Chemical Thermodynamics

FREDERICK D. ROSSINI
Professor and Head of the Department of Chemistry
Carnegie Institute of Technology

JOHN WILEY & SONS, INC., NEW YORK
CHAPMAN & HALL, LIMITED, LONDON

PRINTED IN THE UNITED STATES OF AMERICA

Dedicated to
GILBERT NEWTON LEWIS
inspirer of many to travel
the broad highway of thermodynamics.

Preface

This book on chemical thermodynamics is based on my experiences over a number of years devoted to researches and lectures in various phases of the subject, including the giving of a course in the Graduate School of the National Bureau of Standards. The book is aimed to provide instruction in chemical thermodynamics for those who have studied physical chemistry and some calculus. The basic concepts are introduced in a simple and straightforward manner. Emphasis is laid on the practical application of the laws and principles of thermodynamics to actual physical and chemical systems. Numerous problems are included for testing the reader's capacity. Adequate references to other publications giving more detailed information on the various topics are provided for further study. References to earlier books on chemical thermodynamics are given.

The topics have been arranged in what appears to me to be the most logical order from the standpoint of instruction, and, in so far as appropriate, flow naturally one into the other. Essentially, no topics are developed by reference to statements or proof occurring subsequently in the book. The arrangement of the topics is thus necessarily independent of the order of their actual chronology of development. For example, the chapter (19) on "Thermodynamic functions from statistical calculations" precedes the chapter (20) on "Entropy and the third law of thermodynamics," even though the latter subject was actually developed about twenty years earlier than the preceding subject, because an understanding of the statistical calculations simplifies greatly the presentation of the third law and the comprehension of the apparent exceptions to it.

In order to simplify the presentation and to make the understanding easier, each topic is introduced without discussion of its historical development. Where the historical aspects are significant and important, they are handled by discussion at the end of the appropriate chapter or by reference to other published works.

The symbols and nomenclature follow essentially the practice of Lewis and Randall, which has become well established in this country in the past quarter century. Several exceptions to that system are made, and several additional terms are used, but each exception or addition is clearly explained at the time of its introduction. In the application of the first law to a given system, three kinds of energy are distinguished: (1) heat energy, q; (2) PV work energy, w; and (3) all other energy, u. Infinitesimal quantities of these energies are denoted by δq, δw, and δu, respectively, and are counted as positive when absorbed by the given system for which the differential increment in energy, $\mathrm{d}E$, is being evaluated. In connection with solutions, a new superscript symbol * is used to denote a pure component, and a new superscript symbol 0 is used to denote a solute at zero concentration or infinite dilution. The superscript symbol ° continues to be used to denote the standard state. In the discussion of the equilibrium constant of a reaction, it has been found extremely helpful to introduce a new term, Q, called the "proper quotient of," and to apply it to the activities, pressures, mole fractions, or activity coefficients, etc., of the substances participating in the given reaction.

The first five chapters of this book cover background material of which the reader should have some knowledge before proceeding into the subject of chemical thermodynamics proper. In these chapters is included an account of the present status of the scale of temperature, the fundamental constants, and the calorie and the joule. The next twenty-five chapters give a substantially complete picture of modern chemical thermodynamics. The last five chapters deal with special applications, illustrative calculations, and sources of chemical thermodynamic data.

In the preparation of this book, I am greatly indebted to the following: T. Fraser Young, for many helpful suggestions and a comprehensive critical review of the text before printing; Edgar F. Westrum, Jr., for critically reviewing the text before its being sent to the publishers; Donald D. Wagman and William H. Evans, for carefully checking the text and problems during preparation; Marie T. Lynch and Alberta L. Kelvie, for assistance in the editorial preparation of the manuscript and in proofreading; and Anne L. Rossini and Freddie A. Rossini, for general assistance in arranging and proofreading, and, particularly, for their very great encouragement to complete the book.

I will be very grateful to those readers who will call my attention to any errors found in the book, as well as to those who may make suggestions for improvement of the presentation.

FREDERICK D. ROSSINI

June, 1950

Contents

I

Introduction

Thermodynamics provides laws that govern the passage of energy from one system to another, the transformation of energy from one form to another, and the utilization of energy for useful work. These same laws also govern the change of matter from one molecular or atomic species to another.

All matter of specified composition, in given electrical, magnetic, and gravitational fields, may be considered to have five fundamental thermodynamic properties, namely, pressure, volume, temperature, energy, and entropy. Changes in these properties must conform to the requirements of the first and second laws of thermodynamics. Knowledge of the proper manner of applying these laws to the fundamental properties permits one to subject all transformations of energy and matter to the powerful scrutiny of thermodynamics.

Every physical process or chemical reaction, including biological ones, may be examined thermodynamically. However, the fruitfulness of such examination depends greatly upon the extent to which are known the fundamental properties of the initial and final states of the process or reaction. If the energy and entropy are known, with respect to appropriate reference points, for all values of pressure, volume, and temperature to be covered in the investigation, then the thermodynamic examination can be a complete one.

In such manner can be analyzed problems involving the utilization of a given quantity of energy for the performance of useful work, the transformation of energy from one form to another more useful form, the transfer of heat energy from a cold to a warmer region, and the occurrence of all manner of chemical reactions. It is in the last-named field that thermodynamics has its greatest usefulness for chemists, since every field of chemistry involves chemical reactions of one kind or another.

When under given conditions a chemical reaction takes place naturally of its own accord, it is because the ensemble of atoms and molecules has an opportunity of improving its overall situation with regard to energy and entropy. A group of given atoms will tend to go into that molecular configuration which has a minimum of energy, in which state the atoms are bound most securely one to another, and a maximum of entropy, in which state the atoms have the greatest possible number of states of existence or greatest freedom. The final state of equilibrium is a compromise between these two opposing tendencies, toward maximum security on the one hand and maximum freedom on the other.

Given certain initial and final states of a proposed chemical reaction, it is frequently desirable to ascertain, without possibly costly experimentation, what will be the amounts of the reacting material in the initial and final states, respectively, at thermodynamic equilibrium under the specified conditions. With known data on the differences in energy and in entropy between the two states, under the given conditions of pressure, volume, and temperature, thermodynamics permits calculation of the amounts of material in the two states at equilibrium. If the amount of the material in the final state at equilibrium is very small, the proposed reaction is one which has an unfavorable equilibrium under the specified conditions. If the amount of the material in the final state at equilibrium is large, the proposed reaction is one which has a favorable equilibrium under the given conditions.

Another illustration of the power of chemical thermodynamics is the following: Given ten possible products which may be formed from one starting substance, what are the amounts of the starting substance and of each of the ten possible products at equilibrium under the specified conditions? With a knowledge of the differences in energy and in entropy between the starting substance and each of the ten products, one can answer this question with confidence, without experimentation on the complex reaction involved.

In the foregoing examples, it is important to note that thermodynamics does not evaluate the rate at which the given reaction proceeds or chemical equilibrium is attained, and does not specify the mechanism by which the molecules are transformed from the initial to the final state, and vice versa.

The rate at which molecules pass from the initial state to the final state, and vice versa, in a given chemical reaction is determined by the energy of activation and the temperature. The rate of reaction increases with increase in temperature and with decrease in the energy of activation. By means of a suitable catalyst, the energy of activation can be very materially reduced, producing a correspondingly large increase in the rate of reaction.

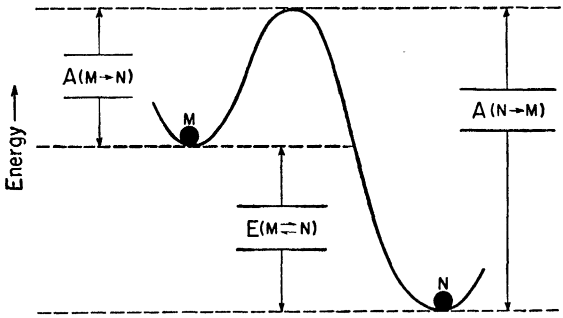


FIGURE 1. Schematic illustration of the relation between energy related to thermodynamic equilibrium and energy related to rate of reaction.

Energy is plotted on the scale of ordinates. In the thermodynamic equilibrium, $m \rightleftharpoons n$, the initial and final states of the atoms and molecules involved in the reaction are represented by m and n, respectively. The state n is at a lower level of energy than the state m, and in this respect n is relatively more stable than m. The energy $E(m \rightleftharpoons n)$ is the energy of reaction, is related to the thermodynamic equilibrium, $m \rightleftharpoons n$, and, combined with the respective entropies, gives a complete description of the thermodynamic equilibrium. The energy $A(m \rightarrow n)$ is the energy of activation in the forward direction, $m \rightarrow n$, and helps to determine the rate at which the molecules in the state m change to those in the state n. The energy $A(n \rightarrow m)$ is the energy of activation in the reverse direction, $n \rightarrow m$, and helps to determine the rate at which the molecules in the state n change to those in the state m. The difference in the energies of activation in the two directions is equal to the energy of reaction, $E(m \rightleftharpoons n)$.

The catalyst serves not only to increase the rate of reaction but also to guide the reaction along the proper path to avoid undesirable other reactions. A highly simplified illustration of the relation between that energy which is related to thermodynamic equilibrium and that energy which is related to rate of reaction is given in Figure 1.

2

Definition of Terms

1. System. A thermodynamic system is that part of the universe which is being subjected to thermodynamic scrutiny. The given system is fixed by a real or an imaginary boundary through which may pass, in or out, energy in one or more of its many forms. The problem may include one or more such systems. Everything which is of thermodynamic interest within the boundary of a given system is to be considered subject to the given thermodynamic study. The system usually contains matter of specified composition and form. The matter may consist of one or more substances.

2. Homogeneous system. A homogeneous system is conventionally defined as one whose properties are the same throughout its extent, with no apparent surfaces of discontinuity, or, if not uniform, vary in a continuous manner. Examples of homogeneous systems are the following: a pure gaseous substance, a pure liquid substance, a pure solid substance, a gaseous solution, a liquid solution, a solid solution.

3. Heterogeneous system. A heterogeneous system is one which is not homogeneous, and consists of two or more different regions of homogeneity. The different distinct regions are called phases and are separated from one another by boundaries in which occur sharp, abrupt changes of properties from one phase to the adjoining one. For the ordinary thermodynamic problems not involving surface tension, adsorption of molecules on surfaces, etc., the boundaries may be considered surfaces of discontinuity having infinitesimal thickness. Examples of heterogeneous systems are the following: a system containing one substance in two or more phases, as liquid and gas, or solid, liquid, and gas, or solid and gas, or two different solid forms; a system containing two or more substances in two or more phases, as two liquid phases, or two solid phases, or a solid and a liquid phase.

4. State of a system. The macroscopic state of a system is adequately specified when its thermodynamic properties and composition are specified with an accuracy comparable to that with which the properties and composition can be measured. The properties of a system of specified composition describe its present state and tell nothing of its previous history.

5. Process. A thermodynamic process constitutes the changes which take place in the system or systems being subjected to thermodynamic study. Such changes may include among others one or more of the following: change in the pressure, volume, temperature, energy and entropy; change in phase, as from solid to liquid or liquid to gas; formation of a solution from two or more pure substances; change in molecular species, as in a chemical reaction. A thermodynamic process takes a system from an initial state to a final state. The initial state and the final state are each specified by the appropriate properties of the system in the two states. The difference in the values of a given thermodynamic property between the two states is fixed entirely by the states themselves and is independent of the path followed by the system in passing from the initial state to the final state.

6. Intensive and extensive properties. The properties of a substance are classed as intensive or extensive, according to whether the given property is independent of or dependent on the mass of the substance. Pressure, temperature, and density are examples of intensive properties. Volume, energy, and mass are examples of extensive properties.

7. Equilibrium. Equilibrium may be considered to exist in a thermodynamic system when its composition and properties undergo no observable change even after the lapse of an indefinite period of time. That is to say, the system is then in a state of rest or state of equilibrium. It follows that any system which is not in a state of rest or equilibrium must be changing continuously toward such a state with more or less rapidity. Sometimes, the rate of change of a system toward its final state of rest or equilibrium is so small as to be imperceptible during the time of observation, and the system may be considered to be in a state of metastable or partial equilibrium. Such cases need introduce no particular difficulty, since in each thermodynamic study there should be known which processes are ones proceeding at measurable speed and therefore subject to thermodynamic scrutiny and which processes are substantially at a standstill and therefore need not be considered in the given problem.

8. Processes and chemical equations. In accordance with the practice of Lewis and Randall (*1*),* equations are used to indicate a given process, with the initial state being described by the material to the left of the equality sign and the final state by the material to the right. In general, the state of each reactant and product is described as adequately as needed for the given problem. Unless otherwise specified, the pressure is assumed to be 1 atmosphere. The temperature is usually indicated along with the thermodynamic property under discussion, or is otherwise adequately specified. In the case of solutions, the concentration is also specified. Examples of equations representing processes are the following:

$$\mathrm{H_2O\ (liq) = H_2O\ (g)}; \quad P = 1\ \mathrm{atm};\ T = 373.16\mathrm{°K}; \tag{1}$$

$$\mathrm{H_2\ (g)} + \tfrac{1}{2}\mathrm{O_2\ (g) = H_2O\ (liq)}; \quad P = 1\ \mathrm{atm};\ T = 298.16\mathrm{°K}; \tag{2}$$

$$\mathrm{NaCl\ (c) = NaCl\ (aq},\ m = 4); \quad P = 1\ \mathrm{atm};\ T = 298.16\mathrm{°K}. \tag{3}$$

The increment of any thermodynamic property G for the given process is the value of G for the final state less the value of G for the initial state and is represented by the symbol ΔG. If A and B designate the initial and final states, respectively, then the increment in G is

$$\Delta G = G_B - G_A. \tag{4}$$

9. Molal properties. In accordance with the convention used by Lewis and Randall (*1*), the value of a thermodynamic property is usually specified per mole or gram-formula-weight of the compound whose chemical formula is written.

10. Mole fraction. The most generally useful expression for giving the composition of a solution is the mole fraction. For a given component, the mole fraction is the ratio of the number of moles of the given component to the total number of moles in the solution. That is, the mole fraction, N_i, of component i in a solution is equal to

$$\mathrm{N}_i = \frac{n_i}{\sum n_i}$$

---

* Italic numbers in parentheses refer to entries in the list of references at the end of each chapter.

when n_i is the number of moles of component i, and $\sum n_i$ is the total number of moles in the solution.

11. Molality. In the case of aqueous solutions, the composition is usually expressed in terms of the molality, m, defined as the number of moles of solute per 1000 grams (or 55.506 moles) of water. Molality, as contrasted to concentration in moles per liter of water or liter of solution, is independent of the temperature.

12. Superscripts. When attached to a symbol representing a given thermodynamic property, as G, the superscript °, making G°, represents the thermodynamic standard reference state of the given substance for which the value of G is given. The superscript * on G, making G^*, represents the pure state of the given substance. For a given substance, the standard state and the pure state may sometimes, but not always, be identical. A zero superscript ^{0} on G, making G^0, represents infinite dilution.

13. Subscripts. When applied to the properties of the components of a solution, the integral number subscripts 1,2,3, etc., refer to the components of the given solution beginning with the solvent. In a solution of two components, the subscripts 1 and 2 refer to the solvent and solute, respectively. The absolute temperature to which a given thermodynamic property applies is indicated by a numerical subscript (corresponding to the absolute temperature) on the given property, as $G_{298.16}$. The latter is the value of G for the given substance at 298.16°K (or 25°C).

REFERENCES

1. G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances,* McGraw-Hill Book Company, New York, 1923.

3

Temperature

1. Temperature. Temperature is one of the most fundamental properties in thermodynamics. The concept of temperature is one easily comprehended in a qualitative way through the human senses. Given five bodies, A, B, C, D, and E, at temperatures, T_A, T_B, T_C, T_D, and T_E, respectively, physical contact with these bodies can permit one to distinguish them with respect to temperature. Suppose one finds A to be warmer than B, B to be warmer than C, C to be neither warmer nor colder than D, and D to be neither warmer nor colder than E. Then the following conclusions may be drawn regarding the several temperatures, within the significance of the observations:

$$T_A > T_B > T_C; \tag{1}$$

$$T_C = T_D = T_E; \tag{2}$$

$$T_A > T_B > T_D; \tag{3}$$

$$T_A > T_B > T_E. \tag{4}$$

2. Quantitative measurement of temperature. Having a qualitative knowledge of temperature, one then desires to make some quantitative measurements. For this purpose, one may select a suitable substance having any readily measured property which changes monotonically with the temperature. The property measured must also be one which has reproducible values when the substance is repeatedly returned to the same temperature. For example, one may use for the thermometric property and the thermometric substance the following: the length of a given piece of copper rod; the volume of a given mass of mercury; the electrical resistance of a given piece of platinum wire; the volume, at constant pressure (or the pressure, at constant volume), of a given mass of oxygen gas. After the selection of the thermometric substance and the thermometric property, it is necessary to specify the mathematical function which is to relate the given property to the temperature. Such a function may be a simple linear one, in which the temperature is proportional to the length of the copper rod, or to the resistance of the platinum wire, or to the volume of mercury, or it may be a complicated logarithmic function relating temperature and the given property.

Any two scales of temperature utilizing different thermometric substances, or different thermometric properties, or both, will not be exactly the same. The reason is that different substances have different values of the percentage rate of change of a given property with temperature and because different properties of the same substance have different values of the percentage rate of change of the properties with temperature. Whenever the volume of a given fluid is measured in containers of different material, it is possible to have two slightly different scales of temperature even though the same property (volume) of the same substance is being used. For example, two scales of temperature, both utilizing the apparent expansion of mercury in glass, will be different if the glass containers in the two cases have different values of expansion with temperature.

It is obviously desirable to have a scale of temperature which is independent of a particular property of a particular substance.

3. "Zero-pressure" gas scale of temperature. It is found that scales of temperature utilizing gases at low pressure (about 1 atmosphere or less), involving either the change of volume at constant pressure or the change of pressure at constant volume, are very nearly (although not exactly) alike. The differences between such scales become less and less as the pressure is diminished. This behavior is corollary to the fact that all real gases approach a common limit in their relations of pressure, volume, and temperature as the pressure is diminished without limit. It is possible therefore to utilize any real gas as a standard thermometric substance by extrapolating its appropriate properties to zero pressure.

With a fixed, but not necessarily measured, quantity of any real gas at a given temperature, T, measurements of the pressure and volume are made at several finite low pressures. These values, in the form of the pressure-volume product, are extrapolated to zero pressure to obtain the value of the pressure-volume product at zero pressure at the given temperature for the quantity of gas involved. If these measurements are repeated at another temperature on the same quantity of the same gas, there is obtained a value of the pressure-volume product at zero pressure for the second temperature. A satisfactory and fundamental scale of temperature is established by letting these values of the pressure-volume product at zero pressure be proportional to the temperature on this zero-pressure gas scale, as

$$(PV)_T^{P=0} = AT. \tag{5}$$

In Equation 5, A is the constant of proportionality for the quantity (preferably moles) of gas involved, and T is the temperature on this zero-pressure gas scale.

The next step is to evaluate the constant of proportionality. This may be done in either of two ways: (*a*) by defining the number of degrees between two selected fixed points which are realizable in the laboratory; or (*b*) by defining the absolute value of temperature to be assigned to one fixed point realizable in the laboratory with reference to the origin or zero on the zero-pressure gas scale of temperature (*2*). In the former method, which is the one currently in use, the difference in the values of temperature between the two selected fixed points is defined and never changed, but the absolute values of the temperature of the two selected fixed points may change as the result of improvements in experimentation with the zero-pressure gas thermometer. In the second method, the absolute value of the temperature of one fixed point with reference to the origin or absolute zero is defined and never changed, but the absolute value of the temperature of any other point may change as the result of improvements in experimentation.

Basic reproducible fixed points on any scale of temperature are most easily realized by using the temperature of the thermodynamic equilibrium between two or more phases of a given pure substance. In general, the equilibrium between a solid and a liquid is easier to reproduce than one between a liquid and a gas, because the temperature of the gas is very much more sensitive to changes in pressure.

In the method currently in use for defining the "zero-pressure" gas scale of temperature, the two realizable fixed points which are employed to define the scale are (*a*) the temperature at which solid water is in thermodynamic equilibrium with liquid water in air at a pressure of 1 atmosphere; and (*b*) the temperature at which liquid water is in thermodynamic equilibrium with gaseous water at a pressure of 1 atmosphere. The difference in the temperature of these two fixed points, which are commonly called the "ice" and "steam" points, respectively, is defined as exactly 100 units or degrees. (It may be noted here that the temperature at which solid water is in thermodynamic equilibrium with liquid water at saturation pressure, in the absence of air, which is the triple point, is 0.0100°C higher than the ice point involving water saturated with air at 1 atmosphere. On the foregoing scale of temperature, the interval between the triple point and the steam point of water is 99.9900°.)

If values of the pressure-volume product at zero pressure have been determined for the quantity of the given gas, at the ice and steam points, respectively, then for the first method of defining the zero-pressure gas scale of temperature, the following relations hold:

$$T_{\text{steam}} - T_{\text{ice}} = 100 \qquad \text{(defined constant)}; \tag{6}$$

$$T_{\text{ice}} = 100 \frac{(PV)_{T\,\text{ice}}^{P=0}}{(PV)_{T_{\text{steam}}}^{P=0} - (PV)_{T_{\text{ice}}}^{P=0}}. \tag{7}$$

Equation 7 serves to evaluate the absolute temperature of the ice point on the "zero-pressure" gas scale of temperature, according to the current method of defining this scale of temperature by using two realizable fixed points.

Figure 1 represents schematically how observations of the pressure-volume product for real gases are extrapolated to zero pressure. In principle, what is required is the measurement, at a given temperature, of pressure and volume at a series of pressures and the extrapolation of these values to zero pressure. Actually, the observations and calculations are rather involved, and the extrapolation to zero pressure is much more complicated than shown schematically in principle in Figure 1.

Figure 2 represents schematically the relation between the values of the temperature and the pressure-volume product at zero pressure, for the zero-pressure gas scale of temperature defined by two realizable defining fixed points.

Equation 7 may be easily derived from Figure 2 by making a

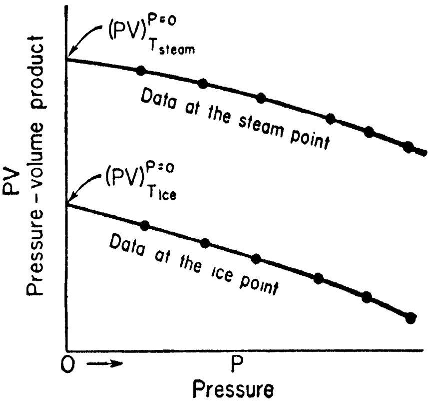


FIGURE 1. Simplified schematic diagram, showing the extrapolation of pressure-volume data to zero pressure.

Values of pressure are plotted on the scale of abscissas, and values of the pressure-volume product are plotted on the scale of ordinates. The data are not plotted to scale.

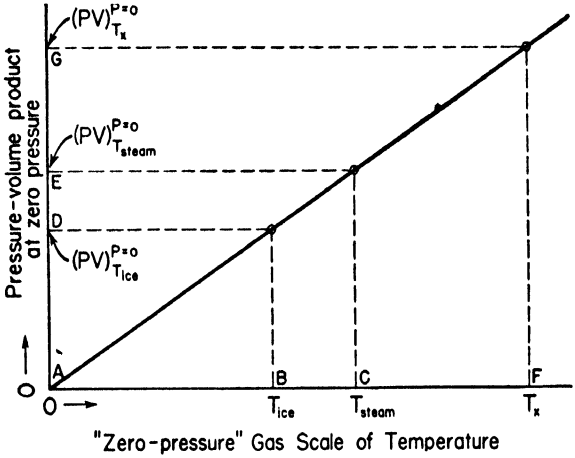


FIGURE 2. Simplified diagram, showing the relation between the pressure-volume product at zero pressure and temperatures on the zero-pressure gas scale.

Temperatures on the zero-pressure gas scale are plotted on the scale of abscissas, and values of the pressure-volume product at zero pressure are plotted on the scale of ordinates.

proportion of the corresponding parts of the two similar right triangles:

$$\frac{\overline{AB}}{\overline{BC}} = \frac{\overline{AD}}{\overline{DE}}, \tag{8}$$

or

$$T_{\text{ice}} = \overline{AB} = \overline{BC}\frac{\overline{AD}}{\overline{DE}}. \tag{9}$$

Any other unknown temperature, including any additional fixed (but not defining) points, may be evaluated fundamentally from measurements on a given but not necessarily measured quantity of a suitable gas. Such measurements would determine the pressure-volume product at zero pressure at the given unknown temperature and at the two defining fixed points, the ice and steam points. The value of the unknown temperature, T_x, on this scale would be given by the following relation:

$$T_x = 100\frac{(PV)_{T_x}^{P=0}}{(PV)_{T_{\text{steam}}}^{P=0} - (PV)_{T_{\text{ice}}}^{P=0}}. \tag{10}$$

Equation 10 may be easily derived from Figure 2 by making a proportion of the corresponding parts of the two similar right triangles:

$$\frac{\overline{AF}}{\overline{BC}} = \frac{\overline{AG}}{\overline{DE}}, \tag{11}$$

or

$$T_x = \overline{AF} = \overline{BC}\frac{\overline{AG}}{\overline{DE}}. \tag{12}$$

In such determinations, maximum precision and accuracy in the evaluation of the unknown temperature T_x are obtained by having the pressure-volume measurements at all three temperatures made with the same apparatus and procedure and by having the extrapolation of the experimental data to zero pressure made uniformly in the same way.

In the second method of defining the zero-pressure gas scale of temperature, using only one realizable fixed point and the origin or absolute zero, the absolute temperature of the ice point is defined and any other unknown temperature, T_x, would be evaluated fundamentally from this defined value of the ice point and the ratio of the pressure-volume product of a suitable gas at zero pressure at the unknown temperature and at the ice point. In this case, arbitrarily defining the absolute value of the ice point according to its present best value on the scale of temperature defined by two realizable fixed points, the relations involved are the following:

$$T_{\text{ice}} = 273.16^\circ \qquad \text{(defined constant)}; \tag{13}$$

$$T_x = 273.16 \frac{(PV)_{T_x}^{P=0}}{(PV)_{T_{\text{ice}}}^{P=0}}. \tag{14}$$

If, instead of the ice point fixed by the thermodynamic equilibrium between water ice and liquid water saturated with air at 1 atmosphere, one used the triple point of water fixed by the same equilibrium in the absence of air, Equations 10, 13, and 14 would be changed to the following Equations 15, 16, and 17, respectively:

$$T_x = 99.9900 \frac{(PV)_{T_x}^{P=0}}{(PV)_{T_{\text{steam}}}^{P=0} - (PV)_{T_{\text{ice, triple pt.}}}^{P=0}}; \tag{15}$$

$$T_{\text{ice, triple pt.}} = 273.17 \qquad \text{(defined constant)}; \tag{16}$$

$$T_x = 273.17 \frac{(PV)_{T_x}^{P=0}}{(PV)_{T_{\text{ice, triple pt.}}}^{P=0}}. \tag{17}$$

4. Practical or working scale of temperature. The evaluation of temperatures by the use of a "zero-pressure" gas thermometer is essentially limited to the national standardizing laboratories and to certain other laboratories possessing the necessary apparatus and experience. The reason is that the use of a zero-pressure gas thermometric system with high precision and accuracy is laborious, difficult, and costly. For general use in science and technology, it has become necessary to establish a practical or working scale of temperature.

To do this, one goes back to the selection of a specified thermometric substance, a specified property of that substance, and a specified mathematical function relating values of the given property of the given substance to values of the temperature.

Before making any measurements on the selected thermometric substance and property, it is necessary to determine experimentally the values of the temperature of a necessary number of fixed points which are to be used in connection with the practical or working scale of temperature. The number of such fixed points will depend upon the number of constants to be evaluated in the selected mathematical function relating, with the necessary precision and accuracy, the values of the selected thermometric property of the selected thermometric substance to the values of the temperature of the selected fixed points.

The absolute value of the temperature of the ice point on the zero-pressure gas scale is currently selected to be 273.160 ± 0.010°, so that the absolute values of the temperature of the water-ice triple point and of the steam point are higher by 0.0100° and 100.0000°, respectively. Additional fixed points necessary to establish a practical or working scale of temperature are selected on the basis of their reproducibility and the range of temperature to be covered. Such basic fixed points, together with the values of temperature which have been assigned to them on the above zero-pressure gas scale of temperature, as a result of measurements with a gas thermometer system, are as follows, with the two defining points, ice and steam, included for completeness.

Substance	Equilibrium	Assigned Temperature (absolute), degrees
Oxygen	Liquid-gas, at 1 atm	90.19
Water	Solid-liquid, in air at 1 atm	273.16
Water	Solid-liquid, saturation pressure	273.17
Water	Liquid-gas, at 1 atm	373.16
Sulfur	Liquid-gas, at 1 atm	717.76
Silver	Solid-liquid, at 1 atm	1233.96
Gold	Solid-liquid, at 1 atm	1336.16

The uncertainties in the absolute values of temperature on the zero-pressure gas scale of temperature assigned to the above fixed points are about 0.01° for the oxygen, ice, and steam points, near 0.1° for the sulfur point, and near 0.5° for the silver and gold points.

For convenience in the use of a practical or working scale of temperature in ordinary scientific and technological work, as well as for historical reasons, the defining ice and steam points are assigned values of 0 and 100°, respectively, and the values of temperature on this practical scale are labeled degrees Celsius (Centigrade), or °C. The above fixed points have the following values on the Celsius (Centigrade) scale, obtained by subtracting 273.16° from the absolute values: oxygen, −182.970°C; ice, 0°C (exactly); ice, triple point, 0.0100°C; steam, 100°C (exactly); sulfur, 444.60°C; silver, 960.80°C; gold, 1063.00°C.

The next step is to select suitable thermometric substances, properties, and mathematical functions. It has been found that the electrical resistance of pure platinum wire increases in a roughly linear manner with temperature. With three or four constants in a second- or third-degree polynomial, it is possible to relate the electrical resistance of platinum to temperature on the above scale with considerable precision and accuracy, from −183° to 630°C, as follows:

For the range −183°C to 0°C, the relation of resistance to temperature is

$$r_t = r_0(1 + at + bt^2 + ct^3), \tag{18}$$

where r_t and r_0 are the electrical resistances of the platinum resistance thermometer at the temperature t and at 0°C, respectively, and a, b, and c are constants evaluated from measurement of the resistance of the thermometer at the oxygen, steam, and sulfur points.

For the range 0°C to 630°C, the relation of resistance to temperature is

$$r_t = r_0(1 + at + bt^2), \tag{19}$$

where the three constants are evaluated from measurement of the resistance of the thermometer at the ice, steam, and sulfur points.

