 1 atmosphere pressure using the Berthelot equation (Prob. 10.13) and the critical constants. Compare with the value derived with the coefficient B.

19.9. The vapor pressure of propylene at 0°C is 5.75 atmospheres and the molar volume of the saturated vapor is 3,410 cc, according to W. E. Vaughn and N. R. Graves [*Ind. Eng. Chem.*, **32,** 1252 (1940)]. The critical constants are $P_c = 45.4$ atm, $T_c = 91.4 + 273.16 = 364.56°\text{K}$, and $\text{v}_c = 180$ cc. When the reduced pressure, $P_r = P/45.4$, has the values 0.05, 0.1, and 0.1267 (saturation pressure), the compressibility factor of the gas $P\text{v}/RT$ has the values, 0.954, 0.907, and 0.875 respectively, at 0°C. According to T. Batuecas [*J. chim. phys.*, **31,** 165 (1934)], the density of propylene gas at 0°C is 1.9149 grams per liter. Plot a suitable function of propylene gas against pressure for the range 0 to 5.75 atmospheres and calculate values of the fugacity of the gas at 0° and the pressures, 0, 1, and 5.75 atmospheres.

CHAPTER 20

REACTIONS IN GALVANIC CELLS

As indicated in the previous chapters, the total reversible work for a reaction that proceeds at constant temperature and pressure is measured by the change in the total work or Helmholtz free energy function A. Similarly, the net or useful reversible work is measured by the change in the Lewis or Gibbs free energy function F. At any given temperature and pressure the value of ΔF for a reaction is calculated from experimental data in one of the four following ways:

1. From known values of the heat of reaction and the entropy of reaction.
2. From measured values of the equilibrium constant or the equilibrium partial pressures or activities of the reacting substances.
3. From tabulated values of the function $(F^\circ - H_0^\circ)/T$ and known values of the heats of formation at the temperature of zero absolute.
4. From the measured reversible value of the emf of a galvanic cell in which the stated reaction occurs.

We have discussed the first three methods in some detail; we shall here discuss the thermodynamic relations as applied to galvanic cells. The reactions of galvanic cells are important because they enable us to measure directly free energies and entropies for solutions of electrolytes that, in general, do not obey the laws of ideal solution.

Galvanic Cells.—In galvanic cells, we meet two classes of electrical conductors: metallic conductors and electrolytic conductors. In metallic conductors, the electricity moves through the conductor without a corresponding movement of the substances of which the conductor is composed. In terms of the electronic theory, the current of electricity consists of a stream of electrons that pass along from one atom to another in the conductor. On the other hand, in electrolytic conductors, called "electrolytes," the carriers of the electricity are of atomic or molecular size, some being positively and some negatively charged. The negatively charged particles have a charge equal to that of one electron or a simple multiple of this charge; the positively charged particles have a charge equal to one or more electronic charges but opposite in sign. In the conduction process, these oppositely charged particles, named "ions" by Faraday, move in opposite directions.

When two metallic conductors, called "electrodes," are dipped into an electrolyte, measurable electric potentials are set up. In chemistry, we are concerned primarily with the potentials at the boundaries between electrode and electrolyte and between electrolyte and electrolyte. However, these potentials can be measured only on formation of a complete electrical circuit that contains, also, boundaries between metal and metal. If the electrodes differ in composition, electrical potentials exist at their junction as well as at the boundaries with which we are concerned. Furthermore, we cannot measure single potentials, so that measurements on galvanic cells give us only *relative* potentials, that is, the differences between potentials and not absolute potentials. However, the assignment of potentials in a circuit can be made in an arbitrary way so long as the observed potential differences are represented. This practice of using relative values, which is inherent in emf measurements, is analogous to the arbitrary assignment of zero relative heat content to the elements in the preparation of heat of formation tables.

When the two electrodes of a galvanic cell with differing potentials are connected by a metallic conductor, a current flows in the circuit. In the external circuit, the conduction is metallic; within the cell, where the conduction is electrolytic, the current is transported bodily by the ions. At the electrode-electrolyte boundary where the change from electrolytic to metallic conduction takes place, the result is a chemical reaction. It is because of these chemical reactions, an essential part of the operation of a galvanic cell, that we study the cells.

Nature of Galvanic Cell Reactions.—In a cell the substance losing electrons to an electrode is being oxidized, and the substance gaining electrons from the other electrode is being reduced. Hence, the chemical reaction accompanying the flow of current is an oxidation-reduction reaction. In an oxidation-reduction reaction in a beaker where the reactants are mixed, the reaction is not reversible; but in the galvanic cell where the oxidation and the reduction take place in parts of the cell physically isolated from each other, the reaction may be made to proceed reversibly. Galvanic cell reactions are especially interesting and important because of their reversible character.

At the same time, we must bear in mind that electrolytes carry the current through the cell; the complete cell reaction must show the materials transported as well as the substances oxidized or reduced at the electrodes. Because electrolytic conduction between the electrodes is an essential requirement of galvanic cells, the types of reaction that can be studied thermodynamically in galvanic cells are limited. A few solid salts are somewhat conducting at temperatures below their melting points, but, as is well known, molten salts and solutions of acids, bases, and salts comprise the chief electrolytic materials, aqueous solutions of electrolytes representing by far the most important type of electrolytic conductors.

In accordance with the laws formulated by Faraday, the extent of an electrode reaction is always directly proportional to the quantity of current passing through the cell, one chemical equivalent of substance being oxidized at one electrode while one equivalent of substance is reduced at the other for each faraday of current passing through the cell. The *faraday*, or equivalent, was previously defined (Chap. 1) as that quantity of electricity, 96,501 int coulombs, which represents the electronic charge per oxidation equivalent of an element or compound. The absolute proportionality between the chemical equivalent and the faraday is a basic fact without which we could not relate the maximum electrical work to the molar free energy change of a reaction. The exactness of Faraday's laws has been fully verified. The number of chemical equivalents deposited per faraday of current is independent of the nature of the dissolved substance, the time or current strength, and the solvent. Richards and Stull[1] found that the same weight of silver, within 0.005 per cent, deposits from fused silver nitrate at 250°c as from an aqueous solution of this salt at 20°c; and Cohen[2] found that the same weight of silver deposits in a coulometer at pressures up to 1,500 atmospheres as in a reference coulometer at atmospheric pressure.

Electrode Reactions.—Because the reducing and the oxidizing action in a galvanic cell take place in different parts of a cell, it is frequently convenient to write separate partial equations for the two simultaneous electrode-electrolyte reactions. These partial equations are called the *half-cell reactions.* We shall consider first some reducing half-cell reactions in which electrons, denoted as e^-, are added to some substance at an electrode. A familiar example is the reduction of silver ions to form a deposit of metallic silver on the electrode as in

$$Ag^+ + e^- = Ag \tag{20.1}$$

This is a common type of electrode reaction for metals. Hydrogen ions react similarly to form a deposit of hydrogen on an inert electrode such as platinum.

$$2H^+ + 2e^- = H_2 \tag{20.2}$$

This electrode is called a *hydrogen electrode;* it is illustrated in Fig. 20.1.

At an inert electrode, many multivalent ions, such as the ferric, stannic, and cupric ions, may be reduced to the corresponding lower valence ions. Thus,

$$Fe^{+++} + e^- = Fe^{++} \tag{20.3}$$

Still another type of reduction is the formation of negative ions from a

---

[1] RICHARDS, T. W., and W. N. STULL, *Proc. Am. Acad. Arts Sci.*, **38**, 409 (1902).

[2] COHEN, E., *Z. Elektrochem.*, **19**, 132 (1913).

neutral substance, such as chlorine gas, at an inert electrode. Thus,

$$Cl_2 + 2e^- = 2Cl^- \qquad (20.4)$$

An electrode at which this reaction takes place is called a *chlorine electrode*. As a modification of equation (20.1) or (20.4), we have the reduction at a silver, silver chloride electrode. This electrode consists of a deposit of crystalline silver chloride on a silver electrode, the electrode reaction being

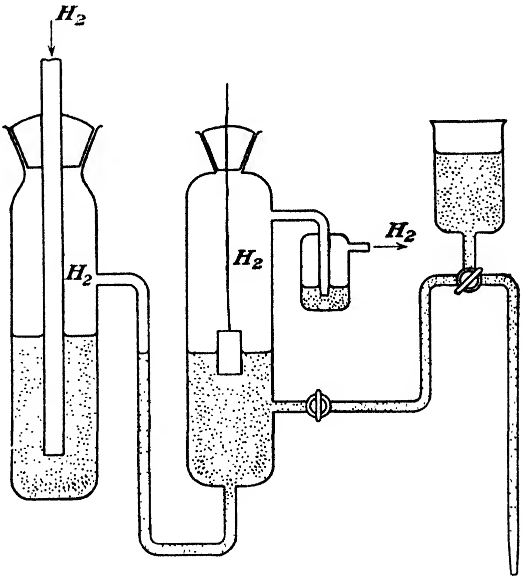


FIG. 20.1.—Diagram of a hydrogen electrode.

$$AgCl(c) + e^- = Ag + Cl^- \qquad (20.5)$$

Figure 20.2 illustrates a silver, silver chloride electrode. The electrode reaction of the calomel half cell, frequently used as a reference electrode, is of this type.

All the above electrode or half-cell reactions are reversible, the direction of the reaction depending only on the direction of the current through the cell. At the electrode where the electrons pass from electrolyte to electrode, the electrode reactions (20.1) to (20.5) are reversed, and the electrode action is an oxidizing one, the oxidizing half-cell reactions being, respectively,

$$\left.\begin{aligned} Ag &= Ag^+ + e^- \\ H_2 &= 2H^+ + 2e^- \\ Fe^{++} &= Fe^{+++} + e^- \\ 2Cl^- &= Cl_2 + 2e^- \\ Ag + Cl^- &= AgCl(c) + e^- \end{aligned}\right\} \qquad (20.6)$$

For each of the electrodes represented by the above reactions, a definite potential exists that depends on the concentration of the various substances and on the temperature and pressure. Because the half-cell reactions do not take place singly but only in pairs, the direction of the reaction depends on the relative potentials of the two half cells that are combined. Thus, if a silver electrode is combined with a hydrogen electrode, reduction takes place at the silver electrode and oxidation at the hydrogen electrode. The cell reaction for the passage of 1 faraday of current through the cell may be represented by a combination of equation (20.1) (reduction) with one-half the reversed equation (20.2) (oxidation), as follows:

$$
\begin{aligned}
Ag^+ + e^- &= Ag \\
\tfrac{1}{2}H_2 &= H^+ + e^- \\
\hline
\tfrac{1}{2}H_2 + Ag^+ &= H^+ + Ag \qquad (20.7)
\end{aligned}
$$

Observe that the sum of the two electrode reactions does not include any negative ion in the reaction. However, during the cell reaction, these negative ions are migrating from the silver electrode toward the hydrogen electrode to preserve the electrical neutrality of the solutions.

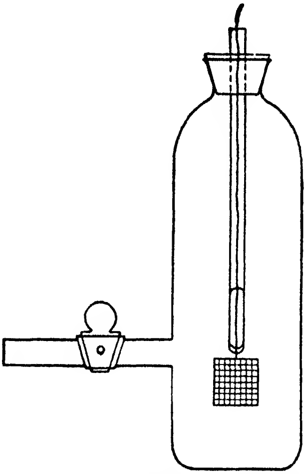


FIG. 20.2.—Diagram of a silver, silver chloride electrode.

Reversible Cell.—In the previous section, we discussed half reactions that could be reversed by the imposition of a sufficient potential. Similarly, when the electrodes are reversible, the cell reaction, such as (20.7), can be reversed if a sufficient emf is opposed to that of the cell. This is not a sufficient criterion of reversibility in the thermodynamic sense, however. As was indicated in Chap. 7, the thermodynamically reversible process is the equilibrium process which may be made to proceed first in one direction and then in the other by an infinitesimal change in one of the thermodynamic functions. If a cell is reversible, the direction of the cell reaction may be controlled by infinitesimal changes in the emf at the electrodes. Thus, if at constant temperature and pressure the emf of the cell is exactly opposed by a counter emf as with a potentiometer, no reaction must take place in the cell. Because small currents pass through the cell in either direction during the process of attaining the balance with the potentiometer, the emf of the cell can remain unchanged at its equilibrium, maximum value only if the electrode reactions are reversible. All the above electrode reactions [equations (20.1) to (20.6)] are reversible in this complete sense.

The statement that the direction of the cell reaction shall be completely controllable by the imposed emf implies that there is no reaction in the cell except at the electrodes, because only the electrode reactions can be controlled by the imposed emf. Any direct reactions among the contents of the cell result in a nonequilibrium process. Furthermore, if the measured emf of a galvanic cell is to be used in thermodynamic calculations it must represent the equilibrium value for some definite known reaction. In some cells, two reactions may proceed at one electrode simultaneously. In such an event, Faraday's laws are not violated because the total quantity of substance liberated at the electrode for each faraday of current is still 1 equivalent of the combined product. Here we cannot be sure, however, whether the measured emf is the equilibrium value for either or neither of the cell reactions. In general, the substances specified in the desired cell reaction should be the strongest oxidizing-reducing agents at their respective electrodes. If not, their reactions must be rapid compared with that of competing reactions. In the words of Gibbs,[1] "If no changes take place in the cell except during the passage of the current, and all changes which accompany the current can be reversed by reversing the current, the cell may be called the perfect electro-chemical apparatus."

A cell is said to be *reproducible* when another cell prepared in the same manner gives the same emf. Obviously, we cannot have confidence in having measured the equilibrium emf of a cell unless the cell is reproducible. However, the reproducibility of a cell does not indicate the nature of the cell reaction. As we shall find on application of thermodynamics, however, the emf of the cell changes in a definite way with a change in concentration of the reacting substances so that unless the emf changes in this fashion when the concentration of a substance is changed the actual cell reaction does not include these substances.

In many cells, a single electrolyte or a uniform electrolyte is present. Cells of this type are said to be *without liquid junctions*. In other cells, however, the two electrodes are bathed in solutions that differ in composition. Where the two half cells of such a cell meet there is an electrolyte-electrolyte boundary of variable thickness between the solutions of different concentration or composition. Such a cell is called a cell *with liquid junction*.

Across this junction, there is diffusion of electrolytes from the solution of higher concentration to that of lower concentration. Because different ions have different mobilities, they tend to diffuse across the boundary at different speeds. A steady state is finally reached in which the faster ions drag the slower oppositely charged ions with them. Accordingly,

---

[1] "The Collected Works of J. Willard Gibbs," p. 338, Vol. 1, "Thermodynamics," Longmans, Green & Company, New York, 1928.

a junction potential is set up that is dependent on the relative speeds of the diffusing ions. The potential of such a junction cannot be measured directly, and it may be difficult to estimate. It can be calculated theoretically for cells with one electrolyte[1]; for more complicated mixtures the treatment is less certain. When a saturated solution of potassium chloride is placed between the two half cells, the liquid junction potential may be reduced to a few millivolts but it is not entirely eliminated. Because of these uncertainties, cells are set up without liquid junctions, whenever possible.

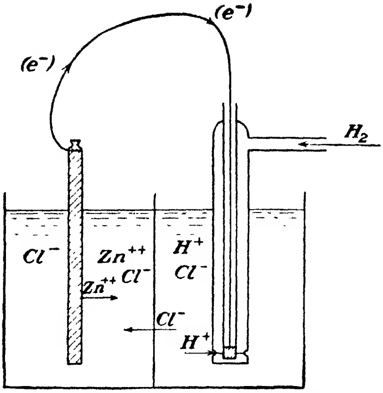


FIG. 20.3.—Diagram of the cell $^-Zn; ZnCl_2:HCl; H_2,Pt^+$.

Conventions.—In Chap. 10, the reaction of zinc with hydrochloric acid was considered for reaction in a beaker and in a galvanic cell. The reaction is not easy to set up in a perfect electrochemical cell, but it will serve to illustrate the conventions used in discussions of cells. A cell for the carrying out of this reaction is illustrated in Fig. 20.3. It consists of a carefully prepared zinc rod, free from strains and impurities, dipping in a solution of zinc chloride, and a hydrogen electrode dipping in a solution of hydrochloric acid. The hydrogen electrode as in Fig. 20.1 consists of a sheet of platinum foil around which pure hydrogen is bubbled. When the surface of the platinum is coated with platinum black, it offers a suitable surface for the reversible fairly rapid oxidation of the hydrogen gas to hydrogen ions. This cell may be summarized in the conventional form

$$^-Zn; ZnCl_2:HCl; H_2,Pt^+ \qquad (A)$$

Here the semicolon (;) designates boundaries between electrode and electrolyte, the colon (:) designates boundaries or junctions between two electrolytes (liquid junctions), and the comma (,) between two formulas indicates that these substances are present together in solution or as coordinate parts of an electrode. The symbol Pt represents the inert electrode that supports the hydrogen gas as electrode material. It is used to represent inert electrodes in general.

---

[1] Methods of calculating liquid junction potentials are discussed in other places. See, for example, D. A. MacInnes, "The Principles of Electrochemistry," Chap. 13, Reinhold Publishing Corporation, New York, 1939, and M. Dole, "Principles of Experimental and Theoretical Electrochemistry," McGraw-Hill Book Company, Inc., New York, 1935.

When a liquid junction potential has been eliminated or has been corrected for, it is customary to indicate the step by the use of double vertical lines as in

$$^{-}\mathrm{Zn};\ \mathrm{ZnCl_2}\ \|\ \mathrm{HCl};\ \mathrm{H_2,Pt^+};\qquad E = \text{approximately } 0.76 \text{ volt} \qquad (B)$$

All remaining potentials are attributed to the electrode-electrolyte junctions. Unless otherwise indicated, all numerical values of E are those for the emf at 25°c.

The equation that represents the cell reaction when 2 faradays of current are produced by cell (B) is

$$\mathrm{Zn} + 2\mathrm{HCl} = \mathrm{ZnCl_2} + \mathrm{H_2};\qquad E = \text{approximately } 0.76 \text{ volt} \qquad (20.8)$$

As this cell reaction proceeds, the negative current passes through cell (B) from right to left; over the external circuit the electrons pass from the zinc electrode to the hydrogen electrode. When measured with the potentiometer, the zinc electrode is found to be negative with respect to the hydrogen electrode as indicated in cell (B).

According to the convention now almost universally adopted, the free energy change is negative for reactions, such as (20.8), that proceed spontaneously from left to right as written, and the emf is given a positive sign. Thus, the emf of the cell reaction (20.8) is +0.76 volt. If the reverse reaction is written, the value of ΔF becomes positive and E becomes −0.76 volt. The approximate value of the emf is here given, for the exact value depends on the concentrations of the electrolytes and the partial pressure of the hydrogen gas.

As written, "positive" electricity travels from left to right in cell (B) for the spontaneous reaction. Unless the reverse polarity is clearly indicated, we shall always diagram cells with the positive electrode on the right so that the positive electricity passes through the cell from left to right for the spontaneous reaction.

Free Energy Change in Galvanic Cell Reactions.—In Chaps. 10 and 11, we discussed the relations among the emf of a cell, the electrical work that can be done by the cell, and the free energy change of the cell reaction. This discussion should be reviewed at this point. In practice, the emf of a cell is compared directly or indirectly with that of a Weston standard cell, which in turn has been compared with the national standards in Washington. The composition and the cell reaction of this cell are indicated in Prob. 20.9. Because the emf of the Weston cell defines the international volt, E is expressed in international volts. The electrical work w_e done by a cell for each faraday of current is, therefore, $96{,}501E$ int joules or $(96{,}501/4.1833)E$ defined calories. For n faradays,

$$w_e = nFE = 96{,}501nE \text{ int joules} = 23{,}068nE \text{ cal} \qquad (20.9)$$

where the faraday constant has the values $F = 96{,}501$ int joules/int volt-equivalent and $F = 23{,}068$ cal/int volt-equivalent.

Because n and F for a given reaction are constant, it follows from equation (20.9) that w_e has the maximum value when E has the maximum equilibrium value, that is, when the reaction is proceeding infinitely slowly. Because the free energy of a reaction is related not to the irreversible work but to the reversible, isothermal, net or useful work, it is clear that only the reversible emf of a cell can be used in thermodynamic calculations. In the subsequent discussion, we shall always use the symbol E to denote this maximum emf of a cell.

Galvanic cells are almost invariably operated under the experimental conditions of constant temperature and pressure. Under these conditions, a cell also does work of expansion, $w_P = P\,\Delta V$, against the atmospheric pressure P whenever an increase in volume results from the reaction. This work is relatively large whenever gases are produced or consumed in the cell reaction. Although the maximum reversible work w_r of a cell is represented by

$$w_r = w_e + w_P \tag{20.10}$$

the net useful work w' is identified with w_e and not with w_r, so that, from equations (10.17) and (10.18),

$$\Delta F_P = -w' = -w_e \tag{20.11}$$

which, when combined with equation (20.9) becomes

$$\Delta F_P = -nFE \tag{20.12}$$

Change of Emf with Temperature.—The application of thermodynamics to electrochemical as well as to other types of equilibrium was first made by Gibbs in his paper "On the Equilibrium of Heterogeneous Substances."[1] Because of the relation of the equilibrium emf of a cell to the free energy, we can derive directly the change of emf with temperature and with pressure. From equation (10.39), we have the general free energy equation

$$dF = -S\,dT + V\,dP - Dw' \tag{20.13}$$

which may be applied to the various constituents of a cell or to the cell as a whole. At constant temperature and pressure, equation (20.13) becomes the familiar expression

$$dF = -Dw'$$

When the change in free energy is the result of a chemical reaction in the

---

[1] *Op. cit.*, pp. 331–349. See also his letters on electrochemical thermodynamics written in 1887 to the British Association for the Advancement of Science, *ibid.*, pp. 406–412.

cell (a change in composition), F_1 being the free energy of the reactants and F_2 that of the products, we have

$$\Delta F = F_2 - F_1 = -w' = -nFE$$

which may be derived directly from equations (20.11) and (20.12).

Again, for the change in free energy of the cell with temperature, the pressure and composition remaining constant, dP and Dw' are equal to zero so that, from equation (20.13) or (17.15),

$$(dF)_{P,N} = -S\,dT \tag{20.14}$$

The subscript N here indicates constant composition.[1] In this process the requirement that Dw' shall be zero means that there shall be no chemical work or work of diffusion taking place in the cell that would cause free energy changes on their own account.

Equation (20.14) can be used to represent constituents of the cell as well as the cell as a whole. Thus, for 1 mole of reactant in the cell at constant pressure and composition, we may write

$$d\overline{F_1} = -\overline{S_1}\,dT \tag{20.15}$$

and, for 1 mole of product of the cell reaction,

$$d\overline{F_2} = -\overline{S_2}\,dT \tag{20.16}$$

The partial molal quantities are used here to emphasize the fact that, although in this change with temperature we are dealing with a cell that does not change in composition, a cell with a different composition would have different partial molal values of these functions. Equation (20.15) may be subtracted from (20.16). For a cell reaction involving only these components

$$d\overline{F_2} - d\overline{F_1} = d(\overline{F_2} - \overline{F_1}) = d\,\Delta F$$

and

$$\overline{S_2} - \overline{S_1} = \Delta S$$

so that we obtain the equation

$$\left(\frac{d\,\Delta F}{dT}\right)_{P,N} = -\Delta S \tag{20.17}$$

previously derived as equation (10.56). The derivation is repeated here to emphasize the basic assumptions behind the equation. Observe that this change of free energy of reaction with temperature is at constant

---

[1] In Chap. 17, we indicated constant composition with the subscript n to show that the number of moles n remain constant during the differentiation. Because we are here using n to indicate the number of faradays or chemical equivalents, we shall indicate constant composition with the subscript N.

pressure and concentration. If the cell reaction now proceeds at the new temperature, an increase in free energy of reaction ΔF must express itself, according to equation (20.12), in a decrease in the emf of the reaction, so that

$$-nF\left(\frac{\mathrm{d}E}{\mathrm{d}T}\right)_{P,N} = -\Delta S \tag{20.18}$$

or

$$\left(\frac{\mathrm{d}E}{\mathrm{d}T}\right)_{P,N} = \frac{\Delta S}{nF} \tag{20.19}$$

This equation was first derived by Gibbs; it was derived independently by Helmholtz. Because ΔS for an isothermal reaction is related to ΔF and ΔH, as in equation (10.51), the Gibbs-Helmholtz equation previously derived as equation (11.19) is readily obtained from equations (20.18) and (20.19). It may be expressed in the form

$$\begin{aligned}\Delta H &= \Delta F + T\,\Delta S\\ &= -nFE + nFT\,\frac{\mathrm{d}E}{\mathrm{d}T}\end{aligned} \tag{20.20}$$

Although this equation may be placed in other forms for specific calculations, we shall, as frequently as possible, utilize the simple fundamental formulas instead of more special forms.

Calculations from the Gibbs-Helmholtz Equation.—Because of the interrelations between the various functions above, it appears that the numerical values of a function may be derived in a number of ways. Thus, ΔF may be calculated from known values of ΔH and ΔS obtained from thermal data or from the measured value of E for the cell reaction. The value of ΔS above may also be derived from the temperature coefficient of a cell, as in equation (20.18), or from spectroscopic data. Similarly, the values of ΔH may be derived from several different types of experiment. Before we undertake detailed calculations, we shall discuss briefly the precision obtained from a combination of different data. The number of equivalents n appears as a factor in the calculations, so that we shall evaluate the functions for 1 equivalent.

If the value of ΔS per equivalent is to be accurate to 0.1 calorie per degree, the value of $\mathrm{d}E/\mathrm{d}T$ must be known to

$$\frac{0.1}{23{,}068} = 0.000004 \text{ volt/deg}$$

In practice, values of $\Delta E/\Delta T$ for a temperature interval of, say 10°, are determined instead of values of the derivative $\mathrm{d}E/\mathrm{d}T$.

If the temperature interval is 10°, the emf of the cell over this interval must be reproducible to 0.00004 volt per degree. This is higher accuracy than is obtained in the majority of measurements. With this accuracy the value at 298.16°K of $T\ \Delta S$, the reversible heat of reaction, can be determined to 30 calories. Again, if the value of ΔF per equivalent is to be accurate to within 30 calories, the value of E for the cell must be accurate to within $30/23{,}068 = 0.0013$ volt. This accuracy has been exceeded for a number of cells. Under such circumstances, the accuracy of a value of ΔH calculated from emf data is likely to be limited more by the uncertainty in ΔS than by that in ΔF.

1. *The Reduction of Silver Chloride by Lead.*—Values of E at 25°C and of $\Delta E/\Delta T$ have been determined by Gerke[1] for the cell

$$\text{Pb(Hg), PbCl}_2\text{; HCl(1m); PbCl}_2\text{, AgCl, Ag} \qquad (C)$$

for which

$$E = 0.4843 \text{ int volt}$$

and

$$\frac{\Delta E}{\Delta T} = -0.000202 \text{ int volt/deg}$$

and for the cell

$$\text{Pb; Pb(ClO}_4)_2\text{; Pb(Hg)} \qquad (D)$$

for which

$$E = 0.0057 \text{ int volt}$$

and

$$\frac{\Delta E}{\Delta T} = 0.000016 \text{ int volt/deg}$$

Crystalline lead chloride was added to the silver, silver chloride electrode so that a uniform concentration of this slightly soluble salt was present throughout the electrolyte. Otherwise, a liquid junction, and therefore a liquid junction potential, resulted.

When cells (C) and (D) are connected in series, the result is equivalent to eliminating the potential of the lead amalgam electrodes and hence equivalent to the cell

$$\text{Pb, PbCl}_2\text{; HCl(1m); PbCl}_2\text{, AgCl, Ag} \qquad (E)$$

for which

$$E = E_C + E_D = 0.4900 \text{ int volt} \qquad (20.21)$$

and

$$\frac{\Delta E}{\Delta T} = \left(\frac{\Delta E}{\Delta T}\right)_C + \left(\frac{\Delta E}{\Delta T}\right)_D = -0.000186 \text{ int volt/deg} \qquad (20.22)$$

Because the cell reaction for the passage of 1 faraday through cell (E) is

$$\tfrac{1}{2}\text{Pb} + \text{AgCl(c)} = \tfrac{1}{2}\text{PbCl}_2\text{(c)} + \text{Ag} \qquad (20.23)$$

---

[1] GERKE, R. H., *J. Am. Chem. Soc.*, **44**, 1684 (1922).

we obtain from the values in equations (20.21) and (20.22), for this reaction

$$\Delta F = -23{,}068(0.4900) = -11{,}303 \text{ cal}$$

and

$$\Delta S = 23{,}068(-0.000186) = -4.29 \text{ cal/deg}$$

whence the reversible heat of reaction is

$$T\,\Delta S = 298.16(-4.29) = -1{,}279 \text{ cal}$$

and the value of ΔH is

$$\Delta H = -11{,}303 - 1{,}279 = -12{,}580 \text{ cal}$$

Let us compare these values of ΔS and ΔH with those calculated from other sources. Using the entropies from Table 11.2 we have

$$\begin{aligned}\Delta S &= \mathrm{s}_{\mathrm{Ag}} + \tfrac{1}{2}\mathrm{s}_{\mathrm{PbCl_2}} - \tfrac{1}{2}\mathrm{s}_{\mathrm{Pb}} - \mathrm{s}_{\mathrm{AgCl}} \\ &= 10.21 + \tfrac{1}{2}(32.6) - \tfrac{1}{2}(15.51) - 23.0 \\ &= -4.2_5 \text{ cal/deg}\end{aligned}$$

Compare this value with the value -4.29 obtained above.

Another value of ΔH is obtained from the heat of formation tables of Bichowsky and Rossini,[1] from which we have, remembering that "heats evolved" are listed in these tables,

$$\begin{aligned}\Delta H &= \mathrm{H}_{\mathrm{Ag}} + \tfrac{1}{2}\mathrm{H}_{\mathrm{PbCl_2}} - \tfrac{1}{2}\mathrm{H}_{\mathrm{Pb}} - \mathrm{H}_{\mathrm{AgCl}} \\ &= 0 - \tfrac{1}{2}(85.71) - 0 + 30.30 \text{ kcal} \\ &= -12{,}560 \text{ cal}\end{aligned}$$

This value may be compared with the value of $-12{,}580$ obtained from the emf data.

2. *The Formation of Silver Chloride.*—Similar calculations may be made with Gerke's[2] data for the cell

$$\mathrm{Ag, AgCl(c); HCl(1m), AgCl(satd\ soln); Cl_2, Pt\text{-}Ir} \qquad (F)$$

for which the cell reaction is

$$\mathrm{Ag(c)} + \tfrac{1}{2}\mathrm{Cl_2(g)} = \mathrm{AgCl(c)} \qquad (20.24)$$

and for which

$$\boldsymbol{E} = 1.1362 \text{ int volts} \qquad \text{and} \qquad \frac{\Delta E}{\Delta T} = -0.000595 \text{ int volt/deg}$$

From these data

$$\begin{aligned}\Delta F &= -26{,}210 \text{ cal} \\ \Delta S &= -13.72 \text{ cal/deg}\end{aligned}$$

---

[1] BICHOWSKY, F. R., and F. D. ROSSINI, "Thermochemistry of Chemical Substances," Reinhold Publishing Corporation, New York, 1936.

[2] *Loc. cit.*

and, T being 298.16°K,

$$T\,\Delta S = -4{,}091 \text{ cal}$$

From these values, we find that

$$\begin{aligned}\Delta H &= -26{,}210 - 4{,}091\\ &= -30{,}300 \text{ cal}\end{aligned}$$

This value is identical with the value recorded in Bichowsky and Rossini's tables for the heat of formation of silver chloride at 18°C. The agreement with the entropy of formation calculated from the entropies in Table 11.2 is satisfactory. Here we find

$$\begin{aligned}\Delta S &= \mathrm{s}_{\mathrm{AgCl}} - \mathrm{s}_{\mathrm{Ag}} - \tfrac{1}{2}\mathrm{s}_{\mathrm{Cl_2}}\\ &= 23.0 - 10.21 - \tfrac{1}{2}(53.31)\\ &= 13.8_6 \text{ cal/deg}\end{aligned}$$

We should warn the student here against misconstruing the kind of check we have just made. In the preparation of entropy or heat of formation tables, evidence is assembled from a variety of sources. It may happen that the particular datum we are comparing was weighted heavily in the preparation of the standard tables so that an apparent check may follow merely because the two values are based on the same experimental data.

In the calculations just made, molar values of S and H were used. This procedure was proper because the cell reaction involved only solids. When the cell reaction includes electrolytes, we must use the corresponding partial molal quantities for the specified concentration. The partial molal quantities may differ widely from the corresponding molar properties of the pure substances. In solutions of electrolytes, the partial molal quantities have proved most necessary and hence most useful.

Change of Emf with Pressure.—The influence of pressure on the free energy of a galvanic cell is easily obtained from the general equation (20.13). At constant temperature, there being no reaction in the cell, $dT = 0$ and $Dw' = 0$, so that $(dF)_{T,N} = V\,dP$. If, now, the reactants and products of the cell reaction are considered separately, we have, for 1 mole of reactant under the same conditions,

$$d\bar{\mathrm{F}}_1 = \bar{\mathrm{v}}_1\,dP \tag{20.25}$$

and, for the products,

$$d\bar{\mathrm{F}}_2 = \bar{\mathrm{v}}_2\,dP \tag{20.26}$$

At constant pressure and composition, for these components

$$d\bar{\mathrm{F}}_2 - d\bar{\mathrm{F}}_1 = d(\bar{\mathrm{F}}_2 - \bar{\mathrm{F}}_1) = d\,\Delta F$$

and $\bar{\mathrm{v}}_2 - \bar{\mathrm{v}}_1 = \Delta V$, so that we obtain for the cell

$$d(\Delta F)_{P,N} = \Delta V\,dP \tag{20.27}$$

and

$$\left(\frac{\mathrm{d}\Delta F}{\mathrm{d}P}\right)_{T,N} = \Delta V \tag{20.28}$$

whence, from equation (20.12),

$$-nF\left(\frac{\partial E}{\partial P}\right)_{T,N} = \Delta V \tag{20.29}$$

These relations were first derived by Gibbs[1] (1878) and by Duhem.[2] In general, we find that for reactions among solids and liquids where the volume changes are relatively small, the work of expansion at moderate pressures may be neglected compared with the work resulting from the chemical reaction. For gases the influence of pressure on emf is much greater and cannot be ignored. If a mole of gas appears from the passage of *n* faradays of current through the cell, the other reacting substances being solid or liquid, we have, approximately,

$$\Delta V \doteq \mathrm{v}_g \doteq \frac{RT}{P}$$

When this value of ΔV is substituted in equation (20.29), we obtain the equation

$$nF\,\mathrm{d}E \doteq -RT\,\mathrm{d}\ln P \tag{20.30}$$

which, when integrated between the limits $E = E_1$ at $P = 1$ atm, and $E = E_P$ at $P = P$ atm, becomes

$$E_P - E_1 \doteq -\frac{RT}{nF}\ln P \tag{20.31}$$

When E is measured in international volts, F in international joules per volt-equivalent, and R is 8.3130 int joules per degree, equation (20.31) at 25°C becomes

$$E_P - E_1 = -\frac{8.3130 \times 298.16 \times 2.3026}{n \times 96{,}501}\log P$$

$$= -\frac{0.059141}{n}\log P \tag{20.32}$$

The factor 0.059141, which represents the slope between the emf and the common logarithm of the concentration, is frequently met in electrochemical calculations.

Calculations on the Pressure Effects. 1. *Cells Involving Only Condensed Phases.*—We have stated that, in cells in which only solids and

---

[1] *Op. cit.*, p. 338.

[2] DUHEM, P., "Le potentiel thermodynamique et ses applications," p. 117, Paris, 1886.

liquids react, the influence of moderate pressure changes on the emf (or free energy) of a galvanic cell may be neglected. It will be interesting to find the order of magnitude of these effects. For the reaction

$$TlCl(c) + CNS^- = TlCNS(c) + Cl^- \qquad (20.33)$$

Cohen and Piepenbroek[1] calculated the value of ΔV at 30°C from density data. At the same temperature, they measured the emf[2] of the cell

$$Tl(Hg),\ TlCNS(c);\ KCNS{:}\ KCl;\ TlCl(c),\ Tl(Hg) \qquad (G)$$

for pressures up to 1,500 atmospheres. From these data, the value of dE/dP for reaction (20.33), obtained directly, may be compared with the value of dE/dP calculated from equation (20.29) and the density data.