For the range from 630°C to 1063°C, the electromotive force of a standard platinum versus platinum-rhodium thermocouple is used for the working scale of temperature, with the following relation:

$$e = a + bt + ct^2. \tag{20}$$

Here e is the electromotive force of the standard thermocouple, one junction of which is kept at 0°C and the other at the given temperature t, and the three constants a, b, and c are evaluated from measurements of the electromotive force of the thermocouple at the antimony, silver, and gold points. The value of the temperature to be assigned to the antimony point in this calibration is evaluated with the platinum resistance thermometer for the given sample of antimony. (Pure antimony has a freezing point of 630.5°C.)

Measurements of temperature below −183°C are made with gas thermometers, or with resistance thermometers or thermocouples that have been calibrated against a gas thermometric system, or with resistance thermometers or thermocouples that have been calibrated against other resistance thermometers or thermocouples that have been calibrated against a gas thermometric system.

Measurements of temperature above the gold point are made with optical pyrometers. The measurements involve determination of the ratio of the intensity of monochromatic visible radiation of a given wave length emitted by a black body at the unknown temperature to the intensity of the same radiation of the same wave length emitted by a black body at the gold point. The unknown temperature T_x is evaluated from the radiation formula:

$$\frac{J_{T_x}}{J_{T_{\mathrm{Au}}}} = \frac{e^{c_2/\lambda T_{\mathrm{Au}}} - 1}{e^{c_2/\lambda T_x} - 1}. \tag{21}$$

In Equation 17, J_{T_x} and $J_{T_{\mathrm{Au}}}$ are the radiant energies per unit wave-length interval at the given wave length, λ (in centimeters), emitted per unit time by unit area of a black body at the temperatures T_x and T_{Au}, respectively; T_x and T_{Au} are the absolute values of the unknown temperature and the temperature of the gold point, respectively; c_2 is the second radiation constant and is equal to hc/k or 1.438 cm degrees.

The International Temperature Scale, which is essentially the practical or working scale described above, was first adopted in 1927 by the Seventh General Conference of Weights and Measures, and was revised in 1948 at the Ninth General Conference of Weights and Measures.

5. Thermodynamic scale of temperature. The zero-pressure gas scale of temperature described in this chapter is identical with the fundamental thermodynamic scale of temperature to be introduced in a subsequent chapter. Temperatures on the thermodynamic scale of temperature are labeled degrees Kelvin, or °K. All temperatures on the zero-pressure gas scale of temperature will henceforth in this book be labeled °K for the sake of uniformity and to avoid unnecessary confusion.

6. Collateral reading. For details concerning temperature and scales of temperature, the reader is referred to the following publications: Kelvin scale of temperature, Thomson (*1*) and Giauque (*2*); International Temperature Scale, Burgess (*3*); temperature, Wensel (*4*); extrapolation of *PV* isotherms, Cragoe (*5*); absolute temperature of the ice point, Beattie (*6*); International Temperature Scale of 1948, Stimson (*7*). See also Beattie, Benedict, Blaisdell, and Kaye (*8*).

REFERENCES

1. W. Thomson, *Phil. Mag.* **33**, 313 (1848).
2. W. F. Giauque, *Nature* **143**, 623 (1939).
3. G. K. Burgess, *J. Research Natl. Bur. Standards* **1**, 635 (1928).
4. H. T. Wensel, Section on "Temperature," in *Temperature. Its Measurement and Control in Science and Industry*, Reinhold Publishing Corporation, New York, 1941.
5. C. S. Cragoe, *J. Research Natl. Bur. Standards* **26**, 495 (1941).
6. J. A. Beattie, Section on "The Thermodynamic Temperature of the Ice Point," in *Temperature. Its Measurement and Control in Science and Industry*, Reinhold Publishing Corporation, New York, (1941).
7. H. F. Stimson, *J. Research Natl. Bur. Standards* **42**, 209 (1949).
8. J. A. Beattie, M. Benedict, B. E. Blaisdell, and J. Kaye, *Proc. Am. Acad. Arts Sci.* **77**, 255 (1949).

PROBLEMS

1. On a certain mass of a real gas, the following values were determined for the pressure in atmospheres and the volume in cubic centimeters, respectively, at 0°C: 1.0000, 19.979; 0.5000, 40.078; 0.2000, 100.375. And similarly at 100°C: 1.0000, 27.447; 0.5000, 54.904; 0.2000, 137.275. From these data, derive the temperature of the ice point, 0°C, in terms of the zero-pressure gas scale of temperature.

2. A mass of 35.0000 g of pure gaseous oxygen, O_2, at the ice point, 0°C, has the following volumes at the indicated pressures: 800 mm Hg, 23,271.5 cm^3; 400 mm Hg, 46,561.7 cm^3; 200 mm Hg, 93,142.0 cm^3. Taking the temperature of the ice point on the zero-pressure gas scale of temperature to be 273.160°K, calculate the value of the gas constant, R, per mole.

3. A zero-pressure gas scale of temperature, labeled X, is fixed by setting $T_{\text{steam}}(°X) - T_{\text{ice}}(°X) = 100(°X)$ and $T_{\text{steam}}(°X)/T_{\text{ice}}(°X) = 1.366086$. A second zero-pressure gas scale of temperature, labeled Y, is fixed by setting $T_{\text{ice}}(°Y) = 273.160(°Y)$. A third zero-pressure gas scale of temperature, labeled Z, is fixed by setting $T_{\text{ice}}(°Z) = 273.100(°Z)$. Assuming that the best experimental value of the ratio of the PV product at zero pressure for a given mass of gas at the steam and ice points is 1.366086, calculate the temperature of the steam point on the three different scales of temperature.

4

Fundamental Constants and Conversion Factors

1. Fundamental constants. In making application of chemical thermodynamics to actual problems, it becomes necessary to have values for the various constants and conversion factors involved in the calculations. In the appendix of this book are given rather complete tables of the constants and conversion factors that may be needed in the calculations of chemical thermodynamics. These values of constants and conversion factors are derived from the lists issued in the tables of *Selected Values of Properties of Hydrocarbons* (*1*) of the American Petroleum Institute Research Project 44 and are adjusted for the recent change in the accepted value of the Faraday constant (*2*, *14*, *21*, *22*). In order to emphasize the derivation of those constants which are most needed in chemical thermodynamics, there are discussed in this chapter certain of these constants with some indication of their origin.

In this connection, distinction must be made among the basic constants, the values of which are determined by experimental measurements, the derived constants, the values of which are obtained by applying physical relations to the basic constants, and defined constants, the values of which are fixed by definition. With regard to the basic and derived constants, it may happen that a given pair of constants related by physical laws may change places from one category to the other, depending upon the relative accuracy with which the values of the two constants may be determined experimentally. The more accurately determined constant is placed in the basic list, leaving the other one to be derived from the value of the first constant with the appropriate physical relation.

The fundamental units in terms of which the measurements of the basic constants are made are those of length, mass, and time (*3*, *4*).

The international standard of length is the meter, which is maintained as the distance at 0°C between the axes of two lines ruled parallel on the International Prototype Meter which is deposited at the International Bureau of Weights and Measures at Sèvres, near Paris, France. The primary standard of length in the United States is the United States Prototype Meter 27, a standard bar made of an alloy of platinum and iridium and having an X-shaped cross section, which is deposited at the National Bureau of Standards in Washington, D.C. The length of the latter meter bar is known in terms of the International Prototype Meter. A supplementary definition of the meter in terms of the wave length of light was adopted provisionally by the Seventh General (International) Conference on Weights and Measures in 1927, and a new movement is now under way to define the meter primarily as a given number of wave lengths of a suitable pure monochromatic radiation.

The international standard of mass is the mass of the International Prototype Kilogram, made of an alloy of platinum and iridium, which is deposited at the International Bureau of Weights and Measures. The primary standard of mass in the United States is the mass of the United States Prototype Kilogram 20, made of an alloy of platinum and iridium, which is deposited at the National Bureau of Standards, and of which the mass is known in terms of the International Prototype Kilogram.

Time is measured by the time of motion of the earth, either on its axis or around the sun. In astronomy, three kinds of time are recognized; sidereal time, which is used exclusively for astronomical purposes; apparent solar time, which is the time shown by the sundial; and mean solar time, which is used in civil life and business and in defining the units employed in the physical sciences.

Sidereal time is defined by the rotation of the earth with respect to the stars, a sidereal day (or 24 sidereal hours or 86,400 sidereal seconds) being the interval of time between two successive passages of a star across a meridian.

Apparent solar time, or the hour angle of the sun, is the time shown by the sundial, its noon being the moment when the center of the sun crosses the meridian. On account of the earth's orbital motion, the sun appears to move eastward along the ecliptic, completing its circuit in a year. Each noon, the sun occupies a place among the stars about a degree farther east than it did the noon before, and so comes to the meridian about 4 minutes later (according to the sidereal time). That is, the solar day is 4 minutes longer than the sidereal day, the difference amounting to exactly 1 day each year. A tropical solar year contains 365.2422 solar days or 366.2422 sidereal days. Since the earth, in its motion around the sun, does not move at a uniform speed, and the sun in its apparent motion does not move along the equator but along the ecliptic, the apparent solar days are not of exactly equal length.

To overcome this difficulty, mean solar time is measured in terms of the motion of a fictitious or "mean" sun, the position of which, at all times, is the same as would be the position of the real sun if the earth moved on its axis at a uniform rate and journeyed around the sun at a uniform rate. The length of the mean solar day is equal to the average length of the apparent solar day. The ratio of the mean solar second to the sidereal second is given by the ratios of the numbers 365.2422 and 366.2422, mentioned above.

2. Basic constants. For the purposes of chemical thermodynamics, at the present time, the basic constants, apart from atomic weights, may be taken as the following:

c, the velocity of light (*5*);
N, the Avogadro constant (*5*);
$\mathcal{F}$, the Faraday constant (*5*);
h, the Planck constant (*5*);
$T_{0°C}$, the absolute temperature of the ice point (*6*);
$(PV)_{0°C}^{P=0}$, the pressure-volume product for 1 mole of a gas at 0°C and zero pressure (*7*);
sec, the mean solar second (*3*, *4*, *8*); and
l, the liter* (*9*).

Following are summarized briefly the kinds of measurements which yield values of the basic constants:

The velocity of light, c, is evaluated from direct experimental measurements involving distance, r, and time, z:

$$c = \frac{r}{z}. \tag{1}$$

The Avogadro number, N, is evaluated from the density, ρ, of an appropriate crystalline substance (as calcium carbonate), its

---

* It is to be noted that the liter can be eliminated as a basic constant by defining it in terms of the cubic centimeter.

molecular weight, M, the X-ray grating space, r, and the crystal structure volume factor, f:

$$N = \frac{M}{2r^3\rho f}. \tag{2}$$

The Faraday constant, $\mathcal{F}$, has classically been evaluated from the gram-molecular weight, M, of a chemical element (as silver), the valence of, or charge on, the ion, z, and the mass, m, of that element deposited by a measured quantity, Q, of electricity:

$$\mathcal{F} = \frac{QM}{mz}. \tag{3}$$

The Planck constant, h, is determined from various spectroscopic, X-ray, and electron measurements, coupled with a number of different relations involving the charge of the electron, e, the mass of the electron, m, the Faraday constant, $\mathcal{F}$, and Avogadro's number, N, as follows: Measurements of the quantum limit of the continuous X-ray spectrum serve to evaluate h/e; electron diffraction measurements of DeBroglie wave lengths for electrons accelerated with a measured voltage serve to evaluate $h/(em)^{1/2}$; X-ray photoelectrons ejected with known quantum energies, and measured by magnetic deflection, serve to evaluate e^2/mh; determinations of the spectroscopic fine-structure constant serve to evaluate e^2/hc; spectroscopic measurements of the Rydberg constant serve to evaluate me^4/h^3c.

The value of the absolute temperature of the ice point is obtained essentially from a determination at two appropriate temperatures (preferably the ice point, 0°C, or the triple point of water, 0.01°C, and the steam point, 100°C) of the PV product at zero pressure for a fixed, but not necessarily measured, quantity of an appropriate gas:

$$T_{0^\circ\mathrm{C}} = 100\frac{(PV)_{0^\circ\mathrm{C}}^{P=0}}{(PV)_{100^\circ\mathrm{C}}^{P=0} - (PV)_{0^\circ\mathrm{C}}^{P=0}}. \tag{4}$$

The value of the product RT is taken as the value of the PV product, at zero pressure and T°K, for one gram mole of an appropriate gas, with the determination preferably being made with oxygen gas at the ice point, 0°C:

$$RT_{0^\circ\mathrm{C}} = (PV)_{0^\circ\mathrm{C}}^{P=0}. \tag{5}$$

The mean solar second is discussed in the preceding section.

The liter is the volume of one kilogram of pure water at the temperature of its maximum density under a pressure of one atmosphere. However, as previously mentioned, it is entirely practicable to define the liter in terms of cubic centimeters.

3. Derived constants. The derived constants of interest in chemical thermodynamics may be taken as the following:

R, the gas constant per mole;
e, the charge on the electron;
k, the Boltzmann constant;
c_2, the second radiation constant;
Y, the constant relating energy and mass; and
Z, the constant relating wave number and energy.

Following are the physical relations from which the values of the foregoing constants are derived, using the values of the basic constants:

The value of the gas constant R is obtained from $T_{0°\mathrm{C}}$ and $(PV)_{0°\mathrm{C}}^{P=0}$, which is $RT_{0°\mathrm{C}}$:

$$R = \frac{(PV)_{0°\mathrm{C}}^{P=0}}{T_{0°\mathrm{C}}}. \tag{6}$$

The charge on the electron, e, is evaluated from the Faraday constant, $\mathcal{F}$, and Avogadro's number, N:

$$e = \frac{\mathcal{F}}{N}. \tag{7}$$

The Boltzmann constant, k, is the gas constant per molecule:

$$k = \frac{R}{N}. \tag{8}$$

The value of the second radiation constant, c_2, which is hc/k, is

$$c_2 = \frac{hc}{k} = \frac{Z}{R}. \tag{9}$$

The constant Y, relating the mass, m, and the energy, E, in the Einstein relation,

$$\Delta E = Y(\Delta m), \tag{10}$$

is evaluated from the square of the velocity of light:

$$Y = c^2. \tag{11}$$

The constant Z, relating the spectroscopic wave number, ν, and the energy, E, in the relation,

$$\Delta E = Z\,(\Delta\nu), \tag{12}$$

is evaluated from Avogadro's number, N, Planck's constant, h, and the velocity of light, c:

$$Z = Nhc. \tag{13}$$

4. Defined constants. The defined constants of importance in chemical thermodynamics are the following:

g_0, the standard value of the acceleration of gravity (*3*);
atm, the standard atmosphere (*3*);
in., the inch (*10*);
lb, the pound (*10*);
gal, the gallon (*10*);
cal, the thermochemical calorie (*11, 12*);
I.T. cal, the steam calorie (*12, 13*); and
BTU, the British thermal unit (*12, 13*).

The values of the foregoing defined constants are discussed in the references cited and are given in the tables of constants and conversion factors in the appendix of this book.

5. Collateral reading. For a detailed presentation of the evaluation of the constants $\mathcal{F}$, N, h, and related quantities, the reader is referred to DuMond and Cohen (*14*) and DuMond (*15*). Earlier extensive surveys of the values of the fundamental constants have been published by Birge (*5, 16, 17*). Before the work of Birge, the most widely used set of constants were those in the *International Critical Tables* (*3*). The status of the fundamental electrical units was reported by Curtis (*18*) and Crittenden (*19*).

The atomic weights are reviewed periodically by the Committee on Atomic Weights of the International Union of Pure and Applied Chemistry (*20*). In this book, the temperature scale is reviewed in Chapter 3 and the calorie and the joule in Chapter 5. For a detailed discussion of the other constants discussed in this chapter, the reader is referred to the publications cited. Reviews of the status of the fundamental constants important in physical chemistry are issued at intervals by the National Research Council Committee on Physical Chemistry (*21*). The new method of evaluating the Faraday constant, which is essentially one of measuring the ratio of the charge to the mass of gaseous hydrogen ion, H^+, is described by Hipple, Sommer, and Thomas (*22*).

REFERENCES

1. F. D. Rossini, K. S. Pitzer, W. J. Taylor, J. P. Ebert, J. E. Kilpatrick, C. W. Beckett, M. G. Williams, and H. G. Werner, American Petroleum Institute Research Project 44, *Natl. Bur. Standards Circ.* 461, U.S. Government Printing Office, Washington, 1947. Also issued currently in loose-leaf form by the American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh (formerly at the National Bureau of Standards, Washington).
2. R. T. Birge, *Phys. Rev.* **77** (1950).
3. *International Critical Tables*, Volume I, McGraw-Hill Book Company, New York, 1926.
4. "Standards of length, mass, and time," *Natl. Bur. Standards Letter Circ.* LC930 (January 1949).
5. R. T. Birge, *Revs. Modern Phys.* **13**, 233 (1941).
6. H. T. Wensel, *J. Research Natl. Bur. Standards* **22**, 375 (1939).
7. C. S. Cragoe, *J. Research Natl. Bur. Standards* **26**, 495 (1941).
8. H. N. Russell, R. S. Dugan, and J. Q. Stewart, *Astronomy*, Ginn and Company, Boston (1945).
9. E. L. Peffer and G. C. Mulligan, "Testing of glass volumetric apparatus," *Natl. Bur. Standards Circ.* 434 (December 1941).
10. "Units of weight and measure; definitions and tables of equivalents," *Natl. Bur. Standards Misc. Pub.* M121 (January 1936).
11. *First Report of the Commission on Thermochemistry*, International Union of Chemistry, Paris, 1934.
12. E. F. Mueller and F. D. Rossini, *Am. J. Phys.* **12**, 1 (1944).
13. "Report of the International Steam Tables Conference," *Mech. Eng.* **51**, 791 (1929); **52**, 120 (1930).
14. J. W. M. DuMond and E. R. Cohen, *Revs. Modern Phys.* **20**, 82 (1948).
15. J. W. M. DuMond, *Phys. Rev.* **75**, 1267 (1949).
16. R. T. Birge, *Revs. Modern Phys.* **1**, 1 (1929).
17. R. T. Birge, *Am. J. Phys.* **13**, 63 (1945).
18. H. L. Curtis, *J. Research Natl. Bur. Standards* **33**, 235 (1944).
19. E. C. Crittenden, "Announcement of changes in electrical and photometric units," *Natl. Bur. Standards Circ.* C459 (May 1947).
20. Committee on Atomic Weights, International Union of Pure and Applied Chemistry, 4 Avenue de l'Observatoire, Paris 6, France.
21. Committee on Physical Chemistry, Division of Chemistry and Chemical Technology, National Research Council, Washington 25, D.C.
22. J. A. Hipple, H. Sommer, and H. A. Thomas, *Phys. Rev.* **76**, 1877 (1949).

PROBLEMS

1. A pure single crystal of sodium chloride is found to have a density of 2.16228 g/cm^3. X-ray data show that the average volume occupied by one molecule of NaCl in the crystal is $(3.5535 \times 10^{-8}\ \text{cm})^3$. Given the molecular weight of NaCl to be 58.454 g/mole, calculate the value of the Avogadro number.

2. It is found that 10,757.97 absolute coulombs of electricity deposit 12.02846 g of silver. If the atomic weight of silver is taken as 107.880 g/mole, calculate the value of the Faraday constant.

3. From the values of the Avogadro number and the Faraday constant obtained in the foregoing problems, calculate the value of the charge on the electron.

4. One mole of a given chemical substance has, under certain conditions, a heat of combustion of 98,000 cal. Express this quantity of energy in terms of the following units: (*a*) absolute joules; (*b*) absolute electron-volts/molecule; (*c*) wave numbers (reciprocal centimeters); (*d*) change in mass (energy equivalent); (*e*) British thermal units; (*f*) absolute kilowatt-hours; (*g*) liter-atmospheres; (*h*) foot-pounds (weight).

5

The Calorie and the Joule

1. Early unit of energy. From the time of the early work of Count Rumford near 1800 to the early part of the present century, the most convenient and readily applicable method of measuring quantities of heat arising from processes occurring at or near room temperature was to observe the rise of temperature produced in a known mass of water contained in a suitable vessel, or calorimeter. In this way, it was possible to measure with considerable precision a quantity of energy in terms of a given mass of water and its rise of temperature. With the calorie defined as the quantity of heat required to raise the temperature of one gram of water through one Centigrade degree, the experimenter was thus able to express the result in calories, obtained as the product of the mass of water in grams and the rise of temperature in Centigrade degrees.

2. Various calories. As the measurements increased in precision, it became necessary to take proper cognizance of the heat capacity of the container, thermometer, stirrer, etc.; to define the scale of temperature; and to specify accurately the various conditions attending the absorption of the heat by the water, such as the mean temperature or the interval of temperature, and the pressure. The specification of the mean temperature gave rise in itself to various calories, such as the 0° calorie, the 4° calorie, the 15° calorie, the 18° calorie, the 20° calorie, and the mean (0 to 100°C) calorie. By about 1905, experimental calorimetry had advanced to a stage where measurements of heat in terms of the heat capacity of water could be made with a precision of about 1 part in 1000.

3. Mechanical equivalent of heat. It was early recognized, however, that, notwithstanding the relative ease with which measurements of heat could be made in terms of the heat capacity of water, it was necessary to ascertain what quantity of energy in absolute units (ergs or joules) a given calorie was equivalent to.

This gave rise to the series of investigations on the mechanical equivalent of heat begun by Joule about 1840 and continued by him over a long period of years (*1*). After Joule, determinations of the heat capacity of water in absolute units were published by Rowland (*2*) in 1880 and by Reynolds and Moorby (*3*) in 1897. Near 1900, extended reviews of the data on the mechanical equivalent of heat were published by Ames (*4*) and by Barnes (*5*). Throughout all this work, it was apparent that the uncertainty of the value giving the number of joules equivalent to a given calorie was always comparable with the uncertainty with which a given quantity of heat could be measured in terms of the heat capacity of water. As long as this situation existed, it was desirable, for purposes of high precision, to continue to use as the unit of heat energy the heat capacity of water under specified conditions.

4. Units of electrical energy. With the development of accurate electrical standards near the beginning of the present century, it became possible to measure electrical energy with high precision. As soon as this precision in the measurement of the electrical energy introduced into a calorimeter became equal to or exceeded that of measuring heat in terms of the heat capacity of water, the real need for retaining the latter as a unit of heat energy was removed. It was not until about 1930, however, that definite steps were taken to separate the calorimetric unit of energy from any connection with the actual heat capacity of water under specified conditions.

Electrical measurements of energy are based upon the mean solar second as the unit of time and upon working standards of electromotive force and resistance maintained at the various national standardizing laboratories. These working standards are saturated cadmium (Weston) cells and wire (usually manganin) resistance coils. When redefined in 1908, the units internationally agreed upon, and specified in terms of the mercury ohm and the silver voltameter, were identical with the absolute units within the limits within which the latter could then be determined (*6*). Since that time, however, the accuracy of the absolute measurements has increased and more accurate determinations of the relation between the international units and the absolute units (ohm and ampere) have been made (*7*). In 1930, the relation between the international and absolute electrical units was such that (*8*)

$$1 \text{ international joule} = 1.0004 \text{ absolute joules.} \qquad (1)$$

Later and more accurate evaluations yielded values nearer unity. In 1939, the relation was (*9*)

$$1 \text{ international joule} = 1.00020 \pm 0.00005 \text{ absolute joules.} \qquad (2)$$

In 1947, the relations selected as best by the National Bureau of Standards (*10*) for purposes of certification of standard cells and resistances were such that

$$1 \text{ international joule} = 1.000165 \pm 0.000025 \text{ absolute joules.} \qquad (3)$$

All measurements of electrical energy made from about 1910 to 1948 by means of standard cells and resistances are actually in terms of international joules. Beginning January 1, 1948, the National Bureau of Standards, along with the national standardizing laboratories of other countries, is certifying standard cells and resistances in absolute volts and ohms, so that the resulting energy is measured in absolute joules (*10*).

5. Joule versus calorie. Notwithstanding the fact that practically all accurate calorimetric measurements made after about 1910 were actually based on electrical energy, most investigators continued until about 1930 to express their final results in such a way as to make it appear that the unit of energy was in some way still connected with the heat capacity of water. Actually, what they did was to convert their values, determined in international joules, into one or more of the several calories based on the heat capacity of water, usually for comparison with older values reported in calories in the literature. This procedure should have been reversed; that is, the older data should have been converted to the modern unit of energy. However, the conversion to the older unit, the calorie, was favored because most chemists and physicists were reluctant to change from their habits of thinking of energy in terms of a unit of the size of a calorie.

An important effort to accustom chemists and physicists to the use of the joule as the unit of energy was made by Washburn in connection with many (but not all) of the tabulations of chemical thermodynamic data in the *International Critical Tables* (*11*), of which he was editor-in-chief. This attempt to change over to the joule was not popular. It appeared then that the calorie would at least have to be retained as the name of the unit of heat energy. It was also realized that there would have to be separated from the new calorie every association with the heat capacity of water, else all the thermodynamic values would have to be changed every time someone determined the heat capacity of water with an accuracy greater than that already existing. It would also be necessary for the new calorie to have a size approximately equal to that of the traditional calorie.

The obvious solution was to have an artificial, conventional calorie, defined as equal to a given number of electrical joules, the unit in which the calorimetric measurements are actually made. The investigators would then report their results in terms of the unit in which the measurements are actually made, and, for the benefit of those who prefer to continue thinking of energy in terms of a unit having the name and size of the calorie, would also give the values in terms of the artificial calorie by using the conventional factor for the conversion.

In line with the foregoing development, there came into use independently about 1930 two different artificial, conventional, defined calories, one in the engineering steam tables and the other in thermochemistry and chemical thermodynamics. (Such calories may also be described as "dry" calories.)

6. Steam calorie. The artificial, conventional calorie used in the engineering steam tables is designated as the I.T. calorie (International Table calorie), which was first defined in 1929 by the International Steam Table Conference (*12*) by the relation

$$\begin{aligned} 1 \text{ I.T. calorie} &= \tfrac{1}{860} \text{ international watt-hour} \\ &= 0.00116279 \text{ international watt-hour.} \qquad (4) \end{aligned}$$

With the 1947 National Bureau of Standards relation between the international and the absolute watt, the same steam calorie would be equal to

$$1 \text{ I.T. calorie} = 0.00116298 \text{ absolute watt-hour.} \qquad (5)$$

As a matter of historical interest, it may be mentioned that the steam calorie was defined so that its value would be near the value of the mean (0° to 100°C) calorie. As indicated by its definition, the steam calorie is independent of the heat capacity of water.

By common consent, the British thermal unit (BTU) used in the engineering steam tables is defined in terms of the steam calorie so as to retain the convenient relation

$$1 \text{ I.T. calorie/gram} = 1.8 \text{ BTU/lb.} \tag{6}$$

7. Thermochemical calorie. The artificial, conventional calorie that was used after about 1930 in all the research laboratories in the United States dealing with thermochemistry and chemical thermodynamics was defined completely by the relation (*13–16*)

$$1 \text{ calorie} = 4.1833 \text{ international joules.} \tag{7}$$

Beginning January 1, 1948, this calorie was redefined in terms of absolute joules, using the 1947 National Bureau of Standards relation between the international and absolute electrical units (*10*), so that

$$1 \text{ calorie} = 4.1840 \text{ absolute joules.} \tag{8}$$

With this redefinition, the thermochemical calorie represents exactly the same quantity of energy as before, and all the values previously reported in terms of the thermochemical calorie remain unchanged. As is obvious from the definition, the thermochemical calorie is independent of the heat capacity of water. All the values of calories reported in this book are in terms of the conventional thermochemical calorie.

The number 4.1833, which originally defined the thermochemical calorie in terms of international joules, now has no particular significance, though for historical interest it may be mentioned that it arose from the quotient 4.185/1.0004, through the attempt to hold to the factor 4.185, selected by the *International Critical Tables* (*11*) for the relation between the absolute joule and the 15° calorie, and the factor 1.0004, selected in 1930 as the then best ratio of the size of the international joule to the absolute joule (*8*).

8. Heat capacity of water. The present best values of the heat capacity of water, in the range 0° to 100°C, appear to be those of Osborne, Stimson, and Ginnings (*17*). These values may be used to convert to joules such thermal data reported in the literature as may have been obtained in terms of the heat capacity of water at a given temperature. (Before this work, Laby and Hercus (*18*) had in 1927 reported a new value for the mechanical equivalent of heat.)

9. Collateral reading. For some additional details regarding the status of the calorie and the joule, the reader is referred to Mueller and Rossini (*19*).

REFERENCES

1. J. P. Joule, *Phil. Mag.* **23**, 263, 347, 435 (1843).
2. H. A. Rowland, *Proc. Am. Acad. Arts Sci.* **15**, 75 (1880).
3. O. Reynolds and W. H. Moorby, *Trans. Roy. Soc.* (*London*) **A190**, 301 (1897).
4. J. S. Ames, *Rapports congress international de physique*, Volume I, pp. 178, 214, Gauthier-Villars, 1900.
5. H. T. Barnes, *Transactions of the International Electrical Congress*, Volume 1, p. 53, St. Louis, 1904.
6. International Congress on Electrical Units and Standards, London, 1908.
7. H. L. Curtis, *J. Research Natl. Bur. Standards* **33**, 235 (1944).
8. *Natl. Bur. Standards Tech. News Bull.* 156 (1930).
9. H. T. Wensel, *J. Research Natl. Bur. Standards* **22**, 375 (1939).
10. *Natl. Bur. Standards Circ.* C459 (1947).
11. *International Critical Tables*, McGraw-Hill Book Company, 1927.
12. "Report of the International Steam Tables Conference (London, 1929)," H. N. Davis, *Mech. Eng.* **51**, 791 (1929).
13. F. D. Rossini, *J. Research Natl. Bur. Standards* **6**, 1 (1931).
14. *First Report of the Permanent Committee on Thermochemistry of the International Union of Chemistry*, Paris, 1934.
15. F. D. Rossini, *Chem. Revs.* **18**, 233 (1936).
16. F. D. Rossini, *Chem. Revs.* **27**, 1 (1940).
17. N. S. Osborne, H. F. Stimson, and D. C. Ginnings, *J. Research Natl. Bur. Standards* **23**, 238 (1939).
18. T. H. Laby and E. O. Hercus, *Trans. Roy. Soc.* (*London*) **A227**, 63 (1927).
19. E. F. Mueller and F. D. Rossini, *Am. J. Phys.* **12**, 1 (1944).

PROBLEM

1. In a given series of calorimetric experiments performed by Julius Thomsen in 1875, the mean temperature of the calorimeter was near 18°C. Thomsen reported the resulting thermochemical values in terms of a calorie that was essentially equal to the heat capacity of water at the mean temperature of the experiments. From the data of Osborne, Stimson, and Ginnings (reference 17 above) and the appropriate other conversion factors, calculate the factor required to convert Thomsen's values to their equivalent in (*a*) international joules, (*b*) absolute joules, and (*c*) thermochemical calories.