TABLE 20.1.—INFLUENCE OF PRESSURE ON THE EMF OF THE CELL*
Tl(Hg), TlCNS(c); KCNS:KCl; TlCl(c), Tl(Hg)

Pressure, atmospheres	E, measured, volts	E, calculated, volts
1	0.00856	0.00856
250	0.00927	0.00927
500	0.00998	0.00998
750	0.01069	0.01069
1,000	0.01139	0.01140
1,250	0.01211	0.01211
1,500	0.01282	0.01282

* Data of E. Cohen and K. Piepenbroek, *Z. physik. Chem.* **170A**, 145 (1934).

For reaction (20.33) the increase in volume is calculated from the densities to be

$$\Delta V_{30^\circ C} = -2.66_6 \pm 0.08_0 \text{ cm}^3$$

From equation (20.29), therefore, at 1 atmosphere pressure,

$$\left(\frac{dE}{dP}\right)_{30^\circ C,\ 1\ atm} = \frac{2.66_6 \times 0.10131}{96{,}501} = 2.80 \times 10^{-6} \text{ int volt/atm}$$

because n is unity and 1 cm^3-atm = 0.10131 int joule.

This value may be compared with that calculated from the emf data in Table 20.1. The experimental emf values in the second column were fitted by the equation

$$E_{30^\circ C} = 0.00856 + 0.00000284P \qquad (20.34)$$

Observe the excellent agreement between the values of E calculated with this formula as listed in the third column and the measured values listed

---

[1] COHEN, E., and K. PIEPENBROEK, *Z. physik. Chem.*, **167A**, 365 (1933).

[2] *Ibid.*, **170A**, 145 (1934).

in the second column. On differentiating equation (20.34), we obtain directly

$$\left(\frac{dE}{dP}\right)_{30°C} = 2.84 \times 10^{-6} \text{ int volt/atm}$$

The two values of dE/dP are in excellent agreement. It is evident that the influence of pressure on solids and liquids at moderate pressures is not important; for this reaction, the emf increases only 3 microvolts per atmosphere.

2. *Cells Involving Gases.*—Because the hydrogen electrode is a standard reference electrode, it is interesting to observe the influence of pressure on cells containing this electrode. MacInnes[1] and his coworkers investigated the hydrogen-calomel cell

$$\text{Pt, H}_2\text{; HCl(0.1}\textsc{m}\text{); Hg}_2\text{Cl}_2\text{, Hg} \qquad (H)$$

up to pressures of 1,000 atmospheres at 25°C, the cell reaction being

$$H_2 + Hg_2Cl_2(c) = 2HCl(0.1\text{M}) + 2Hg \qquad (20.35)$$

We give here the comparison between the calculated and observed emf values for this cell made by these workers.

For reaction (20.35), the volume change is represented by

$$\Delta V = 2\bar{v}_{HCl} + 2v_{Hg} - v_{Hg_2Cl_2} - v_{H_2}$$

the v's representing the respective molar volumes. The partial molal volume of the hydrochloric acid is here written because the molar volume of hydrogen chloride in a 0.1M solution may differ greatly from that of pure liquid hydrogen chloride. However, all the v's except that for the gaseous hydrogen are small and compensating so that, in practice, only the molar volume of the hydrogen need be considered.

At the lower pressures the molar volumes of hydrogen are well represented by the ideal gas equation. Remembering that, because hydrogen gas is consumed in reaction (20.35),

$$\Delta V = -v_{H_2} = -\frac{RT}{P},$$

we obtain, from equation (20.29),

$$E_P - E_1 = \frac{RT}{nF}\ln P \qquad (20.36)$$

This equation, except for sign, is identical with equation (20.31). (Why the difference in sign?) When the proper numerical factors are introduced in equation (20.36), n being 2, we obtain the equation

---

[1] HAINSWORTH, W. R., H. J. ROWLEY, and D. A. MACINNES, *J. Am. Chem. Soc.*, **46**, 1437 (1924).

$$E_P - E_1 = \frac{0.05914}{2}\log P = 0.02957 \log P \qquad (20.37)$$

for the change of emf with pressure. The values of $E_P - E_1$ calculated from equation (20.37) are plotted against log P in Fig. 20.4, forming curve A, which has the theoretical slope 0.02957. The experimental values of $E_P - E_1$ at the same pressures are represented by the circled points on the same graph. Observe the excellent agreement between the calculated and observed values at pressures below 100 atmospheres.

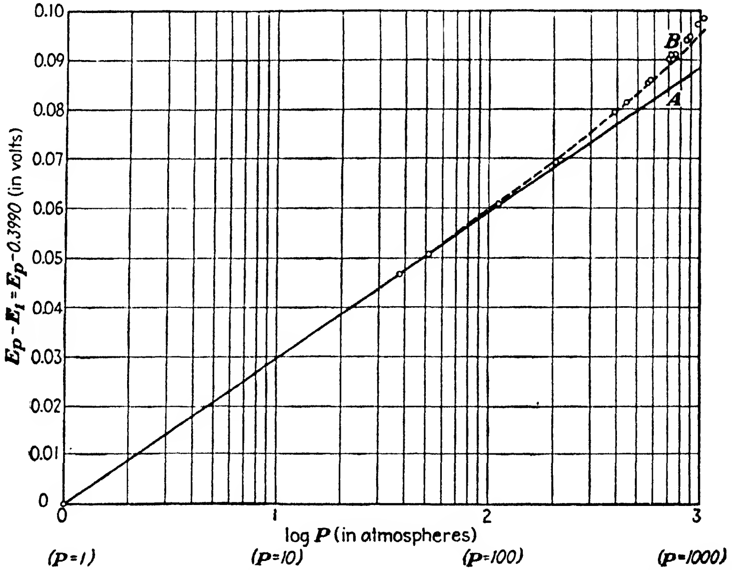


FIG. 20.4.—The change with pressure of the emf of the cell: Pt, H_2; HCl(0.1M); Hg_2Cl_2, Hg.

At higher pressures, the molar volume of hydrogen was calculated from the empirical equation

$$Pv = RT(1 + 0.000537P + 3.5 \times 10^{-8}P^2) \qquad (20.38)$$

the P and P^2 terms on the right representing the corrections for the ideal gas equation at the higher pressures. When this formula is substituted in equation (20.29), we have

$$nF\left(\frac{dE}{dP}\right)_{25^\circ\mathrm{C}} = RT\left(\frac{1}{P} + 0.000537 + 3.5 \times 10^{-8}P\right) \qquad (20.39)$$

which, when integrated between the pressures $P = 1$ atm and $P = P$ atm, becomes

$$E_P - E_1 = \frac{RT}{nF}[\ln P + 0.000537(P - 1) + 1.75 \times 10^{-8}(P^2 - 1)] \qquad (20.40)$$

This equation is represented in Fig. 20.4 by curve *B*, which deviates from curve *A* at pressures above 100 atmospheres. Observe that curve *B* represents the experimental data, indicated by the circles, for pressures up to 600 atmospheres. At still higher pressures, it appears that the molar volume of hydrogen can no longer be used to represent $-\Delta V$ for reaction (20.35).

Change of Emf with Concentration.—We have already derived relations between free energy and concentration for reactions involving ideal gases and solutions. Because the free energy in a galvanic cell is related both to the emf of the cell and to the concentrations of the cell constituents, it appears that emf and concentration must be related to each other. The change of emf of a cell with pressure of hydrogen was discussed above. We shall here derive the general relationship between emf and concentration.

For ideal gases and solutions, the differential expression for the relation between free energy and concentration for any constituents is given by equations such as (19.1) and (19.2), namely,

$$\mathrm{d}F = RT\,\mathrm{d}\ln P$$
$$\mathrm{d}F = RT\,\mathrm{d}\ln N$$

However, solutions of strong electrolytes show the widest departures from the laws of ideal solutions, so that concentrations cannot be related to the free energy and emf according to the ideal solution equations. For this reason, Lewis introduced the empirical activity function *a*, defined in equation (19.4), which we shall here write in the partial molal form

$$\mathrm{d}\overline{F} = RT\,\mathrm{d}\ln a \tag{20.41}$$

This function is applied only to the nonideal constituents. When ideal gases participate in cell reactions, we shall continue to represent their activities by their partial pressures.

Consider again the general chemical reaction

$$a\mathrm{A} + b\mathrm{B} = d\mathrm{D} + e\mathrm{E} \tag{20.42}$$

in which the participating substances A, B, D, and E, may represent reacting ions in a cell reaction. When a'_{A} is the initial activity and a_{A} the equilibrium activity of the substance A, the change in free energy when 1 mole of A is transferred from the initial to the equilibrium state is represented by the equation

$$\overline{F}_{\mathrm{A}} - \overline{F}'_{\mathrm{A}} = RT\ln\frac{a_{\mathrm{A}}}{a'_{\mathrm{A}}} \tag{20.43}$$

which may be obtained by integration of equation (20.41). Corresponding equations may be written for the substances B, D, and E. When the partial molal free energy equations for these substances are combined according to the methods of Table 12.1 and equation (12.16), we have, for reaction (20.42),

$$\begin{aligned}\Delta F &= a(\overline{\mathrm{F}}_{\mathrm{A}} - \overline{\mathrm{F}}'_{\mathrm{A}}) + b(\overline{\mathrm{F}}_{\mathrm{B}} - \overline{\mathrm{F}}'_{\mathrm{B}}) + d(\overline{\mathrm{F}}'_{\mathrm{D}} - \overline{\mathrm{F}}_{\mathrm{D}}) + e(\overline{\mathrm{F}}'_{\mathrm{E}} - \overline{\mathrm{F}}_{\mathrm{E}}) \\ &= RT\left[\ln\left(\frac{a}{a'}\right)_{\mathrm{A}}^{a} + \ln\left(\frac{a}{a'}\right)_{\mathrm{B}}^{b} + \ln\left(\frac{a'}{a}\right)_{\mathrm{D}}^{d} + \ln\left(\frac{a'}{a}\right)_{\mathrm{E}}^{e}\right] \\ &= RT\ln\frac{a'^{d}_{\mathrm{D}}a'^{e}_{\mathrm{E}}}{a'^{a}_{\mathrm{A}}a'^{b}_{\mathrm{B}}} - RT\ln\frac{a_{\mathrm{D}}{}^{d}a_{\mathrm{E}}{}^{e}}{a_{\mathrm{A}}{}^{a}a_{\mathrm{B}}{}^{b}} \qquad (20.44)\end{aligned}$$

We here remind ourselves that the a''s represent the initial activities of the reactants and the final activities of the products and the a's represent the equilibrium values. The ratio of the a's in the last term of equation (20.44) is, therefore, the equilibrium constant K_a, previously defined in equation (12.84). When equation (20.44) is combined with (20.12), due regard being paid to sign, the result is

$$E = -\frac{RT}{nF}\ln\frac{a'^{d}_{\mathrm{D}}a'^{e}_{\mathrm{E}}}{a'^{a}_{\mathrm{A}}a'^{b}_{\mathrm{B}}} + \frac{RT}{nF}\ln K_a \qquad (20.45)$$

Observe that the emf of a cell is a function of the initial and final activities of the reactants and products as well as of the equilibrium constant.

The change of emf of a cell with concentration may be expressed by other formulas. If E'' is the emf of a cell in which the initial activities of the reactants and the final activities of the products are expressed as a'''s, as in the equation

$$E'' = -\frac{RT}{nF}\ln\frac{a''^{d}_{\mathrm{D}}a''^{e}_{\mathrm{E}}}{a''^{a}_{\mathrm{A}}a''^{b}_{\mathrm{B}}} + \frac{RT}{nF}\ln K_a \qquad (20.46)$$

and E' is the corresponding value of E in equation (20.45), where the initial and final activities are expressed as a''s, equations (20.45) and (20.46) may be combined to give the equation

$$E'' - E' = \frac{RT}{nF}\ln\frac{a'^{d}_{\mathrm{D}}a'^{e}_{\mathrm{E}}}{a'^{a}_{\mathrm{A}}a'^{b}_{\mathrm{B}}} - \frac{RT}{nF}\ln\frac{a''^{d}_{\mathrm{D}}a''^{e}_{\mathrm{E}}}{a''^{a}_{\mathrm{A}}a''^{b}_{\mathrm{B}}} \qquad (20.47)$$

Equation (20.47) contains no term corresponding to the equilibrium constant, although the activity terms have the same form as the equilibrium constant term. *Observe that the a's in these terms are not the equilibrium values but the values for the constituents in the cell as set up and measured.*

This ratio of the a's, which appears in the general free energy expression and in the emf formulas and which represents the initial-final and not the equilibrium values, may be represented conveniently by the symbol Q. Thus, for the a''s,

$$Q' = \frac{a'^{d}_{\mathrm{D}}a'^{e}_{\mathrm{E}}}{a'^{a}_{\mathrm{A}}a'^{b}_{\mathrm{B}}} \qquad (20.48)$$

The ratio Q has a value fixed only by the activities of the constituents of the cell. This value may be varied at will, but there is only a single value of K for a given cell reaction at constant temperature and pressure. When Q' and Q'' are written for the ratios of the a''s and the a'''s in equation (20.47), this becomes

$$E'' - E' = \frac{RT}{nF} \ln Q' - \frac{RT}{nF} \ln Q'' \tag{20.49}$$

Equations of the form of (20.47) and (20.49) are especially useful in the treatment of *concentration cells* whose emf results entirely from changes in the concentrations of the cell constituents rather than from changes in their nature.

Standard Emf of a Cell.—In dealing with free energies, it is convenient to fix the initial and final concentrations so that they represent the standard states of the pure substances at which partial pressures or concentrations are unity. Under these conditions, the standard free energy equation takes on the simple form

$$\Delta F^\circ = -RT \ln K \tag{20.50}$$

as in equation (12.21). The standard states of pure substances can be realized in practice. If the reacting substances are not at their standard states, they can be brought to these states by known manipulations with known or measurable free energy changes. In this way, the standard free energy can be evaluated and then used to derive the numerical value of the equilibrium constant.

If each reacting substance in a galvanic cell is in its standard state so that its value of a' is unity, the first term in equation (20.45) disappears, and the cell has the standard emf E° defined by the equation

$$E^\circ = \frac{RT}{nF} \ln K_a \tag{20.51}$$

which corresponds to equation (20.50). The mathematical step is here simple, but the experimental realization of the standard state for electrolytes is difficult. Indeed, there is no direct experimental procedure by which a solution can be prepared in which all the constituents have a desired activity. We can prepare a one molal or a one molar solution of sodium chloride even though other substances are present in the solution, but we cannot set up a solution in which the chloride ion has an activity of one molal regardless of the character of the other constituents of the cell. On the other hand, the emf of a cell changes with activity of the chloride ion whenever this ion is one of the reacting substances even though the molality of the ion remains unchanged, but the emf remains constant when the activity remains unchanged even though the concentration of the chloride ion is altered.

An inspection of equations (20.44) and (20.45) shows that these equations give only *ratios* of activities and not the absolute values of these activities. It appears, therefore, that emf measurements in themselves cannot evaluate the activities of substances whose standard states cannot be realized directly. If a value of K_a can be obtained by some independent method, it can be used to set up a value of $E°$, which can then be combined with the experimental value to E to give values of activity relative to those of the standard state. Or the experimental data can be extrapolated to infinite dilution as we did for the cadmium amalgams in Chap. 19. Numerical values of the a's in the experimental range relative to the standard state can then be obtained.

If $E°$ has been evaluated by an extrapolation method or by some independent method, this value may be substituted in equation (20.45) to give

$$E = E° - \frac{RT}{nF} \ln \frac{a_D'^d a_E'^e}{a_A'^a a_B'^b} \tag{20.52}$$

From the definition of Q in equation (20.48), it appears that equation (20.52) may be written in the form

$$E = E° - \frac{RT}{nF} \ln Q \tag{20.53}$$

which has special usefulness in the so-called "oxidation-reduction" reactions. When Q is made equal to K the cell is at equilibrium and E (and ΔF) become equal to zero.

Standard States for Electrodes.—For metallic electrodes, the standard state usually chosen is that of the electrode in its stable crystalline form at the cell temperature. In some cells, the metal in a saturated two-phase amalgam is chosen as the standard state because the electrode so formed is more reproducible than the electrode of pure metal. Examples of amalgam electrodes are given in Table 20.2. In a two-phase amalgam the activity of the metal in both phases is identical and, therefore, independent of the gross composition of the mixture.

Because the activity of a perfect gas is directly proportional to its pressure, the partial pressure of the reacting gas at a gas electrode must be carefully defined, the standard state for the gas being unit partial pressure or unit fugacity. When the partial pressure or fugacity of the gas at the electrode is P rather than unity, the change in emf of the cell with P may be calculated from equation (20.49). Consider a cell in which 1 mole of gas D is produced for n faradays of current. If all the other activities remain unchanged during this change in partial pressure of D, we have

$$a_A' = a_A'', \qquad a_B' = a_B'', \qquad a_D' = 1, \qquad a_D'' = P, \qquad a_E' = a_E''$$

so that, from equation (20.49),

$$E'' - E' = 0 - \frac{RT}{nF} \ln P \tag{20.54}$$

which is identical with equation (20.31) derived for the change of emf with pressure. As stated earlier, this equation is based on the assumption that all other activities in the cell remain constant and that the activity of the gas is measured by its pressure. Figure 20.4 and the accompanying discussion show the pressure limits for the validity of these assumptions for one particular cell.

Standard States for Electrolytes.—Early work showed that the emf of a cell is not uniquely defined by the concentration of reacting ions when these concentrations are expressed in normalities or molarities of these ions as estimated from so-called "degrees of ionization." For this reason, the standard state of an ion is now defined in terms of the hypothetical state of unit activity. As we stated in Chap. 19, however, the activity of a solute may be so defined that its value equals unity when expressed (1) in mole fraction units, (2) in molal units, and (3) in moles per liter, the standard state of unit activity being different in each case. The usual practice is to express the standard ion activity in terms of molalities so that $a = 1$ for an ion when $m\gamma = 1$.