6

Energy and the First Law of Thermodynamics

1. Energy. There exists a property of every thermodynamic system called its energy, E, which is characterized by the fact that it is fully conserved over all systems in every process. Energy can enter or leave a system only through its surroundings. The existence of energy is manifested to us through observations of the changes which it produces in material things. It is important to note that distinction between various kinds of energy is made only as regards energy being transferred from one system to another. Once a given quantity of energy of a given kind has been taken up by a system, it is merged into the energy of the given system as a whole.

2. Magnitudes of changes in energy. Different processes may have associated with them quite appreciably different amounts of energy. The following examples illustrate the tremendous variation in the magnitude of the changes in energy which accompany different processes:

1. *Processes involving changes in the nuclei of atoms.* In the nuclear fission of uranium 235 with one neutron to form one atom of barium, one atom of krypton, and an assumed number of three neutrons,

$$^{235}\mathrm{U} + n = \mathrm{Ba} + \mathrm{Kr} + 3n, \tag{1}$$

the energy given up by the system to the surroundings is approximately 4 × 10^{12} cal/mole.

2. *Processes involving changes in the valence electrons of atoms or molecules.* In the recombination of an electron with a proton to form a neutral hydrogen atom,

$$\theta + \mathrm{H}^{+} = \mathrm{H}, \tag{2}$$

the energy given up by the system to the surroundings is about 3×10^5 cal/mole.

3. *Processes involving changes in molecular structure.* In the reaction of hydrogen with oxygen to form water,

$$H_2 + \tfrac{1}{2}O_2 = H_2O, \tag{3}$$

the energy given up by the system to the surroundings is about 6×10^4 cal/mole.

4. *Processes involving changes of state, as from solid to liquid or liquid to gas.* In the condensation of water vapor to liquid water,

$$H_2O\ (g) = H_2O\ (liq), \tag{4}$$

the energy given up by the system to the surroundings is about 1×10^4 cal/mole.

5. *Processes involving changes in translational, rotational, and vibrational energy in a molecule.* In the process of cooling gaseous water from 1000°K to 300°K,

$$H_2O\ (g, 1000°K) = H_2O\ (g, 300°K), \tag{5}$$

the energy given up by the system is about 5×10^3 cal/mole.

6. *Processes involving changes in mechanical potential energy.* When a mass of water is dropped from a height of 555 ft, the energy given up by the system to its surroundings is about 7 cal/mole.

7. *Processes involving changes in mechanical kinetic energy.* In the stopping of a mass of water traveling with a speed of 50 miles/hour, the energy given up by the system to its surroundings is about 1 cal/mole.

3. Manner in which a system possesses energy. Although thermodynamics is not concerned with the mechanism of a process, it is nevertheless frequently helpful in thermodynamic studies to have some picture of how a system possesses energy. There may be said to be two general ways in which a system may possess energy.

In the first way, a system acquires or loses energy because of some change in the position of the system as a whole with respect to its surroundings. That is to say, the system may gain or lose energy because of a gain or loss, for the system as a whole, of its directed kinetic energy or of its potential energy of position in the gravitational field of the earth.

In the second way, a system acquires or loses energy because of a change in its internal chemical structure, that is, a change in the condition of its constituent atoms and molecules, or a change in the neutrons, protons, and electrons that go to make up the atoms. In addition to changes in atomic and molecular structure, there are included here changes in the translational, rotational, and vibrational energy of the molecules of which the system is composed.

4. The first law of thermodynamics. In every process that occurs, every change in energy must be in accord with the first law of thermodynamics. This law governs not only the transfer of energy from one place to another, but also all the transformations of energy in any of its many forms, as heat energy, mechanical potential energy, mechanical kinetic energy, electrical energy, radiation energy, latent molecular energy, etc.

The first law of thermodynamics was contained implicitly in the work of Carnot (*1*) in 1824 and of Mayer (*2*) in 1842, but was first stated unambiguously by Helmholtz (*3*) in 1847. The first law may be summed up in the statement that, whenever any process occurs, the sum of all the changes in energy, taken over all the systems participating in the process, is zero:

$$\sum \mathrm{d}E = 0. \tag{6}$$

In Equation 1, E represents the energy of a given thermodynamic system, and the summation is to cover all systems.

In subjecting a given process to the scrutiny of the first law, it is usually convenient to specify or define a particular system which is enclosed by a surface through which passes, in or out, energy in its various forms, and to let all the other possible systems constitute one large surrounding system. Whenever any process occurs, the net energy taken up by the given system will be exactly equal to the energy lost by the surroundings, and vice versa. The increase in the energy of a given system participating in a process will be equal to the sum of all the different kinds of energy taken up by the system from the surroundings less the sum of all the different kinds of energy given up by the system to the surroundings. For convenience in later derivations and calculations, it is desirable to distinguish three kinds of energy transferred between the system and its surroundings and to take the algebraic sign of each as positive when the given energy is taken up or absorbed by the system. This may be expressed by the relation*:

$$\mathrm{d}E = \delta q + \delta w + \delta u. \tag{7}$$

In Equation 7, $\mathrm{d}E$ is the differential increase in the energy of the system and δq, δw, and δu are infinitesimal quantities of the different kinds of energy taken up by the system, with q representing heat energy, w representing PV work energy, and u representing all other forms of energy. In order to be added properly, the energies q, w, and u must be expressed in the same unit of energy, and must be labeled properly with respect to sign. Positive values of q, w, or u, respectively, indicate that the given energy has been taken up by the system from the surroundings. Correspondingly, negative values of q, w, or u indicate that the given energy has been lost by the system to the surroundings.

Figure 1 illustrates schematically the various kinds of energy that may be taken up or lost by a given system when a process occurs. In the example shown in Figure 1, the increase in energy of the system as it passes from an initial state A to a final state B is

$$E_B - E_A = \Delta E = a - b + c - d + f - g + h - i + j - k. \tag{8}$$

In the general case, for a finite change from state A to state B, the increase in the energy of a system is

$$\Delta E = q + w + u, \tag{9}$$

where q, w, and u represent, respectively, the heat energy, the PV work energy, and all other forms of energy, absorbed by the given system. That is to say, the numerical values assigned to q, w, and u will be positive or negative, respectively, according to whether the net energy of the given kind is absorbed or given out by the system.

Since the energy of the system in the state A is fixed completely by the properties of state A, and similarly for state B, the increase

---

[*] The differential symbol d is used to mean the infinitesimal increment or differential increase of a given property, as $\mathrm{d}E$, the increment or differential increase in the energy of the system. The variation symbol δ is used to represent an infinitesimal quantity of something, as of one of the kinds of energy transferred in the process, as δq, an infinitesimal quantity of heat energy absorbed by the system. The variation symbol δ is to be distinguished from the differential symbol d.

in energy, $E_B - E_A$, or ΔE, as the system passes from state A to state B, is independent of the path followed in going from A to B. That is to say, for given states A and B, the value of ΔE is invariant. But q, w, and u may have any values whatsoever so long as their algebraic sum is equal to ΔE.

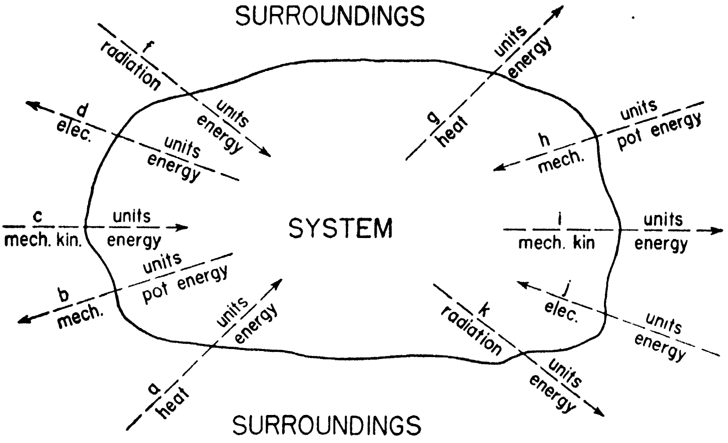


FIGURE 1. Schematic illustration of different kinds of energy taken up or lost by a system in a given process.

The arrows indicate the direction of passage of the different kinds of energy, into or out of, the given system during a given thermodynamic process.

If the process is one in which w and u are both zero, and the only energy involved is the heat energy, q, then

$$\Delta E = q. \tag{10}$$

If the process is one in which q and u are both zero, and the only energy involved is the PV work energy, w, then

$$\Delta E = w. \tag{11}$$

Similarly, if the process is one in which no heat or PV work energy is involved, and the only energy is some other form, as, for example, electrical energy, then

$$\Delta E = u. \tag{12}$$

If the process is one in which the system passes through a complete closed cycle, with the final state B being identical with the initial state A, then

$$\Delta E = 0, \tag{13}$$

and the sum of all the different energies absorbed or given out by the system must algebraically add to zero:

$$q + w + u = 0. \tag{14}$$

It is important to note that the first law of thermodynamics is concerned only with changes in the energy of material systems and not with the absolute value of the energy of any system. However, in making thermodynamic calculations of energy, particularly of the energy of chemical reactions, it is convenient to select certain reference states of the substances to which are assigned values of zero energy. Such reference states may be, for example, the chemical elements in the physical state in which they occur naturally at 25°C, or they may be the chemical atoms in the gaseous monatomic state at the absolute zero of temperature, or they may be, also at the absolute zero of temperature, the neutrons, protons, and electrons from which atoms may be formed. The selection of any such set of reference states, including the last named, is essentially arbitrary, since it is conceivable that even more fundamental units of matter may be discovered. The use of any given set of arbitrary reference states for assigning values of energy is desirable in so far as it facilitates the making of thermodynamic calculations.

REFERENCES

1. Sadi Carnot, *Reflexions sur la puissance motrice du feu*, Paris, 1824.
2. J. R. Mayer, *Liebigs Ann. Chem.* **42**, 233 (1842).
3. H. von Helmholtz, *Ueber die Erhaltung der Kraft*, G. Reimer, Berlin, 1847.

PROBLEMS

1. A given mass of fluid, X, is contained in a vertical cylinder under pressure by means of a piston held in place by stops, a–a. The piston has a mass of m g and a cross-section of r cm^2, and is in contact with the atmosphere, the pressure of which is 760 mm Hg. The cylinder is in contact with a thermostat. The following isothermal process occurs: The stops a–a are released; the fluid, X, forces the piston upward against the stops b–b, which are a vertical distance of h cm above the stops a–a, and, in this process, q joules of heat energy pass from the thermostat through the walls of the cylinder into the fluid, X. Assuming that no energy is involved in releasing the stops a–a, calculate the increase in the internal energy of the fluid, X.

2. A thermodynamic system and its surroundings participate in the following isothermal process involving four steps: (1) 100 cal of heat energy pass from the system to the surroundings; (2) the thermodynamic system expands

in volume 4000 cm^3 against the constant pressure of 1 atm exerted by the surroundings; (3) for a time of 2000 sec, an electric current of 2 amp passes from the surroundings into the system where it flows through a resistance coil of 20 ohms and returns to the surroundings; (4) a mass of 1 kg falls from a stationary location in the surroundings into the system where it comes to a stop after a total vertical fall of 30 m. Calculate the increase in energy of the system.

7

Equivalence of Mass and Energy

1. Relation between mass and energy. Shortly after the beginning of the present century, developments in the field of mathematical physics yielded a fundamental basis for evaluating the energy of material systems on an absolute basis. Embodied in the principle of relativity announced by Einstein (*1*) in 1905 is the following important relation:

$$E = \frac{m_0c^2}{(1 - v^2/c^2)^{1/2}}. \tag{1}$$

In this equation, E is the energy of the body (system), m_0 is the mass of the body at rest, v is the velocity of the body, and c is a constant whose value is the velocity of light. The expression on the right side of Equation 1 may be expanded into the following series:

$$E = m_0c^2 + \tfrac{1}{2}m_0v^2 + \tfrac{3}{8}m_0\frac{v^4}{c^2} + \tfrac{5}{16}m_0\frac{v^6}{c^4} + \cdots. \tag{2}$$

At ordinary velocities, the terms on the right side of Equation 2 beyond the second are negligible, so that, for velocities which are small compared to the velocity of light, the relation is

$$E = m_0c^2 + \tfrac{1}{2}m_0v^2. \tag{3}$$

In Equation 3, the term $\frac{1}{2}m_0v^2$ is the ordinary mechanical kinetic energy of a moving body, and the term m_0c^2 is the energy of the body at rest.

For systems at rest, the foregoing equation reduces to

$$E = m_0c^2. \tag{4}$$

According to Equation 4, the energy of a system at rest is equal to the square of the velocity of light into the mass of the system.

This then provides a fundamental basis for the assignment of absolute values of energy to material systems.

However, the assignment of absolute values of energy on this basis would add very large and unwieldy constants to the numbers which would be added and subtracted to obtain changes of energy taking place in systems participating in ordinary thermodynamic processes. The great practical usefulness of Einstein's theory, as expressed in Equation 4, lies in the fact that it relates changes of mass with changes of energy. If Equation 4 is applied to a given thermodynamic system that has gone from an initial state A to a final state B, the following relations hold:

$$E_B - E_A = [(m_0)_B - (m_0)_A]c^2, \tag{5}$$

or

$$\Delta E = c^2 \, \Delta m_0. \tag{6}$$

According to Equation 6, any gain or loss in energy by a given system is accompanied by a corresponding and proportional gain or loss in the mass of the given system. Letting the Einstein constant of proportionality be represented by the symbol Y, one may write Equation 6 as

$$\Delta E = Y \, \Delta m_0. \tag{7}$$

The value of the Einstein constant Y is 2.14784×10^{13} cal/g. That is to say, a gain in mass of 1 g corresponds to a gain in energy of more than 2.1×10^{13} cal or 2.5×10^{7} kw-hr.

2. Changes in mass in thermodynamic processes. At this point, it will be instructive to calculate the changes in mass accompanying the several representative types of thermodynamic processes listed in the preceding chapter. Equation 7 may be rewritten as

$$\Delta m_0 = \frac{\Delta E}{Y}\cdot \tag{8}$$

The changes in mass for the given reactions are as follows:

$$^{235}\mathrm{U} + n = \mathrm{Ba} + \mathrm{Kr} + 3n, \tag{9}$$

$$\Delta E = -4 \times 10^{12}\ \mathrm{cal/mole}; \quad \Delta m_0 = -0.2\ \mathrm{g/mole}; \tag{9a}$$

$$\theta + \mathrm{H}^+ = \mathrm{H}, \tag{10}$$

$$\Delta E = -3 \times 10^{5}\ \mathrm{cal/mole}; \quad \Delta m_0 = -1.4 \times 10^{-8}\ \mathrm{g/mole}; \tag{10a}$$

$$H_2 + \tfrac{1}{2}O_2 = H_2O, \tag{11}$$

$$\Delta E = -0.6 \times 10^5 \text{ cal/mole}; \quad \Delta m_0 = -3 \times 10^{-9} \text{ g/mole}; \tag{11a}$$

$$H_2O \text{ (g)} = H_2O \text{ (liq)}, \tag{12}$$

$$\Delta E = -1 \times 10^4 \text{ cal/mole}; \quad \Delta m_0 = -5 \times 10^{-10} \text{ g/mole}; \tag{12a}$$

$$O_2 \text{ (g, 1000°K)} = O_2 \text{ (g, 0°K)}, \tag{13}$$

$$\Delta E = -5 \times 10^3 \text{ cal/mole}; \quad \Delta m_0 = -2 \times 10^{-10} \text{ g/mole}. \tag{13a}$$

In each of the foregoing processes involving a decrease in energy, there is a corresponding decrease in mass. But, except for the reaction involving nuclear fission, the changes in mass are too small to be detected on the most sensitive balance available. The greatest sensitivity available in weighing with a balance is near 10^{-7} g/g. For a system whose mass is about 100 g, such a balance could detect a change in mass of 10^{-5} g, which would be equivalent to a change in energy of 2×10^8 cal. Energies of this magnitude are about 1000 times greater than the energies of ordinary chemical reactions, and hence can not be detected by weighing. That is to say, every system that has a change in energy has at the same time a corresponding and proportional change in mass, although for all ordinary chemical reactions and processes the change in mass is far too small to be detected, let alone measured. If it were possible to have a balance of unlimited sensitivity, measurements of energy could be made entirely by means of such a balance and calorimetric measurements would no longer need to be made.

It is interesting to note that Landolt (*2*) in 1893 and Manley (*3*) in 1913 made attempts to measure changes in mass accompanying ordinary chemical reactions.

3. Nuclear reactions. In 1919, Rutherford (*4*) discovered that alpha particles from radium brought about a nuclear reaction with nitrogen. In 1932, Chadwick (*5*) discovered the neutron, and Cockcroft and Walton (*6*) brought about a nuclear reaction involving lithium and artificially accelerated protons. Since nuclear reactions usually involve extremely large changes in energy, it became possible for the first time to subject the Einstein relation between mass and energy to experimental test. It was found that the changes in mass and energy were in accord with the Einstein relation within the accuracy and precision of the experimental observations.

Consider the above nuclear reaction in which a high-speed proton reacts with lithium to form two atoms of helium:

$$^{1}\text{H} + {}^{7}\text{Li} = 2\,{}^{4}\text{He}. \tag{14}$$

The masses of the atoms involved in this reaction are, on the physical scale (^{16}O = 16.0000), as follows: ^{1}H, 1.008123; ^{7}Li, 7.01822; ^{4}He, 4.00390.
Therefore, for reaction,

$$\Delta m_0 = -0.01854 \text{ g/mole}; \tag{15}$$

$$\Delta E = -3.982 \times 10^{11} \text{ cal/mole}. \tag{16}$$

By measuring the kinetic energy of the protons striking the stationary lithium target, and evaluating the kinetic energy of the atoms of helium produced, the energy of the reaction may be determined experimentally and compared with the value calculated from the change in mass.

The nuclear reaction of protons with lithium to form helium is one in which the system undergoes a decrease in mass and a decrease in energy. The energy lost by the reacting system is given up to the surroundings. However, this is not a reaction which may be used as a source of energy because many of the high-speed protons do not react and the kinetic energy that was given to them is wasted. The energy which is supplied to the many non-reacting protons is far greater than the energy released by the few reacting atoms. That is to say, a far greater quantity of energy is required to maintain the reaction than is liberated by it.

In each nuclear reaction for which it has been possible to determine both the change in energy and the change in mass, complete accord with the Einstein relation has been found within the limits of uncertainty of the experimental observations (*7*, *8*). In those reactions where only the change in energy has been measured, and the mass of one of the products (or reactants) is unknown, it has been possible by means of the Einstein relation to evaluate the unknown mass.

In those reactions where the masses of all the reactants and products are known, the energy of any given nuclear reaction may be calculated with an accuracy comparable to the accuracy of the value of the change in mass.

4. Self-sustaining nuclear reactions. In 1939, the discovery of the fission of uranium was reported (*9*). As was made evident by the truly tremendous amount of work done on this nuclear reaction during the recent war period (*10*), the fission of uranium can be made a self-sustaining chain reaction. In such reactions, one or more of the products are particles which are reactants necessary to maintain the reaction. For example, the fission of the uranium atom of mass 235 may be represented as follows, assuming the production of three neutrons (*10, 11*):

$$+ {}^{235}\mathrm{U} = \mathrm{Ba} + \mathrm{Kr} + 3n. \tag{17}$$

The neutrons produced in the reaction have an opportunity of being captured by other atoms of uranium 235 to maintain the fission reaction.

In the fission of uranium 235, the decrease in mass is about 0.001 g/g. Therefore, the fission of 1 g of uranium 235 would result in the transfer to the surroundings of an energy equal to 2.1×10^{10} cal, or about 2.5×10^{4} kw-hr. These figures mean that the energy released in the fission of 1 mass unit of uranium 235 is about the same as that released in the combustion of 3,000,000 mass units of coal. It is obvious that such a process has most enticing possibilities as a source of energy for power.

5. Collateral reading. For detailed discussion regarding atomic masses, nuclear reactions, nuclear energy for power, etc., the reader is referred to Seaborg (*8*), Bethe (*7*), Smyth (*10*), and Darrow (*11*).

REFERENCES

1. A. Einstein, *Ann. Physik* **18**, 639 (1905).
2. H. Landolt, *Berichte* **26**, 1820 (1893).
3. J. J. Manley, *Trans. Roy. Soc.* (*London*) **A212**, 227 (1913).
4. E. Rutherford, *Phil. Mag.* **37**, 581 (1919).
5. J. Chadwick, *Proc. Roy. Soc.* (*London*) **A136**, 692 (1932).
6. J. D. Cockcroft and E. T. S. Walton, *Proc. Roy. Soc.* (*London*) **A137**, 229 (1932).
7. H. A. Bethe, *Elementary Nuclear Theory*, John Wiley & Sons, New York, 1947.
8. G. T. Seaborg, *Revs. Modern Phys.* **16**, 1 (1944).
9. O. Hahn and F. Strassman, *Naturwissenschaften* **27**, 11, 89 (1939).
10. H. D. Smyth, *Atomic Energy for Military Purposes*, Princeton University Press, Princeton, N.J., 1945.
11. K. K. Darrow, *Atomic Energy*, John Wiley & Sons, New York, 1948.

PROBLEMS

1. A given radiating body loses mass at the rate of 0.00100 g every 24 hr. Calculate the rate of emission of radiation energy by the body in terms of kilowatts.

2. For the reaction of dissociating gaseous diatomic hydrogen into gaseous monatomic hydrogen,

$$^{1}H_2\ (g) = 2\ ^{1}H\ (g),$$

the change in energy, $\Delta E°$, is 104.18 kcal/mole at 25°C. Calculate the difference in mass, at 25°C, between 1 mole of $^{1}H_2$ (g) and 2 moles of ^{1}H (g).

3. The energy of the reaction

$$^{7}Li + {}^{2}H = 2\ ^{4}He + n$$

is $\Delta E_0° = -14.7 \times 10^6$ absolute electron-volts/molecule. On the scale $^{16}O = 16.0000$, the atomic masses are: $^{7}Li = 7.0182$, $^{2}H = 2.0147$, $^{4}He = 4.0039$. Calculate the mass of the neutron, n.

4. On the scale of $^{16}O = 16.0000$, the atomic masses are $^{1}H = 1.0081$, $^{35}Cl = 34.9803$, and $^{38}A = 37.974$. Calculate the change in energy, $\Delta E_0°$, for the reaction

$$^{35}Cl + {}^{4}He = {}^{38}A + {}^{1}H.$$

5. The mass of the electron is 0.00055 g/mole. Calculate the change in energy of a process in which an electron is completely converted into radiation energy: electron = radiation energy.

6. Given the following masses, in grams per mole: $^{1}H = 1.00786$; neutron, $n = 1.00870$. Calculate the change in energy for the process

$$n = {}^{1}H.$$

8

Energy, Heat Content (Enthalpy), and Heat Capacity

1. Change in energy. When a system participates in any process, we have seen (Chapter 6) that the increase in energy of the system is equal to the sum of all the different kinds of energy absorbed by the system from the surroundings less the sum of all the different kinds of energy given up by the system to the surroundings. Distinguishing, as before, three kinds of energy, and taking the quantity of each energy as positive when absorbed by the system and negative when given up by the system, the increase in the energy of the system is

$$\mathrm{d}E = \delta q + \delta w + \delta u. \tag{1}$$

In Equation 1, q, w, and u represent, respectively, heat energy, PV work energy, and all other kinds of energy.

When a given process involves only heat energy and PV work energy, then Equation 1 reduces to

$$\mathrm{d}E = \delta q + \delta w. \tag{2}$$

Suppose that the system is in pressure equilibrium with the surroundings in the sense that, if the pressure exerted by the system on the surroundings is P, then the pressure exerted by the surroundings on the system is either $P + \mathrm{d}P$ or $P - \mathrm{d}P$. Under these circumstances, the PV work energy is

$$\delta w = -P\,\mathrm{d}V, \tag{3}$$

where $\mathrm{d}V$ is the differential increase in the volume of the system. If the volume of the system increases, then the value of $\mathrm{d}V$ is positive and the value of δw is negative, indicating that the system gives up a positive amount of PV work energy to the surroundings. If the volume of the system decreases, then the value of $\mathrm{d}V$ is negative and the value of δw is positive, indicating that in such case the system takes up a positive amount of PV work energy from the surroundings. When the pressure exerted by the surroundings on the system is constant, then Equation 3 becomes

$$\delta w = -\mathrm{d}(PV). \tag{4}$$

For such a process at constant pressure, with only heat energy and PV work energy involved, Equation 2 becomes

$$\mathrm{d}E = \delta q - \mathrm{d}(PV). \tag{5}$$

Equation 5 may be transformed to

$$\mathrm{d}(E + PV) = \delta q. \tag{6}$$

Equation 6 tells us that, for any process occurring at constant pressure, with only heat energy and PV work energy involved, the heat absorbed from the surroundings is equal to the increment in the function $E + PV$.

2. Heat content (enthalpy). Because many processes actually occur at constant pressure, often that of the atmosphere, with only heat energy and PV work energy involved, and because under these circumstances the heat energy absorbed by the system from the surroundings is equal to the increment in the value of the function $E + PV$ for the system, it has been found convenient, largely as a matter of shorthand in writing, to let

$$H = E + PV. \tag{7}$$

The function H is called the heat content or enthalpy. With this nomenclature, Equation 6 becomes

$$\mathrm{d}H = \delta q. \tag{8}$$

If the given process of this kind takes place between an initial state A and a final state B, then, on integration,

$$\int_A^B \mathrm{d}H = H_B - H_A = \Delta H, \tag{9}$$

and

$$\Delta H = q. \tag{10}$$

Calorimetric measurements of the heat energy associated with a process occurring in a calorimetric reaction vessel at constant pressure, with no other energy involved than heat energy and work energy of the PV kind, yield a value for the increment in heat content (or enthalpy) of the given process, in accordance with Equation 10.

Just as was the value of ΔE, the value of ΔH is uniquely determined for a given system by the initial and final states, A and B, respectively, and is independent of the path followed in going from state A to state B.

Although the thermodynamic function, $H = E + PV$, has been defined chiefly because of its utility in connection with processes occurring at constant pressure, the fact that it is a thermodynamic property of a system makes its use possible under any conditions. For example, one may be interested in evaluating, at a constant temperature of 25°C, the change in heat content of 1 mole of gaseous oxygen as it passes from an initial state having a pressure of 1 atmosphere to a final state having a pressure of 20 atmospheres. Here again, the value of ΔH for this process is independent of the path followed in going from A to B.

3. Heat capacity. The heat capacity, C, of a system is defined as the ratio of the heat energy absorbed by the system from the surroundings to the increase in temperature of the system, as

$$C = \frac{\delta q}{\mathrm{d}T}\cdot \tag{11}$$

In general, the heat capacity of a system is determined by adding a measured quantity of heat energy to it and measuring the resulting change in temperature, with the quantity of heat energy added being such as to produce not too large a change in temperature, so that

$$C = \frac{\delta q}{\mathrm{d}T} = \frac{\Delta q}{\Delta T}\cdot \tag{12}$$

The heat capacity defined by Equation 11 is perfectly general and may be applied to any system of one or more components and of one or more phases.

4. Heat capacity at constant volume. The heat capacity at constant volume, C_V, of a system is defined as the ratio of the heat energy absorbed by the system from the surroundings to the increase in temperature of the system, while the system remains at constant volume, as

$$C_V = \left(\frac{\delta q}{\partial T}\right)_V\cdot \tag{13}$$

In this process, there is no work energy of the PV kind because the volume is constant, and the only energy involved is heat energy. Application of the first law to this process yields

$$\mathrm{d}E = \delta q. \tag{14}$$

Denoting the constancy of volume, we write

$$(\partial E)_V = (\delta q)_V. \tag{15}$$

Dividing both sides of Equation 15 by $(\partial T)_V$, one obtains

$$\left(\frac{\partial E}{\partial T}\right)_V = \left(\frac{\delta q}{\partial T}\right)_V. \tag{16}$$

Combination of Equations 13 and 16 yields

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V. \tag{17}$$

That is, the heat capacity at constant volume is equal to the change of the energy with temperature at constant volume.

5. Heat capacity at constant pressure. The heat capacity at constant pressure, C_P, of a system is defined as the ratio of the heat energy absorbed by the system from the surroundings to the increase in temperature of the system, all at constant pressure, as

$$C_P = \left(\frac{\delta q}{\partial T}\right)_P. \tag{18}$$

In this process, the work energy is of the PV kind, and, since the pressure is constant, is equal to the pressure times the change in volume. Application of the first law yields

$$\mathrm{d}E = \delta q + \delta w, \tag{19}$$

or

$$\mathrm{d}E = \delta q - P\,\mathrm{d}V. \tag{20}$$

Since the pressure is constant

$$P\,\mathrm{d}V = \mathrm{d}(PV), \tag{21}$$

and Equation 20 becomes

$$\mathrm{d}(E + PV) = \delta q, \tag{22}$$

or

$$\mathrm{d}H = \delta q. \tag{23}$$

Indicating the constancy of pressure in the equation itself,

$$(\partial H)_P = (\delta q)_P. \tag{24}$$

Dividing both sides of Equation 24 by $(\partial T)_P$, one obtains

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\delta q}{\partial T}\right)_P. \tag{25}$$

Combination of Equations 18 and 25 yields

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P. \tag{26}$$

That is, the heat capacity at constant pressure is equal to the change of the heat content (or enthalpy) with temperature at constant pressure.

6. Relation between C_V and C_P. The relation between the heat capacity at constant volume and the heat capacity at constant pressure may be derived as follows: From the definition of the heat content,

$$H = E + PV. \tag{27}$$

Differentiating with respect to temperature at constant pressure, one obtains

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P. \tag{28}$$

The energy, E, may be expressed as a function of volume and temperature:

$$E = f(V,T). \tag{29}$$

Then

$$\mathrm{d}E = \left(\frac{\partial E}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial E}{\partial T}\right)_V \mathrm{d}T. \tag{30}$$

Indicating the constancy of the pressure by appropriate subscripts, one obtains

$$(\partial E)_P = \left(\frac{\partial E}{\partial V}\right)_T (\mathrm{d}V)_P + \left(\frac{\partial E}{\partial T}\right)_V (\partial T)_P. \tag{31}$$

Dividing each term by $(\partial T)_P$, one may write

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial E}{\partial T}\right)_V. \tag{32}$$

From Equations 28 and 32, we obtain

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial E}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial E}{\partial T}\right)_V + P\left(\frac{\partial V}{\partial T}\right)_P. \tag{33}$$

Then

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial V}{\partial T}\right)_P\left[P + \left(\frac{\partial E}{\partial V}\right)_T\right], \tag{34}$$

and

$$C_P - C_V = \left(\frac{\partial V}{\partial T}\right)_P\left[P + \left(\frac{\partial E}{\partial V}\right)_T\right]. \tag{35}$$

An equation similar to Equation 35 but containing the pressure as a variable instead of the volume may be derived by letting the energy be expressed as a function of pressure and temperature, as

$$E = f(P,T), \tag{36}$$

and proceeding as in the derivation of Equation 35.

PROBLEMS

1. Derive the relation

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

2. Derive the relation

$$\left(\frac{\partial H}{\partial P}\right)_T - V = P\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial E}{\partial P}\right)_T.$$

3. Assuming the change of energy with volume at constant temperature to be negligible, and taking the expansion at 25°C and constant pressure of 1 atm to be $(\partial V/\partial T)_P = 0.10$ cm^3/deg mole, calculate the value of $C_P - C_V$ for a given system at 25°C and 1 atm.

9

Gases and the First Law of Thermodynamics

1. Isothermal process. Any process that takes place at a constant temperature, or any process that is fully specified by initial and final states which are at the same temperature, is an isothermal process.

2. Adiabatic process. Any process occurring in such a way that no heat energy is absorbed or lost by the given system through the boundary which separates the system from the surroundings is an adiabatic process.

3. Reversible process. A reversible process is one occurring in such a manner that the restoring force differs from the deforming force only by a differential amount. In the reversible expansion of a gas, the deforming force is the pressure, P, of the gas itself, and the restoring force is represented by an opposing pressure, $P - \mathrm{d}P$. Similarly, in the reversible compression of a gas, the deforming force is an external pressure, $P + \mathrm{d}P$, operating against a restoring force represented by the pressure, P, of the gas.

4. Irreversible process. An irreversible process is one in which the deforming and restoring forces differ by more than a differential amount.

5. Ideal gas. In any discussion concerning the thermodynamic properties of a gaseous substance, it is convenient to define what has come to be known as the ideal gas. In the words of Lewis and Randall (*1*), the ideal gas is an invented substance, defined by certain properties which are not possessed by any actual substance, but which are supposed to be approached by every actual gas as its pressure is indefinitely diminished. That is to say, as the pressure becomes smaller and smaller, or the volume becomes larger and larger, the pressure-volume-temperature relations for every real gas approach each other, and in the limit become those attributed to the ideal gas.

The ideal gas is defined by the following relations:

$$PV = RT, \tag{1}$$

$$\left(\frac{\partial E}{\partial V}\right)_T = 0. \tag{2}$$

Equation 1 refers to one mole of gas and indicates the manner in which the pressure, volume, and temperature of the ideal gas are related. Equation 2 states that for the ideal gas at constant temperature the energy is independent of the volume, and hence also of the pressure.

6. Work of expansion or compression of a gas. The work performed in the expansion or compression of a gas is evaluated from the physical relation that the amount of work is equal to the pressure multiplied by the change in volume. If w is the PV work energy absorbed by the gas during a given process, then, during either expansion or compression,

$$\delta w = -P\,\mathrm{d}V, \tag{3}$$

and

$$w = -\int P\,\mathrm{d}V. \tag{4}$$

In Equations 3 and 4, P is the pressure of the gas if the process is a reversible one. If the process is not reversible, then the work is measured by the resisting pressure, whatever that may be.

Consider the plot of pressure versus volume of a gas, as shown in Figure 1. On the expansion of the gas from the volume V_A to the volume V_B, different amounts of work may be performed by the gas on the surroundings, depending upon the resisting pressure. If the expansion is performed reversibly, with the resisting pressure differing from the pressure of the gas itself only by a differential amount, then the work done by the gas on the surroundings is a maximum and is evaluated by the area, $ABCD$, under the curve. If during the expansion the resisting pressure is a constant and equal to the final pressure, P_B, then the work done by the gas is evaluated by the rectangular area, $BCDE$, or $P_B(V_B - V_A)$. If the resisting pressure during the expansion is zero, as by expansion of the gas into an evacuated space, then the work performed by the gas is zero, and may be represented by the line DC.

If the relation between the pressure and volume of the gas undergoing reversible expansion or compression is known and expressible by means of an equation explicit in terms of either the pressure or the volume, then the PV work energy may be calculated analytically more readily than by graphical integration.

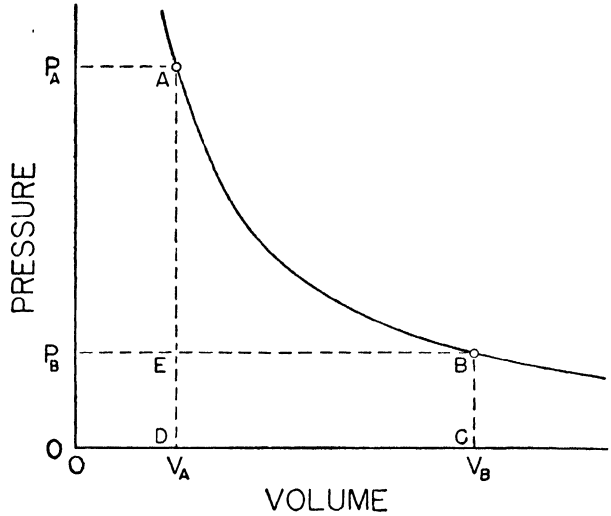


FIGURE 1. Schematic diagram of pressure as a function of volume for a gas.

For example, in the case of one mole of an ideal gas at constant temperature,

$$\delta w = -P\,\mathrm{d}V = -\frac{RT}{V}\,\mathrm{d}V = -RT\mathrm{d}\ln V, \tag{5}$$

or, for the finite change from an initial volume V_A to a final volume V_B,

$$w = -RT\ln\frac{V_B}{V_A}. \tag{6}$$

7. Isothermal expansion or compression of an ideal gas. When an ideal gas is expanded or compressed, with only heat energy and PV work energy involved, the process conforms to the first law by the relation

$$\mathrm{d}E = \delta q + \delta w. \tag{7}$$

In Equation 7, $\mathrm{d}E$ is the increase in energy of the system, here taken as the gas itself, δq is the heat energy absorbed by the system (gas) from the surroundings, and δw is the PV work energy absorbed by the system (gas) from the surroundings. For a finite change, as from state A to state B, Equation 7 becomes

$$\Delta E = q + w. \tag{8}$$

Since the energy of an ideal gas at constant temperature is constant and independent of the volume, then in the isothermal expansion or compression of an ideal gas,

$$\Delta E = 0, \tag{9}$$

and

$$q + w = 0, \tag{10}$$

or

$$q = -w. \tag{11}$$

Equation 11 tells us that, in the isothermal expansion of an ideal gas, the heat energy taken up by the gas from the surroundings is equal to the PV work energy performed by the gas on the surroundings (which is the negative of the PV work energy absorbed by the gas from the surroundings). Similarly, in the isothermal compression of an ideal gas, the PV work energy absorbed by the gas from the surroundings is equal to the heat energy given up by the gas to the surroundings (which is the negative of the heat energy absorbed by the gas from the surroundings).

In the reversible expansion or compression of any gas,

$$\delta w = -P\,\mathrm{d}V. \tag{12}$$

For the ideal gas in an isothermal process, we have seen that, since

$$P = \frac{RT}{V}, \tag{13}$$

we can write

$$\delta w = -\frac{RT}{V}\,\mathrm{d}V = -RT\mathrm{d}\ln V, \tag{14}$$

and integrate between the initial volume V_A and the final volume V_B, to obtain

$$w = -RT\ln\frac{V_B}{V_A}\cdot \tag{15}$$

Equation 15 gives the value of the PV work energy in the isothermal expansion or compression of one mole of an ideal gas. Since, for such a process, the heat energy absorbed is, by Equation 11, equal to the negative of the PV work energy absorbed (or equal directly to the PV work energy given up by the gas to the surroundings) we can also write the heat energy absorbed in such a process to be

$$q = RT \ln \frac{V_B}{V_A}. \tag{16}$$

Because for an ideal gas

$$\frac{V_B}{V_A} = \frac{P_A}{P_B}, \tag{17}$$

Equations 15 and 16 may also be expressed in terms of the initial and final pressures.

8. Adiabatic expansion or compression of an ideal gas. In the adiabatic expansion or compression of a gas, with only PV work energy involved, the first law reduces to

$$\mathrm{d}E = \delta w. \tag{18}$$

For the ideal gas, the energy is independent of the volume,

$$\left(\frac{\partial E}{\partial V}\right)_T = 0. \tag{19}$$

From Chapter 8,

$$\mathrm{d}E = C_V\,\mathrm{d}T. \tag{20}$$

For a reversible expansion or compression,

$$\delta w = -P\,\mathrm{d}V. \tag{21}$$

Combination of Equations 18, 20, and 21 yields

$$C_V\,\mathrm{d}T = -P\,\mathrm{d}V. \tag{22}$$

For one mole of an ideal gas,

$$P = \frac{RT}{V}, \tag{23}$$

and Equation 22 may be written as

$$\frac{\mathrm{d}T}{T} + \left(\frac{R}{C_V}\right)\left(\frac{dV}{V}\right) = 0, \tag{24}$$

or

$$d \ln T + \frac{R}{C_V} d \ln V = 0. \tag{25}$$

Equation 25 can not be integrated until the value of C_V for the ideal gas is known as a function of temperature. However, in the simple case where, over the given range of temperature, C_V may be assumed constant, Equation 25 may be integrated to yield

$$\ln T + \frac{R}{C_V} \ln V = c, \tag{26}$$

or

$$\ln T + \ln V^{R/C_V} = c. \tag{27}$$

In Equations 26 and 27, c is the constant of integration. Equation 27 may be further transformed to

$$\ln TV^{R/C_V} = c, \tag{28}$$

or

$$TV^{R/C_V} = e^c = c'. \tag{29}$$

Strictly, Equation 29 applies only to an ideal gas for which the value of C_V is constant.

9. Isothermal expansion or compression of a real gas. The isothermal expansion or compression of a real gas, with only heat energy and PV work energy involved in the process, is governed by the relation

$$dE = \delta q + \delta w, \tag{30}$$

or, for the finite change,

$$\Delta E = q + w. \tag{31}$$

In the case of the ideal gas, Equations 30 and 31 are simplified because at constant temperature the change in energy is zero. Further, with the ideal gas in an isothermal reversible process, the PV work energy is readily evaluated (Equation 15) from the initial and final volumes and hence the heat energy becomes known (Equation 16). With a real gas in an isothermal reversible expansion or compression, however, the application of Equation 31 requires (1) a knowledge of how the energy of the gas changes with pressure or volume, in order to evaluate ΔE, and (2) a knowledge of how the pressure is related to the volume, in order to evaluate the PV work energy through the relation

$$w = -\int P\,\mathrm{d}V. \tag{32}$$

10. Adiabatic expansion or compression of a real gas. In the adiabatic expansion or compression of a gas, with only PV work energy involved, the first law becomes

$$\mathrm{d}E = \delta w. \tag{33}$$

If the expansion or compression is reversible, then

$$\delta w = -P\,\mathrm{d}V,$$

and

$$\mathrm{d}E = -P\,\mathrm{d}V. \tag{34}$$

In order to apply Equation 33 to the adiabatic expansion or compression of a real gas, data are needed on the P-V-T relations of the gas or on the energy as a function of the volume and temperature covered in the process.

REFERENCE

1. G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill Book Company, New York, 1923.

PROBLEMS

1. Show that the value of $C_P - C_V$ for an ideal gas is equal to the gas constant R.

2. One mole of an ideal gas is permitted to expand at 25°C isothermally and reversibly from an initial pressure of 20 atm to a final pressure of 1 atm. Calculate the value, in joules and in kilowatt-hours, of the PV work energy performed by the gas on the surroundings. What is the value, in joules and in calories, of the heat energy absorbed by the gas from the surroundings?

3. One mole of a real gas is compressed isothermally and reversibly from an initial pressure of 1 atm to a final pressure of 100 atm, at a temperature of 25°C. At this temperature, and over this range of pressure, the following relations for this real gas hold: $E = a - 2P$, where a is a constant, E is in calories per mole, and P is in atmospheres; $PV = RT\ (1 - 0.005P)$, where P is in atmospheres. Calculate the work and heat of compression, in calories.

4. One mole of an ideal gas expands at 25°C isothermally from an initial pressure of 50 atm to a final pressure of 1 atm, against a constant pressure of 1 atm. What is the heat energy absorbed by the gas from the surroundings during this process?

5. One mole of a real gas undergoes an adiabatic reversible expansion from an initial state A, with properties P_A, V_A, T_A, and E_A, to a final state B, with properties P_B, V_B, T_B, and E_B. In terms of the given properties of the states A and B, give the value of the work performed by the gas on the surroundings during this expansion.

10

Energy of Substances in Relation to Temperature and Physical State

1. Change of energy of substances with temperature and physical state. Since energy is one of the important properties of matter, it is helpful to have some knowledge of how the energy of a substance varies with the temperature and with its physical state (solid, liquid, or gas).

Figure 1 gives a schematic diagram of how the energy (or the related property, the heat content or enthalpy) of a substance usually varies with the temperature and the physical state, the example being a substance that has two stable crystalline forms. Starting at the absolute zero of temperature, the substance passes through the following states*:

a. From the absolute zero, 0°K, to the transition temperature, *Ttr*, the substance is in the stable crystalline form II, with its energy increasing relatively slowly with temperature at a rate given by the heat capacity of crystalline form II;

b. At the transition temperature, *Ttr*, the substance absorbs a considerable amount of energy (energy or heat of transition) and is transformed from the stable crystalline form II to the stable crystalline form I;

c. From the transition temperature, *Ttr*, to the melting temperature, *Tm*, the substance is in the stable crystalline form I, with its energy increasing relatively slowly with temperature at a rate given by the heat capacity of crystalline form I;

d. At the melting temperature, *Tm*, the substance absorbs a considerable amount of energy (energy or heat of melting or fusion)

---

* The crystalline forms are labeled I, II, III, etc., beginning with the form in equilibrium with the liquid at the normal melting temperature, and continuing in regular order to the forms stable at lower temperatures.

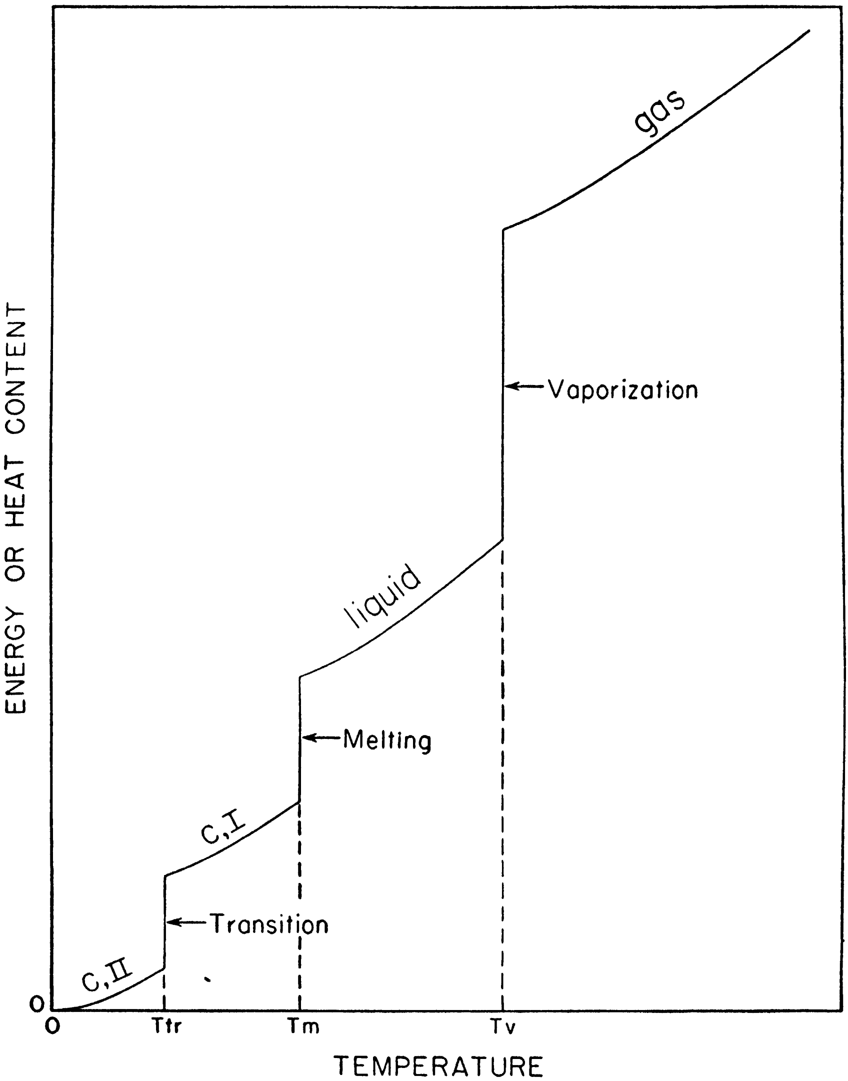


FIGURE 1. Schematic diagram of the energy or the heat content of a substance as a function of the temperature.

The scale of ordinates represents the energy or the heat content, referred to its value at the absolute zero, while the scale of abscissas gives the absolute temperature. The notations c,I and c,II represent crystalline forms I and II, respectively. *Ttr*, *Tm*, and *Tv* represent the temperatures of transition, melting, and vaporization, respectively.

and is transformed from the stable crystalline form I to the liquid state;

e. From the melting temperature, Tm, to the vaporization temperature, Tv, the substance is in the liquid state, with its energy increasing relatively slowly with temperature at a rate given by the heat capacity of the liquid;

f. At the vaporization temperature, Tv, the substance absorbs a considerable amount of energy (energy or heat of vaporization) and is transformed from the liquid state to the gaseous state;

g. Above the vaporization temperature, Tv, the substance is in the gaseous state, with its energy increasing relatively slowly with temperature at a rate given by the heat capacity of the gas.

If, in Figure 1, the scale of ordinates represents the heat content, H, of the given substance at constant pressure, then the slope of the curve at any point gives the heat capacity at constant pressure at that temperature:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \cdot \tag{1}$$

At the temperatures of transition, melting, and vaporization, the slopes are infinite and the value of the heat capacity at these temperatures is of course infinite.

Referred to the heat content of crystalline form II at 0°K, the heat content of the given substance in the gaseous state at the temperature T is given by the relation

$$H\ (\mathrm{g}) = H_0\ (\mathrm{c,II}) + \int_0^{Ttr} C_P\ (\mathrm{c,II})\, \mathrm{d}T + \Delta Htr + \int_{Ttr}^{Tm} C_P\ (\mathrm{c,I})\, \mathrm{d}T + \Delta Hm + \int_{Tm}^{Tv} C_P\ (\mathrm{liq})\, \mathrm{d}T + \Delta Hv + \int_{Tv}^{T} C_P\ (\mathrm{g})\, \mathrm{d}T. \tag{2}$$

2. Solid state. A substance in the solid crystalline state is characterized by a regularity in the arrangement of the atoms or molecules which compose it. In general, from the standpoint of the energy required to disperse a crystal into its atomic or molecular components, crystalline solids may be classed as predominantly (*a*) molecular or non-bonded atomic, (*b*) metallic, (*c*) bonded atomic, and (*d*) ionic.

Molecular or non-bonded atomic crystals are ones in which the building blocks are molecules composed of two or more atoms, as the diatomic molecule, I_2, and the polyatomic molecule, C_6H_6. Non-bonded atomic crystals are ones in which the building blocks are non-bonded atoms, such as those of the rare gases, Ne, A, Kr, and Xe. In such crystals, the forces binding the atoms together in the molecule are relatively very large, whereas the forces holding the molecules or the non-bonded atoms together to form the crystal are relatively much smaller and are called van der Waals forces.

Metallic crystals are ones in which the building blocks are the atoms of the given metallic element, with the atoms being strongly bonded together, as in a crystal of copper. Metals are characterized by the relative ease with which electrons pass through the crystal to produce the phenomenon of high electrical conductivity.

Bonded atomic crystals are ones made up of atoms strongly bound to one another to form what may be called a giant molecule. A good example of such a crystal is diamond, in which each carbon atom is strongly bound by four single bonds to four neighboring carbon atoms, along the angles of a tetrahedron.

Ionic crystals are ones in which the building blocks are charged ions held in position in the crystal largely by strong electrostatic forces. An example is the crystal of sodium chloride, which is made up of positive sodium ions, Na^+, and negative chloride ions, Cl^-, each ion having as its nearest neighbors six ions of the opposite sign.

3. Melting or fusion. As a given crystalline substance is taken from the absolute zero of temperature to a higher temperature, the energy absorbed by the crystalline substance may be looked upon as resident in the crystal mainly in the form of vibrational motions of the atoms and molecules. When the energy so absorbed reaches a given value, with consequent considerable motion among the component parts of the crystal, the forces holding the substance in the crystalline form will be in a sort of state of balance with the forces arising from the thermal motions, and any additional energy put into the substance will serve to break down the crystal lattice and permit the molecules or atoms comprising the crystal to transform to the liquid state. This energy is the energy of melting or fusion.

4. Liquid state. The forces holding the atoms or molecules of a given substance together in the form of a liquid are very similar to the forces existing in the solid state, but the thermal motion has destroyed the regularity of arrangement that is characteristic of the crystalline state. The liquid state is characterized, in general, by a randomness of arrangement of the molecules or atoms of which it is composed.

5. Vaporization. As a given substance in the liquid state is taken from the normal melting temperature to a higher temperature, the energy absorbed in the process may be looked upon as resident in the liquid in the form of vibrational, rotational, and translational motions of the molecules and atoms. When the energy so absorbed reaches a particular value, at some given pressure, the intermolecular forces holding the molecules or atoms together as a liquid will be in a sort of state of balance with the forces arising from the thermal motions, and any additional energy sent into the liquid will serve to overcome the intermolecular forces, and the molecules or atoms will be transformed to the gaseous state. This energy is the energy of vaporization.

6. Sublimation. In the process of sublimation, a given substance passes directly from the solid state to the gaseous state. This process may occur for any substance below its melting temperature provided the pressure of the given substance in the gas phase is suitably low. At the temperature of sublimation, the forces holding the substance in the solid form are in a sort of state of balance with the forces arising from the thermal motions, and any additional energy put into the substance will serve to break down the crystalline lattice and set the molecules or atoms composing the crystal free to exist in the gaseous state. The energy of sublimation, particularly at a low pressure, may be looked upon as a measure of the energy associated with the forces holding the component parts of the crystal together. From our qualitative knowledge of the magnitude of the forces operating in crystals, we can see that the energy of sublimation of molecular or nonbonded atomic crystals, in which the intermolecular forces are van der Waals forces, will be much smaller than the energy of sublimation of metallic, bonded atomic, or ionic crystals, in which the atoms or ions are strongly bound together.

7. Gaseous state. The energy of a substance in the gaseous state near zero pressure is substantially all intramolecular, since the molecules are so far apart as to make the intermolecular forces negligible. As energy is taken up by such gaseous molecules, the temperature increases. The energy is resident in these molecules (*a*) as translational energy of the molecule as a whole, (*b*) as rotational energy of the molecule as a whole and, in some cases, of component parts of the molecule, (*c*) as vibrational energy of the component parts of the molecule, and (*d*), at sufficiently high temperatures, as electronic energy (of excitation of one or more of the valence electrons) of the molecule.

If, at a given temperature, the pressure of the gas is increased, the molecules are brought closer together, intermolecular forces will come into play, and the various motions of the molecules, and their component parts, will be affected in such a way as to decrease the energy of the molecules. In the limit, of course, if the temperature is below the critical temperature, the molecules may be brought so close together with increasing pressure as to permit the intermolecular forces to bring about the liquefaction or solidification of the substance.

8. Transition in the solid state. Certain substances can exist in more than one stable crystalline form at a given pressure. Absorption of energy by such a substance in the crystalline form stable at the lower temperature will bring it to a state at which the existing intermolecular forces in the crystal may be overcome by the thermal agitation of its component parts. But instead of yielding in favor of the liquid state as additional energy is absorbed, the given crystalline form will change to another crystalline form, which is usually less rigid and more mobile than its predecessor and which is capable of maintaining its existence in the face of the tendency toward liquefaction.

The new crystalline form will be stable from the temperature of the foregoing transition up to the temperature of melting, where the forces maintaining the crystalline form yield to the forces tending to bring about the liquid state. In some substances, several successive crystalline forms may be passed through as the temperature is raised toward the melting point, each of these crystalline forms being successive stops on the way to the liquid state.

In certain hydrocarbons, the transition from one stable crystalline form to another is accompanied by an absorption of energy which is comparable in magnitude to the normal energy of melting, with the energy of melting for such compounds being smaller than normal. In such cases, the transition is a process in which the given substance has almost, but not quite, melted.

When the transition is from one definite crystalline form to another, the temperature of transition will, at a given pressure, be a constant characteristic of the given substance. For pure substances, the energy of transition will be absorbed with no change in temperature, and, as in the processes of melting and vaporization, the heat capacity at this temperature will be infinite in value.

In addition to normal transitions of the first kind mentioned above, which are characterized by a discontinuity in the energy as a function of temperature and an infinite rate of change of energy with temperature (or an infinite value of the heat capacity) at the temperature of transition, there occur for some substances transitions of a second kind. These latter are called transitions of the second order and are characterized by having no discontinuity in the energy as a function of temperature, but having a discontinuity in the heat capacity as a function of temperature, without the heat capacity becoming infinite in value. This type of transition occurs over a range of temperature with the substance absorbing energy above its normal rate over the given range of temperature.

In a plot, as in Figure 1, of energy against temperature, for a crystalline solid, a transition of the second order would appear as a gradual upward displacement over the given range of temperature in the given curve.

There appear to be three general kinds of transitions of the second order, as follows (*4*): those involving ferromagnetic changes in a crystal, with a change from a magnetized state at lower temperatures to a non-magnetized state at higher temperature; those involving an order-disorder transition in alloys; and those involving internal rotation or rearrangement in crystals. These transitions of the second order occur with no change in the crystalline form of the substance.

9. Collateral reading. For a detailed discussion of the structure of matter in the solid, liquid, and gaseous states, the reader is referred to the following: Pauling (*1*), Rice and Teller (*2*), Mayer and Mayer (*3*), Slater (*4*), Seitz (*5*), and Hildebrand (*6*).

REFERENCES

1. L. Pauling, *The Nature of the Chemical Bond,* Cornell University Press, Ithaca, N.Y., 1940.

2. F. O. Rice and E. Teller, *The Structure of Matter,* John Wiley & Sons, New York, 1949.

3. J. E. Mayer and M. G. Mayer, *Statistical Mechanics,* John Wiley & Sons, New York, 1940.

4. J. C. Slater, *Introduction to Chemical Physics,* McGraw-Hill Book Company, New York, 1939.

5. F. Seitz, *The Modern Theory of Solids,* McGraw-Hill Book Company, New York, 1940.

6. J. H. Hildebrand, *Chem. Revs.* **44**, 37 (1949).

PROBLEMS

1. What thermodynamic property is a measure of the energy associated with the intermolecular forces holding together, in a given crystal form, the molecules of a van der Waals solid?

2. In the study of elastomers, or rubber-like solids, and the monomers from which they are made, an important property is what is called by some the "cohesive energy density," which is defined, for van der Waals liquids, as the energy, per unit volume, associated with the intermolecular forces holding the molecules together as a liquid. How would one determine the value of the cohesive energy density for a given van der Waals liquid? What is the relation between the cohesive energy density and Hildebrand's "solubility parameter"?

II

Entropy and the Second Law of Thermodynamics

1. Spontaneous change. Every system, if left to itself, changes spontaneously at a slow or rapid rate in such a way as to approach a definite final state of rest or equilibrium. Some simple examples of such spontaneous change are the following: (*a*) the expansion of a gas from a region of high pressure to one of low pressure, (*b*) the diffusion of a solute from a region of high concentration to one of low concentration, (*c*) the passage of heat from a region of high temperature to one of low temperature, and (*d*) the occurrence of a chemical reaction, as the combustion of carbon in oxygen to produce carbon dioxide. As these systems move toward equilibrium, they lose some measure of their capacity for spontaneous change. In each of these cases, the spontaneous change continues until equilibrium is attained, that is, until (*a*) the pressure becomes uniform, (*b*) the concentration becomes uniform, (*c*) the temperature becomes uniform, and (*d*) what we may at this point call the thermodynamic stability becomes uniform.

In each of the above examples, it follows that the reverse change of moving away from equilibrium will not occur spontaneously, and, further, that some external energy or force is necessary to move the given system in a direction away from the state of equilibrium, that is, to increase the capacity for spontaneous change in the given system. It is obvious, also, that in each of the above cases the capacity of the given system for spontaneous change is greater (*a*) the greater the difference in pressure, (*b*) the greater the difference in concentration, (*c*) the greater the difference in temperature, and (*d*) the greater the difference in the thermodynamic stability between the initial state and the equilibrium state.

It is important to note that in many such spontaneous changes there may be no change whatever in the energy of the given system. A simple example is the isothermal expansion of an ideal gas, in which expansion the gas loses some measure of its capacity for spontaneous change, but undergoes no change in energy.

2. Entropy. This brings us to the idea that there exists a property of every thermodynamic system called its entropy, S, that is associated with its capacity for spontaneous change. This property of entropy of a system increases in value as the system undergoes some spontaneous change and hence loses some of its capacity for spontaneous change. That is, in the isothermal expansion of an ideal gas, the entropy of the gas would increase with increase in its volume and decrease with decrease in its volume.

3. Reversible process. Given a system capable of spontaneous change from state A to state B, it would be possible theoretically to include in the process a mechanism whereby, as the spontaneous change occurred and the capacity for spontaneous change of the given system decreased, an increase in capacity for spontaneous change would be built up in the surroundings in an amount equal in magnitude to the decrease in capacity for spontaneous change occurring in the given system. Such a process would be what we have already called (Chapter 9) a reversible process, wherein there exist no forces (or pressures) differing by more than a differential amount, and wherein no heat energy is produced from other kinds of energy by friction, electrical resistance, etc.

In the isothermal expansion of an ideal gas, it is easy to see how the process may be arranged to operate reversibly and thus conserve the capacity for spontaneous change. Suppose that we have two systems, each of which consists of one mole of an ideal gas, with the initial volume and pressure of the first gas being the same as the final volume and pressure of the second gas, and vice versa. A suitable mechanism is interposed between the two systems so that the work done by the first gas in its reversible expansion from a volume V_A to a volume V_B is used in the reversible compression of the second gas from a volume V_B to a volume V_A. Thus, in this reversible process, the capacity for spontaneous change lost by the first system is gained by the second system, in like amount.

We thus arrive at the idea that, if a spontaneous change in one given system occurs reversibly, and that system thereby loses capacity for spontaneous change, there is built up in the surroundings or second system an increase in capacity for spontaneous change. We can then say that, for all processes occurring reversibly, the sum of the capacities for spontaneous change of all the systems involved remains unchanged.

It is important to note that a reversible process is one from which have been eliminated all friction, electrical resistance, and other causes of the dissipation of energy. The reversible process is therefore not an actual process but an ideal process which is approached in the limit by an actual process as the dissipation of energy through friction, etc., is reduced further and further. Every actual process that occurs, therefore, is accompanied by a decrease in capacity for spontaneous change, or an increase in entropy, the decrease in capacity for spontaneous change, or the increase in entropy, being greater the greater the departure from reversibility of the given process.