Standard Single Electrode Potentials.—The potential of a single electrode cannot be measured. However, all electrodes may be compared with some standard reference electrode and their potentials evaluated relative to the potential of this reference electrode. The standard hydrogen electrode with hydrogen gas at unit pressure and hydrogen ion at unit molal activity has been chosen as this reference electrode, its potential being arbitrarily called zero at all temperatures. The standard emf for the cell in which the standard hydrogen electrode is one electrode then becomes the standard single electrode potential of the other electrode. The sign of the single electrode potential still remains undefined. According to one convention, an electrode is given a positive sign when reduction at the electrode, as indicated in equations (20.1) to (20.5), is spontaneous compared with the reduction of hydrogen ion in equation (20.2). According to another convention, the electrode is given a positive sign when oxidation, as indicated in equations (20.6), is spontaneous compared with the oxidation of hydrogen. We shall follow the former convention; when the positive end of a cell is always written on the right, the emf of the cell and the single electrode potentials E_R and E_L of the right-hand and the left-hand electrode, respectively, are related by the equation

$$E = E_R - E_L \tag{20.55}$$

TABLE 20.2.—STANDARD ELECTRODE POTENTIALS* AT 25°C
(Standard states: gases at unit fugacity, ions at unit molal activity)

Electrode	Electrode reaction	Standard potential $E°$, volts
Li^+; Li	$Li^+ + e^- = Li$	−3.0243
K^+; K	$K^+ + e^- = K$	−2.9239
Rb^+; Rb	$Rb^+ + e^- = Rb$	−2.9239
Na^+; Na	$Na^+ + e^- = Na$	−2.7139
OH^-, H_2O; H_2, Pt	$H_2O + 2e^- = 2OH^- + H_2$	−0.8279
Zn^{++}; Zn	$Zn^{++} + 2e^- = Zn$	−0.7611
OH^-, PbO(c); Pb	$PbO(c) + H_2O + 2e^- = 2OH^- + Pb$	−0.5785
Cd^{++}; Cd	$Cd^{++} + 2e^- = Cd$	−0.4021
Cd^{++}; Cd(Hg)	$Cd^{++} + 2e^- = Cd(Hg)(satd)$	−0.3516
SO_4^{--}, $PbSO_4$(c); Pb(Hg)	$PbSO_4(c) + 2e^- = SO_4^{--} + Pb(Hg)(satd)$	−0.3505
Tl^+; Tl	$Tl^+ + e^- = Tl$	−0.3385
Co^{++}; Co	$Co^{++} + 2e^- = Co$	−0.283
Ni^{++}; Ni	$Ni^{++} + 2e^- = Ni$	−0.236
I^-, AgI(c); Ag	$AgI(c) + e^- = I^- + Ag$	−0.1522
Sn^{++}; Sn	$Sn^{++} + 2e^- = Sn$	−0.1405
Pb^{++}; Pb	$Pb^{++} + 2e^- = Pb$	−0.1265
H^+; H_2, Pt	$2H^+ + 2e^- = H_2$	±0.0000
Br^-, AgBr(c); Ag	$AgBr(c) + e^- = Br^- + Ag$	+0.0711
OH^-, HgO(c); Hg	$HgO(c) + H_2O + 2e^- = 2OH^- + Hg$	+0.0976
H^+, Sb_2O_3(c); Sb	$Sb_2O_3(c) + 6H^+ + 6e^- = 3H_2O + 2Sb$	+0.1445
Cu^{++}, Cu^+; Pt	$Cu^{++} + e^- = Cu^+$	+0.159
Cl^-, AgCl(c); Ag	$AgCl(c) + e^- = Cl^- + Ag$	+0.2225
Cl^-, Hg_2Cl_2(c); Hg	$\frac{1}{2}Hg_2Cl_2(c) + e^- = Cl^- + Hg$	+0.2681
Cu^{++}; Cu	$Cu^{++} + 2e^- = Cu$	+0.339
I^-, I_2(c); Pt	$I_2 + 2e^- = 2I^-$	+0.5350
OH^-, MnO_4^-, MnO_2(c); Pt	$MnO_4^- + 2H_2O + 3e^- = 4OH^- + MnO_2(c)$	+0.587
SO_4^{--}, $HgSO_4$(c); Hg	$HgSO_4(c) + 2e^- = SO_4^{--} + Hg$	+0.6141
H^+, quinhydrone; Au	Quinone(c) + $2H^+ + 2e^-$ = hydroquinone	+0.6994
Fe^{+++}, Fe^{++}; Pt	$Fe^{+++} + e^- = Fe^{++}$	+0.783
Ag^+; Ag	$Ag^+ + e^- = Ag$	+0.799
Hg^{++}, Hg_2^{++}; Pt	$2Hg^{++} + 2e^- = Hg_2^{++}$	+0.906
Br^-, Br_2 (liq); Pt	$Br_2(liq) + 2e^- = 2Br^-$	+1.0651
Mn^{++}, MnO_2(c); Pt	$MnO_2(c) + 4H^+ + 2e^- = 2H_2O + Mn^{++}$	+1.236
Cl^-; Cl_2(g); Pt	$Cl_2(g) + 2e^- = 2Cl^-$	+1.3587
H^+, Au_2O_3(c); Au	$Au_2O_3(c) + 6H^+ + 6e^- = 3H_2O + 2Au$	+1.360
Pb^{++}, PbO_2(c); Pb	$PbO_2(c) + 4H^+ + 2e^- = 2H_2O + Pb^{++}$	+1.467
MnO_4^-, MnO_2(c); Pt	$MnO_4^- + 4H^+ + 3e^- = 2H_2O + MnO_2$	+1.586
Ce^{++++}, Ce^{+++}; Pt	$Ce^{++++} + e^- = Ce^{+++}$	+1.609
SO_4^{--}, PbO_2(c), $PbSO_4$(c); Pt	$PbO_2(c) + SO_4^{--} + 4H^+ + 2e^- = 2H_2O + PbSO_4(c)$	+1.685

---

* These are the values selected by D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corporation, New York, 1939.

Thus, for the cell

$$Zn; Zn^{++}(a = 1) \parallel H^+(a = 1); H_2, Pt \qquad (I)$$

whose emf is $E° = 0.7611$ volt,

$$E° = E^{\circ}_{H_2} - E^{\circ}_{Zn} = 0.7611 \text{ volt}$$
$$E^{\circ}_{Zn} = 0 - 0.7611 = -0.7611 \text{ volt}$$

Single electrode potentials calculated in this way, all for substances in their standard states, are tabulated in Table 20.2. The corresponding half-cell reactions, all for the reducing action at an electrode, are listed opposite the standard potential. Table 20.2 therefore gives complete information on the reactions corresponding to each potential. If any of the half-cell reaction equations is reversed to show oxidation, the corresponding potential must be given the opposite sign.

From Table 20.2, for example,

$$2H^+ + 2e^- = H_2; \qquad E^\circ_H = 0$$
$$Zn^{++} + 2e^- = Zn; \qquad E^\circ_{Zn} = -0.7611 \text{ volt}$$

When the second equation is subtracted from (or reversed and added to) the first, the equation for the reaction of cell (*I*) is obtained, namely,

$$Zn + 2H^+ = Zn^{++} + H_2; \qquad E^\circ = 0 + 0.7611 = 0.7611 \text{ volt}$$

In this way the standard emf for any cell can be calculated from the single potential values.

Problems

20.1. According to W. G. Parks and V. K. La Mer [*J. Am. Chem. Soc.*, **56**, 90 (1934)], who studied the cell

$$Cd(c); CdSO_4(0.5m); Cd \text{ (satd with Hg)}$$

for which the cell reaction is

$$Cd(c) = Cd\text{(satd with Hg)}$$

the emf of the cell can be represented by the formula

$$10^5E = 5{,}538 - 14.8t - 0.385t^2 + 0.0075t^3$$

between 0 and 30°c, *t* being in degrees centigrade. For the transfer of 1 mole of cadmium to the saturated amalgam at 20°c calculate ΔF, ΔH, and ΔS. If the pure cadmium is selected as the standard state, calculate the activity of the cadmium in the saturated amalgam at 0, 10, 20, and 30°c.

20.2. Write the half-cell reactions for the cell in Prob. 20.1. Does the potential of each half cell depend on the concentration of the electrolyte? Does the emf of the cell?

20.3. From the standard electrode potentials (Table 20.2), calculate the standard emf of the cell

$$Pt, H_2; HCl(a = 1); Cl_2, Pt$$

Write the cell reaction. Calculate the standard free energy change and the value of the equilibrium constant for the cell reaction at 25°c.

20.4. The chlorine at a chlorine electrode may be diluted by an inert gas, nitrogen. Calculate the emf of the cell in Prob. 20.3 if the partial pressure of the chlorine is 0.75 atmosphere. 0.50 atmosphere.

20.5. A hydrogen electrode is used in a solution in which the partial pressure of the water vapor is 22 mm at 25°c. The atmospheric pressure is 748 mm. What is the difference in potential between this electrode and one whose partial pressure of hydrogen is 1 atmosphere?

20.6. For the cell

$$\text{Ag, AgCl; 0.1m KCl; HgCl, Hg at 25°c,} \qquad 10^3\frac{dE}{dP} = 2.66 \pm 0.2 \text{ mv/atm}$$

Write the chemical equation for the cell reaction and the equation for the emf as a function of the activity of the cell constituents. What is the volume change for this reaction? Compare with the volume change calculated from the necessary density data.

20.7. Write the cell reaction equations and the equations for the emf as a function of the activity of the cell constituents for the following cells. Where liquid junctions occur, assume that the liquid junction potentials have been eliminated.

(*a*) Pt, H_2; $HCl(m_1) \| HCl(m_2)$; H_2, Pt
(*b*) Pt, H_2; $HCl(m_1) \| KOH(m_1)$; H_2, Pt
(*c*) $Zn(N_1)$, (Hg); $ZnSO_4(m_1)$; $Zn(N_2)$, (Hg)
(*d*) Pt, H_2; $H_2SO_4(C)$; Hg_2SO_4, Hg
(*e*) Ag, AgCl; $HCl(m_1)$; H_2, Pt; $HCl(m_2)$; AgCl, Ag
(*f*) Cd(Hg); $CdCl_2(m_1)$; AgCl, Ag
(*g*) Cd; $CdCl_2(m_1)$; Cl_2, Pt
(*h*) Pt, I_2(c); $KI(m_1) \| KCl(m_2)$; Cl_2, Pt

20.8. Write the cell reactions and calculate the emf of the following cells at 25°c. Assume that liquid junctions have been eliminated.

(*a*) Pt; $Fe^{++}(a = 1)$, $Fe^{+++}(a = 1) \| Cl^-(a = 1)$; $Cl_2(P = 0.5)$, Pt
(*b*) Zn; $Zn^{++}(a = 0.1) \| I^-(a = 0.1)$; I_2(c), Pt
(*c*) Pb, PbO(c); $OH^-(a = 0.1)$; HgO(c), Hg
(*d*) Ag, AgI(c); $I^-(a = 0.01)$; I_2(c), Pt
(*e*) Pt, $Hg_2^{++}(a = 1)$, $Hg^{++}(a = 0.1) \| H^+(a = 0.1)$; H_2, Pt

20.9. The Weston standard cell may be represented as follows:

$$\text{Cd(amalgam); CdSO}_4\text{(satd soln), Hg}_2\text{SO}_4\text{(satd soln); Hg(liq)}$$

The chemical reaction upon the passage of 2 faradays of current through the cell is represented specifically by the equation

$$\text{Cd(amalgam)} + \text{Hg}_2\text{SO}_4\text{(c)} + \tfrac{8}{3}\text{H}_2\text{O(satd soln of CdSO}_4) = \text{CdSO}_4 \cdot \tfrac{8}{3}\text{H}_2\text{O(c)} + 2\text{Hg(liq)}$$

As the reaction proceeds, the $CdSO_4$ formed by the cell reaction removes $\frac{8}{3}$ mole of water per mole of $CdSO_4$ from the saturated solution, resulting in the precipitation of more $CdSO_4$ than the above reaction calls for. The equation is, therefore, revised to

$$\text{Cd(amalgam)} + \text{Hg}_2\text{SO}_4\text{(c)} + x\text{CdSO}_4\text{(aq)} + m\text{H}_2\text{O} = (1 + x)\text{CdSO}_4 \cdot \tfrac{8}{3}\text{H}_2\text{O(c)} + 2\text{Hg(liq)}$$

where $m = \frac{8}{3}(1 + x)$.

This reaction may be considered the sum of three reactions. Its heat of reaction at 18°c may be calculated from the following data:

(*a*) $Cd\gamma = \text{Cd(amalgam)}$ $\qquad \Delta H_1 = -5{,}675$ cal
(*b*) $Cd\gamma + Hg_2SO_4\text{(c)} = CdSO_4\text{(c)} + 2Hg\text{(liq)}$ $\qquad \Delta H_2 = \cdots$
(*c*) $CdSO_4\text{(c)} + xCdSO_4\text{(aq)} + mH_2O = (1 + x)CdSO_4 \cdot \frac{8}{3}H_2O$ $\qquad \Delta H_3 = -7{,}890$ cal

For ΔH_2, the "International Critical Tables" values give −46,340 calories, and the data of E. C. Cohen and J. J. Wolters [*Z. physik. Chem.*, **96**, 253 (1920)] give $-45,346$ calories.

(1) From the above data, calculate the heat of reaction for the standard cell reaction.

(2) In the "International Critical Tables," find, for the above cell, the equation for its emf as a function of temperature. From this equation, calculate E_{291}, dE/dT, and hence ΔF_{291} and ΔH_{291}. Compare the latter with the value calculated from thermal data in (1).

CHAPTER 21

SOLUTIONS OF ELECTROLYTES

For the reasons previously given, the concentration of nonelectrolytes is best expressed in terms of mole fraction; the activity coefficient α then becomes a true measure of the departure of the solution from the laws of ideal solution. For historical and practical reasons, however, the concentration of solutions of electrolytes has generally been expressed in terms of the volume and mole ratio units, molarity and molality, respectively. Because of the influence of charged particles on each other and on the solvent, solutions of strong electrolytes deviate from the laws of ideal solution even though proper allowance is made for the increased number of solute particles resulting from the separation of the solute into ions. Furthermore, salts are usually not completely miscible with water, so the entire range of solutions represents only part of the entire mole fraction range. Indeed, for many solutions the entire concentration range is represented by solutions so dilute that mole fractions, molalities, and molarities are proportional to each other for all possible concentrations. Under these conditions, the various activity coefficients indicate the influence and nature of the specific interactions of ions and solvent. In more concentrated solutions, they will, of course, indicate also the departure from ideality resulting from the use of a function of the wrong form, as was stated in connection with equation (19.77).

In this chapter, we shall apply all three of the methods of expressing concentration to solutions of electrolytes for all are used by important workers. The relations between the different concentration units discussed in Chap. 19 should, therefore, be reviewed at this point. Because the concentration of the ions in an electrolyte is not always identical with the concentration of the electrolyte that furnishes the ions, some additional definitions and conventions are required. Most of the relations that follow are applicable to solutions of electrolytes in general, but all of them can be applied specifically to aqueous solutions.

Activity of Ions.—Because the properties of a strong electrolyte such as potassium chloride are essentially the properties of a mixture of potassium ions and chloride ions and because the solution has no properties that need interpretation in terms of un-ionized molecules, we shall follow the usage of the theory of complete ionization of strong electrolytes without further comment.

Consider a solution of potassium chloride. In this solution, the activity of the potassium ion expressed as the usual function of the partial molal free energy of the potassium ion is

$$\bar{F}_{K^+} - \bar{F}^0_{K^+} = RT \ln a_{K^+} \tag{21.1}$$

and the activity of the chloride ion in the same solution is expressed by the equation

$$\bar{F}_{Cl^-} - \bar{F}^0_{Cl^-} = RT \ln a_{Cl^-} \tag{21.2}$$

In a formal way, the activity of the potassium chloride may be defined similarly, as in the equation

$$\bar{F}_{KCl} - \bar{F}^0_{KCl} = RT \ln a_{KCl} \tag{21.3}$$

If the standard states are so defined that

$$\bar{F}^0_{KCl} = \bar{F}^0_{K^+} + \bar{F}^0_{Cl^-}$$

and the partial molal free energies of these constituents in the solution at nonstandard states have the same relation, we obtain, on combining these equations,

$$\begin{aligned}\bar{F}_{KCl} - \bar{F}^0_{KCl} &= (\bar{F}_{K^+} + \bar{F}_{Cl^-}) - (\bar{F}^0_{K^+} + \bar{F}^0_{Cl^-}) \\ &= RT \ln a_{KCl} = RT \ln a_{K^+}a_{Cl^-}\end{aligned} \tag{21.4}$$

Under these conditions, it is evident that

$$a_{KCl} = a_{K^+}a_{Cl^-} \tag{21.5}$$

Equation (21.5) serves as a definition of the relation between the activity of the salt and the activities of the component ions.

In order to substitute numerical values for the activities in equation (21.5), we must be able to evaluate separately the activities of one or both of the ions. However, these ions coexist in the solution so that the activity of one kind of ion in the absence of the other cannot be determined. Because the individual ion activities are not determined, a *mean activity* $a_\pm$, is introduced; this mean activity may then be substituted for the individual ion activities regardless of sign.

When $a_\pm$ is substituted for a_{K^+} and a_{Cl^-} in equation (21.5), we have the equations

$$\left.\begin{aligned} a_{KCl} &= a_{K^+}a_{Cl^-} = a_\pm^2 \\ a_\pm &= (a_{K^+}a_{Cl^-})^{\frac{1}{2}} \end{aligned}\right\} \tag{21.6}$$

Equations (21.6) serve as a definition for the mean activity of the ions in this salt. Observe that the mean activity is a geometric mean.