With regard to the quantitative measure of the decrease in capacity for spontaneous change, or increase in entropy, we may consider two different kinds of spontaneous change.

First, let us consider that there is available a given quantity of mechanical energy and that this energy may be (*a*) absorbed as heat energy by a reservoir A at a temperature T_A, or (*b*) be absorbed as heat energy by a second reservoir B at a lower temperature T_B. The latter result could also be reached by letting the energy be (*a*) absorbed as heat energy by the reservoir A and then (*c*) flow spontaneously to the reservoir B. It follows that the decrease in capacity for spontaneous change, or the increase in entropy, must be greater for step (*b*) than for step (*a*), since the increase in entropy for step (*b*) is equal to that in step (*a*) plus that in step (*c*). Therefore, the measure of the decrease in capacity for spontaneous change, or the increase in entropy, must be such that a simple function of the temperature is involved as a denominator to the quantity of heat energy. For example, the increase in entropy in a reversible process might be defined as

$$dS = \frac{\delta q}{f(T)}, \tag{1}$$

where the value of $f(T)$ increases with increase in temperature.

Second, consider the isothermal expansion at some temperature T of an ideal gas from a volume V_A to a larger volume V_B and then to a still larger volume V_C. Here again, the measure of the decrease in capacity for spontaneous change, or the increase in entropy, must be such that the change directly from A to C is greater than the change from A to B, and greater than the change from B to C. In this example, since the energy of the ideal gas is constant, we can write, according to the first law,

$$q = -w. \tag{2}$$

If, in the expansion, the gas performs no work, then

$$q = -w = 0. \tag{3}$$

But if the expansion is made to occur reversibly, then, for the change from A to B,

$$q_{AB} = -w_{AB} = RT \ln \frac{V_B}{V_A}, \tag{4}$$

and for the change from B to C,

$$q_{BC} = -w_{BC} = RT \ln \frac{V_C}{V_B}, \tag{5}$$

and for the change from A to C,

$$q_{AC} = -w_{AC} = RT \ln \frac{V_C}{V_A}. \tag{6}$$

Using the same function as above to measure the increase in entropy for each change occurring reversibly, and letting

$$f(T) = T, \tag{7}$$

we have for A to B,

$$S_B - S_A = \frac{q_{AB}}{T} = R \ln \frac{V_B}{V_A}, \tag{8}$$

and similarly for B to C,

$$S_C - S_B = \frac{q_{BC}}{T} = R \ln \frac{V_C}{V_B}, \tag{9}$$

and similarly for the change A to C,

$$S_C - S_A = \frac{q_{AC}}{T} = R \ln \frac{V_C}{V_A}. \tag{10}$$

It may be noted that the sum of Equations 8 and 9 is Equation 10.

In the isothermal expansion of the ideal gas, as from state A to state C, we may note the following: (*a*) there is no change in the energy of the gas; (*b*) there is no heat energy associated with the process if no work is done by the gas; (*c*) if the expansion is made to occur reversibly, the gas will perform work on the surroundings equal to

$$-w_{AC} = RT \ln \frac{V_C}{V_A}, \tag{11}$$

and heat energy will be absorbed by the gas in the amount of

$$q_{AC} = RT \ln \frac{V_C}{V_A}; \tag{12}$$

and (*d*), although the expansion from V_A to V_C may take place along an infinite number of paths, the increase in the property of entropy of the gas (or decrease in its capacity for spontaneous change) is fixed entirely by the initial and final states, being independent of the path, and the increase in entropy must have the same value over all the paths.

4. Second law of thermodynamics. The second law of thermodynamics was contained implicitly in the work of Carnot (*1*) as early as 1824, but was first clearly enunciated by Clausius (*2*) in 1850 and independently by Kelvin (*3*) in 1851. According to the second law, entropy is fully conserved over all systems in every reversible process. That is, for a reversible process, the sum of all the changes in entropy, taken over all the systems participating in the process, is zero:

$$\sum \mathrm{d}S = 0. \tag{13}$$

If the process is not a reversible one, then, for all systems participating, the sum of all the changes in entropy is greater than zero:

$$\sum \mathrm{d}S > 0. \tag{14}$$

We can then say that for any process that may occur, for all systems participating, the sum of all the changes in entropy will be equal to or greater than zero:

$$\sum \mathrm{d}S \geqq 0. \tag{15}$$

In the foregoing equations, S represents the entropy of a given thermodynamic system and the summation is to cover all systems.

In subjecting a given process to the scrutiny of the second law, it is usually convenient to specify or define a particular system which is inclosed by a surface and to let all the other possible systems constitute one large surrounding system. Whenever any reversible process occurs, the entropy gained by the system will be exactly equal to the entropy lost by the surroundings, and vice versa. Quantitatively, the increase in entropy of a given system participating in a reversible process is defined as

$$dS = \frac{\delta q}{T}. \tag{16}$$

At the same time, the surroundings will undergo a decrease in entropy of exactly the same amount.

Equation 16 above may also be written as

$$\delta q = T\,dS, \tag{17}$$

indicating that in a reversible process the heat energy absorbed by a given system is equal to the increase in entropy multiplied by the temperature.

From the foregoing, it is now clear how we may measure the change in entropy for any actual process that may occur in a nonreversible manner. The procedure is to restore the given system from the final state B to the initial state A along a reversible path. The change in entropy from B to A is thus measurable, and the value will be the negative of the change from A to B. For example, consider the difference in entropy between a volume V_A and a volume V_B for one mole of an ideal gas at a temperature T. What is desired is the value of $S_B - S_A$. To evaluate this, the gas is restored from the volume V_B to the volume V_A along a reversible path. In this process, the gas will absorb from the surroundings an amount of heat energy equal to

$$q_{B\rightarrow A} = -w_{B\rightarrow A} = RT \ln \frac{V_A}{V_B}, \tag{18}$$

and the change in entropy from B to A is

$$S_A - S_B = \Delta S_{B\rightarrow A} = \frac{q_{B\rightarrow A}}{T} = R \ln \frac{V_A}{V_B}. \tag{19}$$

The desired quantity is for the change from A to B and is

$$S_B - S_A = -(S_A - S_B) = -R \ln \frac{V_A}{V_B} = R \ln \frac{V_B}{V_A}. \tag{20}$$

5. Entropy and probability. We have seen how the property of entropy of a system is associated with its capacity for spontaneous change, with the value of entropy reaching a maximum as the capacity for spontaneous change reaches a minimum. To appreciate better the significance of the property of entropy, it is helpful to associate entropy with probability. Here we are concerned with the relation between the entropy of a system in a particular state as related to the probability of its existence in that particular one of its (usually many) allowable states of existence.

Consider a system, at a given temperature, T, consisting of a rectangular box having a volume V_B and containing one single molecule of an ideal gas. Suppose the box is arranged in such a way that, without involving any energy, a partition can be passed through the walls to separate instantaneously a volume V_A of the total volume V_B. The probability that the molecule of gas will at a given instant be found in the volume V_A is equal to the ratio of the volume V_A to the total volume V_B. The value of the probability will, of course, range from a minimum of zero, when the volume V_A is zero (as when the partition coincides with the near end on the box), through the value $\frac{1}{2}$, when the volume V_A is just half of the total volume V_B, to a maximum value of 1, when the volume V_A is equal to the total volume V_B (as when the partition coincides with the far end of the box).

If the box contained two molecules of the ideal gas instead of one, the probability that both molecules would at any instant be found in the volume V_A is $(V_A/V_B)^2$. If the box contained x molecules of the ideal gas, the probability that all the molecules would at any instant be found in the volume V_A is $(V_A/V_B)^x$, and if the box contained one mole, N, of molecules of the ideal gas, then the probability, W, that all the molecules would at any instant be found in the volume V_A is

$$W = \left(\frac{V_A}{V_B}\right)^N. \tag{21}$$

Since the probability for the existence of the molecules in the total volume V_B is unity, Equation 21 also gives the ratio of the probability of the existence of the molecules in the volume V_A to the probability for their existence in the total volume V_B, as

$$\frac{W_A}{W_B} = \left(\frac{V_A}{V_B}\right)^N, \tag{22}$$

or

$$\frac{W_B}{W_A} = \left(\frac{V_B}{V_A}\right)^N. \tag{23}$$

Let us now arbitrarily define the following relation between probability and entropy, per mole of molecules in the ideal gas state:

$$S = k \ln W. \tag{24}$$

In Equation 24, the constant of proportionality is the Boltzmann gas constant. According to this relation, for the one mole of molecules in the ideal gas state, the increase in entropy from the state A to the state B is

$$S_B - S_A = k \ln \frac{W_B}{W_A}. \tag{25}$$

Substituting from Equation 23, one obtains

$$S_B - S_A = k \ln \left(\frac{V_B}{V_A}\right)^N = Nk \ln \frac{V_B}{V_A} = R \ln \frac{V_B}{V_A}. \tag{26}$$

The relation between entropy and volume for an ideal gas as given by Equation 26 is identical with that given by Equation 8.

We thus have reached the idea that a system that is undergoing spontaneous change is moving toward a state of higher probability, and that, in the limit, when the system will have exhausted its capacity for spontaneous change, it will have reached a state of maximum probability. In the words of Lewis and Randall (*1*), we may say that "every system which is left to itself will, on the average, change toward a condition of maximum probability. This law, which is true for average changes in any system, is also true for any changes in a system of many molecules."

6. Collateral reading. For extended and detailed discussions of entropy, and its relation to probability and to changes occurring in nature, including certain philosophical aspects of the problem, the reader is referred to Lewis and Randall (*4*), Gibbs (*5*), Boltzmann (*6*), and Tolman (*7*).

REFERENCES

1. Sadi Carnot, *Reflexions sur la puissance motrice du feu*, Paris, 1824.
2. Clausius, *Pogg. Ann.* **19**, 368, 500 (1850).

3. W. Thomson, *Phil. Mag.* **4**, 8, 105, 160 (1851).

4. G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill Book Company, New York, 1923.

5. J. Willard Gibbs, *Collected Works*, Longmans, Green, and Company, New York, 1931.

6. L. Boltzmann, *Vorlesungen über Gas Theorie*, Barth, Leipzig, 1912.

7. R. C. Tolman, *The Principles of Statistical Mechanics*, Oxford University Press, New York, 1938.

PROBLEMS

1. Calculate the change in entropy of 1 mole of an ideal gas when it expands freely into an evacuated space from an initial pressure of 10 atm to a final pressure of 1 atm, at 25°C.

2. What is the change in entropy of a system as it passes reversibly from a state A to a state B if, for the given change from T_A to T_B, $q = a + bT$? What is the change in entropy of the surroundings?

12

Entropy and Thermodynamic Engines

1. Thermodynamic engines. One of the important practical applications of entropy is in the examination of the several devices to which we may apply the general name of thermodynamic engines. A thermodynamic engine is any system or combination of systems set up to convert heat energy into work energy or to utilize work energy to effect the transfer of heat energy from a region of given temperature to one of higher temperature. The three thermodynamic engines considered here will be called (*a*) the work engine, (*b*) the refrigerating engine, and (*c*) the heating engine.

2. Work engine. The thermodynamic work engine is used to convert heat energy into work energy. It involves the availability of a given amount of heat energy in a reservoir at a temperature T_A, the conversion of as much as possible of that heat energy to work energy, and the discharge of the remainder of the heat energy to a second reservoir at a lower temperature T_B.

Figure 1 gives a schematic diagram of the thermodynamic work engine, showing the hot reservoir, A, the cold reservoir, B, and the machine for performing work, C. The process consists in having available q_A units of heat energy in a hot reservoir at the temperature T_A, converting u_C units of this to work energy, and discharging q_B units of heat energy to the cold reservoir at T_B, with each step of the process operated reversibly. The problem is to determine what fraction of the heat energy originally available is obtainable as work energy, namely, the ratio u_C/q_A.

For a reversible process, the first and second laws of thermodynamics provide the following relations:

$$\sum \Delta E = 0; \tag{1}$$

$$\sum \Delta S = 0. \tag{2}$$

From the first law, covering the three systems involved,

$$-q_A + q_B + u_C = 0, \tag{3}$$

or

$$u_C = q_A - q_B. \tag{4}$$

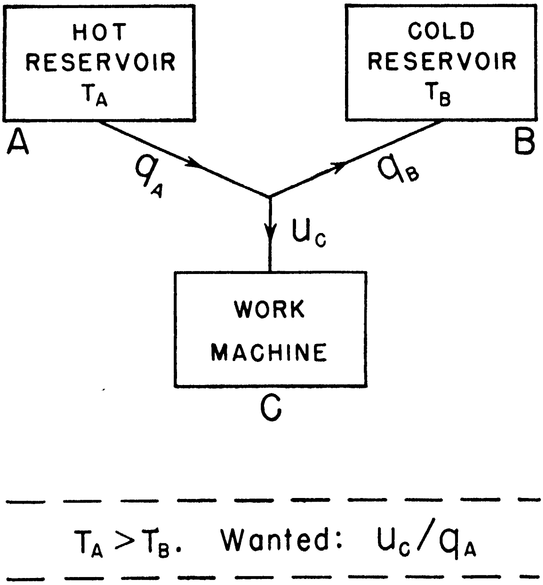


FIGURE 1. Schematic diagram of the thermodynamic work engine.

From the second law, covering the three systems involved,

$$-\frac{q_A}{T_A} + \frac{q_B}{T_B} = 0, \tag{5}$$

or

$$\frac{q_B}{q_A} = \frac{T_B}{T_A}. \tag{6}$$

Subtracting 1 from each side of Equation 6 and rearranging gives

$$\frac{q_B - q_A}{q_A} = \frac{T_B - T_A}{T_A}. \tag{7}$$

Multiplying each term in Equation 7 by −1 yields

$$\frac{q_A - q_B}{q_A} = \frac{T_A - T_B}{T_A}. \tag{8}$$

Combination of Equations 4 and 8 gives

$$\frac{u_C}{q_A} = \frac{T_A - T_B}{T_A}, \tag{9}$$

which is the desired result. Equation 9 shows that the maximum possible fraction of the available heat energy which is convertible into work energy is equal to the difference in temperature between the hot and the cold reservoirs divided by the temperature of the hot reservoir. This ratio varies from a value of zero, when $T_A = T_B$ and $T_B > 0$, to a value of unity, when $T_A > T_B$ and $T_B = 0$.

In the application of Figure 1 to a simple steam engine, the hot reservoir, *A*, corresponds to the boiler, the cold reservoir, *B*, corresponds to the condenser, and the work machine, *C*, corresponds to the source of the mechanical energy.

3. Refrigerating engine. The thermodynamic refrigerating engine expends work energy for the purpose of removing a given amount of heat energy from a given refrigerated space and discharging it to the warmer surroundings. Such an engine may be used to maintain a refrigerated space at a given low temperature by expending work energy to "pump" away to the warmer surroundings the heat energy which leaks in to the refrigerated space because of imperfect thermal insulation, as in a common refrigerator. Or this engine may be used in an ice plant to remove heat energy from liquid water and obtain ice, in which case the heat energy, along with the work energy expended for the operation of the engine, is, as before, discharged to the warmer surroundings.

Figure 2 gives a schematic diagram of the thermodynamic refrigerating engine, showing the hot reservoir, *A*, the cold reservoir, *B*, and the machine for performing work, *C*. The process consists in utilizing u_C units of work energy to "pump" q_B units of heat energy from the cold reservoir at T_B into the hot reservoir at T_A, with each step of the process operated reversibly. The problem is to determine the ratio of the heat energy removed from the cold reservoir to the work energy expended, namely, q_B/u_C.

To this reversible process, we apply the first and second laws of thermodynamics as given above by Equations 1 and 2. From the first law, covering the three systems involved,

$$q_A - q_B - u_C = 0, \tag{10}$$

or

$$u_C = q_A - q_B. \tag{11}$$

From the second law, covering the three systems involved,

$$\frac{q_A}{T_A} - \frac{q_B}{T_B} = 0, \tag{12}$$

or

$$\frac{q_A}{q_B} = \frac{T_A}{T_B}. \tag{13}$$

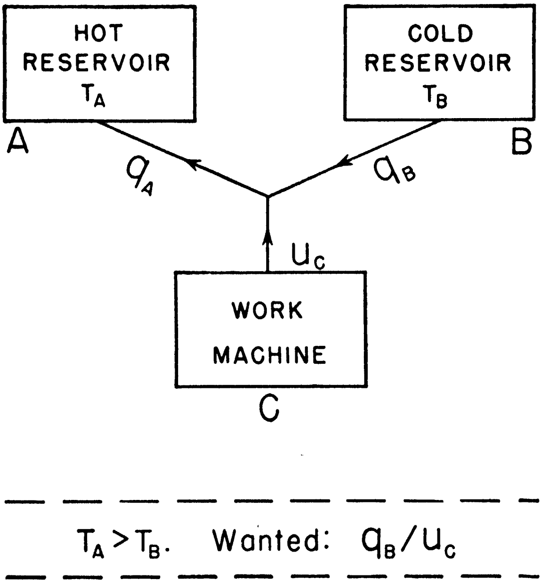


FIGURE 2. Schematic diagram of the thermodynamic refrigerating engine.

Subtracting 1 from each side and rearranging, we obtain

$$\frac{q_A - q_B}{q_B} = \frac{T_A - T_B}{T_B}. \tag{14}$$

Combination of Equations 11 and 14 and rearrangement give

$$\frac{q_B}{u_C} = \frac{T_B}{T_A - T_B} \tag{15}$$

which is the desired result. Equation 15 shows that the ratio of the heat energy removed from the cold reservoir to the work energy expended is equal to the temperature of the cold reservoir divided by the difference in temperature between the hot and cold reservoirs. This ratio varies from a value of infinity, when $T_A = T_B$ and $T_B > 0$, to a value of zero, when $T_A > T_B$ and $T_B = 0$.

In the application of Figure 2 to a simple household electric refrigerator, the cold reservoir, B, corresponds to the interior of the refrigerator, the hot reservoir, A, corresponds to the surroundings of the refrigerator, as the room in which it is located, and the work machine, C, corresponds to the electric motor and compressor.

4. Heating engine. The thermodynamic heating engine expends work energy for the purpose of "pumping" a given amount of heat energy into a given warm space from the colder surroundings. Such an engine may be used to provide heat for a house or building in cold weather, utilizing electrical energy to "pump" heat energy into the warm building from the colder surroundings.

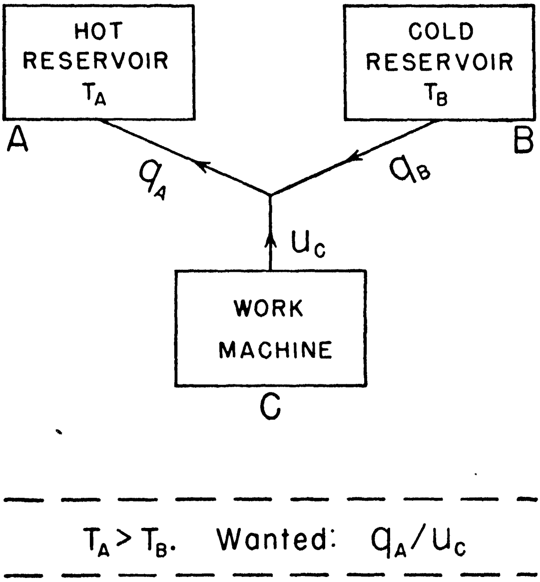


FIGURE 3. Schematic diagram of the thermodynamic heating engine.

Figure 3 gives a schematic diagram of the thermodynamic heating engine, showing the hot reservoir, A, the cold reservoir, B, and the machine for performing work, C. The process consists in utilizing u_C units of work energy to pick up q_B units of heat energy from the cold reservoir at T_B, giving q_A units of heat energy to the hot reservoir at T_A, with each step of the process operated reversibly. The problem is to determine the ratio of the heat energy made available to the hot reservoir to the work energy expended, namely, the ratio, q_A/u_C.

To this reversible process, we apply the first and second laws of thermodynamics as given above by Equations 1 and 2. From the first law, covering the three systems involved,

$$q_A - q_B - u_C = 0, \tag{16}$$

or

$$u_C = q_A - q_B. \tag{17}$$

From the second law, covering the three systems involved,

$$\frac{q_A}{T_A} - \frac{q_B}{T_B} = 0, \tag{18}$$

or

$$\frac{q_B}{q_A} = \frac{T_B}{T_A}. \tag{19}$$

Subtracting 1 from each side of Equation 19 and rearranging yields

$$\frac{q_B - q_A}{q_A} = \frac{T_B - T_A}{T_A}. \tag{20}$$

Combining Equations 17 and 20 and rearranging, we obtain

$$\frac{q_A}{u_C} = \frac{T_A}{T_A - T_B}, \tag{21}$$

which is the desired result. Equation 21 shows that for each unit of work energy expended there is available for heating the warm space a number of units of heat energy equal to the temperature of the hot reservoir, T_A, divided by the difference in temperature between the hot and cold reservoirs. The number of units of heat energy available for each unit of work energy varies from a value of one, when $T_A > T_B$ and $T_B = 0$, to a value of infinity, when $T_A = T_B$ and $T_B > 0$.

In the application of Figure 3 to a heating plant for a building, the hot reservoir, A, corresponds to the interior of the house being heated, the cold reservoir, B, corresponds to the colder surroundings, and the work machine, C, corresponds to the electric motor and compressor. The heat energy to which the work energy is converted is added to the heat energy picked up from the surroundings for deposit within the heated space.

PROBLEMS

1. A steam engine, operating with boiler and condenser at temperatures of 200°C and 30°C, respectively, is used to generate electrical energy. Ten tons of coal are burned each hour, liberating at the boiler 15,000 BTU/lb. Calculate the maximum power in kilowatts available from this engine.

2. A residence requires 200 million BTU for heating in a given winter season, where the average indoor temperature is 21°C and the average outdoor temperature is 5°C. Assuming that electrical energy costs 2 cents per kilowatt-hour, calculate the minimum cost of operating a thermodynamic engine for heating this residence in the given season.

3. A household refrigerator costs 75 cents to operate for 1 month of 30 days, the average temperature within the refrigerator being 4°C and the room temperature being 25°C. If electrical energy costs 2.5 cents per kilowatt-hour, calculate the maximum number of calories of heat energy passing from the room into the interior of the refrigerator per hour.

4. The heat of fusion of water ice at 0°C is 1436.3 cal/mole. If the surroundings are at a temperature of 25°C, and electrical power costs 2 cents per kilowatt-hour, calculate the minimum cost of energy for making 1 ton of ice with a suitable thermodynamic engine.

13

Entropy of Substances in Relation to Temperature, Volume, Pressure, and Physical State

1. Relation involving the five fundamental thermodynamic properties of a substance. If any substance is subjected to a reversible process in which only heat energy and PV work energy are involved, then, according to the first law,

$$\mathrm{d}E = \delta q + \delta w, \tag{1}$$

or, since

$$\delta w = -P\,\mathrm{d}V, \tag{2}$$

$$\mathrm{d}E = \delta q - P\,\mathrm{d}V. \tag{3}$$

But, according to the second law,

$$\delta q = T\,\mathrm{d}S. \tag{4}$$

Combination of Equations 3 and 4 yields

$$\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V. \tag{5}$$

Equation 5 is an important relation describing how the five fundamental thermodynamic properties of a given substance are related as that substance is subjected to reversible changes in which are involved only heat energy and the PV work energy arising from the reversible changes in pressure and volume.

2. Variation of entropy with temperature. If a given substance absorbs a small amount of heat energy, δq, in a reversible process with no other energy involved except PV work energy, there will occur, in general, corresponding changes in the five fundamental thermodynamic properties as $\mathrm{d}P$, $\mathrm{d}V$, $\mathrm{d}T$, $\mathrm{d}E$, and $\mathrm{d}S$. But we have defined the increase in entropy to be

$$\mathrm{d}S = \frac{\delta q}{T}, \tag{6}$$

and the heat capacity to be

$$C = \frac{\delta q}{\mathrm{d}T}. \tag{7}$$

Therefore, combination of Equations 6 and 7 yields the relation

$$T\,\mathrm{d}S = C\,\mathrm{d}T, \tag{8}$$

or

$$\mathrm{d}S = \frac{C}{T}\,\mathrm{d}T = C\mathrm{d}\ln T. \tag{9}$$

If the pressure is constant, the heat capacity is that at constant pressure, C_P, and we can write, for constant pressure,

$$\mathrm{d}S = \frac{C_P}{T}\,\mathrm{d}T = C_P\mathrm{d}\ln T; \qquad P \text{ constant}, \tag{10}$$

or, in general,

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}. \tag{11}$$

Similarly, if the process occurs at constant volume, we can write the corresponding equation,

$$\mathrm{d}S = \frac{C_V}{T}\,\mathrm{d}T = C_V\mathrm{d}\ln T; \qquad V \text{ constant}, \tag{12}$$

or, in general,

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}. \tag{13}$$

The foregoing equations can be appropriately integrated to give the increase in entropy of a substance in a given physical state from one temperature to another when the values of the heat capacity are known as a function of temperature. For example, Equation 10 may be integrated as follows:

$$\int_A^B \mathrm{d}S = S_B - S_A = \int_{T_A}^{T_B} \frac{C_P}{T}\,\mathrm{d}T = \int_{T_A}^{T_B} C_P\mathrm{d}\ln T. \tag{14}$$

That is to say, on a plot of C_P/T against T, or a plot of C_P against $\ln T$, the area under the curve from T_A to T_B gives the increase in entropy from the temperature T_A to the temperature T_B.

Since

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P, \tag{15}$$

Equation 11 may be written as

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{1}{T}\right)\left(\frac{\partial H}{\partial T}\right)_P. \tag{16}$$

Differentiating both sides with pressure at constant temperature, we have

$$\frac{\partial^2 S}{\partial T\,\partial P} = \left(\frac{1}{T}\right)\left(\frac{\partial^2 H}{\partial T\,\partial P}\right) = \left(\frac{1}{T}\right)\left(\frac{\partial C_P}{\partial P}\right)_T, \tag{17}$$

or

$$\frac{\partial^2 H}{\partial T\,\partial P} = T\frac{\partial^2 S}{\partial T\,\partial P}. \tag{18}$$

Similarly, we can derive the relation

$$\frac{\partial^2 S}{\partial T\,\partial V} = \left(\frac{1}{T}\right)\left(\frac{\partial^2 E}{\partial T\,\partial V}\right) = \left(\frac{1}{T}\right)\left(\frac{\partial C_V}{\partial V}\right)_T, \tag{19}$$

or

$$\frac{\partial^2 E}{\partial T\,\partial V} = T\frac{\partial^2 S}{\partial T\,\partial V}. \tag{20}$$

3. Variation of entropy with volume. For a substance subjected to a reversible process at constant temperature, with only heat energy and *PV* work energy involved, Equation 5 may be written as

$$(\mathrm{d}E)_T = T(\mathrm{d}S)_T - P(\mathrm{d}V)_T. \tag{21}$$

Dividing by $(\mathrm{d}V)_T$, we obtain the relation

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P. \tag{22}$$

Differentiating with temperature at constant volume, we obtain

$$\frac{\partial^2 E}{\partial V\,\partial T} = T\frac{\partial^2 S}{\partial V\,\partial T} + \left(\frac{\partial S}{\partial V}\right)_T - \left(\frac{\partial P}{\partial T}\right)_V. \tag{23}$$

But, from Eq~~uation 20, we note that the term on~~ the left side is equal to the first term on the right side, so that we have

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V. \tag{24}$$

Equation 24 gives the change of entropy with volume at constant temperature in terms of the change of pressure with temperature at constant volume. For example, we can write

$$\mathrm{d}S = \left(\frac{\partial P}{\partial T}\right)_V \mathrm{d}V; \qquad T \text{ constant.} \tag{25}$$

For an ideal gas,

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_V = \frac{R}{V}, \tag{26}$$

so that

$$\mathrm{d}S = \frac{R}{V}\mathrm{d}V = R\mathrm{d}\ln V; \qquad T \text{ constant.} \tag{27}$$

For a change of volume from V_A to V_B at a temperature T, the change in entropy for an ideal gas would be

$$S_B - S_A = R\ln\frac{V_B}{V_A}. \tag{28}$$

In general,

$$S_B - S_A = \int_{V_A}^{V_B}\left(\frac{\partial P}{\partial T}\right)_V \mathrm{d}V; \qquad T \text{ constant.} \tag{29}$$

Equation 29 shows that for any substance at constant temperature, its change of entropy from one volume to another can be evaluated from a knowledge of its change of pressure with temperature at constant volume in the given range of volume.

4. Variation of entropy with pressure. From the definition

$$H = E + PV, \tag{30}$$

we can write

$$\mathrm{d}H = \mathrm{d}E + P\,\mathrm{d}V + V\,\mathrm{d}P. \tag{31}$$

Combination of Equations 5 and 31 yields

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}P. \tag{32}$$

For a substance subjected to a reversible process at constant temperature, with only heat energy and PV work energy involved, Equation 32 may be written as

$$(\mathrm{d}H)_T = T(\mathrm{d}S)_T + V(\mathrm{d}P)_T. \tag{33}$$

Dividing by $(\mathrm{d}P)_T$, we obtain the relation

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V. \tag{34}$$

Differentiating with temperature at constant pressure, we obtain

$$\frac{\partial^2 H}{\partial P\,\partial T} = T\frac{\partial^2 S}{\partial P\,\partial T} + \left(\frac{\partial S}{\partial P}\right)_T + \left(\frac{\partial V}{\partial T}\right)_P. \tag{35}$$

But from Equation 18, we note that the term on the left side is equal to the first term on the right side, so that

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P. \tag{36}$$

Equation 36 gives the change of entropy with pressure at constant temperature in terms of the negative of the change of volume with temperature at constant pressure. We can write

$$\mathrm{d}S = -\left(\frac{\partial V}{\partial T}\right)_P \mathrm{d}P; \qquad T \text{ constant}, \tag{37}$$

and, for the change in entropy of any substance at constant temperature from a pressure P_A to a pressure P_B,

$$S_B - S_A = -\int_{P_A}^{P_B} \left(\frac{\partial V}{\partial T}\right)_P \mathrm{d}P. \tag{38}$$

For a change of pressure from P_A to P_B at a temperature T, the change in entropy for an ideal gas would be

$$S_B - S_A = -R \ln \frac{P_B}{P_A}. \tag{39}$$

Equation 38 shows that for any substance at constant temperature its change of entropy from one pressure to another can be evaluated from a knowledge of its change of volume with temperature at constant pressure in the given range of pressure.

5. Change in entropy with change in phase. At some given temperature and pressure, a substance can change from one phase to another with the absorption or liberation of heat energy.

Examples of such changes in phase that involve absorption of heat energy, with a corresponding increase in the energy content of the phase that is formed, are (see Figure 1 in Chapter 10) the transition from crystalline form II to crystalline form I, melting of crystalline form I to the liquid state, vaporization of the liquid to the gaseous state, and sublimation of a solid to the gaseous state. In each case, at the given temperature and pressure, the reverse process occurs with liberation of energy by the substance.

At the given equilibrium temperature and pressure, we can write for the change in phase, in general terms,

$$\text{MX (phase } A) = \text{MX (phase } B). \tag{40}$$

Since this is a reversible process, with the change from one phase to another taking place on the absorption or liberation of heat energy, we may write from the second law,

$$\mathrm{d}S = \frac{\delta q}{T}. \tag{41}$$

But, from Equation 8 of Chapter 8, we have found that for a process taking place at constant pressure,

$$\delta q = \mathrm{d}H. \tag{42}$$

Therefore, Equation 41 becomes

$$\mathrm{d}S = \frac{\mathrm{d}H}{T}, \tag{43}$$

and, since the temperature is constant,

$$S_B - S_A = \frac{H_B - H_A}{T}, \tag{44}$$

or

$$\Delta S = \frac{\Delta H}{T}. \tag{45}$$

For the several kinds of changes in phase, Equation 45 would be written as follows:

$$\Delta S\text{ (transition)} = \frac{\Delta H\text{ (transition)}}{T}; \tag{46}$$

$$\Delta S\text{ (melting)} = \frac{\Delta H\text{ (melting)}}{T}; \tag{47}$$

$$\Delta S \text{ (vaporization)} = \frac{\Delta H \text{ (vaporization)}}{T}; \tag{48}$$

$$\Delta S \text{ (sublimation)} = \frac{\Delta H \text{ (sublimation)}}{T}. \tag{49}$$

It should be noted that the foregoing equations are applicable only for the temperature and pressure at which the two given phases are in equilibrium. For example, for the equilibrium process,

$$H_2O \text{ (liq, 0°C, 1 atm)} = H_2O \text{ (c, 0°C, 1 atm)}, \tag{50}$$

the change in entropy is

$$\Delta S \text{ (crystallization at 0°C)} = \frac{\Delta H \text{ (crystallization at 0°C)}}{273.16}. \tag{51}$$

But, for the non-equilibrium process,

$$H_2O \text{ (liq, }-10\text{°C, 1 atm)} = H_2O \text{ (c, }-10\text{°C, 1 atm)}, \tag{52}$$

the change in entropy is

$$\Delta S \text{ (crystallization at }-10\text{°C)} = \int_{263.16}^{273.16} C_P\,[H_2O\text{ (liq)}]\,d\ln T + \frac{\Delta H \text{ (crystallization at 0°C)}}{273.16} + \int_{273.16}^{263.16} C_P\,[H_2O\text{ (c)}]\,d\ln T. \tag{53}$$

Equation 53 may also be written as

$$\Delta S \text{ (crystallization at }-10\text{°C)} = \frac{\Delta H \text{ (crystallization at 0°C)}}{273.16} - \int_{263.16}^{273.16} \{C_P[H_2O\text{ (c)}] - C_P[H_2O\text{ (liq)}]\}\,d\ln T. \tag{54}$$

The three terms on the right side of Equation 53 represent the integral of $\delta q/T$ along the reversible path from liquid water at -10°C to solid water at -10°C. The first term takes the liquid water from −10° to 0°C; the second term applies to the crystallization, at 0°C, of liquid water to solid water ice, and the third term takes the solid water ice from 0°C to −10°C.

Considering the same substance as in Figure 1 of Chapter 10, the increase in entropy of the substance from crystalline form II at the absolute zero to the gaseous state at some temperature T would be equal to

$$\begin{aligned} S\ (\mathrm{g}) = S_0\ (\mathrm{c, II}) &+ \int_0^{Ttr} C_P\ (\mathrm{c, II})\ d \ln T \\ &+ \frac{\Delta Htr}{Ttr} + \int_{Ttr}^{Tm} C_P\ (\mathrm{c, I})\ d \ln T \\ &+ \frac{\Delta Hm}{Tm} + \int_{Tm}^{Tv} C_P\ (\mathrm{liq})\ d \ln T \\ &+ \frac{\Delta Hv}{Tv} + \int_{Tv}^{T} C_P\ (\mathrm{g})\ d \ln T. \qquad (55) \end{aligned}$$

In Equation 55, the first term on the right is the entropy of crystalline form II at 0°K.

6. Entropy of mixing ideal gases. Given $n_1, n_2, n_3, \cdots, n_i$ moles of different ideal gases, each at the same pressure, P, and temperature, T, and having volumes $V_1, V_2, V_3, \cdots, V_i$, respectively. Suppose that these gases are in adjoining compartments in a large box, with the partitions between the compartments occupying an insignificant volume. It is desired to evaluate the change in entropy occurring when the partitions are removed and the several gases are permitted to mix, all at constant temperature, and with the pressure remaining unchanged. After mixing, the total volume is the sum of the volumes of the separate gases before mixing, and the mole fraction, N_i, of each gas in the mixture, is equal to its original volume divided by the total volume. That is,

$$\mathrm{N}_i = \frac{n_i}{\sum n_i} = \frac{V_i}{\sum V_i}. \qquad (56)$$

On mixing, each gas passes from its original volume, V_i, to the common final volume, $\sum V_i$. The increase in entropy for this change in volume for each gas is independent of the presence of the other ideal gases, and the total change in entropy is obtained by adding together the increases in entropy for each of the gases. If the total amount of all the gases is taken as one mole, then the number of moles of each gas is equal to its mole fraction:

$$n_i = \mathrm{N}_i. \tag{57}$$

The increase in entropy, ΔS_i, for each gas on passing from its original volume to the final volume is given by Equation 28, multiplied by the number of moles of the given gas:

$$\Delta S_i = \mathrm{N}_i R \ln \frac{\sum V_i}{V_i}. \tag{58}$$

Substituting, from Equation 56, the mole fraction of the given component for the ratio of the initial volume to its final volume, Equation 58 becomes

$$\Delta S_i = \mathrm{N}_i R \ln \frac{1}{\mathrm{N}_i} = -R\, \mathrm{N}_i \ln \mathrm{N}_i. \tag{59}$$

The sum of the increases in entropy for all the gases involved is, per mole of the mixture,

$$\Delta S_{\text{mixing}} = \sum \Delta S_i = -R \sum \mathrm{N}_i \ln \mathrm{N}_i. \tag{60}$$

Equation 60 gives the entropy of mixing ideal gases when the pressures of the different gases before mixing are identical and the same as the final pressure after mixing. In such case, it follows that the final volume of the mixture is the sum of the original volumes of the separate gases. Equation 60 also shows that for ideal gases the entropy of a given kind of gas occupying a given volume is independent of what other gases occupy the identical space.

To calculate the entropy of mixing ideal gases which are originally at different pressures to form a mixture in which the final pressure is also different, a simple procedure is to evaluate the change in entropy for bringing each of the different gases to a common pressure, according to Equation 39; to evaluate the entropy of mixing the gases at this common pressure, according to Equation 60; and to evaluate the change in entropy on bringing the final mixture from this common pressure to the specified final pressure, according to Equation 39. The sum of all these changes in entropy will give the total entropy of mixing for the specified case.

PROBLEMS

1. For a given substance in the solid state, over the range 300° to 1000°K, $C_P = 5.74 + 0.00062T - 100{,}000/T^2$ cal/deg mole. Calculate the value of $S_{800} - S_{400}$ for this solid substance.

2. For MX (c), the expansion with temperature at 25°C, at various pressures, is given by the equation

$$\left(\frac{\partial V}{\partial T}\right)_P = a + bP + cP^2.$$

Calculate, in terms of the constants a, b, and c, the change in entropy of MX (c) as it is compressed at 25°C from 1 atm to 100 atm.

3. The boiling point of MX under a pressure of 1 atm is 50°C. The heat of vaporization of MX at 50°C is $\Delta H = 8500$ cal/mole. Assuming the gas to be ideal, calculate the change in entropy for the following process:

$$\text{MX (liq, 50°C, 1 atm)} = \text{MX (g, 50°C, 0.1 atm)}.$$

4. For water, at a pressure of 1 atm, the heat of fusion at 0°C is $\Delta H = 1436.3$ cal/mole, the heat of vaporization at 100°C is $\Delta H = 9717.1$ cal/mole, and the mean heat capacity of the liquid from 0°C to 100°C is 18.046 cal/deg mole. Calculate the value of $S_{373.16}$ [H_2O (g, 1 atm)] $- S_{273.16}$ [H_2O (c, 1 atm)].

5. Calculate the entropy of mixing five different ideal gases, each at 1 atm and 25°C, to form a mixture, at the same pressure and temperature, containing 0.10 mole of gas A, 0.20 mole of gas B, 0.30 mole of gas C, 0.25 mole of gas D, and 0.15 mole of gas E. How would the result be affected if the pressure were 10 atm? If the temperature were 1000°K?

6. Given 0.5 mole each of two different ideal gases, each at the same pressure and temperature, and being contained in two identical rectangular boxes with two sides adjacent. Suppose that the two adjacent sides are made permeable and the two boxes are pushed together to coincide. The resulting mixture of gases will now occupy the same volume as each of the gases before mixing, and the pressure of the mixture will be double the initial pressure. Calculate the change of entropy for this process of mixing.

14

Energy of Substances in Relation to Pressure and Volume

1. Variation of energy with volume. Combination of Equations 22 and 24 of Chapter 13 yields the following equation:

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P. \tag{1}$$

Equation 1 permits us to calculate for any substance its change of energy with volume at constant temperature from a knowledge of the temperature, pressure, and the change of pressure with temperature at constant volume. In other words, if the P-V-T relations for any substance (solid, liquid, or gas) are known, the change of energy with volume at constant temperature may be calculated.

2. Variation of heat content with pressure. Combination of Equations 34 and 36 of Chapter 13 yields the following equation:

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V. \tag{2}$$

Equation 2 makes it possible to calculate the change of heat content (enthalpy) with pressure at constant temperature of any given substance from a knowledge of the temperature, volume, and the change of volume with temperature at constant pressure. The change of heat content with pressure at constant temperature may be calculated for any substance (solid, liquid, or gas) for which the P-V-T relations are known.

3. Variation of energy with pressure. From the definition of the heat content, we may write

$$E = H - PV. \tag{3}$$

Differentiating with pressure at constant temperature, we obtain

$$\left(\frac{\partial E}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T - V. \tag{4}$$

Combination of Equations 2 and 4 yields

$$\left(\frac{\partial E}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T. \tag{5}$$

Equation 5 permits the calculation of the change of energy with pressure at constant temperature for any substance for which the P-V-T relations are known or for which specifically are known the values of the expansion with temperature and the compression with pressure.

4. Energy and heat content of gases as a function of volume or pressure. The foregoing Equations 1, 2, and 5 on the change of energy and heat content with volume or pressure are applicable to any substance in any physical state. In general, however, the change in energy with pressure for a condensed substance, liquid or solid, is not large because the values of expansion with temperature and compression with pressure are not large and, further, are of opposite sign and largely tend to cancel.

With regard to gases, we have seen that for the ideal gas, by definition, the energy is independent of the volume or pressure at constant temperature. For real gases, however, there is a measurable change of energy with pressure or volume, and several methods of measurement have been developed and used to obtain data on the change of energy or heat content with volume or pressure. The following sections describe some of these methods of measurement and the properties determined by them.

5. Joule experiment. In 1845, Joule (*1*) described the results of the following experiment: Two large spheres, connected by a valve, were placed in a water bath the temperature of which was measured with a thermometer. One sphere was filled with a gas at a given pressure, and the other sphere was evacuated. When equilibrium with temperature was established, the thermometer was read. Then the valve was opened and the gas permitted to flow into the second sphere until the pressure was equalized. The thermometer was again read. Joule found that there was no observable change in temperature. He concluded, therefore, that, within the limits of precision of his measurements, the value of $(\Delta E/\Delta V)_T$ was zero. We know now, however, that Joule's experiment was not sensitive enough to measure the small change in energy involved in such an experiment.

6. Adiabatic Joule-Thomson experiment. In 1853, Joule and Thomson (*2*) reported the results of a different and much more sensitive kind of measurement designed to disclose the change of energy or heat content of a gas with change in pressure. In this experiment, which is shown schematically in Figure 1, a gas is made to flow continuously through a tube containing a porous plug. At state A, in Figure 1, one mole of the continuously flowing gas is outlined momentarily on the inlet side of the porous plug, and at state B the same mole of gas is outlined at an appropriate later time on the exit side of the porous plug. The drop in pressure due to the flow of gas in the open tube is negligible, for the given rate of flow, compared to the drop in pressure caused by the flow of the gas through the porous plug. The entire tube is completely isolated thermally from the surroundings, so that no heat enters or leaves the gas through the walls of the tube. The process is, therefore, an adiabatic one.

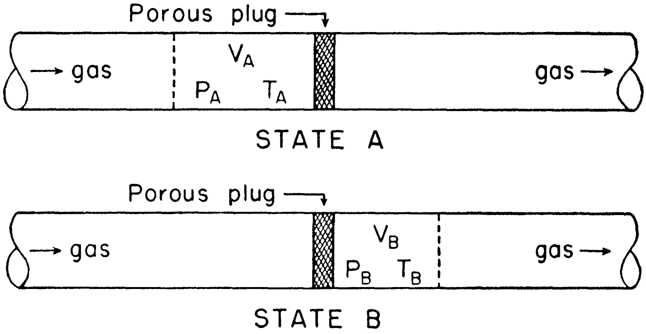


FIGURE 1. Schematic diagram of the adiabatic Joule-Thomson experiment.

In state A, one mole of gas has a pressure, P_A, volume, V_A, and temperature, T_A, and in state B, the corresponding values P_B, V_B, and T_B. The process may be looked upon as transferring one mole of gas from state A to state B. As the gas enters the porous plug from the inlet side, it is being acted upon by the gas behind it at a pressure P_A through the volume V_A. As the gas leaves the porous plug on the exit side, it is acting upon the gas ahead of it at a pressure P_B through the volume V_B. The system is taken as the one mole of the gas. Then, according to the first law,

$$E_B - E_A = \Delta E = q + w + u. \tag{6}$$

Since the process is adiabatic, and no work other than PV work is involved,

$$q = 0, \tag{7}$$

and

$$u = 0. \tag{8}$$

The net PV work energy absorbed by the system is equal to

$$w = P_A V_A - P_B V_B. \tag{9}$$

Hence

$$E_B - E_A = P_A V_A - P_B V_B = -(P_B V_B - P_A V_A), \tag{10}$$

or

$$(E_B + P_B V_B) - (E_A + P_A V_A) = 0, \tag{11}$$

or

$$H_B - H_A = 0, \tag{12}$$

or

$$\Delta H = 0. \tag{13}$$

The given process is therefore one that occurs with no change in heat content or that occurs at constant H.

In the experiment, the quantities that are measured are the initial or the final pressure, the change in pressure, $\Delta P = P_B - P_A$, and the change in temperature, $\Delta T = T_B - T_A$. The property measured, therefore, may be written as $(\Delta T/\Delta P)_H$, for given values of pressure. Since ΔP may be made small, with corresponding small values of ΔT, the property measured can be made not to differ significantly from $(\partial T/\partial P)_H$. This latter is called the Joule-Thomson coefficient and is usually labeled with the Greek letter μ, so that we may write

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H. \tag{14}$$

If the measured values of ΔP and ΔT are large, they may be treated analytically or graphically to obtain the values of the differential coefficient, $(\partial T/\partial P)_H$, for given values of pressure.

The relation of the Joule-Thomson coefficient to the change in heat content with pressure at constant temperature can be derived as follows:

Given

$$H = f(P,T). \tag{15}$$

Therefore,

$$\mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial H}{\partial P}\right)_T \mathrm{d}P. \tag{16}$$

At constant H,

$$\mathrm{d}H = 0; \tag{17}$$

so that

$$0 = \left(\frac{\partial H}{\partial T}\right)_P (\mathrm{d}T)_H + \left(\frac{\partial H}{\partial P}\right)_T (\mathrm{d}P)_H, \tag{18}$$

or

$$0 = \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H + \left(\frac{\partial H}{\partial P}\right)_T, \tag{19}$$

or

$$\left(\frac{\partial H}{\partial P}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H. \tag{20}$$

Therefore

$$\left(\frac{\partial H}{\partial P}\right)_T = -C_P\,\mu. \tag{21}$$

Equation 21 permits the calculation of the change of heat content with pressure at constant temperature from values of the heat capacity, C_P, and the Joule-Thomson coefficient, μ.

7. Isothermal Joule-Thomson experiment. The Joule-Thomson experiment is one in which the heat content is constant and changes occur in the pressure and temperature. In 1903, Buckingham (*3*) suggested, and later Keyes and Collins (*4*) and Eucken, Clusius, and Berger (*5*) independently carried out, the porous-plug experiment in a new way, by adding heat energy to the gas on the exit side of the porous plug to maintain the temperature of the gas the same before and after the change in pressure.

Figure 2 gives a schematic diagram of the experiment, which involves a gas flowing continuously through the porous plug. At state A, in Figure 2, one mole of the continuously flowing gas is outlined momentarily on the inlet side of the porous plug, and at state B the same mole of gas is outlined at an appropriate later time on the exit side of the porous plug. As in the Joule-Thomson experiment, the drop in pressure due to the flow of gas in the tube is negligible, for the given rate of flow, compared to the drop in pressure caused by the flow of gas through the porous plug. The quantities measured in this experiment are the following: the pressure on one side of the porous plug, the drop in pressure through the porous plug or the difference in pressure between the two sides of the porous plug, the amount of gas flowing in unit time, and the electrical power input.

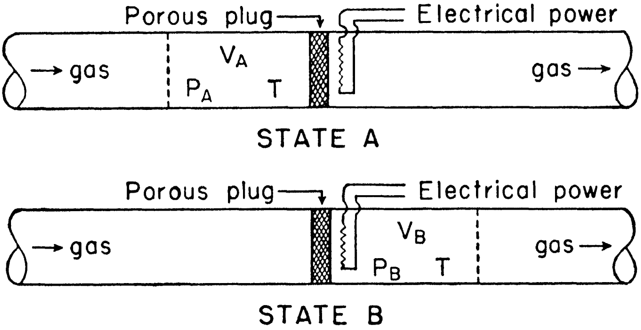


FIGURE 2. Schematic diagram of the isothermal Joule-Thomson experiment.

Applying the first law to the process occurring between the states A and B, we can write:

$$\Delta E = E_B - E_A = q + w + u. \tag{22}$$

But

$$u = 0, \tag{23}$$

$$W = -(P_B V_B - P_A V_A), \tag{24}$$

and q is measured electrically.

Hence

$$q = E_B - E_A + P_B V_B - P_A V_A = H_B - H_A = \Delta H. \tag{25}$$

The property measured in this experiment may therefore be written as $(\Delta H/\Delta P)_T$ or, if the change in pressure is sufficiently small compared with the variation of heat content with pressure, as $(\partial H/\partial P)_T$.

If the measured differences in pressure, ΔP, are large, the experimental values of ΔH and ΔP may be related analytically, or plotted graphically, in such a way as to permit evaluation of the values of $(\partial H/\partial P)_T$ by appropriate differentiation.

8. Washburn experiment. In the Washburn (*6*) experiment, a known quantity of gas is contained at a known pressure in a suitable vessel in a calorimeter and permitted to expand against the pressure of the atmosphere, at constant temperature.

Figure 3 gives a schematic diagram of the experiment, showing at state A the gas before expansion and at state B the gas after expansion to the pressure of the atmosphere. In this experiment, the quantities measured are the following: the mass, m, the pressure, P_A, and the volume, V_A, of the gas in the vessel at the beginning of the experiment; the quantity of electrical energy required to be added to the system to maintain the temperature constant; and the pressure of the atmosphere, P_B. In the expansion of the gas from the initial pressure, P_A, to the final pressure, P_B, work is performed by the gas on the surroundings in an amount equal to the constant pressure of the atmosphere, P_B, multiplied by the change in volume, $V_B - V_A$. In the actual experiment, it is not practical to contain all the gas in the calorimeter at its final volume, but the same result is obtained by letting the gas escape from the calorimeter, at the constant temperature, through a long length of coiled tubing immersed in the water of the calorimeter. It is also necessary to see that the gas issuing from the calorimeter possesses no significant amount of directed kinetic energy or to take account of it if significant.

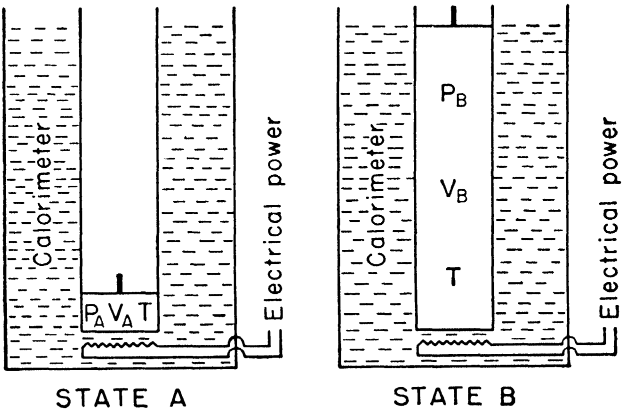


FIGURE 3. Schematic diagram of the Washburn experiment.

The opening at the exit end of the tubing may be made large so that the issuing gas has a small velocity.

In the Washburn experiment, the temperature is constant, the electrical energy is absorbed by the system as heat energy, and the system performs some PV work on the surroundings. According to the first law, the change in energy of the gas from the initial pressure, P_A, to the final pressure, P_B, is equal to

$$E_B - E_A = \Delta E = q + w, \tag{26}$$

where q is the heat produced by the measured electrical energy, and w is the negative of the work done by the gas in "pushing back" the atmosphere, or $-P_B(V_B - V_A)$.

Hence

$$E_B - E_A = q - P_B(V_B - V_A), \tag{27}$$

or

$$E_B - E_A = q + P_B V_A - P_B V_B. \tag{28}$$

In Equation 28, the first and second terms on the right are evaluated from the directly measured quantities. Since the final volume, V_B, is not measured, the last term on the right side is evaluated from the value of the PV product for the given gas at the given temperature and the atmospheric pressure. For the gases which are likely to be subjected to measurements in the Washburn experiment, there will be known the value of the compressibility factor, $z = PV/RT$, at the given temperature and atmospheric pressure.

At this pressure, the compressibility factor will be nearly unity, so that the value of $P_B V_B$ will be nearly equal to RT. In any case,

$$P_B V_B = z_B RT, \tag{29}$$

so that Equation 28 may be written as

$$E_B - E_A = q + P_B V_A - z_B RT, \tag{30}$$

and the value of each of the terms on the right side is known. Measurements are made for different values of the initial pressure, P_A, and there results a series of values of $E_B - E_A$ for different values of $P_A - P_B$, where P_B is near 1 atmosphere and P_A covers the range of values of the initial pressure. Suitable analytical or graphical treatment of the data will yield values of the coefficient

$(\Delta E/\Delta P)T$, or, in the limit, $(\partial E/\partial P)_T$. The Washburn experiment, therefore, evaluates the change of energy of the gas with pressure at constant temperature.

9. Collateral reading. For additional information regarding the energy of substances as a function of pressure and volume, the reader is referred to the following: On the Joule-Thomson effect, Roebuck (*7*), Johnston (*8*), Pattee and Brown (*9*), Sage, Kennedy, and Lacey (*10*); on the Washburn experiment, Rossini and Frandsen (*11*).

REFERENCES

1. J. P. Joule, *Phil. Mag.* **26**, 369 (1845).
2. J. P. Joule and W. Thomson, *Proc. Roy. Soc.* (*London*) **143**, 357 (1853).
3. E. Buckingham, *Phil. Mag.* **6**, 518 (1903).
4. F. G. Keyes and S. C. Collins, *Proc. Natl. Acad. Sci. U.S.* **18**, 328 (1932).
5. A. Eucken, K. Clusius, and W. Berger, *Z. tech. Physik* **13**, 267 (1932).
6. E. W. Washburn, *J. Research Natl. Bur. Standards* **9**, 521 (1932).
7. J. R. Roebuck, *Proc. Am. Acad. Art. Sci.* **60**, 537 (1925); **64**, 287 (1930).
8. H. L. Johnston, *J. Am. Chem. Soc.* **68**, 2362 (1946).
9. E. C. Pattee and G. G. Brown, *Ind. Eng. Chem.* **26**, 511 (1934).
10. B. H. Sage, E. R. Kennedy, and W. N. Lacey, *Ind. Eng. Chem.* **28**, 601 (1936).
11. F. D. Rossini and M. Frandsen, *J. Research Natl. Bur. Standards* **9**, 733 (1932).

PROBLEMS

1. For a given gas: $C_P = 10.34 + 0.00274T - 195{,}500/T^2$ cal/deg mole; $V = RT/P + (9/128)(RT_c/P_c)\,[1 - 6(T_c/T)^2]$, with V in liters per mole, P in atmospheres, $T_c = 304.2°\text{K}$, and $P_c = 72.9$ atm. Calculate the following at 25°C and 1 atm: (*a*) $(\partial H/\partial P)_T$; (*b*) $(\partial E/\partial P)_T$; (*c*) $(\partial T/\partial P)_H$.

2. In a Washburn experiment at 25°C, 1 mole of gaseous oxygen is contained in a 1-liter vessel in a calorimeter at a pressure of 40.0 atm. The gas is permitted to expand isothermally against the prevailing atmosphere, the pressure of which is 750 mm Hg, and 640.0 cal of heat energy are added, electrically, to maintain the temperature of the calorimeter constant. For oxygen at 25°C and near 1 atm, the compressibility factor is $z = 0.9995$. Calculate the value of $E^{P=1} - E^{P=40}$ for oxygen from this experiment. Assuming that the change of energy with pressure is constant, what is the value of $(\partial E/\partial P)_T$ for oxygen over this range of pressure at 25°C?

3. In an adiabatic Joule-Thomson experiment on a given gas at a mean temperature of 25°C, it is found that the ratio of $\Delta T/\Delta P$ is -0.20°C/atm. If the heat capacity of the gas over the given range of temperature is 7.0 cal/deg mole, calculate the value of $(\partial H/\partial P)_T$ for the gas. If this Joule-Thomson experiment were performed isothermally, how much electrical energy would need to be added on the low-pressure side of the porous plug for each mole of gas flowing?

4. For a given substance at 25°C and 1 atm, the molal volume is 90 cm^3, the value of $(1/V)(\partial V/\partial P)_T$ is -0.000100/atm, and the value of $(1/V)(\partial V/\partial T)_P$ is 0.00100/deg. Calculate the change of energy with pressure for this substance at 25°C and 1 atm.

5. For water at 25°C, at a pressure, P, from 0 to 1000 atm: $V = 18.066 - 0.000715P + 0.000000046P^2$ cm^3/mole; $(\partial V/\partial T)_P = 0.0045 + 0.0000014P$ cm^3/deg mole. Calculate (*a*) the work necessary to compress isothermally at 25°C 1 mole of liquid water from 1 to 1000 atm; and (*b*) the change in energy of liquid water from 1 to 1000 atm, $E^{P=1000} - E^{P=1}$, at 25°C.

6. For a given gas at 0°C, $PV = RT(1 - 0.0010P + 0.000002P^2)$. Calculate the difference between $(\partial H/\partial P)_T$ and $(\partial E/\partial P)_T$ for this gas at 0°C and 10 atm.

15

Heat Capacity of Substances

1. Heat capacity in relation to temperature and physical state. A schematic diagram representing the heat capacity of a substance as a function of the temperature and the physical state is given in Figure 1, the example being, as in Figure 1 of Chapter 10, a substance having two stable crystalline forms. On this plot, the ordinate at any given temperature is, on a proper scale at the given temperature, the slope of the corresponding curve in Figure 1 of Chapter 10. At the temperatures of transition, melting, and vaporization, the heat capacity is infinite in value, and at these temperatures the curves of heat capacity are discontinuous.

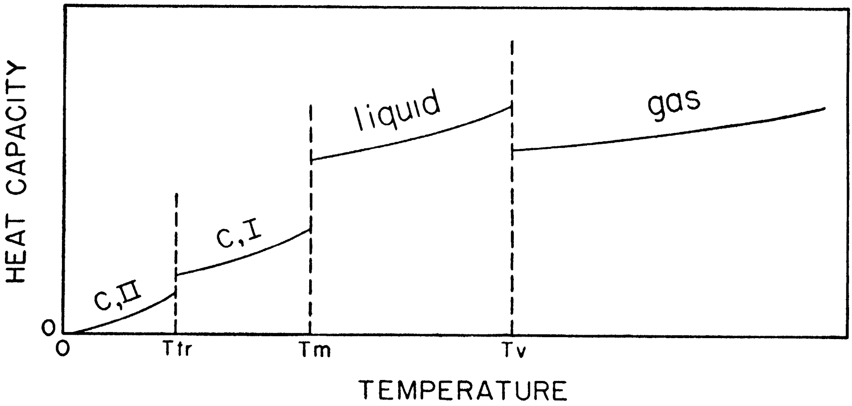


FIGURE 1. Schematic diagram of the heat capacity of a substance as a function of the temperature.

The scale of ordinates represents the heat capacity, while the scale of abscissas gives the absolute temperature. The notations c,I and c,II represent crystalline forms I and II, respectively. *Ttr*, *Tm*, and *Tv* represent the temperatures of transition, melting, and vaporization, respectively.

It should also be noted that in Figure 1 the area under the curve of the heat capacity of crystalline form II from the absolute zero up to any given temperature below the transition temperature is equal to the value of the ordinate of the corresponding curve in Figure 1 of Chapter 10 for the energy or heat content at the given temperature. In Figure 1, the area under the curve of the heat capacity of crystalline form I, from the transition temperature to the melting temperature, is equal to the increase in energy or heat content of crystalline form I from the transition temperature to the melting temperature, as given by the ordinates in Figure 1 of Chapter 10. Similarly, in Figure 1 the area under the curve of the heat capacity of the liquid, from the melting temperature to the vaporization temperature, is equal to the increase in energy or heat content of the liquid from the melting temperature to the vaporization temperature, as given by the ordinates in Figure 1 of Chapter 10.

2. Equations for heat capacity and heat content as a function of temperature. It has been largely a matter of experimental convenience that data on the change of energy or heat content with temperature have been obtained mostly in the form of heat capacity at various temperatures rather than as energy or heat content at various temperatures. The values of heat capacity are then expressed analytically or graphically as a function of the temperature, and the values of the energy or heat content as a function of the temperature are obtained from the equations by analytical integration or from the plots by graphical integration. The heat capacity of a substance in a given physical state may be expressed analytically as a function of temperature over a specified range of temperature, as (*1*, *2*)

$$C_P = a + bT + cT^2 + \cdots, \tag{1}$$

or in the form (*3*)

$$C_P = a + bT + \frac{e}{T^2}. \tag{2}$$

It is important to note that all such equations must be labeled as to the physical state and the range of temperature for which they are applicable.