Consider next a solution of barium chloride that furnishes two moles of chloride ion per mole of salt. The free energy of the chloride ion in such a solution is

$$2\bar{F}_{Cl^-} - 2\overline{F^{\circ}_{Cl^-}} = 2RT \ln a_{Cl^-} = RT \ln a_{Cl^-}{}^2 \tag{21.7}$$

and that of the barium is represented by an equation corresponding to (21.1). For 1 mole of this salt, the free energy may be expressed in a form analogous to equation (21.4), namely,

$$\begin{aligned} \bar{F}_{BaCl_2} - \overline{F^{\circ}_{BaCl_2}} &= (\bar{F}_{Ba^{++}} + 2\bar{F}_{Cl^-}) - (\overline{F^{\circ}_{Ba^{++}}} + 2\overline{F^{\circ}_{Cl^-}}) \\ &= RT \ln a_{BaCl_2} = RT \ln a_{Ba^{++}}a_{Cl^-}{}^2 \end{aligned} \tag{21.8}$$

For barium chloride, it appears that the activity of salt and the activity of the ions are related by the equation

$$a_{BaCl_2} = a_{Ba^{++}}a_{Cl^-}{}^2 \tag{21.9}$$

If, as before, the mean activity represents the geometric mean of the product of the individual ion activities regardless of sign, it is related to the activities in equation (21.9) by the equations

$$\left.\begin{aligned} a_{BaCl_2} &= a_{Ba^{++}}a_{Cl^-}{}^2 = a_{\pm}{}^3 \\ a_{\pm} &= (a_{Ba^{++}}a_{Cl^-}{}^2)^{\frac{1}{3}} \end{aligned}\right\} \tag{21.10}$$

It is apparent that these relations among the activity of a salt, the individual ion activities, and the mean activity of the ions can be generalized. Consider the strong electrolyte B, which contributes ν_+ positive ions indicated as D^+ and ν_- negative ions, indicated as D^-. Here the $_+$ and $_-$ subscripts indicate merely the sign of the charges and not the number of charges on the several ions. For this electrolyte,

$$B = \nu_+D^+ + \nu_-D^- \tag{21.11}$$

If, as before, the free energy per mole of electrolyte is the sum of the ionic free energies, the standard free energy of the electrolyte being related to the standard free energy of the ions by the relation

$$\overline{F^{\circ}_B} = \nu_+\overline{F^{\circ}_+} + \nu_-\overline{F^{\circ}_-} \tag{21.12}$$

the activities of electrolyte and constituent ions are related by the equation

$$a_2 = a_+{}^{\nu_+}a_-{}^{\nu_-} = (a_{\pm})^{\nu_+}(a_{\pm})^{\nu_-} = (a_{\pm})^{\nu} \tag{21.13}$$

where $\nu = \nu_+ + \nu_-$. From equation (21.13), it follows that the mean activity is related to the activity of the electrolyte by the equation

$$a_{\pm} = (a_2)^{\frac{1}{\nu}} \tag{21.14}$$

Molality of Ions and the Mean Molality.—The relations indicated in equations (21.1) to (21.14) serve to define the relations between the activities of the various constituents of a salt. Although these activities may be expressed in any of the usual units, they are most frequently applied to data expressed in molalities. For this reason, we shall utilize the molal system in the following section.

Consider again the solution of barium chloride. In an m molal solution of the salt the molalities of the barium ion and the chloride ion are related to that of the salt by the equations

$$\begin{aligned} m_{\mathrm{Ba}^{++}} &= m \\ m_{\mathrm{Cl}^-} &= 2m \end{aligned} \tag{21.15}$$

If the solution is dilute enough so that the activity coefficient is unity, the activities of the ions become equal to the molalities of the ions so that $a_{\mathrm{Ba}^{++}} = m_{\mathrm{Ba}^{++}} = m$ and $a_{\mathrm{Cl}^-} = m_{\mathrm{Cl}^-} = 2m$. It follows from equation (21.9) that

$$a_{\mathrm{BaCl}_2} = (m_{\mathrm{Ba}^{++}})(m_{\mathrm{Cl}^-})^2 = (m)(2m)^2 \tag{21.16}$$

In this solution in which the activity coefficients are unity, the *mean molality* $m_\pm$ may be defined as equal to the mean activity. From equations (21.9) and (21.10) and this definition of mean molality, we have, the activity coefficient still being unity,

$$a_\pm{}^3 = m_\pm{}^3 = 2^2m^3 \tag{21.17}$$

so that

$$a_\pm = m_\pm = m(2^2)^{\frac{1}{3}} \tag{21.18}$$

From the derivation of this equation, it follows that for the general electrolyte indicated in equation (21.11) the mean molality is related to the molality of the electrolyte by the relation

$$m_\pm = m(\nu_+{}^{\nu_+}\nu_-{}^{\nu_-})^{\frac{1}{\nu}} \tag{21.19}$$

Because we have made no approximations that restrict these relations to solutions in which activity is expressed in molalities, we may immediately define *mean molarity* of ions and a *mean mole fraction* of ions by the equations corresponding to equation (21.19), namely,

$$C_\pm = C(\nu_+{}^{\nu_+}\nu_-{}^{\nu_-})^{\frac{1}{\nu}} \tag{21.20}$$

and

$$N_\pm = N(\nu_+{}^{\nu_+}\nu_-{}^{\nu_-})^{\frac{1}{\nu}} \tag{21.21}$$

These methods of deriving the mean molality of a salt may be extended to a mixture of salts. Thus, in a solution in which potassium chloride is 0.1m and barium chloride is 0.1m, we have $m_{\mathrm{K}^+} = 0.1$, $m_{\mathrm{Cl}^-} = 0.3$, $m_{\mathrm{Ba}^{++}} = 0.1$ so that, for the potassium chloride

$$m_\pm = (m_{K^+}m_{Cl^-})^{\frac{1}{2}} = (0.1 \times 0.3)^{\frac{1}{2}}$$

and, for the barium chloride,

$$m_\pm = (m_{Ba^{++}}m_{Cl^-}{}^2)^{\frac{1}{3}} = [0.1 \times (0.3)^2]^{\frac{1}{3}}$$

Ion Activity Coefficients and the Mean Activity Coefficient.—From the relations between activities, concentrations, and activity coefficients defined in Chap. 19, we can now find the relation between the activity coefficients of the individual ions and the mean activity coefficient. For the general electrolyte in equation (21.11), let the activity coefficient of the positive ions be γ_+ and that of the negative ions be γ_-. From equation (21.13) for the activity of this electrolyte and the general relation between m_+, m_-, and m, we may write

$$a_2 = a_+{}^{\nu_+}a_-{}^{\nu_-} = (m_+\gamma_+)^{\nu_+}(m_-\gamma_-)^{\nu_-} = m^\nu(\nu_+{}^{\nu_+}\nu_-{}^{\nu_-})(\gamma_+{}^{\nu_+}\gamma^{\nu_-}) \tag{21.22}$$

But, from equations (21.14) and (21.19),

$$(a_2)^{\frac{1}{\nu}} = a_\pm = m_\pm(\gamma_+{}^{\nu_+}\gamma_-{}^{\nu_-})^{\frac{1}{\nu}} \tag{21.23}$$

Let us now define the mean activity coefficient $\gamma_\pm$ as

$$\gamma_\pm = (\gamma_+{}^{\nu_+}\gamma_-{}^{\nu_-})^{\frac{1}{\nu}} \tag{21.24}$$

From equation (21.23), it appears, therefore, that the mean activity coefficient may also be defined as

$$\gamma_\pm = \frac{a_\pm}{m_\pm} \tag{21.25}$$

The mean activity coefficients for the other concentration units may be defined in an analogous manner. Thus, for concentration in moles per liter,

$$f_\pm = \frac{a_\pm}{C_\pm} = (f_+{}^{\nu_+}f_-{}^{\nu_-})^{\frac{1}{\nu}} \tag{21.26}$$

and, for concentration in mole fractions,

$$\alpha_\pm = \frac{a_\pm}{N_\pm} = (\alpha_+{}^{\nu_+}\alpha_-{}^{\nu_-})^{\frac{1}{\nu}} \tag{21.27}$$

As stated earlier, the individual ion activities cannot be measured experimentally. For this reason, the mean activity coefficients and not the individual ion activity coefficients are derived in practice. Where no qualifying subscripts are indicated, we shall, therefore, assume that the value of an activity coefficient is that of the mean coefficient. Observe, as before, that "mean" refers to the geometric mean.

Activity and Ionic Strength.—In the application of the law of mass action to strong electrolytes, it was early recognized that the equilibrium constant does not remain constant when the "active masses" of ions in the equilibrium constant expression are represented by the concentrations of these ions as calculated from the Arrhenius theory of the incomplete dissociation of the strong electrolytes. It was originally assumed that all electrolytes are incompletely dissociated because the conductivity of electrolytes increases with dilution, the limiting conductivity at infinite dilution being assumed to represent complete dissociation. However, strong electrolytes do not follow the Ostwald dilution law. Furthermore, the solubility of slightly soluble strong electrolytes can be treated by the mass action law only as long as the total concentration of electrolytes is small, the solubility increasing markedly in the presence of indifferent electrolytes that do not react with the dissolving salt and do not have an ion in common with it.

The increased solubility of a slightly soluble salt in a strong salt solution could not be explained satisfactorily on the basis of the Arrhenius theory. On the other hand, the enhanced solubility follows from the empirical rule that the presence of electrolytes of moderate concentration decreases the activity of the dissolved salt so that a greater quantity must dissolve to maintain a definite activity and the corresponding partial molal free energy.

After a study of the general decrease in the activity coefficient of an electrolyte in the presence of indifferent electrolytes in the dilute range, Lewis and Randall[1] concluded that in any dilute solution of a mixture of strong electrolytes of the same valence type the activity coefficient of each electrolyte depends solely on the total concentration. Because salts of the higher valence types have a much greater effect than univalent salts, Lewis and Randall introduced a new term, *ionic strength*, μ, to permit the correlation of data on the influence of salts of all types.

In a solution of a strong electrolyte, the ionic strength of the solution is defined as one-half the sum of the ion molalities, each multiplied by the square of its charge, the factor $\frac{1}{2}$ being included because the sum includes both the positive and the negative ions. If z_i is the charge of the ion i, this definition may be expressed as

$$\mu = \frac{1}{2} \sum m_i z_i^2 \tag{21.28}$$

With this definition, Lewis and Randall[2] were able to state their *principle of ionic strength* concerning the influence of electrolytes on the activity

---

[1] LEWIS, G. N., and M. RANDALL, *J. Am. Chem. Soc.*, **43**, 1112 (1921).

[2] *Loc. cit.*

coefficient: *In dilute solutions the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength.* As we shall see, this empirical rule proved to have a theoretical basis. It holds only as a limiting law, and it may be applied with reasonable accuracy only in dilute solutions (below 0.2m); even where it does not hold quantitatively, it furnishes a convenient qualitative rule.

For a uni-univalent electrolyte the ionic strength is identical with the concentration, that is, $\mu = (m + m)/2$. For a uni-bivalent electrolyte such as potassium sulfate,

$$\mu = \frac{(2m + 4m)}{2} = 3m$$

and, for a bi-bivalent electrolyte such as copper sulfate,

$$\mu = \frac{(4m + 4m)}{2} = 4m$$

In other words the effectiveness of these salts in influencing activities is in the order of 1:3:4.

DEBYE-HÜCKEL EQUATION

The first successful theoretical explanation of the observed activity of strong electrolytes was the theory of Debye and Hückel,[1] which explains the deviation of electrolytes from the laws of ideal solution in terms of the interionic attraction of the charged ions in the solution. The theory rests on a successful calculation of the potential of an ion surrounded by an ionic atmosphere that contains more oppositely charged ions than ions of the same kind of charge. Although limiting mathematical approximations and physical assumptions are made in the derivation that restrict its precise application, the equation has established its usefulness in dilute solutions where the approximations are valid.

Electric Potential of an Ion.—Consider a positive ion in a solution surrounded by the charges of the remainder of the solution. Because of the attraction of opposite charges, a positive ion is surrounded by more negative ions than positive ions, the orienting force of the charges tending to overcome the dispersive forces of the thermal agitation of the ions. The potential of the central ion Debye and Hückel found to be of the form

$$\psi = \frac{Ae^{-\kappa r}}{r} \tag{21.29}$$

where A is an integration constant, e the base of the natural logarithms,

---

[1] DEBYE, P., and E. HÜCKEL, *Physik. Z.*, **24**, 185 (1923). The theory as we shall outline it was not complete in this paper. It has been developed and improved by the authors and others.

r the distance for which the value of the potential ψ is calculated, and κ an important quantity defined by the equation

$$\kappa = \sqrt{\frac{4\pi e^2 \Sigma n_i z_i^2}{DkT}} \tag{21.30}$$

In equation (21.30), e is the electronic charge (positive); n_i the number of ions of the charge z_i per cubic centimeter; D the dielectric constant of the solvent; k the Boltzmann gas constant, that is, R/N, the gas constant per molecule; and T the absolute temperature. For the simple case of a uni-univalent electrolyte for which z for both positive and negative ions is unity, equation (21.30) becomes simplified to

$$\kappa = \sqrt{\frac{4\pi e^2 n}{DkT}} \tag{21.31}$$

The reciprocal of κ has the dimensions of length. It is interpreted as the effective radius of the ionic atmosphere about the central ion. This radius is large for small values of κ, that is, when the concentration of ions is small. Equation (21.30) shows also the importance of the charge of ions, the ions of high charge having much greater influence on κ than univalent ions.

The integration constant A can be evaluated for the limiting case of a very dilute solution where the concentration of ions is so small that κ is very small and $e^{-\kappa r} = 1$. The entire potential of the ion at the distance r can then be attributed to the charge on the ion itself and not to any potential because of the ionic atmosphere. Because this potential for a point charge is

$$\psi_0 = \frac{z_i e}{Dr} \tag{21.32}$$

it appears on comparison with equation (21.29) that $A = z_i e/D$ so that equation (21.29) becomes

$$\psi = \frac{z_i e}{Dr} e^{-\kappa r} \tag{21.33}$$

An important step is now made in dividing the potential into two parts, one ψ_0 due to the charge of the ion itself and one ψ_i due to the ionic atmosphere around the central ion. Thus, $\psi = \psi_0 + \psi_i$. But, if ψ_0 has the value in equation (21.32), the potential due to the ionic atmosphere, from equation (21.33), is

$$\psi_i = \psi - \psi_0 = \frac{z_i e}{Dr}(e^{-\kappa r} - 1) \tag{21.34}$$

The term $e^{-\kappa r}$ can be expanded in a series; for small values of κr the series becomes approximately equal to $1 - \kappa r$ so that equation (21.34) becomes

$$\psi_i = -\frac{z_i e \kappa}{D} \tag{21.35}$$

Equation (21.35) was derived on the basis of several simplifying assumptions. If the ions are not considered to be point charges but to have an effective radius so that the distance of nearest approach is a, equation (21.35) has the more complicated form

$$\psi_i = -\frac{z_i e}{D}\frac{\kappa}{1 + \kappa a} \tag{21.36}$$

For ions of a single size, a represents the diameter of the ions; for a mixture of ions of different sizes, a must represent the mean effective diameter of the ions. Observe that, for very dilute solutions where κ is small, equation (21.36) reduces to equation (21.35).

Free Energy of Transfer of an Ion.—In an ideal solution, the free energy of transfer of a mole of substance from the concentration N_1 to the concentration N_2 is given by $RT \ln (N_2/N_1)$. From the definition of activity, the corresponding free energy of transfer in a nonideal solution is given by $RT \ln (a_2/a_1)$. For a single molecule, the ideal and actual free energy change is, respectively, $kT \ln (N_2/N_1)$ and $kT \ln (a_2/a_1)$. Because of the relation $a = N\alpha$, we may divide the free energy of transfer into two parts, as in the equation

$$\Delta F = RT \ln \frac{a_2}{a_1} = RT \ln \frac{N_2\alpha_2}{N_1\alpha_1} = RT \ln \frac{N_2}{N_1} + RT \ln \frac{\alpha_2}{\alpha_1} \tag{21.37}$$

where the term $RT \ln (\alpha_2/\alpha_1)$ represents the free energy change in excess of the ideal free energy change. This division of the free energy change into an ideal and a nonideal portion is used in explaining the deviations of ionic solutions from the ideal solution laws.

Let us consider the reversible work of bringing a charged ion from an infinitely dilute solution to a solution in which its concentration is N and its activity coefficient is α_i. In the infinitely dilute solution where $N = N_0$, the activity coefficient is unity. Let the ion be discharged while in the dilute solution, transferred without charge into its final ionic atmosphere in the final solution, and there charged reversibly. Because the reversible work done by a system is related to the free energy change of the system by the relation $\Delta F = -w'$, ΔF for this process is numerically equal to the reversible work done on the system.

On the assumption that the ion without its charge behaves as an ideal solute, it follows that the work done on it in transferring it from the dilute to the concentrated solution is given by the equation

$$\text{Ideal work on the ion} = \frac{\Delta F}{N}\,(\text{ideal}) = kT \ln \frac{N}{N_0} \tag{21.38}$$

But the electrical work of discharging and charging the ions is also a part of the reversible work of transfer. Per ion it is,

$$\text{Electrical work on the ion} = \frac{\Delta\text{F}}{N}\,(\text{electrical}) = kT \ln \alpha_i \qquad (21.39)$$

for α in the dilute solution is unity. For N ions, we obtain the important relations

$$\left.\begin{aligned} \Delta\text{F} &= \Delta\text{F}(\text{ideal}) + \Delta\text{F}(\text{electrical}) \\ \Delta\text{F}(\text{ideal}) &= NkT \ln \frac{N}{N_0} = RT \ln \frac{N}{N_0} \\ \Delta\text{F}(\text{electrical}) &= NkT \ln \alpha_i = RT \ln \alpha_i \end{aligned}\right\} \qquad (21.40)$$

which relate the activity coefficient to the electrical work of transfer.

The Debye-Hückel theory has been called the "theory of complete ionization" because it undertakes to explain the deviation of a solution of ions from the ideal laws entirely on the basis of the electric charges instead of on an assumed existence of un-ionized molecules in the ionic solution. Indeed, it has been so successful that the concept of the complete ionization of strong electrolytes is utilized almost universally. In solutions in which the solvent has a low dielectric constant, the association of ions into more complex particles becomes important, but these associated complexes do not necessarily correspond to neutral un-ionized molecules. There is nothing in theory as developed, however, which prohibits its application to solutions of weak electrolytes that are known to be only partly dissociated into ions. When we apply the equations to strong electrolytes, we assume that the numerical values for the number of ions to be substituted in the formulas is the maximum number that the electrolyte can give, and for weak electrolytes we use the number of ions actually present.