In order to obtain the heat content explicitly as a function of temperature, the foregoing equations may be integrated. From Chapter 8, the heat capacity at constant pressure is related as follows to the heat content:

$$dH = C_P\, dT. \tag{3}$$

Then, if the range of applicability is from T_A to T_B, one obtains by integration

$$H_B - H_A = \int_{T_A}^{T_B} C_P\, dT, \tag{4}$$

or, for any temperature T in the range T_A to T_B,

$$H - H_A = \int_{T_A}^{T} C_P\, dT. \tag{5}$$

With the heat capacity given in the form of Equation 1, Equation 5 becomes

$$\begin{aligned} H - H_A &= \int_{T_A}^{T} (a + bT + cT^2 + \cdots)\, dT = \\ &(aT + \tfrac{1}{2}bT^2 + \tfrac{1}{3}cT^3 + \cdots) - (aT_A + \tfrac{1}{2}bT_A{}^2 + \tfrac{1}{3}cT_A{}^3 + \cdots) \end{aligned} \tag{6}$$

or, for some temperature T in the given range of applicability,

$$H - H_A = (\text{constant}) + aT + \tfrac{1}{2}bT^2 + \tfrac{1}{3}cT^3 + \cdots \tag{7}$$

where

$$(\text{constant}) = -(aT_A + \tfrac{1}{2}bT_A{}^2 + \tfrac{1}{3}cT_A{}^3 + \cdots). \tag{8}$$

With the heat capacity given in the form of Equation 2, the corresponding equations are

$$\begin{aligned} H - H_A &= \int_{T_A}^{T} \left(a + bT + \frac{e}{T^2}\right) dT = \\ &\left(aT + \tfrac{1}{2}bT^2 - \frac{e}{T}\right) - \left(aT_A + \tfrac{1}{2}bT_A{}^2 - \frac{e}{T_A}\right), \end{aligned} \tag{9}$$

or, for the given range of applicability,

$$H - H_A = (\text{constant}) + aT + \tfrac{1}{2}bT^2 - \frac{e}{T}, \tag{10}$$

where

$$(\text{constant}) = -\left(aT_A + \tfrac{1}{2}bT_A{}^2 - \frac{e}{T_A}\right). \tag{11}$$

It should be noted again that equations such as the above giving the heat content as a function of temperature for a given physical state of the substance should be used only in the range of temperature for which the corresponding equations for heat capacity are valid.

In the case where the heat content itself is measured as a function of the temperature, then equations for heat content of the form of Equations 7 and 10 may be obtained directly from the experimental data, and the corresponding equations for heat capacity are obtained by differentiation. Such equations for heat capacity will be valid only in the range of temperature for which the corresponding equations for heat content hold.

3. Difference between C_P and C_V. From Equation 40 of Chapter 8, we have the following relation between the heat capacity at constant pressure and that at constant volume:

$$C_P - C_V = \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]. \tag{12}$$

From Equation 1 of Chapter 14, we have the change of energy with volume at constant temperature expressed in terms of the P-V-T relations, as follows:

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P. \tag{13}$$

Combination of Equations 12 and 13 yields

$$C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V. \tag{14}$$

But, for a given substance, the pressure can be expressed as a function of volume and temperature,

$$P = f(V,T), \tag{15}$$

so that

$$\mathrm{d}P = \left(\frac{\partial P}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial P}{\partial T}\right)_V \mathrm{d}T. \tag{16}$$

At constant pressure, this becomes

$$0 = \left(\frac{\partial P}{\partial V}\right)_T (\mathrm{d}V)_P + \left(\frac{\partial P}{\partial T}\right)_V (\mathrm{d}T)_P, \tag{17}$$

or

$$(\partial P/\partial T)_V = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}. \tag{18}$$

Substituting in Equation 14, we obtain

$$C_P - C_V = -T\frac{(\partial V/\partial T)_P{}^2}{(\partial V/\partial P)_T}. \tag{19}$$

Letting the coefficient of expansion be

$$\alpha = \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_P \tag{20}$$

and the coefficient of compressibility be

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T, \tag{21}$$

we may write Equation 19 as

$$C_P - C_V = \frac{\alpha^2}{\beta}VT. \tag{22}$$

In Equations 20, 21, and 22, the properties C_P, C_V, and V each apply to one mole of the given substance.

For most solid substances, the value of $C_P - C_V$ is small, though it becomes appreciable for substances having large values of the coefficient of expansion. The following values illustrate the magnitude of $C_P - C_V$ for a number of elements in the solid state at room temperature, in calories per degree mole (*4*): Li, 0.3; C, 0.0; Na, 0.5; Al, 0.2; Si, 0.1; S, 0.4; K, 0.6; Cr, 0.1; Mn, 0.1; Fe, 0.1; Co, 0.1; Ni, 0.2; Cu, 0.2; Zn, 0.3; As, 0.0; Ag, 0.3; Cd, 0.3; I, 0.9; W, 0.1; Pt, 0.2; Au, 0.3; Pb, 0.4; Th, 0.1. These values range up to 10 percent of the value of C_V.

For a substance in the liquid state, the value of $C_P - C_V$ is usually larger than for the same substance in the solid state, since the value of the coefficient of expansion is usually greater for the liquid state.

For the ideal gas, the value of $C_P - C_V$ can be derived simply from Equation 12, using the two conditions that define the ideal gas, namely,

$$PV = RT, \tag{23}$$

and

$$\left(\frac{\partial E}{\partial V}\right)_T = 0. \tag{24}$$

Combination of Equations 12, 23, and 24, with appropriate operation, yields for the ideal gas

$$C_P - C_V = R. \tag{25}$$

For real gases at low pressure, the value of $C_P - C_V$ is not greatly different from R.

4. Variation of heat capacity with pressure and volume. From Chapter 13, we have the relation

$$\frac{\partial^2 S}{\partial T\, \partial P} = \left(\frac{1}{T}\right)\left(\frac{\partial C_P}{\partial P}\right)_T. \tag{26}$$

But from Equation 36 of Chapter 13,

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P, \tag{27}$$

so that

$$\frac{\partial^2 S}{\partial T\, \partial P} = -\left(\frac{\partial^2 V}{\partial T^2}\right)_P. \tag{28}$$

Combination of Equations 26 and 28 yields

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P. \tag{29}$$

At constant temperature, the change in heat capacity of a substance from a pressure P_A to a pressure P_B is

$$C_{P_B} - C_{P_A} = -T\int_{P_A}^{P_B}\left(\frac{\partial^2 V}{\partial T^2}\right)_P \mathrm{d}P. \tag{30}$$

That is, the change in heat capacity from P_A to P_B is equal to the area under a curve, from P_A to P_B, of the second derivative of volume with temperature at constant pressure plotted against the pressure, all multiplied by the negative of the temperature.

Similarly, utilizing Equations 19 and 24 of Chapter 13, we can derive the relation

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V. \tag{31}$$

At constant temperature, the change in heat capacity of a substance from a volume V_A to a volume V_B is

$$C_{V_B} - C_{V_A} = T \int_{V_A}^{V_B} \left(\frac{\partial^2 P}{\partial T^2}\right)_V dV. \tag{32}$$

That is, the change in heat capacity from V_A to V_B is equal to the area under a curve, from V_A to V_B, of the second derivative of pressure with temperature at constant volume plotted against volume, all multiplied by the temperature.

5. Heat capacity of solids. It is interesting to trace chronologically the considerable amount of work which has been done in interpreting the heat capacity of solid substances in terms of molecular structure.

In 1819, Dulong and Petit (*5*) announced their famous empirical rule that for all solid elements the value of the heat capacity per gram atom was a constant with a value near 6 cal/deg. This rule was extended by Kopp (*6*) in 1864 to include compounds, by assigning a given constant value to each element for its contribution to the heat capacity of any given solid compound.

In 1871, Boltzmann (*7*) derived the Dulong and Petit relation on the basis of the classical kinetic theory, and showed that the value of the constant was 3 times the gas constant, or 5.96 cal/deg gram atom. In this derivation, Boltzmann showed that for a vibrating body, as each atom in a solid element may be assumed to be, the mean kinetic energy and the mean potential energy each have a value $RT/2$ for each degree of freedom (or direction of motion), or an energy of RT for each degree of freedom or $3RT$ for the 3 degrees of freedom. If the energy is

$$E = 3RT, \tag{33}$$

then the heat capacity is

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3R. \tag{34}$$

In 1904, Dewar (*8*) published the results of his measurements of the mean heat capacity of some solid elements between the temperatures of 77°K (obtained with liquid air) and 20°K (obtained with liquid hydrogen). Dewar's data showed that for most elements the value of the mean heat capacity between 20°K and 77°K was considerably below the classical value of $3R$.

In 1907, Lewis (*9*) made a rigorous comparison of the existing data with Boltzmann's theory and the rule of Dulong and Petit and found that, for 15 elements at 20°C, the value of the heat capacity at constant volume, C_V, was equal to 5.90 ± 0.09 cal/deg mole. This comparison included only elements above potassium in atomic weight because many of the lighter elements were found to have smaller values for C_V at 20°C. In this work, Lewis properly made the correction for the difference between C_P and C_V in order to obtain from the existing data for C_P the values for C_V required by the Boltzmann theory.

Einstein (*10*) was the first to sense the theoretical significance of the decrease in the heat capacity of solid elements at lower temperatures and published the results of his study in 1907. Einstein showed that the average energy (kinetic plus potential) of an oscillator vibrating with a characteristic frequency, ν, was to be taken, not as kT for each degree of vibrational freedom, but as

$$\frac{kTx}{e^x - 1}, \tag{35}$$

where

$$x = \frac{h\nu}{kT} = \frac{\theta}{T}, \tag{36}$$

h being Planck's constant and $\theta = h\nu/k$.

According to Einstein, the energy of 1 mole, N, of vibrating atoms, counting all 3 degrees of freedom, is

$$E = \frac{3NkTx}{e^x - 1} = \frac{3RTx}{e^x - 1}, \tag{37}$$

and the heat capacity becomes

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{3Rx^2e^x}{(e^x - 1)^2}. \tag{38}$$

According to the foregoing equations,

$$\text{as } T \rightarrow 0, \qquad E \rightarrow 0, \quad C_V \rightarrow 0, \tag{39}$$

and

$$\text{as } T \rightarrow \text{large value}, \qquad E \rightarrow 3RT, \quad C_V \rightarrow 3R. \tag{40}$$

Although Einstein's equation for heat capacity constituted a very remarkable improvement, it was found that appreciable departures still existed at low temperatures.

In 1912, Debye (*11*) published the results of his theoretical investigation of the problem. In his derivation, Debye modified Einstein's procedure by letting each oscillator vibrate with all possible frequencies from zero up to a maximum frequency, ν_{max}, characteristic for each substance. Debye obtained the following relations for the energy and heat capacity, per gram atom of the crystalline solid:

$$E = 3RT\left[3\left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} \left\{\frac{x^3}{e^x - 1}\right\} dx\right], \tag{41}$$

and

$$C_V = 3R\left[3\left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} \left\{\frac{x^4 e^x}{(e^x - 1)^2}\right\} dx\right]. \tag{42}$$

In the foregoing equations, the following abbreviations are used:

$$x = \frac{h}{kT}\,\nu, \tag{43}$$

$$\theta = \frac{h}{k}\,\nu_{\text{max}}, \tag{44}$$

$$\frac{\theta}{T} = \frac{h}{kT}\,\nu_{\text{max}} = x_{\text{max}}. \tag{45}$$

The Debye equations lead to the following limiting values of energy and heat capacity:

$$\text{as } T \rightarrow \text{large value,} \qquad E \rightarrow 3RT, \quad C_V \rightarrow 3R; \tag{46}$$

$$\text{as } T \rightarrow 0, \qquad E \rightarrow 0, \quad C_V \rightarrow 0. \tag{47}$$

For sufficiently small values of temperature, the Debye equations for energy and heat capacity reduce to the following values, per gram atom:

$$E \approx 3R\,\frac{\pi^4}{5\theta^3}\,T^4 = aT^4; \tag{48}$$

$$C_V \approx 3R\,\frac{4\pi^4}{5\theta^3}\,T^3 = 4aT^3; \tag{49}$$

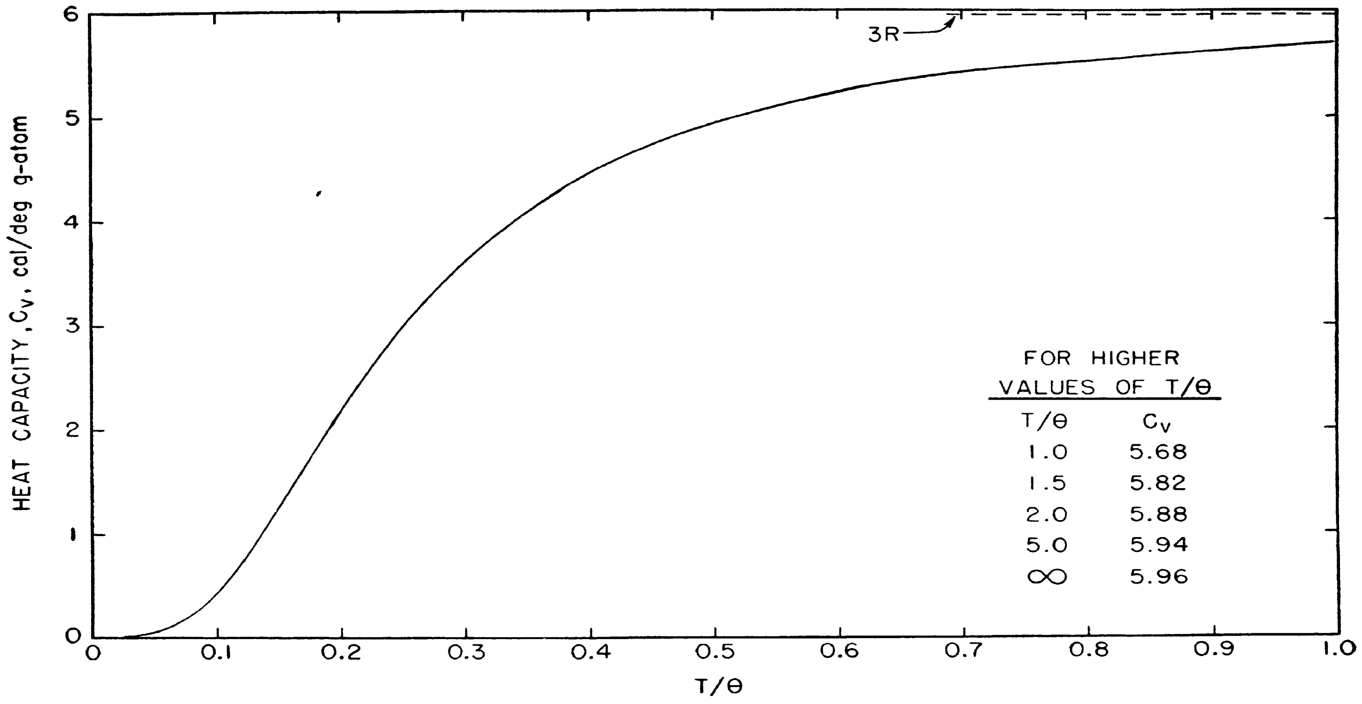


FIGURE 2. The heat capacity, C_V, calculated from the Debye equation for the heat capacity of solids, plotted as a function of T/θ.

The scale of ordinates gives the value of the heat capacity at constant volume, C_V, per gram atom, as given by the Debye equation, and the scale of abscissas gives the value of the absolute temperature divided by the Debye constant, T/θ.

where

$$a = 3R\frac{\pi^4}{5\theta^3}\cdot \tag{50}$$

The heat capacities of practically all elements in the solid crystalline state, and of most compounds in the isotropic crystalline state, are fairly well represented as a function of the temperature by the Debye relation, Equation 42 above. Figure 2 gives a plot of C_V against T/θ, as given by Equation 42. The values of C_V for most isotropic crystalline solids fall on or near this curve. If the value of θ is known for a given isotropic crystalline solid, the value of its heat capacity, C_V, at any given temperature can be estimated. Similarly, if the temperature is known at which the heat capacity, C_V, for a given solid has a known value between about $\frac{1}{2}R$ and $\frac{5}{2}R$ per gram atom, the value of θ can be deduced and values of the heat capacity, C_V, for other temperatures can be estimated.

Values of the Debye θ, evaluated from the values of the heat capacity, C_V, as a function of temperature, for a number of elements and compounds in the crystalline state, are approximately as follows (*12, 13*): Cs, 68; Rb, 85; Pb, 88; Tl, 96; Hg, 97; I_2, 106; Bi, 111; Sn, 119; K, 115; Cd, 165; Au, 175; Na, 180; Ag, 215; Pt, 225; Ca, 226; Zn, 235; Ge, 290; Mg, 290; W, 310; Cu, 315; Fe, 370; Ni, 375; Al, 396; Fe, 420; Li, 510; Be, 900; C (diamond), 1850; KBr, 177; KCl, 220; NaCl, 287; CaF_2, 474; FeS_2, 630.

Examination of Equation 42 and Figure 2 shows that when T/θ has the value unity, that is, when $\theta = T$, the heat capacity, C_V, per gram atom will be approximately 0.95 of the limiting high-temperature value of $3R$, or about 5.67 cal/deg. It may be noted that the heat capacity, C_V, will have attained this value of $(0.95)3R$ at or below room temperature in the case of the first 17 elements and the first 3 compounds listed. For a number of the elements and compounds, the heat capacity, C_V, per gram atom will not attain the value $(0.95)3R$ until relatively high temperatures are reached. It is important to note that the heat capacity, C_V, of solids of complicated crystalline structure may deviate appreciably from the relation given by Equation 42.

Following the work of Debye, Born and von Karman (*14*), Blackman (*15*), Raman (*17*), Venkateswaran (*18*), and Blackman and Born (*19*) made some theoretical studies calculated to improve the agreement of theory and experiment in connection with the heat capacity of solid substances.

6. Heat capacity of liquids. Relatively little advance has been made in the quantitative theoretical evaluation of the heat capacity of substances in the liquid state in terms of molecular structure. The problem is exceedingly more difficult than for the crystalline state because the molecular motions are much more complex. In the liquid state, the molecules possess motions that may be resolved into those of the translational, rotational, and vibrational kinds, but each of these is affected by the intermolecular forces characteristic of the liquid state. The heat capacity of a substance in the liquid state is usually, but not always, greater than its heat capacity in the solid state.

7. Heat capacity of gases. A gas at low pressure may be looked upon as an ensemble of molecules each of which is so far removed from the others that the intermolecular forces are negligible. In such case, the value of a given thermodynamic property for 1 mole of the gas is Avogadro's number, N, times the value for each molecule.

For the property of heat capacity, the picture may be developed in a simple way in terms of the several classical degrees of freedom of the gaseous molecule. For any gaseous molecule, the total number of degrees of freedom allocated to translation, rotation, and vibration is $3n$, where n is the number of atoms in the molecule. Each molecule has 3 degrees of translational freedom, each of which, when fully excited, carries a contribution of $\frac{1}{2}R$ to the heat capacity. The sum of the degrees of freedom for rotation and vibration is therefore $3n - 3$. If the molecule is monatomic, with $n = 1$, there are no degrees of freedom for rotation or vibration. If the molecule is polyatomic ($n > 1$), there are 2 degrees of freedom for rotation if the molecule is linear or 3 degrees of freedom if the molecule is non-linear, with each degree of rotational freedom contributing, when fully excited, $\frac{1}{2}R$ to the heat capacity. For polyatomic molecules ($n > 1$), the number of degrees of freedom for vibration is therefore $3n - 5$ for linear molecules and $3n - 6$ for non-linear molecules, with each degree of freedom for vibration contributing, when fully excited, R to the heat capacity (the energy of the fully excited vibrator being $\frac{1}{2}RT$ for the mean kinetic energy and $\frac{1}{2}RT$ for the mean potential energy, or a total energy of RT). Table 1 summarizes the foregoing discussion regarding classical degrees of freedom and their contributions to the heat capacity of gaseous molecules.

Figure 3 shows schematically how the heat capacity, C_V, for an ideal diatomic gas varies with the temperature. This plot indicates how the degrees of freedom for translation are fully excited even near the absolute zero of temperature; how, as the temperature is increased, the degrees of freedom for rotation become fully excited; and how, after that, the degrees of freedom for vibration become fully excited. The curve in Figure 3 also illustrates the difficulty of expressing the heat capacity of a gas over the entire range of temperature by means of one simple mathematical function.

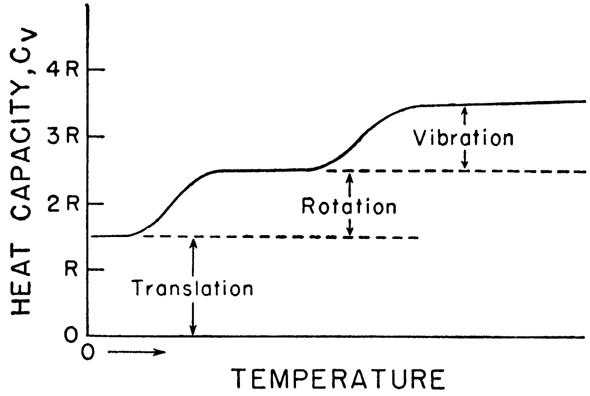


Figure 3. Schematic diagram of the heat capacity, C_V, of an ideal diatomic gas as a function of the temperature.

For the ideal gas, we have seen that the difference between C_P and C_V is the gas constant, R:

$$C_P - C_V = R. \tag{51}$$

For the ideal gas, or for real gases near zero pressure, therefore, the value of the ratio of the heat capacity at constant pressure to that at constant volume has certain simple values, from the relation:

$$\frac{C_P}{C_V} = 1 + \frac{R}{C_V}. \tag{52}$$

TABLE 1. CLASSICAL DEGREES OF FREEDOM AND THEIR CONTRIBUTIONS TO THE HEAT CAPACITY OF GASEOUS MOLECULES

Gaseous Molecule	Classical Degrees of Freedom (Total = $3n$)*			Contributions to the Heat Capacity, C_V, When the Given Degrees of Freedom Are Fully Excited			
	For Translation	For Rotation	For Vibration*	For Translation	For Rotation	For Vibration	Total
Monatomic	3	0	0	$\frac{3}{2}R$	0	0	$\frac{3}{2}R$
Polyatomic, linear	3	2	$3n - 5$	$\frac{3}{2}R$	R	$(3n - 5)R$	$(3n - \frac{5}{2})R$
Polyatomic, non-linear	3	3	$3n - 6$	$\frac{3}{2}R$	$\frac{3}{2}R$	$(3n - 6)R$	$(3n - 3)R$

* n is the number of atoms in the molecule.

For the ideal gas, composed of monatomic molecules,

$$\frac{C_P}{C_V} = 1\tfrac{2}{3}. \tag{53}$$

For the ideal gas composed of polyatomic linear molecules with the degrees of freedom for translation and rotation being fully excited but with the degrees of freedom for vibration being not excited at all,

$$\frac{C_P}{C_V} = 1\tfrac{2}{5}. \tag{54}$$

For the ideal gas composed of polyatomic non-linear molecules with the degrees of freedom for translation and rotation being fully excited but with the degrees of freedom for vibration being not excited at all,

$$\frac{C_P}{C_V} = 1\tfrac{1}{3}. \tag{55}$$

For the ideal gas composed of diatomic molecules with all the degrees of freedom for translation, rotation, and vibration being fully excited,

$$\frac{C_P}{C_V} = 1\tfrac{2}{7}. \tag{56}$$

For real gases, the value of the ratio C_P/C_V may change markedly with pressure, especially at low temperatures.

8. Collateral reading. For detailed discussion of the heat capacities of substances the reader is referred to Mayer and Mayer (*16*) and the other references given above.

REFERENCES

1. G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill Book Company, New York, 1923.
2. H. M. Spencer, *Ind. Eng. Chem.* **40**, 2152 (1948).
3. K. K. Kelley, *U.S. Bur. Mines Bull.* 371 (1934).
4. G. N. Lewis and G. E. Gibson, *J. Am. Chem. Soc.* **39**, 2554 (1917).
5. P. L. Dulong and A. T. Petit, *Ann. chim. et phys.* **10**, 395 (1819).
6. H. Kopp, *Ann. Chem. Pharm. Suppl.* **3**, 1, 289 (1864).
7. L. Boltzmann, *Sitzbes kgl. preuss. Akad. Wiss. Wien* **2**, 679 (1871).
8. J. Dewar, *Proc. Roy. Soc.* (*London*), **A74**, 122 (1904).
9. G. N. Lewis, *J. Am. Chem. Soc.* **29**, 1165, 1516 (1907).
10. A. Einstein, *Ann. Physik* **22**, 180 (1907).
11. P. Debye, *Ann. Physik* **39**, 789 (1912).
12. M. N. Saha and B. N. Srivastava, *A Treatise On Heat*, Indian Press, Calcutta, India, 1935.
13. A. Eucken, "Energie and Warmeinhalt," Volume VIII, Part 1, *Handbuch der experimental Physik*, Akademische Verlagsgesellschaft M.B.H., Leipzig, Germany, 1929.
14. M. Born and T. von Karman, *Physik. Z.* **13**, 294 (1912); **14**, 15 (1913).
15. M. Blackman, *Proc. Roy. Soc.* (*London*) **A159**, 416 (1937).
16. J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, John Wiley & Sons, New York, 1940.
17. C. V. Raman, *Proc. Indian Acad. Sci.* **14A**, 459 (1941).
18. C. S. Venkateswaran, *Proc. Indian Acad. Sci.* **14A**, 506 (1941).
19. M. Blackman and M. Born, *Nature* **150**, 55 (1942).

PROBLEMS

1. Given for MX (g) at 1 atm, in the range 300° to 1000°K, $C_P = 8.05 + 0.00023T - 156{,}300/T^2$ cal/deg mole. Calculate the increase in heat content of the gas at 1 atm from 500° to 900°K.

2. Calculate the value of $C_P - C_V$ for a solid substance at 25°C, for which the coefficient of expansion is 5.8×10^{-5}/deg, the coefficient of compressibility is 1.0×10^{-6}/atm, and the volume is 10.3 cm^3/mole.

3. Assuming the Debye equation for the heat capacity of solids to hold, estimate from the curve in Figure 2 the value of C_V at 25°C for a solid for which θ has the value 1000.

4. The value of C_V at 100°C for a given element in the solid state is measured to be 4.00 cal/deg mole. Estimate the value of C_V at -100°C for this solid.

5. Estimate values of C_P for the following gases at low pressure, as indicated: He; O_2, assuming all degrees of freedom fully excited; N_2, assuming only

translational and rotational degrees of freedom fully excited; CO_2, linear molecule, assuming all degrees of freedom fully excited; CH_4, non-linear molecule, assuming only translational and rotational degrees of freedom fully excited; CS_2, non-linear molecule, assuming all degrees of freedom fully excited.

16

Useful Energy; Free Energy; Criteria of Equilibrium

1. Useful energy. One of the most important relations in thermodynamics is obtained by applying the first and second laws of thermodynamics to a reversible process which involves the transfer, between the system and its surroundings, of energy in addition to heat energy and PV work energy. For such a general process, we can write from the first law

$$\mathrm{d}E = \delta q + \delta w + \delta u, \tag{1}$$

where, as before, $\mathrm{d}E$ is the increase in energy of the system, δq is the heat energy, δw is the PV work energy, and δu is all other energy, absorbed by the system from the surroundings. From the second law, we can write

$$\mathrm{d}S = \frac{\delta q}{T}. \tag{2}$$

Since the process is reversible, we can also set the PV work equal to

$$\delta w = -P\,\mathrm{d}V. \tag{3}$$

Combination of Equations 1, 2, and 3 gives the relation

$$\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V + \delta u, \tag{4}$$

where δu represents all energy other than heat energy and PV work energy absorbed by the system from the surroundings.

The term δu, therefore, is identified as useful energy absorbed by the system from the surroundings. Conversely, the useful energy made available by the system to the surroundings is $-\delta u$. From Equation 4, we can write the useful energy made available by the system to the surroundings as

$$-\delta u = -(\mathrm{d}E + P\,\mathrm{d}V - T\,\mathrm{d}S). \tag{5}$$

Equation 5 is a most important relation, because it tells us that, for any process performed reversibly, the useful energy obtainable from the system is completely expressible in terms of the five fundamental thermodynamic properties, P, V, T, E, and S.

It is important to note the simplification occurring in the value of the useful energy in terms of the fundamental thermodynamic properties for various special cases, as follows:

At constant volume,

$$\mathrm{d}V = 0, \tag{6}$$

and Equation 5 becomes

$$-\delta u = -(\mathrm{d}E - T\,\mathrm{d}S). \tag{7}$$

At constant pressure,

$$P\,\mathrm{d}V = \mathrm{d}(PV), \tag{8}$$

and Equation 5 becomes

$$\begin{aligned} -\delta u &= -[\mathrm{d}E + \mathrm{d}(PV) - T\,\mathrm{d}S] \\ &= -[\mathrm{d}(E + PV) - T\,\mathrm{d}S] = -(\mathrm{d}H - T\,\mathrm{d}S). \end{aligned} \tag{9}$$

At constant temperature,

$$T\,\mathrm{d}S = \mathrm{d}(TS), \tag{10}$$

and Equation 5 becomes

$$\begin{aligned} -\delta u &= -[\mathrm{d}E + P\,\mathrm{d}V - \mathrm{d}(TS)] \\ &= -[\mathrm{d}(E - TS) + P\,\mathrm{d}V]. \end{aligned} \tag{11}$$

At constant entropy,

$$\mathrm{d}S = 0, \tag{12}$$

and Equation 5 becomes

$$-\delta u = -(\mathrm{d}E + P\,\mathrm{d}V). \tag{13}$$

At constant volume and constant entropy, Equation 5 becomes

$$-\delta u = -\mathrm{d}E. \tag{14}$$

At constant pressure and constant entropy, Equation 5 becomes

$$-\delta u = -[\mathrm{d}E + \mathrm{d}(PV)] = -\mathrm{d}(E + PV) = -\mathrm{d}H. \quad (15)$$

At constant volume and constant temperature, Equation 5 becomes

$$-\delta u = -[\mathrm{d}E - \mathrm{d}(TS)] = -\mathrm{d}(E - TS). \quad (16)$$

At constant pressure and constant temperature, Equation 5 becomes

$$\begin{aligned} -\delta u &= -[\mathrm{d}E + \mathrm{d}(PV) - \mathrm{d}(TS)] \\ &= -\mathrm{d}(E + PV - TS) = -\mathrm{d}(H - TS). \quad (17) \end{aligned}$$

2. Free energy. Because many processes occur at constant pressure and constant temperature, the particular combination of the five fundamental thermodynamic properties occurring in Equation 17, namely, $E + PV - TS$ or $H - TS$, recurs with great frequency in thermodynamic calculations. It has accordingly been found desirable to use an abbreviation, F, for this particular combination of properties and to call this function the free energy. Thus, by definition,

$$F = E + PV - TS = H - TS. \quad (18)$$

This function is sometimes called the Gibbs' or Lewis' free energy. From Equation 17, it is seen that, for a reversible process occurring at constant pressure and temperature, the useful energy, $-\delta u$, is equal to $-\mathrm{d}(E + PV - TS)$, or $-\mathrm{d}(H - TS)$ or, by our new definition, $-\mathrm{d}F$. That is, Equation 17 becomes,

$$-\delta u = -\mathrm{d}F. \quad (19)$$

That is to say, for a reversible process at constant pressure and temperature, the decrease in the free energy is the energy which is free to be put to some useful purpose.