Electrical Work of Transfer.—In the previous section, we indicated that the electrical work of transfer, which has been equated with a function of the activity coefficient in equation (21.39), can be derived from the reversible work of charging the ion in its new environment. This work evidently depends on the potential of the ion in the new and in the old environment. In equations (21.32) to (21.35), this potential was divided into two parts, that due to the charge of the ion itself and that due to the ionic atmosphere. But the ion in the dilute solution has the same charge as it has in the concentrated solution, although it has no ionic atmosphere in the extremely dilute solution. It follows that the work of discharge of the ion in the dilute solution at the potential of its own charge is exactly equal and opposite to the work of charging the ion at that part of the potential ψ_0 due to its own charge in the new solution. The new electrical work of the transfer, therefore, arises from the potential ψ_i of the ion due to its ionic atmosphere, as indicated in equations (21.35) and (21.36). The electrical work has been shown to be equal to one-half the product of the potential and the charge of the ion so that we have, per ion of charge z_i,

$$\frac{\Delta F}{N} \text{ (electrical)} = \frac{1}{2} \psi_i z_i e \tag{21.41}$$

From this equation and equations (21.35) and (21.36), we have

$$\frac{\Delta F}{N} \text{ (electrical)} = -\frac{z_i^2 e^2 \kappa}{2D} \tag{21.42}$$

as the simple form and

$$\frac{\Delta F}{N} \text{ (electrical)} = -\frac{z_i^2 e^2}{2D} \frac{\kappa}{1 + \kappa a} \tag{21.43}$$

as a more exact form. We shall develop equation (21.42) only. The corresponding equations obtained with equation (21.43) can be readily derived. From equation (21.42), the electrical free energy of transfer per mole of the ion is readily found to be

$$\Delta F\text{(electrical)} = -\frac{z_i^2 e^2 N}{2D} \kappa \tag{21.44}$$

The negative sign indicates that the transfer of the charge to the ionic environment proceeds with a decrease in free energy; that is, the process is spontaneous, tending to oppose the tendency of the ions to diffuse into the more dilute solution.

Activity Coefficient of an Ion.—From equations (21.40) and (21.44), it is clear that the activity coefficient is related to the maximum electrical work of transfer of N ions from the solution where the coefficient is unity to the solution where it is α_i by the equation

$$-RT \ln \alpha_i = \frac{z_i^2 e^2 N}{2D} \kappa \tag{21.45}$$

Here α_i is the activity coefficient of the ion that is transferred and z_i is its charge. By the rules previously derived, α_i is related to the mean activity coefficient. From equation (21.45), we have

$$-\ln \alpha_i = \frac{z_i^2 e^2 N}{2DRT} \kappa = \frac{z_i^2 e^2}{2DkT} \kappa \tag{21.46}$$

where κ contains the term for the concentration of ions. Before we substitute for κ in equation (21.46), we shall call attention to the fact that its concentration unit is the number of ions per cubic centimeter, a volume unit, and α is the activity coefficient for the mole fraction unit.

The further assumption is, therefore, made at this point that $\alpha_i = f_i$, the activity coefficient of the ion for the concentration in molar units. This step is equivalent to a substitution of C/C_0 for N/N_0 in equations (21.40). This approximation is valid for the dilute solutions in which the final equation is found to hold. If other deviations from the Debye-Hückel equation did not appear in the more concentrated solutions, it would be necessary to introduce a correction term for the deviation of f from α in the more concentrated solutions. A similar statement applies when the molal activity coefficient γ is substituted for α. With f_i as the activity coefficient of the ion which is transferred, equation (21.46) becomes

$$-\ln f_i = \frac{z_i^2 e^2}{2DkT}\kappa \tag{21.47}$$

The value of κ is indicated in equation (21.30), which contains a factor $\Sigma n_i z_i^2$ in addition to the constants found in equation (21.47), n_i being the number of ions of a particular kind and z_i the charge of this kind of ions. This factor is readily converted to gram-ionic weights per liter, because, for one kind of ion,

$$C_i = \frac{1{,}000 n_i}{N}$$

Accordingly, $n_i z_i^2 = (N/1{,}000)C_i z_i^2$. With this substitution, equation (21.30) becomes

$$\kappa = \sqrt{\frac{4\pi e^2 N}{1{,}000DkT}\sum C_i z_i^2} \tag{21.48}$$

But the summation of the molar concentrations of the various ions, each multiplied by the square of the charge of the ion, corresponds, except for the factor $\frac{1}{2}$ and the use of C_i for m_i, to the definition of ionic strength in equation (21.28). If the ionic strength is here defined on the molar basis rather than on the molal basis, it is evident that we may substitute 2μ for $\Sigma C_i z_i^2$ in equation (21.48). This equation may now be substituted in equation (21.47). When natural logarithms are converted to common logarithms, this equation then becomes

$$-\log f_i = \frac{z_i^2 e^3 \sqrt{2\pi N/1{,}000}}{2.3026(DkT)^{\frac{3}{2}}}\sqrt{\mu} = z_i^2 A \sqrt{\mu} \tag{21.49}$$

The factor A in equation (21.49) contains terms for the dielectric constant D and the temperature T in addition to the universal constants. Because $\boldsymbol{k} = \boldsymbol{R}/\boldsymbol{N}$, the factor A in equation (21.49) has the value

$$A = \frac{A'}{(DT)^{\frac{3}{2}}} = \frac{e^3 N^2 \sqrt{2\pi/1{,}000}}{2.3026R^{\frac{3}{2}}(DT)^{\frac{3}{2}}} = \frac{1.8243 \times 10^6}{(DT)^{\frac{3}{2}}} \tag{21.50}$$

where the constants have the values given in Appendix I. This equation can be used for any solvent at any temperature. If the dielectric constant[1] of water has the values 88.25, 82.27, 80.35, and 78.49, respectively, at the temperatures 0, 15, 20, and 25°c, the values of A for aqueous solutions at these temperatures are, respectively, 0.4873, 0.4997, 0.5045, and 0.5095. The latter, 25° value of A, corresponds to the value 0.505 commonly found in the chemical literature, and based on the older Millikan value of 4.774×10^{-10} abs esu for the electronic charge.

Mean Activity Coefficient.—Equation (21.49) and the preceding equations express the relations for the activity coefficient of a single ion species, the factor z_i being the charge of this species. As was mentioned earlier, however, the activity of a single ion species in the absence of other ions cannot be measured experimentally. Because the mean activity coefficient is what is determined, it will be necessary to find the relation between f_i and $f_\pm$.

We shall do this for a binary electrolyte of the kind illustrated in equation (21.11) for which the relation between the activity coefficients of the positive and negative ions and the mean activity coefficient is given by equation (21.26). From this equation,

$$\log f_\pm = \frac{1}{\nu}(\nu_+ \log f_+ + \nu_- \log f_-) \tag{21.51}$$

If the ith ion in equation (21.49) is alternately the positive ion and the negative ion, we have, on substitution in equation (21.51),

$$-\log f_\pm = \left(\frac{\nu_+ z_+{}^2 + \nu_- z_-{}^2}{\nu}\right) A \sqrt{\mu} \tag{21.52}$$

But, the solution is electrically neutral so that

$$\nu_+ z_+ = \nu_- z_-$$

It can, therefore, be readily shown that equation (21.52) may be expressed in the form

$$-\log f_\pm = z_+ z_- A \sqrt{\mu} \tag{21.53}$$

In a pure uni-univalent electrolyte in water at 25°c, equation (21.53) has the simple form

$$-\log f_\pm = 0.5095 \sqrt{\mu} = 0.5095 \sqrt{C} \tag{21.54}$$

because the ionic strength equals the concentration for such a salt. When the logarithm of the activity coefficient of such an electrolyte is

---

[1] The values of the dielectric constant are taken or calculated from the tabulation of N. E. Dorsey, "Properties of Ordinary Water-substance," Table 174, pp. 364–365, Reinhold Publishing Corporation, New York, 1940.

plotted against the square root of the molarity or molality, the slope should be -0.5. This limiting slope is approached by all strong electrolytes of this type in dilute solutions (below 0.01m). This agreement affords one of the tests of the Debye-Hückel equation.

In a uni-bivalent electrolyte, $z_+z_- = 2$ and

$$-\log f_\pm = 1.0\sqrt{\mu} \tag{21.55}$$

Here, μ is no longer equal to C.

For a uni-tervalent electrolyte, it is evident that

$$-\log f_\pm = 1.5\sqrt{\mu} \tag{21.56}$$

The limiting slopes 0.5, 1.0, and 1.5 for the three types of salt have been confirmed by experiment. This experimental confirmation of the theoretical slopes supports the general logic of the Debye-Hückel equation. At the same time, the Debye-Hückel equation affords an excellent theoretical basis for the empirical principle of ionic strength of Lewis and Randall.

More Complete Forms of the Debye-Hückel Equation.—In the derivation of the Debye-Hückel equation, a number of simplifying assumptions were made. In part because of these approximations and in part because the specific properties of the individual ions become more important in concentrated solutions, the simple linear forms of the equation are approached only as limiting values, that is, in very dilute solutions. Various attempts have been made to extend the range of validity of the equation. One, of course, starts with the more exact equation (21.43) instead of equation (21.42) so that equation (21.53) becomes

$$-\log f_\pm = \frac{z_+z_-A}{1+\kappa a}\sqrt{\mu} \tag{21.57}$$

Because κ is a function of the ionic strength expressible as $B\sqrt{\mu}$, equation (21.57) may be put in the form

$$-\log f_\pm = \frac{z_+z_-A\sqrt{\mu}}{1+Ba\sqrt{\mu}} \tag{21.58}$$

B may be evaluated from the constants for κ in equation (21.30). However, when equation (21.58) is then fitted to the experimental data, a may or may not have values that are reasonable when interpreted as the mean ionic diameter. In practice, therefore, a is usually treated as an empirical constant. Equation (21.58) provides for the observed deviation from the straight line when $\log f$ is plotted against $\sqrt{\mu}$. It does not provide for the minimum actually found for $\log f$ in the more concentrated solutions, the values of $\log f$ then rising at higher concentrations.

In the above derivations, the dielectric "constant" D was treated as a constant, the value for pure water being used for the salt solutions. In these solutions, however, the properties of the solvent water are no longer identical with those of the pure solvent. Some correction for this effect may be made by the addition of another term to equation (21.58) so that it now becomes

$$-\log f_{\pm} = \frac{z_+z_-A\sqrt{\mu}}{1 + Ba\sqrt{\mu}} - C\mu \qquad (21.59)$$

In practice, C in this equation is treated as an empirical constant, being given a value that fits the equation to the observed data. Equation (21.59) is sometimes simplified to

$$-\log f_{\pm} = z_+z_-A\sqrt{\mu} - C'\mu \qquad (21.60)$$

As we stated previously, the values of $\log f$ in these equations are really the values of $\log \alpha$. From the relations between α, γ, and f given in equations (19.113), (19.114), and (19.115), the true values of f and γ may be obtained by the addition of the proper corrective terms to the above equations.

Among the extensions of the Debye-Hückel equation must be included that of Gronwall, LaMer, and Sandved,[1] which takes into account the higher terms in the series expansion used in the evaluation of the potential ψ. The result is a complicated correction term to equation (21.57). This equation is successful in interpreting the activity coefficients of bi-bivalent electrolytes, such as zinc sulfate,[2] that are not represented by the simpler equations.

MEASUREMENT OF ACTIVITY COEFFICIENTS

If the limiting equation of Debye and Hückel is to be tested, experimental values of activity coefficients must be available for dilute solutions. In these dilute solutions, the chances for experimental errors are great. The testing, therefore, must be made by methods that are accurate. These methods may be classified into three groups, solubility measurements, emf measurements, and measurements on the solvent. The solubility method may be used for nonelectrolytes as well as for electrolytes. The emf method is limited to electrolytes that participate in reversible reactions at electrodes. The solvent properties usually measured are freezing point lowering, boiling point rise, and vapor pressure lowering. The latter measurements may obviously be made on solutions of either electrolytes or nonelectrolytes, but they give the

---

[1] GRONWALL, T. H., V. K. LAMER, and K. SANDVED, *Physik. Z.*, **29**, 358 (1928).

[2] COWPERTHWAITE, I. A., and V. K. LAMER, *J. Am. Chem. Soc.*, **53**, 4333 (1931).

activity of the solvent directly. The activity of the solute must be obtained with the aid of the Gibbs-Duhem equation.

Solubility of Salts.—For the solution of a slightly soluble salt, such as silver chloride, to form a saturated solution, we may write

$$\mathrm{AgCl(c)} = \mathrm{Ag}^+ + \mathrm{Cl}^-; \qquad \Delta F = 0 \tag{21.61}$$

and

$$\Delta F - \Delta F^\circ = RT \ln a_+ + RT \ln a_- = RT \ln a_+a_- \tag{21.62}$$

But, because $\Delta F = 0$,

$$\Delta F^\circ = -RT \ln K = RT \ln a_+a_- \tag{21.63}$$

whence,

$$K = a_+a_- \tag{21.64}$$

This equilibrium constant K is the well-known *activity solubility product.*

The solubility product constant was first derived in terms of the concentrations of the ions rather than in activities; it was defined by the equation

$$K_C = C_+C_- \tag{21.65}$$

For a salt of the uni-univalent type, $C_+ = C_- = s$, where s is the solubility in moles per liter. Accordingly, $s = \sqrt{K_C}$ for the silver chloride. It was early recognized, however, that the solubility of a slightly soluble salt is greatly influenced by the presence of other salts that do not furnish an ion in common and therefore do not change the concentration of either the positive or the negative ion. Furthermore, the product C_+C_- does not remain constant when either C_+ or C_- is changed by the addition of some electrolyte containing one of these ions.

These results can be explained in terms of the activity solubility product because

$$K = a_+a_- = (C_+f_+)(C_-f_-) = (C_\pm)^2(f_\pm)^2 = K_C(f_\pm)^2 \tag{21.66}$$

If the result of an increased salt concentration in the solvent is to lower the activity coefficient of the saturating salt, $f_\pm$ takes on a value of less than unity and K_C must increase to preserve the constancy of K. Furthermore, since the Debye-Hückel equation gives a quantitative estimate of the change of f with salt concentration, it should give a quantitative estimate of the influence of additional salts on the solubility of the saturating salt. A measurement of the solubility of a salt in salt solutions may therefore be used as a test of the validity of the Debye-Hückel equation.

When the measurements are carried out in pure water or in salt water containing no ions in common, the calculations are simple. Consider the general case of a slightly soluble salt of the type indicated in equation

(21.11). The salt must not be too soluble lest the ionic strength become too high. For this salt, we may set up, in the usual manner,

$$\Delta F^\circ = RT \ln K = RT \ln a_+^{\nu_+} a_-^{\nu_-} \tag{21.67}$$

whence we obtain, for the activity solubility product,

$$K = (a_+^{\nu_+})(a_-^{\nu_-}) = (C_+f_+)^{\nu_+}(C_-f_-)^{\nu_-} = (C_\pm)^\nu(f_\pm)^\nu \tag{21.68}$$

$$K = K_C(f_\pm)^\nu \tag{21.69}$$

These general equations may be applied either in the presence or in the absence of a common ion. If a common ion is not present and s is the solubility, $C_+ = \nu_+ s$, $C_- = \nu_- s$, so that

$$K_C = s^\nu(\nu_+^{\nu_+}\nu_-^{\nu_-}) \tag{21.70}$$

Let us now compare the solubility s_0 of the salt in pure water and its solubility s in a salt solution, f_0 being the activity coefficient of the saturating salt in pure water and f the corresponding value in the salt solution. It follows from equations (21.69) and (21.70), therefore, that, because ν_+ and ν_- remain constant,

$$sf = s_0 f_0 = \frac{K}{\nu_+^{\nu_+}\nu_-^{\nu_-}} = \text{const} \tag{21.71}$$

and

$$\frac{s}{s_0} = \frac{f_0}{f} \tag{21.72}$$

The ratio of the solubilities in salt solution and in pure water gives directly the ratio of the activity coefficients in these two solutions.

One of the first tests of the Debye-Hückel equation was given by the data of Brønsted and LaMer[1] on the solubility of some complex cobaltammines at 15°C. These salts are sparingly soluble, their solubilities in water at 15°C ranging from 0.00049 to 0.00005M. Analysis of these saturated solutions was simplified, for a number of equivalents of ammonia could be released and titrated for each mole of the complex salt. These workers tested the Debye-Hückel equation by the following method:

From equations (21.53) and (21.72) is obtained the general equation

$$\log \frac{s}{s_0} = \log f_0 - \log f = z_+z_-A\,(\sqrt{\mu} + \sqrt{\mu_0}) \tag{21.73}$$

For the uni-univalent saturating salt

$$[Co(NH_3)_4(NO_2)(CNS)]^+[Co(NH_3)_2(NO_2)_2(C_2O_4)]^-$$

for which $z_+ = z_- = 1$, equation (21.73) becomes

$$\log \frac{s}{s_0} = \log f_0 - \log f = 0.5\sqrt{\mu} + \text{const} \tag{21.74}$$

BRØNSTED, J. N., and V. K. LAMER, *J. Am. Chem. Soc.*, **46**, 555 (1924).

because the ionic strength μ_0 in water is constant. For the uni-bivalent saturating salt $[Co(NH_3)_4C_2O_4]_2{}^{+}(S_2O_6)^{--}$ for which $z_+ = 1, z_- = 2$, equation (21.73) becomes

$$\log \frac{s}{s_0} = \log f_0 - \log f = 1.0 \sqrt{\mu} + \text{const} \tag{21.75}$$

For the ter-univalent saturating salt $[Co(NH_3)_6]^{+++}[Co(NH_3)_2(NO_2)_2(C_2O_4)]_3{}^{-}$ for which $z_+ = 3$, $z_- = 1$, equation (21.73) becomes

$$\log \frac{s}{s_0} = \log f_0 - \log f = 1.5 \sqrt{\mu} + \text{const} \tag{21.76}$$

Various values of the ionic strength μ were obtained by the addition of known quantities of salts such as sodium chloride, potassium nitrate, barium chloride, potassium sulfate, magnesium sulfate, and potassium cobalticyanide to the solvent water. In the solutions tested, the value of log (s/s_0) when plotted against $\sqrt{\mu}$ gave straight lines as required by equations (21.74), (21.75), and (21.76), the slope in each case being the slope of 0.5, 1.0, or 1.5 as required by the theory.

In order to evaluate log f, however, it is necessary to know the value of log f_0, f_0 being the activity coefficient of the saturated water solution of the salt. Because of the linear relation between log (s/s_0) and $\sqrt{\mu}$, it is possible to extrapolate the curve through the measured value of $\sqrt{\mu_0}$ for the saturated value in pure water to $\mu = 0$, where the ions are so widely separated that $f = 1$, the extrapolated value of s in this hypothetical solution having the value s^*. Because

$$\log \frac{s}{s^*} = -\log f = z_1 z_2 0.5 \sqrt{\mu} + \text{const} \tag{21.77}$$

values of log s/s^* found in this way give values of $-\log f$ directly.

Figure 21.1 shows the degree of correspondence between the activity coefficients measured in the different salt solutions and the limiting slopes predicted by the Debye-Hückel equations for the different types of salts. The equations for the uni-univalent salt, the uni-bivalent salt, and the ter-univalent salt are represented, respectively, by curves A, B, and C. The agreement between the experimental and theoretical values is good. We should point out, however, that, when higher valence solvent salts are used with higher valence saturating salts, deviations from the linear relations begin to appear at low concentrations.

Activity Coefficients from Emf Measurements.—Galvanic cells offer a convenient and accurate method of obtaining the activity coefficients of electrolytes. This method can be used whenever a cell can be set up that has a cell reaction involving the activities of the desired substances. The concentration of the electrolytes in a cell are usually expressed in molalities, especially when the cell reaction is studied at different temperatures, hence γ is the activity coefficient evaluated by this method.

When the value of $E°$ for a cell is known, the activities of the constituents can be derived by a simple calculation. The values so derived, however, rest on the value of $E°$ that is adopted, and this value in turn rests on an extrapolation of experimental data to zero concentration. Because the activity coefficient approaches unity when the concentration approaches zero, the precision with which this limiting value can be estimated depends on the rate of change of activity with concentration at concentrations below those which can be measured directly. If the Debye-Hückel equation is valid as the limiting relation, it is evident that γ for an electrolyte cannot equal unity at any finite concentration. In other words, an electrolytic solution cannot be ideal at any finite concentration so that an extrapolation to zero concentration cannot be avoided. Some of the problems met in the extrapolation of experimental data and therefore inherent in the setting up of a table of activity coefficients will be illustrated.

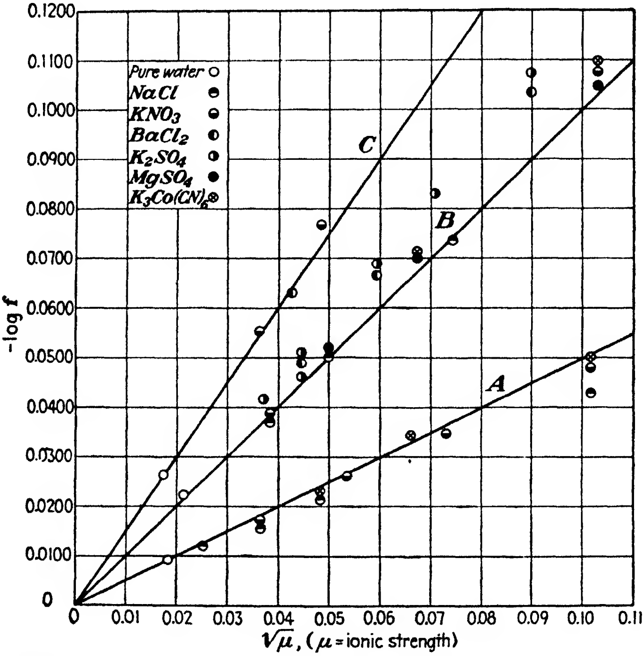


FIG. 21.1.—Relations between activity coefficient and ionic strength from the solubility of salts of different types in salt solutions.

Consider the cell

$$\text{Pt, H}_2\text{; HCl}(m)\text{; AgCl(c), Ag} \qquad (A)$$

for which the cell reaction is

$$\tfrac{1}{2}H_2 + AgCl(c) = H^+(m) + Cl^-(m) + Ag \qquad (21.78)$$

The activity of the solids, silver and silver chloride, remains constant and is, therefore, assigned a value of unity in accordance with the usual definitions of the standard states so that, for this reaction

$$E' = E^\circ - \frac{RT}{nF} \ln \frac{a_{H^+}a_{Cl^-}}{P_{H_2}^{\frac{1}{2}}} \qquad (21.79)$$

The emf of this cell depends, as indicated, on the experimental partial pressure of the hydrogen gas. The emf data reported in the chemical literature are usually for the cell with a standard hydrogen electrode, P_{H_2} being 1 atmosphere. Under these conditions, equation (21.79) becomes

$$E = E^\circ - \frac{RT}{nF} \ln a_{H^+}a_{Cl^-} = E^\circ - \frac{RT}{nF} \ln (m_{H^+}\gamma_{H^+})(m_{Cl^-}\gamma_{Cl^-}) \qquad (21.80)$$

where

$$E = E' - \frac{RT}{nF} \ln P_{H_2}^{\frac{1}{2}}$$

For reaction (21.78) as written, $n = 1$, so that equation (21.80) may be put into the forms

$$\left.\begin{aligned} E &= E^\circ - \frac{RT}{F} \ln (m_\pm)^2 - \frac{RT}{F} \ln (\gamma_\pm)^2 \\ E &= E^\circ - 2\,\frac{(2.3026)RT}{F} \log m_\pm - 2\,\frac{(2.3026)RT}{F} \log \gamma_\pm \end{aligned}\right\} \qquad (21.81)$$

Activity Coefficient of Hydrochloric Acid.—For cell (A), Harned and Ehlers[1] report values of the emf at temperatures of 0 to 35°C and for concentrations of hydrochloric acid ranging from 0.003m to 0.12m, the value at 25° for 0.1m hydrochloric acid being $E = 0.35240$ volt. In order to use equation (21.81) to calculate the activity coefficient of hydrogen chloride in this solution, we must have the value of E°. From their data, Harned and Ehlers derive the value of $E^\circ = 0.22239$ volt. From substantially identical data, MacInnes[2] calculated

$$E^\circ = 0.2225 \text{ volt}$$

---

[1] HARNED, H. S., and R. W. EHLERS, *J. Am. Chem. Soc.*, **54**, 1350 (1932).

[2] MACINNES, D. A., "The Principles of Electrochemistry," p. 186, Reinhold Publishing Corporation, New York, 1939.

The "International Critical Tables"[1] value based on older data is 0.2221 volt.

A simple calculation shows how the values of the activity coefficient depend on the adopted value of $E°$. Let us calculate the values for 0.1m hydrochloric acid from the above data. From equation (21.81),

$$2 \times 0.059141 \log \gamma_{\pm} = E° - 2 \times 0.059141 \log (0.1) - E$$

Using the Harned and Ehlers value of $E°$ and $E = 0.35240$,

$$\log \gamma_{\pm} = \frac{0.22239 + 0.11828 - 0.35240}{0.11828}$$
$$= -0.09917$$

With $E° = 0.2225$ volt and the same E,

$$\log \gamma_{\pm} = -0.09824$$

With $E° = 0.2221$ volt,

$$\log \gamma_{\pm} = -0.10162$$

From these values of $\log \gamma_{\pm}$ the values obtained for the activity coefficient of 0.1m hydrochloric acid at 25°c are, respectively, 0.7958, 0.7976, and 0.7914. Values of the activity coefficient of additional electrolytes are given in Table 21.1.

TABLE 21.1.—ACTIVITY COEFFICIENTS* γ OF SOME ELECTROLYTES AT 25°C

Electrolyte	Concentration, moles of electrolyte/1,000 grams of water											
	0.005	0.01	0.02	0.05	0.10	0.20	0.50	1.00	1.50	2.00	3.00	4.00
NaCl	0.928	0.903	0.872	0.821	0.778	0.732	0.680	0.656	0.655	0.670	0.719	0.791
KCl	0.927	0.902	0.869	0.817	0.770	0.719	0.652	0.607	0.587	0.578	0.574	
HCl	0.930	0.906	0.878	0.833	0.798	0.768	0.769	0.811	0.898	1.011	1.31	1.74
HBr	0.930	0.906	0.879	0.838	0.805	0.782	0.790	0.871				
NaOH	. . . . .	0.899	0.86_0	0.80_5	0.75_9	0.71_9	0.68_1	0.66_7	0.67_1	0.68_5		
$CaCl_2$	0.789	0.732	0.699	0.584	0.524	0.491	0.510	0.725	. . . . .	1.554	3.384	
$ZnCl_2$	0.767	0.708	0.642	0.556	0.502	0.448	0.376	0.325	0.290			
H_2SO_4	0.643	0.545	0.455	0.341	0.266	0.210	0.155	0.131	. . . . .	0.125	0.142	0.172
$ZnSO_4$	0.477	0.387	0.298	0.202	0.148	0.104	0.063	0.044	0.037	0.035	0.041	
$CdSO_4$	0.476	0.383	. . . . .	0.199	0.137	. . . . .	0.061	0.042	0.039	0.030	0.026	

* MACINNES, D. A., "The Principles of Electrochemistry," p. 167, Reinhold Publishing Corporation, New York, 1939. References to the original literature are given by MacInnes.

According to the calculations of Randall and Young,[2] the value of γ at 25°c both from freezing point lowering and emf measurements is

---

[1] "International Critical Tables," Vol. 6, p. 332, McGraw-Hill Book Company, Inc., New York, 1926.

[2] RANDALL, M., and L. E. YOUNG, *J. Am. Chem. Soc.*, **50**, 989 (1928).

0.796, in agreement with the Harned and Ehlers value. However, Randall and Young secure the E° value of 0.2221 with this value of γ. This means that their value of $E^\circ = 0.2221$ volt is based on an observed value of E for the cell (A) different from that reported by Harned and Ehlers.

Evaluation of E°.—In the previous section, we listed three different values of E° for the cell (A). The "International Critical Tables" value of 0.2221 rests on a different experimental value of E for cell (A) than do the other values. Thus, if $\gamma = 0.796$ is accepted as the activity coefficient of hydrochloric acid and $E = 0.35240$, we have from equation (21.81) the value

$$\begin{aligned} E^\circ &= 0.35240 + 2 \times 0.05914 \log (0.0796) \\ &= 0.35240 - 0.13000 \\ &= 0.2224 \text{ volt} \end{aligned}$$

in agreement with that derived by Harned and Ehlers.

However, the value of E° calculated by MacInnes rests substantially on the same data as those of Harned and Ehlers, the difference in E° resulting from different extrapolation methods. We shall, therefore, review these extrapolation methods briefly.

1. *Method of Hitchcock.*[1]—Equation (21.81) may be placed in the form

$$E + 2k \log m = E_0 - 2k \log \gamma \tag{21.82}$$

where $k = 2.3026RT/F$. Plotting the left side of equation (21.82) against $m^{\frac{1}{2}}$, on a large-scale plot, Harned and Ehlers obtained values of E for rounded values of m. Now, using the method of Hitchcock, who assumed that $\log \gamma$ varies according to equation (21.60) so that

$$\log \gamma = -0.5m^{\frac{1}{2}} + bm \tag{21.83}$$

we find on combining equations (21.82) and (21.83) that

$$E + 2k \log m - km^{\frac{1}{2}} = E^\circ - 2k\, bm \tag{21.84}$$

The left side of equation (21.84) is now plotted against m. The graph has only a slight curvature; it may, therefore, be extrapolated to $m = 0$ where the ordinate reading gives E° directly.

2. *Method of Brown and MacInnes.*[2]—With the above data, MacInnes[3] used the more exact equation (21.58) to represent γ, namely,

$$-\log \gamma = \frac{A'\sqrt{m}}{1 + B'a\sqrt{m}} \tag{21.85}$$

---

[1] Hitchcock, D. I., *J. Am. Chem. Soc.*, **50**, 2076 (1928).

[2] Brown, A. S., and D. A. MacInnes, *J. Am. Chem. Soc.*, **57**, 1356 (1935).

[3] "The Principles of Electrochemistry," p. 185.

where A' and B' differ from the constants A and B by the factor $\sqrt{d^\circ}$ as required by equation (19.93). From equation (21.82), therefore, E'' being defined by the relation

$$E'' = E + 2k \log m$$

we have, on combination with equation (21.85),

$$E'' - E^\circ = -2k \log \gamma = 2k \frac{A' \sqrt{m}}{1 + B'a\sqrt{m}} \tag{21.86}$$

Equation (21.86) may be rearranged to

$$E'' - 2kA' \sqrt{m} = E^\circ - (E'' - E^\circ)B'a\sqrt{m} \tag{21.87}$$

It appears from equation (21.87) that a plot of the left side of the equation against $(E'' - E^\circ)\sqrt{m}$ as abscissa should be a straight line with a slope of $B'a$ and an intercept of E°. A tentative value of E° is necessary for this method. Using this method on the data of Harned and Ehlers and of Roberts,[1] MacInnes obtained a straight line through the data, instead of the curved line of Hitchcock. This straight line indicates the value $E^\circ = 0.2225$ volt. It appears, therefore, that the method used in extrapolation to infinite dilution is of some importance in the calculation of E° values and the establishment of an activity coefficient scale.

Activities from Freezing Point Measurements.—Consider ice in equilibrium with water in a solution, the fugacity of the ice being $f_{(c)}$ and its molar heat content being $\text{H}_{(c)}$. From equation (19.51), the change of fugacity of the ice with temperature is

$$\frac{\partial \ln f_{(c)}}{\partial T} = \frac{\text{H}^* - \text{H}_{(c)}}{RT^2} \tag{21.88}$$

where H^* is the heat content at a standard state of unit fugacity.

Consider next pure undercooled water with a fugacity f° and a heat content H_1. For this substance,

$$\frac{\partial \ln f^\circ}{\partial T} = \frac{\text{H}^* - \text{H}_1}{RT^2} \tag{21.89}$$

From equations (21.88) and (21.89), therefore,

$$\frac{\partial \ln f_{(c)}}{\partial T} - \frac{\partial \ln f^\circ}{\partial T} = \frac{\partial \ln (f_{(c)}/f^\circ)}{\partial T} = \frac{\text{H}_1 - \text{H}_{(c)}}{RT^2} \tag{21.90}$$

But, at equilibrium, the fugacity of the ice equals the fugacity f_1 of the water in the solution. The activity of the water at equilibrium may, therefore, be defined as

$$a_1 = \frac{f_1}{f^\circ} = \frac{f_{(c)}}{f^\circ} \tag{21.91}$$

---

[1] ROBERTS, E. J., *J. Am. Chem. Soc.*, **52**, 3877 (1930).

Observe that the standard state here selected for the water is the undercooled water at the freezing temperature. From equations (21.90) and (21.91), therefore,

$$\frac{\partial \ln a_1}{\partial T} = \frac{\mathrm{H}_1 - \mathrm{H}_{(c)}}{RT^2} = \frac{\Delta \mathrm{H}_f}{RT^2} \tag{21.92}$$

where $\Delta \mathrm{H}_f$ is the heat of melting of ice at this temperature. Equation (21.92) corresponds to the ideal solubility equation (13.26) previously derived, the two equations becoming identical when $a_1 = N$.

For dilute solutions, the usual approximations may be made in integrating equation (21.92). If $\Delta \mathrm{H}_f$ is assumed to remain constant, we find on integration between the limits $a_1 = a_1$ and $a_1 = 1$, where $T = T$ and $T = T_0$, respectively,

$$\ln a_1 = -\frac{\Delta \mathrm{H}_f}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) = -\frac{\Delta \mathrm{H}_f}{R}\left(\frac{T_0 - T}{TT_0}\right) \tag{21.93}$$

For dilute solutions, TT_0 is approximately equal to T_0^2, and $T_0 - T$ is the observed freezing point lowering, which may be designated as θ. Equation (21.93) may, therefore, be put in the forms

$$\ln a_1 = -\frac{\Delta \mathrm{H}_f}{RT_0^2}\,\theta \tag{21.94}$$

and

$$d \ln a_1 = -\frac{\Delta \mathrm{H}_f}{RT_0^2}\,d\theta \tag{21.95}$$

Equations (21.94) and (21.95) give relations between the activity of the solvent and the observed freezing point lowering. For the ideal solution where $a_1 = N_1$, the relation between activity of the solute and the observed lowering is obtained by a simple substitution of $1 - N_2$ for N_1. For the nonideal solution, however, we must turn to the Gibbs-Duhem relation. Thus, from equation (19.104), the relation between the activity of the solvent and that of the solute is given by

$$d \ln a_2 = -\frac{N_1}{N_2}\,d \ln a_1 = -\frac{n_1}{n_2}\,d \ln a_1 \tag{21.96}$$

Equation (21.95) may, therefore, be written

$$d \ln a_2 = \frac{n_1}{n_2}\frac{\Delta \mathrm{H}_f}{RT_0^2}\,d\theta \tag{21.97}$$

For an aqueous solution in which $n_1 = 1{,}000/M_1$, M_1 being the molar weight of water, and n_2 equals the molality m, equation (21.97) becomes

$$d \ln a_2 = \frac{1{,}000\Delta \mathrm{H}_f}{M_1RT_0^2}\frac{d\theta}{m} = \frac{1}{k_f}\frac{d\theta}{m} \tag{21.98}$$

where k_f is the molality freezing point constant previously defined in equation (13.44). Equation (21.98) may be used for nonelectrolytes as well as electrolytes. For electrolytes, the activity of the solute is related to the mean ion activity as in equation (21.14). In terms of the mean activity, equation (21.98), therefore, becomes

$$d \ln a_\pm = \frac{1}{\nu} d \ln a_2 = \frac{1}{\nu m k_f} d\theta \tag{21.99}$$

Equation (21.99) may be evaluated by graphical integration. The computation is simplified, however, by the introduction of the j function of Lewis and Randall.

Let j be defined by the equation

$$j = 1 - \frac{\theta}{\nu m k_f} \tag{21.100}$$

Because the observed lowering θ becomes identical with $\nu m k_f$ at infinite dilution, j becomes zero at infinite dilution. When equation (21.100) is differentiated and rearranged, it becomes

$$\frac{d\theta}{\nu m k_f} = (1 - j)\frac{dm}{m} - dj \tag{21.101}$$

A comparison with equation (21.99) shows immediately that

$$d \ln a_\pm = (1 - j)\frac{dm}{m} - dj \tag{21.102}$$

In equation (21.19), we indicated the relation between the mean ion molality $m_\pm$ and the molality m of the solute. From this equation, it appears that

$$\ln m_\pm = \ln m + \ln (\nu_+^{\nu_+}\nu_-^{\nu_-})^{\frac{1}{\nu}}$$

which, when differentiated, becomes

$$d \ln m_\pm = d \ln m \tag{21.103}$$

for the ν's remain constant during the change in concentration. If equation (21.103) is now subtracted from equation (21.102), we obtain

$$d \ln \frac{a_\pm}{m_\pm} = d \ln \gamma_\pm = -j\frac{dm}{m} - dj \tag{21.104}$$

Equation (21.104), therefore, gives a relation between the mean activity coefficient and j. Integrating equation (21.104) between the limits $m = m$, and $m = 0$ where $j = 0$ and $\gamma = 1$, we have

$$\ln \gamma_\pm = -\int_0^m \frac{j}{m} dm - j \tag{21.105}$$

The value of the integral may be obtained graphically. It may also be obtained from the empirical relation of Lewis and Linhart,[1] which expresses j in terms of m.

$$j = \beta m^{\alpha} \tag{21.106}$$

When equations (21.104) and (21.106) are combined and the resulting equation integrated, we obtain

$$\begin{aligned}\ln \gamma_{\pm} &= -\frac{\beta m^{\alpha}}{\alpha} - \beta m^{\alpha} \\ &= -\frac{\beta(\alpha + 1)}{\alpha} m^{\alpha}\end{aligned} \tag{21.107}$$

A comparison with the Debye-Hückel equation indicates that α in this empirical equation should have the limiting value of $\frac{1}{2}$. It is evident that equation (21.105) may be combined directly with one of the forms of the Debye-Hückel equation, which expresses a value of $\log \gamma_{\pm}$. In this way the empirical function [equation (21.106)] may be replaced by a function with a semitheoretical basis.

Ionization Constants of Weak Electrolytes.—In the previous discussion, we treated strong electrolytes that are essentially completely ionized. The same general methods may be used to treat weak electrolytes when proper methods are available for evaluating the actual concentration of the ions. Let us consider a weak acid HA, which dissociates according to the equation

$$\mathrm{HA} = \mathrm{H}^{+} + \mathrm{A}^{-} \tag{21.108}$$

and for which the thermodynamic ionization constant is

$$K = \frac{a_{\mathrm{H}^+} a_{\mathrm{A}^-}}{a_{\mathrm{HA}}} \tag{21.109}$$

In general, the activities of the ions are functions of the ionic strength so that the simple "dissociation constants"

$$K_C = \frac{C_{\mathrm{H}^+} C_{\mathrm{A}^-}}{C_{\mathrm{HA}}} \tag{21.110}$$

and

$$K_m = \frac{m_{\mathrm{H}^+} m_{\mathrm{A}^-}}{m_{\mathrm{HA}}} \tag{21.111}$$

do not remain constant during variations in the salt concentration of the acid solution. The relation between the K and K_m at any temperature as obtained from equations (21.109) and (21.111) is

$$K = \frac{(m_{\mathrm{H}^+}\gamma_{\mathrm{H}^+})(m_{\mathrm{A}^-}\gamma_{\mathrm{A}^-})}{m_{\mathrm{HA}}\gamma_{\mathrm{HA}}} = \frac{\gamma_{\mathrm{H}^+}\gamma_{\mathrm{A}^-}}{\gamma_{\mathrm{HA}}} K_m \tag{21.112}$$

---

[1] LEWIS, G. N., and G. A. LINHART, *J. Am. Chem. Soc.*, **41**, 1951 (1919).

The corresponding relation between the thermodynamic ionization constant and the "constant" in terms of molarities is, evidently,

$$K = \frac{f_{H^+}f_{A^-}}{f_{HA}} K_c \tag{21.113}$$

Similar methods may be used to set up the constants for weak bases or for water.

Ionization Constant of Acetic Acid.—Harned and his coworkers have determined the dissociation constants of a number of weak acids over a range of temperatures. The method will be illustrated by the data of Harned and Ehlers[1] on acetic acid. The emf of the cell

$$\text{Pt, H}_2\text{; HOAc}(m_1)\text{, NaOAc}(m_2)\text{, NaCl}(m_3)\text{; AgCl, Ag} \tag{B}$$

was measured at various temperatures and for various values of m_1, m_2, and m_3. The cell is without liquid junctions; hence, the potentials are defined unambiguously. The cell reaction for this cell is

$$\tfrac{1}{2}H_2 + AgCl = H^+ + Cl^- + Ag \tag{21.114}$$

as for the reaction (21.78) of cell (A). The pressure of the hydrogen being 1 atmosphere, equation (21.80) is valid so that, for the cell

$$E = E^\circ - \frac{RT}{F} \ln (m_{H^+}\gamma_{H^+}m_{Cl^-}\gamma_{Cl^-}) \tag{21.80}$$

But, acetic acid ionizes like the weak acid in equation (21.108), so that

$$K = \frac{\gamma_{H^+}\gamma_{OAc^-}}{\gamma_{HOAc}} \cdot \frac{m_{H^+}m_{OAc^-}}{m_{HOAc}} \tag{21.115}$$

Between these two equations, m_{H^+} may be eliminated to give the equation

$$E = E^\circ - \frac{RT}{F} \ln \frac{m_{HOAc}m_{Cl^-}}{m_{OAc^-}} \cdot \frac{\gamma_{H^+}\gamma_{Cl^-}\gamma_{HOAc}}{\gamma_{H^+}\gamma_{OAc^-}} K \tag{21.116}$$

This equation may be rearranged to the form

$$E - E^\circ + \frac{RT}{F} \ln \frac{m_{HOAc}m_{Cl^-}}{m_{OAc^-}} = -\frac{RT}{F} \ln \frac{\gamma_{H^+}\gamma_{Cl^-}\gamma_{HOAc}}{\gamma_{H^+}\gamma_{OAc^-}} - \frac{RT}{F} \ln K \tag{21.117}$$

The values of E° have been accurately determined, and the values of E are measured at various known values of m_{HOAc}, m_{Cl^-}, and m_{OAc^-}. In the more dilute solutions, enough of the acetic acid dissociates so that the concentration of the acetate ion from this source must be added to that from the sodium acetate in the calculation of m_{OAc^-}. Similarly, the concentration of the undissociated acetic acid must be used for m_{HOAc}.

---

[1] *Loc. cit.*

However, these corrections remain small in the presence of the excess of sodium acetate, and they may be readily made with the aid of a preliminary value of the ionization constant so that the accuracy of the final calculation is not altered.

The values on the left side of equation (21.117) are, therefore, all known or measured in this experiment. They may be plotted against the ionic strength μ as abscissa. Now the ratio

$$\frac{\gamma_{H^+}\gamma_{Cl^-}}{\gamma_{H^+}\gamma_{OAc^-}}$$

equals unity at $\mu = 0$, and it varies little from unity at low ionic strengths. The same is true of the activity coefficient of the undissociated acetic acid γ_{HOAc}. Because the first term on the right of equation (21.117) varies in this fashion with μ and the last term is constant, the curve representing the plot of the left-hand terms of equation (21.117) against μ should be nearly straight and its extrapolated value at $\mu = 0$ gives the desired value of

$$-\frac{RT}{F}\ln K$$

A second method of plotting may be used. Equation (21.117) may be placed in the form

$$E - E^\circ + \frac{RT}{F}\ln\frac{m_{HOAc}m_{Cl^-}}{m_{OAc^-}} = -\frac{RT}{F}\ln K' \qquad (21.118)$$

where

$$K' = \frac{\gamma_{H^+}\gamma_{Cl^-}\gamma_{HOAc}}{\gamma_{H^+}\gamma_{OAc^-}}K$$

From the known values of the left-hand terms at various values of μ, K' can be calculated. These values of K' may now be plotted against μ. Because the fraction expressing the ratio of the activity coefficients approaches unity at zero ionic strength as previously indicated, $K' = K$ at $\mu = 0$. By this method, the value of the thermodynamic ionization constant of acetic acid at 25°C was found to be $K = 1.754 \times 10^{-5}$.

Thermodynamic Ionization Constant of Water.—Similar methods may be used in the calculation of the ionization of water. Thus, the concentration of hydrogen ion in the cell without liquid junction

$$\text{Pt, H}_2\text{; KOH}(m_1)\text{, KCl}(m_2)\text{; AgCl, Ag} \qquad (C)$$

is controlled by that of the hydroxyl ion according to the reaction

$$H_2O = H^+ + OH^- \qquad (21.119)$$

For this ionization, the thermodynamic ionization constant is represented by the equation

$$K_w = \frac{a_{H^+}a_{OH^-}}{a_{H_2O}} = m_{H^+}m_{OH^-}\frac{\gamma_{H^+}\gamma_{OH^-}}{\gamma_{H_2O}} \tag{21.120}$$

By convention, the molality of water in 1,000 grams of water is assigned a value of unity.

As before, let the cell reaction for cell (*C*) be represented by equation (21.114), there being, however, a further reaction according to equation (21.119), so that OH^- is consumed and H_2O produced in the cell reaction.

Between equations (21.80) and (21.120), m_{H^+} may be eliminated so that

$$E = E^\circ - \frac{RT}{F}\ln\frac{m_{Cl^-}}{m_{OH^-}}\cdot\frac{\gamma_{H^+}\gamma_{Cl^-}\gamma_{H_2O}}{\gamma_{H^+}\gamma_{OH^-}}K_w \tag{21.121}$$

This equation may be written in the form similar to equation (21.117), namely,

$$E - E^\circ + \frac{RT}{F}\ln\frac{m_{Cl^-}}{m_{OH^-}} = -\frac{RT}{F}\ln\frac{\gamma_{H^+}\gamma_{Cl^-}\gamma_{H_2O}}{\gamma_{H^+}\gamma_{OH^-}} - \frac{RT}{F}\ln K_w \tag{21.122}$$

As already discussed for acetic acid, the right-hand side of equation (21.122) may be placed equal to $-(RT/F)\ln K'$, where

$$K' = \frac{\gamma_{H^+}\gamma_{Cl^-}\gamma_{H_2O}}{\gamma_{H^+}\gamma_{OH^-}}K_w$$

The quantity K' is evaluated at various values of m_{Cl^-}/m_{OH^-} and at various temperatures from the measured values of E, and these values are plotted against the ionic strength. At each temperature, the activity coefficient ratio approaches unity at $\mu = 0$ so that an extrapolation of the value of K' to $\mu = 0$ gives K_w directly. From the data of Harned and Hamer[1] the value of K_w at 25°c is $K_w = 1.008 \times 10^{-14}$.

Problems

21.1. Calculate the mean molality $m_\pm$ for each of the following m molal solutions: $CuSO_4$, $Al_2(SO_4)_3$, $KHSO_4$. What is the mean molality of $CuSO_4$ and of K_2SO_4 in a solution containing 0.2 mole of $CuSO_4$ and 0.2 mole of K_2SO_4 per 1,000 grams of water?

21.2. Calculate the ionic strength of a 0.01m solution of aluminum sulfate. Compare with a 0.01m solution of copper sulfate. What is the ionic strength of a solution containing 0.1 mole of $NaNO_3$, 0.1 mole of $BaCl_2$, and 0.2 mole of Na_2SO_4 in 1,000 grams of water?

21.3. Calculate the value of B in equation (21.58) for water solutions at 25°c.

21.4. Prove that the Brønsted definition of ionic strength of a simple salt,

$$\mu = c\left(\frac{z_+ + z_-}{2}\right)$$

where c is the *number of equivalents* per liter, is identical with the Lewis and Randall

---

[1] HARNED, H. S., and W. J. HAMER, *J. Am. Chem. Soc.*, **55**, 2194 (1933).

definition in terms of molarities. For a mixture of salts show that

$$\mu = \tfrac{1}{2}(c_1 z_1 + c_2 z_2 + \cdots)$$

21.5. If the "mean ionic diameter" a has the value 3.5×10^{-8} cm, what percentage error in the value of f will result from using equation (21.53) instead of (21.58) for a solution with an ionic strength of 1? 0.1? 0.001?

21.6. From the relation between the ionic strength and the concentration of a pure uni-bivalent salt and a pure uni-tervalent salt, calculate the limiting slope at low concentrations when $-\log f_{\pm}$ is plotted against $\sqrt{C}$ for these salts.

21.7. At 25°c the limiting solubility of silver chloride is 1.309×10^{-5} mole per liter. What is the limiting molality? Calculate the solubility of silver chloride in 0.01m potassium chloride solution and 0.01m sodium nitrate solution, the mean activity coefficients of these salts being 0.902 and 0.90, respectively.

21.8. From the single electrode potential in Table 20.2 of the hydrogen electrode in solutions of H^+ ions and OH^- ions, respectively, calculate the value of K_w for the ionization of water.

APPENDIX

TABLE I.—SOME ACCEPTED CONSTANTS*

Ice point (0°C) = 273.160 ± 0.010°K
Liter = 1,000.028 ± 0.004 cm^3
Atmosphere, standard (atm) ≡ 1.013250 × 10^6 dynes/cm^2
$(Pv)_{i,0°C} = (\boldsymbol{R}T)_{0°C}$ = 22,414.6 ± 0.4 cm^3 atm/mole
= 22.4140 ± 0.0004 liter atm/mole
International ohm = 1.000494 ± 0.000015 abs ohm
International coulomb = 0.999838 ± 0.000025 abs coulomb
International volt = 1.000332 ± 0.000029 abs volts
International joule = 1.000170 ± 0.000052 abs joules
Calorie (cal) ≡ 4.1833 int joules
= 4.18401 ± 0.00020 abs joules
Faraday constant, $\boldsymbol{F}$ = 96,501.2 ± 10.0 int joule/int volt equiv
= 23,068.2 ± 2.4 cal/int volt equiv
= 23,060.6 ± 2.4 cal/abs volt equiv
Molar gas constant, $\boldsymbol{R}$ = 8.31439 ± 0.00034 abs joules/deg mole
= 8.31298 ± 0.00054 int joules/deg mole
= 1.98718 ± 0.00013 cal/deg mole
= 82.0567 ± 0.0034 cm^3 atm/deg mole
= 0.0820544 ± 0.0000034 liter atm/deg mole
Avogadro number, $\boldsymbol{N}$ = (6.02283 ± 0.0022) × 10^{23}/mole
Boltzmann gas constant $\left(\boldsymbol{k} = \frac{\boldsymbol{R}}{\boldsymbol{N}}\right)$ = (1.38048 ± 0.00050) × 10^{-16} erg/deg
Planck constant, $\boldsymbol{h}$ = (6.6242 ± 0.0044) × 10^{-27} erg sec
Velocity of light, $\boldsymbol{c}$ = (2.99776 ± 0.00008) × 10^{10} cm/sec
Electronic charge, $\boldsymbol{e}$ = (1.60200 ± 0.00060) × 10^{-19} abs coulomb
= (4.80240 ± 0.00180) × 10^{-10} abs esu

---

* American Petroleum Institute Research Project 44 at the National Bureau of Standards. Selected Values of Properties of Hydrocarbons. Table α, Values of Constants, Dec. 31, 1944; revised, Mar. 31, 1945.

TABLE II.—RELATIONS AMONG VARIOUS ENERGY UNITS*

To convert any value expressed in one of the units in the left-hand column to the corresponding value expressed in one of the units in the top row of the table, multiply the former value by the factor in the block common to both units.

	Calorie	Abs joule	Int joule	Liter-atm	Int kilowatt-hr
1 calorie	1	4.18401	4.1833	4.12918×10^{-2}	1.162028×10^{-6}
1 abs joule	0.239005	1	0.999830	9.86896×10^{-3}	2.77731×10^{-7}
1 int joule	0.239046	1.000170	1	9.87063×10^{-3}	2.77778×10^{-7}
1 liter atm	24.2179	101.3278	101.3106	1	2.81418×10^{-5}
1 int kilowatt-hr	860,565	3,600,612	3,600,000	35,534.3	1

---

* American Petroleum Institute Research Project 44 at the National Bureau of Standards. Selected Values of Properties of Hydrocarbons. Table β (Part 8), Conversion Factors. Units of Energy, Jan. 31, 1945; revised, Mar. 31, 1945.

TABLE III.—SOME FREQUENTLY USED FACTORS

Factor	Numerical value	Common logarithm
Ice point in °K	273.16	2.43642
25°C in °K	298.16	2.47445
Steam point in °K	373.16	2.57190
273.16^2	74,616	4.87283
298.16^2	88,899	4.94890
373.16^2	139,248	5.14379
273.16^3	2.0382×10^7	7.30925
298.16^3	2.6506×10^7	7.42334
373.16^3	5.1962×10^7	7.71569
$\ln 10 = \ln x/\log x$	2.30259	0.36222
R: In cal/deg mole	1.9872	0.29824
In int joules/deg mole	8.3130	0.91976
In liter atm/deg mole	0.082054	$\bar{2}.91410$
F: In cal/int volt equiv	23,068	4.36301
In int joules/int volt equiv	96,501	4.98453

In the following ***R*** is in calories per degree, ***F*** in calories per international volt-equivalent

2.3026 (298.16)	686.54	2.83667
2.3026 R	4.5757	0.66046
2.3026 R (298.16)	1,364.28	3.13491
2.3026 R (298.16)/F	0.059141	$\bar{2}.77189$

NAME INDEX

SUBJECT INDEX