Abbreviations similar to that in Equation 18 may be substituted for other combinations of the fundamental properties, as, for example, the combination $E - TS$, for which the symbol A is frequently used (*1,2*), so that, by definition, one may write

$$A = E - TS. \quad (20)$$

This function is sometimes called the Helmholtz free energy. However, it would appear desirable to avoid the introduction of additional abbreviations unless such abbreviations are justified by the extent of the occurrence in actual problems of the combination of properties represented by them. In the present work, little use will be made of the abbreviation given by Equation 20.

3. Spontaneous change and useful energy. Every system if left to itself tends to change toward its final state of rest or equilibrium. If a given system has some capacity for spontaneous change, an appropriate mechanism can, in principle, always be introduced to harness the system to obtain some amount of useful energy as the system passes reversibly from its initial state toward the state of equilibrium. For every process that occurs spontaneously, therefore, some amount of useful energy may be obtained from the system. To make the given system move away from the state of equilibrium, that is, in a non-spontaneous or unnatural direction, it is necessary to supply some useful energy to the system. The algebraic sign of the useful energy obtainable from the system, therefore, serves to tell us whether the given process is one in which the system is moving toward or away from equilibrium. If the value of δu is negative, useful energy is obtainable from the system and we know that the change is a naturally occurring one in the direction toward the state of equilibrium. If the value of δu is positive, useful energy is required to be supplied to the given system to bring about the desired change and we know that the change is an unnatural one in the direction away from equilibrium. It follows that, if the value of δu is zero, the system is already at the state of equilibrium with respect to the prescribed change.

4. General criterion of equilibrium. The value of δu for any given system in any reversible process is given by Equation 5 in terms of the five fundamental thermodynamic properties of the system:

$$\delta u = (\mathrm{d}E + P\,\mathrm{d}V - T\,\mathrm{d}S). \tag{21}$$

We have just seen that, when the value of δu is zero for any given change in a reversible process, the system is at the state of equilibrium. This condition may therefore be used as the general criterion of equilibrium. That is, equilibrium exists in a system with respect to any prescribed change occurring reversibly whenever

$$\delta u = 0, \tag{22}$$

or, from Equation 21, whenever

$$dE + P\,dV - T\,dS = 0. \tag{23}$$

Equation 23 is the general criterion of equilibrium for any system for any prescribed change in a reversible process.

5. Criteria of equilibrium for special cases. Just as in Equations 6 to 17 it was desirable to evaluate the useful energy for special conditions, it is important to ascertain the simplification occurring in the general criterion of equilibrium as given by Equation 23 for various special cases.

The criterion of equilibrium reduces to the following for the indicated special conditions:

Conditions	Criterion of Equilibrium	
Constant volume	$dE - T\,dS = 0.$	(24)
Constant pressure	$dH - T\,dS = 0.$	(25)
Constant temperature	$d(E - TS) + P\,dV = 0.$	(26)
Constant entropy	$dE + P\,dV = 0.$	(27)
Constant volume and entropy	$dE = 0.$	(28)
Constant pressure and entropy	$dH = 0.$	(29)
Constant volume and temperature	$d(E - TS) = 0.$	(30)
Constant pressure and temperature	$d(E + PV - TS) = d(H - TS)$ $= dF = 0.$	(31)

REFERENCES

1. G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill Book Company, New York, 1923.

2. J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, John Wiley & Sons, New York, 1940.

PROBLEMS

1. The following processes occur at a pressure of 1 atm:

a. H_2O (c, 0°C) = H_2O (liq, 0°C);
b. H_2O (c, −5°C) = H_2O (liq, −5°C);
c. H_2O (g, 98°C) = H_2O (liq, 98°C);
d. Combustion of carbon in oxygen at 25°C;
e. Decomposition of water into hydrogen and oxygen at 25°C;
f. NaCl (aq, $m = 2$) = NaCl (aq, $m = 1$).

Give for each process the following information:

i. Identification as spontaneous, non-spontaneous, or equilibrium;
ii. Sign of the useful energy, $-\delta u$, for the process, as positive, negative, or zero.
iii. Sign of dF for the process, as positive, negative, or zero.

2. Derive the equation giving the criterion for equilibrium at (*a*) constant volume and entropy and (*b*) constant pressure and entropy.

17

Relations among the Thermodynamic Properties and Functions

1. Relation involving the five fundamental properties. When a substance is subjected to a reversible process involving only heat energy and PV work energy, application of the first and second laws yields the following important relation (Chapter 13):

$$\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V. \tag{1}$$

Equation 1 tells us that, when a given substance is subjected to a reversible process involving no energy except heat energy, represented by the term $T\,\mathrm{d}S$, and PV work energy, represented by the term $-P\,\mathrm{d}V$, the increase in energy is given completely by the sum of these two terms.

2. Relations involving the defined functions. For the same process for which Equation 1 is valid, namely, a reversible process involving only heat energy and PV work energy, similar equations may be derived to give the corresponding relations for the defined thermodynamic functions, H, A, F, as follows:

By definition,

$$H = E + PV. \tag{2}$$

On differentiation,

$$\mathrm{d}H = \mathrm{d}E + P\,\mathrm{d}V + V\,\mathrm{d}P. \tag{3}$$

Combination of Equations 1 and 3 yields

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}P. \tag{4}$$

By definition,

$$A = E - TS. \tag{5}$$

On differentiation,

$$\mathrm{d}A = \mathrm{d}E - T\,\mathrm{d}S - S\,\mathrm{d}T. \tag{6}$$

Combination of Equations 1 and 6 yields

$$dA = -S\,dT - P\,dV. \tag{7}$$

By definition,

$$F = E + PV - TS. \tag{8}$$

On differentiation,

$$dF = dE + P\,dV + V\,dP - T\,dS - S\,dT. \tag{9}$$

Combination of Equations 1 and 9 yields

$$dF = -S\,dT + V\,dP. \tag{10}$$

3. Special cases. Interesting and important thermodynamic relations may be obtained from Equations 1, 4, 7, and 10, for various special cases, as follows:

From Equation 1, we have at constant volume,

$$dE = T\,dS, \tag{11}$$

or

$$\left(\frac{\partial E}{\partial S}\right)_V = T; \tag{12}$$

and at constant entropy,

$$dE = -P\,dV, \tag{13}$$

or

$$\left(\frac{\partial E}{\partial V}\right)_S = -P. \tag{14}$$

From Equation 4, we have at constant pressure,

$$dH = T\,dS, \tag{15}$$

or

$$\left(\frac{\partial H}{\partial S}\right)_P = T; \tag{16}$$

and at constant entropy,

$$dH = V\,dP, \tag{17}$$

or

$$\left(\frac{\partial H}{\partial P}\right)_S = V. \tag{18}$$

From Equation 7, we have at constant volume,

$$dA = -S\,dT, \tag{19}$$

or

$$\left(\frac{\partial A}{\partial T}\right)_V = -S; \tag{20}$$

and at constant temperature,

$$dA = -P\,dV, \tag{21}$$

or

$$\left(\frac{\partial A}{\partial V}\right)_T = -P. \tag{22}$$

From Equation 10, we have at constant pressure,

$$dF = -S\,dT, \tag{23}$$

or

$$\left(\frac{\partial F}{\partial T}\right)_P = -S; \tag{24}$$

and at constant temperature,

$$dF = V\,dP, \tag{25}$$

or

$$\left(\frac{\partial F}{\partial P}\right)_T = V. \tag{26}$$

The exact differential Equations 1, 4, 7, and 10, given above, lead to important relationships among the differential coefficients of the various thermodynamic properties. The general differential equations may be written in the form

$$dG = M\,dx + N\,dy. \tag{27}$$

But

$$dG = \left(\frac{\partial G}{\partial x}\right)_y dx + \left(\frac{\partial G}{\partial y}\right)_x dy. \tag{28}$$

Hence,

$$M = \left(\frac{\partial G}{\partial x}\right)_y; \quad N = \left(\frac{\partial G}{\partial y}\right)_x \cdot \tag{29}$$

But

$$\frac{\partial^2 G}{\partial x\, \partial y} = \frac{\partial^2 G}{\partial y\, \partial x}, \tag{30}$$

so that

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y. \tag{31}$$

In this way, for example, Equation 4 yields

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P, \tag{32}$$

and Equation 10 yields

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T. \tag{33}$$

The power and usefulness of relations such as those given above should not be overlooked. For example, it may be noted that according to Equation 24 the change of the free energy of a substance with temperature at constant pressure is equal to the negative of its entropy. Similarly, Equation 26 shows that the change of the free energy of a substance with pressure at constant temperature is equal to its volume.

4. Identity of the scales of temperature provided by the ideal gas and by the second law. In earlier chapters, we introduced the absolute temperature by means of the definition of the ideal gas, and again independently by the second law of thermodynamics by the quantitative definition of change in entropy. It is now possible to show that these two scales of temperature, as previously defined, are identical. The ideal gas was defined by the two relations:

$$PV = RT, \tag{34}$$

and

$$\left(\frac{\partial E}{\partial V}\right)_T = 0. \tag{35}$$

By the second law of thermodynamics, the absolute temperature was defined through the following relation for a reversible process:

$$\delta q = T\, dS. \tag{36}$$

By application of the first and second laws of thermodynamics to a substance participating in a reversible process involving only heat energy and PV work energy, the following relations (Chapter 14) were derived:

$$\left(\frac{\partial E}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V, \tag{37}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P. \tag{38}$$

Equations 37 and 38 may be rewritten explicitly in terms of pressure and volume, as

$$P = T\left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial E}{\partial V}\right)_T, \tag{39}$$

$$V = T\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial H}{\partial P}\right)_T. \tag{40}$$

It is important to note that Equations 39 and 40 have been derived independently of the equations defining the ideal gas, and the temperature is the thermodynamic temperature. If, therefore, Equations 39 and 40 are completely in accord with the equations defining the ideal gas, the two scales of temperature are proportional and may be considered identical if the constant of proportionality between the two scales is taken as unity. The accord of Equations 39 and 40 with the definition of the ideal gas may be shown by substituting the ideal gas relations into the right side of Equations 39 and 40 and seeing whether the resulting terms yield the pressure in Equation 39 and the volume in Equation 40. In Equation 39, the values of T, $(\partial P/\partial T)_V$, and $(\partial E/\partial V)_T$ from the relations of the ideal gas are introduced, the substitutions being T, R/V, and 0, respectively, which yield P for the sum of the two terms. Similarly, in Equation 40, the values of T, $(\partial V/\partial T)_P$, and $(\partial H/\partial P)_T$ are introduced from the relations for the ideal gas, the substitutions being T, R/P, and 0, which yield V for the sum of the two terms.

5. Condensed summary of thermodynamic formulas. It is possible to derive a great number of thermodynamic formulas such as those listed above, following the procedure given by Bridgman (*1*) and used by Lewis and Randall (*2*). The procedure is to write

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{(\partial x)_z}{(\partial y)_z}, \tag{41}$$

and

$$(\partial x)_y = -(\partial y)_x, \tag{42}$$

where x, y, and z may represent any one of the five fundamental properties, P, V, T, E, S, or the three defined functions, H, A, F. Letting

$$(\partial T)_P = 1, \tag{43}$$

it is then possible to derive the following 28 Bridgman (*1*) formulas, which are expressed in terms of the fundamental properties and the three derivatives most readily capable of experimental measurement, namely, $(\partial V/\partial T)_P$, $(\partial V/\partial P)_T$, and $(\partial H/\partial T)_P$ or C_P:

$$(\partial T)_P = -(\partial P)_T = 1. \tag{44}$$

$$(\partial V)_P = -(\partial P)_V = \left(\frac{\partial V}{\partial T}\right)_P. \tag{45}$$

$$(\partial S)_P = -(\partial P)_S = \frac{C_P}{T}. \tag{46}$$

$$(\partial E)_P = -(\partial P)_E = C_P - P\left(\frac{\partial V}{\partial T}\right)_P. \tag{47}$$

$$(\partial H)_P = -(\partial P)_H = C_P. \tag{48}$$

$$(\partial F)_P = -(\partial P)_F = -S. \tag{49}$$

$$(\partial A)_P = -(\partial P)_A = -\left[S + P\left(\frac{\partial V}{\partial T}\right)_P\right]. \tag{50}$$

$$(\partial V)_T = -(\partial T)_V = -\left(\frac{\partial V}{\partial P}\right)_T. \tag{51}$$

$$(\partial S)_T = -(\partial T)_S = \left(\frac{\partial V}{\partial T}\right)_P. \tag{52}$$

$$(\partial E)_T = -(\partial T)_E = T\left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial P}\right)_T. \tag{53}$$

$$(\partial H)_T = -(\partial T)_H = -V + T\left(\frac{\partial V}{\partial T}\right)_P \cdot \tag{54}$$

$$(\partial F)_T = -(\partial T)_F = -V. \tag{55}$$

$$(\partial A)_T = -(\partial T)_A = P\left(\frac{\partial V}{\partial P}\right)_T \cdot \tag{56}$$

$$(\partial S)_V = -(\partial V)_S = \left(\frac{1}{T}\right)\left[C_P\left(\frac{\partial V}{\partial P}\right)_T + T\left(\frac{\partial V}{\partial T}\right)_P^2\right] \cdot \tag{57}$$

$$(\partial E)_V = -(\partial V)_E = C_P\left(\frac{\partial V}{\partial P}\right)_T + T\left(\frac{\partial V}{\partial T}\right)_P^2 \cdot \tag{58}$$

$$(\partial H)_V = -(\partial V)_H = C_P\left(\frac{\partial V}{\partial P}\right)_T + T\left(\frac{\partial V}{\partial T}\right)_P^2 - V\left(\frac{\partial V}{\partial T}\right)_P \cdot \tag{59}$$

$$(\partial F)_V = -(\partial V)_F = -\left[V\left(\frac{\partial V}{\partial T}\right)_P + S\left(\frac{\partial V}{\partial P}\right)_T\right] \cdot \tag{60}$$

$$(\partial A)_V = -(\partial V)_A = S\left(\frac{\partial V}{\partial P}\right)_T \cdot \tag{61}$$

$$(\partial E)_S = -(\partial S)_E = \left(\frac{P}{T}\right)\left[C_P\left(\frac{\partial V}{\partial P}\right)_T + T\left(\frac{\partial V}{\partial T}\right)_P^2\right] \cdot \tag{62}$$

$$(\partial H)_S = -(\partial S)_H = -\frac{VC_P}{T} \cdot \tag{63}$$

$$(\partial F)_S = -(\partial S)_F = -\left(\frac{1}{T}\right)\left[VC_P - ST\left(\frac{\partial V}{\partial T}\right)_P\right] \cdot \tag{64}$$

$$(\partial A)_S = -(\partial S)_A = \left(\frac{1}{T}\right)\left\{P\left[C_P\left(\frac{\partial V}{\partial P}\right)_T + T\left(\frac{\partial V}{\partial T}\right)_P^2\right] + ST\left(\frac{\partial V}{\partial T}\right)_P\right\} \cdot \tag{65}$$

$$(\partial H)_E = -(\partial E)_H = -V\left[C_P - P\left(\frac{\partial V}{\partial T}\right)_P\right] - P\left[C_P\left(\frac{\partial V}{\partial P}\right)_T + T\left(\frac{\partial V}{\partial T}\right)_P^2\right] \cdot \tag{66}$$

$$(\partial F)_E = -(\partial E)_F = -V\left[C_P - P\left(\frac{\partial V}{\partial T}\right)_P\right] + S\left[T\left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial P}\right)_T\right]. \tag{67}$$

$$(\partial A)_E = -(\partial E)_A = P\left[C_P\left(\frac{\partial V}{\partial P}\right)_T + T\left(\frac{\partial V}{\partial T}\right)_P^2\right]. \tag{68}$$

$$(\partial F)_H = -(\partial H)_F = -V(C_P + S) + TS\left(\frac{\partial V}{\partial T}\right)_P. \tag{69}$$

$$(\partial A)_H = -(\partial H)_A = -\left[S + P\left(\frac{\partial V}{\partial T}\right)_P\right]\cdot\left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] + P\left(\frac{\partial V}{\partial P}\right)_T. \tag{70}$$

$$(\partial A)_F = -(\partial F)_A = -S\left[V + P\left(\frac{\partial V}{\partial P}\right)_T\right] - PV\left(\frac{\partial V}{\partial T}\right)_P. \tag{71}$$

Any of the thermodynamic relations may be derived from the above summary. Some examples are the following:

$$\left(\frac{\partial F}{\partial P}\right)_T = \frac{(\partial F)_T}{(\partial P)_T} = \frac{-V}{-1} = V. \tag{72}$$

$$\left(\frac{\partial F}{\partial T}\right)_P = \frac{(\partial F)_P}{(\partial T)_P} = \frac{-S}{1} = -S. \tag{73}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{(\partial S)_T}{(\partial P)_T} = \frac{(\partial V/\partial T)_P}{-1} = -\left(\frac{\partial V}{\partial T}\right)_P. \tag{74}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{(\partial H)_T}{(\partial P)_T} = \frac{-V + T(\partial V/\partial T)_P}{-1} = V - T\left(\frac{\partial V}{\partial T}\right)_P. \tag{75}$$

6. Collateral reading. For detailed discussion of condensed thermodynamic formulas and their derivation, the reader is referred to Bridgman (*3*), Koenig (*4*), Tobolsky (*5*), and Prins (*6*).

REFERENCES

1. P. W. Bridgman, *Phys. Rev.* **3**, 273 (1914).
2. G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill Book Company, New York, 1923.

3. P. W. Bridgman, *Condensed Collection of Thermodynamic Formulas*, Harvard University Press, Cambridge, Mass., 1926.
4. F. O. Koenig, *J. Chem. Phys.* **3**, 29 (1935).
5. A. Tobolsky, *J. Chem. Phys.* **10**, 644 (1942).
6. J. A. Prins, *J. Chem. Phys.* **16**, 65 (1948).

PROBLEMS

1. Using Bridgman's formulas, derive the equivalent of the following: $(\partial H/\partial P)_S$, $(\partial H/\partial S)_P$, $(\partial E/\partial S)_V$, $(\partial E/\partial V)_S$, $(\partial E/\partial P)_T$, $(\partial E/\partial S)_T$, $(\partial H/\partial S)_T$, $(\partial F/\partial T)_S$, $(\partial F/\partial P)_S$, $(\partial F/\partial S)_P$.

2. For a given substance at 25°C and 1 atm, $C_P = 33.0$ cal/deg mole, $V = 90.0$ cm^3/mole, $(\partial V/\partial T)_P = 0.0900$ cm^3/deg, and $(\partial V/\partial P)_T = -0.00900$ cm^3/atm. Calculate $(\partial E/\partial P)_T$, $(\partial H/\partial P)_T$, and the Joule-Thomson coefficient.

3. For a given substance, at $T = 25$°C, and $P = 0$ to 10,000 atm, $V = a + bP + cP^2$ cm^3/mole. Calculate the increase in free energy of 1 mole of this substance at 25°C as the pressure is increased from 1000 to 10,000 atm.

18

Heats and Energies of Reactions and Processes

1. Specification of the reaction or process. One of the important thermodynamic facts to be known about a given chemical reaction or process is the change, or increment, in energy, ΔE, or heat content, ΔH, associated with the reaction or process at some specified temperature, as at 25°C, with each of the reactants and products in an appropriate reference state. As will be seen later, such reference states, usually called standard states and denoted by a superscript on the thermodynamic symbol, as $H°$, may be ones realizable only in theory but are such that a given substance can be readily converted from the actual state to the appropriate standard state with the necessary data. In written equations, it is assumed that a given reaction or process involves each of the reactants and products in its standard state, unless otherwise specified. Unless the context provides a complete description of the reaction or process, as to temperature, pressure, concentrations, etc., such information should be given explicitly in the writing of the chemical equation describing the process. Some examples follow:

$$H_2O\text{ (liq, sat'n press.)} = H_2O\text{ (g, sat'n press.)};$$

$$\Delta H_{298.16} = x\text{ kcal/mole.} \tag{1}$$

$$H_2O\text{ (liq)} = H_2O\text{ (g)};$$

$$\Delta H_{298.16}\text{(sat'n press.)} = x\text{ kcal/mole.} \tag{2}$$

$$H_2O\text{ (liq)} = H_2O\text{ (g)};$$

$$\Delta H^\circ_{298.16} = x'\text{ kcal/mole.} \tag{3}$$

$$H_2\text{ (g, 2 atm)} + \tfrac{1}{2}O_2\text{ (g, 5 atm)} = H_2O\text{ (liq, 1 atm)};$$

$$\Delta H_{298.16} = y\text{ kcal/mole.} \tag{4}$$

$$\mathrm{H_2\ (g) + \tfrac{1}{2}O_2\ (g) = H_2O\ (liq)};$$

$$\Delta H^\circ_{298.16} = y'\ \text{kcal/mole}. \tag{5}$$

$$\mathrm{HCl\ (aq,}\ m = 2, P = 2\ \mathrm{atm) + Ag\ (c,}\ P = 2\ \mathrm{atm)}$$

$$= \mathrm{AgCl\ (c,}\ P = 2\ \mathrm{atm) + \tfrac{1}{2}H_2\ (g, 2\ atm)};$$

$$\Delta H_{298.16} = z\ \text{kcal/mole}. \tag{6}$$

$$\mathrm{HCl\ (aq,}\ m = 2) + \mathrm{Ag\ (c) = AgCl\ (c) + \tfrac{1}{2}H_2\ (g)};$$

$$\Delta H_{298.16}\ (P = 2\ \text{atm}) = z\ \text{kcal/mole}. \tag{7}$$

$$\mathrm{HCl\ (aq) + Ag\ (c) = AgCl\ (c) + \tfrac{1}{2}H_2\ (g)};$$

$$\Delta H^\circ_{298.16} = z'\ \text{kcal/mole}. \tag{8}$$

In the above equations, it should be noted that Equations 1 and 2 are different ways of saying the same thing; and similarly for Equations 6 and 7.

2. Specification of the thermodynamic property. In addition to specifying the actual state of each of the reactants and products participating in the given reaction or process, it is important to specify the thermodynamic property which is measured, as the increment in energy, ΔE, or the increment in heat content, ΔH.

In chemical reactions, the thermodynamic property measured may usually be labeled as ΔE or ΔH, depending upon whether the substances participating in the reaction are confined at constant volume or at constant pressure. Consider, for example, the reaction of a stoichiometric mixture of two diatomic ideal gases, MX and X_2, to form the triatomic ideal gas, MX_2:

$$\mathrm{MX\ (g) + \tfrac{1}{2}X_2\ (g) = MX_2\ (g)}. \tag{9}$$

If the reaction takes place in a calorimeter in a closed bomb at constant volume, and if the total pressure of the reactant gases is P_A, then the reaction may be specified as follows, at the given temperature:

$$\mathrm{MX}\ (\mathrm{g}, P_{\mathrm{MX}} = \tfrac{2}{3}P_A) + \tfrac{1}{2}\mathrm{X_2}\ (\mathrm{g}, P_{\mathrm{X_2}} = \tfrac{1}{3}P_A)$$

$$= \mathrm{MX_2}\ (\mathrm{g}, P_{\mathrm{MX_2}} = \tfrac{2}{3}P_A). \tag{10}$$

According to the first law, for any process,

$$\Delta E = q + w + u, \tag{11}$$

where q is the heat energy, w is the PV work energy, and u is any other energy, each absorbed by the system during the process. But, in this calorimetric experiment, u is zero, and, since the volume is constant, w is also zero. Hence, the calorimetrically measured heat energy absorbed, q, is equal to ΔE, and for the reaction given by Equation 10, we may write,

$$\Delta E = q. \tag{12}$$

Since the gases are ideal, the designation of pressure is unnecessary, as the energy of ideal gases is independent of the pressure and of the presence of other gases. For real gases, however, the specification of the pressure must be made in so far as it is significant.

In general, the absorbed heat energy associated with any chemical reaction that takes place in a calorimeter in a vessel at constant volume may be placed equal to ΔE for the specified reaction or process.

If the reaction given by Equation 9 takes place in a calorimeter at constant pressure, with each reactant gas disappearing at the pressure P_A, and the product gas appearing at the pressure P_A, then the reaction may be specified as follows at the given temperature:

$$\mathrm{MX}\ (\mathrm{g}, P_A) + \tfrac{1}{2}\mathrm{X}_2\ (\mathrm{g}, P_A) = \mathrm{MX}_2\ (\mathrm{g}, P_A). \tag{13}$$

According to the first law, for any process,

$$\Delta E = q + w + u. \tag{14}$$

But, in this calorimetric experiment, u is zero. Since the system undergoes a change in volume and is subjected to a constant confining pressure, the PV work energy is

$$w = -\int P\,\mathrm{d}V = -P\int \mathrm{d}V = -P\,\Delta V. \tag{15}$$

Substituting in Equation 14 gives

$$\Delta E = q - P\,\Delta V. \tag{16}$$

Hence

$$\Delta E + P\,\Delta V = q,$$

and

$$\Delta E + \Delta(PV) = \Delta(E + PV) = q. \tag{17}$$

Finally, since

$$E + PV = H, \tag{18}$$

we may write

$$\Delta H = q. \tag{19}$$

That is, the calorimetrically measured heat energy absorbed, q, is equal to ΔH, the increment in heat content for the given reaction.

In general, the absorbed heat energy associated with any chemical reaction that takes place in a calorimeter at constant pressure may be placed equal to ΔH for the specified reaction or process.

For any specified reaction or process, the difference between the values of ΔE and ΔH may be evaluated from the relation

$$\Delta H = \Delta E + \Delta(PV). \tag{20}$$

In Equation 20, $\Delta(PV)$ is simply the sum of the product of pressure and volume for each of the products less the sum of the product of pressure and volume for each of the reactants, for the specified reaction or process. The value of PV for liquid and solid substances will be small compared to the value of PV for gaseous substances. For reactions in which all the reactants and products are liquids or solids, therefore, the difference between ΔE and ΔH will be relatively small. For reactions in which the number of moles of gaseous reactants is the same as the number of moles of gaseous products, the difference between ΔE and ΔH will also be relatively small. For other reactions, the difference between ΔE and ΔH will depend on the difference in the number of moles, Δn, of gaseous reactants and gaseous products.

In the reaction given by Equation 9, wherein each of the substances involved is an ideal gas, the difference between ΔE and ΔH may be readily evaluated as follows:

$$\Delta H = \Delta E + \Delta(PV). \tag{21}$$

But

$$\Delta(PV) = (\Delta n)RT = -\tfrac{1}{2}RT. \tag{22}$$

Hence

$$\Delta H = \Delta E - \tfrac{1}{2}RT. \tag{23}$$

In general, for reactions involving only ideal gases, the difference between ΔE and ΔH is given by the relation

$$\Delta H = \Delta E + RT\,\Delta n, \tag{24}$$

where

$$\Delta n = \sum n_{\text{products}} - \sum n_{\text{reactants}}, \tag{25}$$

n being the number of moles of gas.

In processes such as those of transition, fusion, and vaporization, occurring in a calorimeter, the calorimetrically measured value of the heat energy is equivalent to ΔH if the process occurs at constant pressure and ΔE if the process occurs at constant volume.

Similarly, if the process is one of simply taking a given substance from one temperature to a slightly higher temperature in order to determine the heat capacity of the given substance, as the ratio of the heat absorbed to the rise in temperature (see Chapter 8), the measured property will be the heat capacity at constant volume, C_V, if the process occurs at constant volume, and the heat capacity at constant pressure, C_P, if the process occurs at constant pressure. In any case, the property will be that for the substance in the physical state or states in which it actually exists in the calorimetric vessel in which it is contained.

3. Variation of the heat of reaction with temperature. When the value of the change in heat content, ΔH, is known for a specified reaction or process at some temperature, the value at any other temperature may be readily calculated if there are known, for each of the individual reactants and products, the values of heat capacity, C_P, or of the heat content, H (referred to some selected temperature), over the range of temperature for which the calculation is to be made.

Consider the simple reaction,

$$\mathrm{M} = \mathrm{N}, \tag{26}$$

with the state of each substance being adequately specified. The change in heat content for this reaction at the given temperature, T, is equal to

$$\Delta H = H_{\mathrm{N}} - H_{\mathrm{M}}. \tag{27}$$

At constant pressure,

$$\frac{\mathrm{d}(\Delta H)}{\mathrm{d}T} = \frac{\mathrm{d}H_{\mathrm{N}}}{\mathrm{d}T} - \frac{\mathrm{d}H_{\mathrm{M}}}{\mathrm{d}T}. \tag{28}$$

Since, at constant pressure,

$$\frac{\mathrm{d}H}{\mathrm{d}T} = C_P, \tag{29}$$

it follows that

$$\frac{\mathrm{d}(\Delta H)}{\mathrm{d}T} = C_{P_\mathrm{N}} - C_{P_\mathrm{M}} = \Delta C_P. \tag{30}$$

Suppose that over a given range of temperature, T_1 to T_2,

$$C_{P_\mathrm{N}} = a_\mathrm{N} + b_\mathrm{N}T + c_\mathrm{N}T^2, \tag{31}$$

and

$$C_{P_\mathrm{M}} = a_\mathrm{M} + b_\mathrm{M}T + c_\mathrm{M}T^2. \tag{32}$$

Subtraction of Equation 32 from Equation 31 gives

$$\Delta C_P = (\Delta a) + (\Delta b)T + (\Delta c)T^2, \tag{33}$$

where

$$\Delta a = a_\mathrm{N} - a_\mathrm{M}, \tag{34}$$

$$\Delta b = b_\mathrm{N} - b_\mathrm{M}, \tag{35}$$

and

$$\Delta c = c_\mathrm{N} - c_\mathrm{M}. \tag{36}$$

Combination of Equations 30 and 33 gives, for constant pressure,

$$\frac{\mathrm{d}(\Delta H)}{\mathrm{d}T} = (\Delta a) + (\Delta b)T + (\Delta c)T^2. \tag{37}$$

Equation 37 may be readily integrated over the given range of temperature to give the value of ΔH at some temperature T within the given range with reference to the value of ΔH at T_1:

$$\Delta H_T - \Delta H_{T_1} = (\Delta a)(T - T_1) + \tfrac{1}{2}(\Delta b)(T^2 - T_1{}^2) + \tfrac{1}{3}(\Delta c)(T^3 - T_1{}^3). \tag{38}$$

Equation 38 serves to evaluate ΔH at the temperature T, between T_1 and T_2, when the value of ΔH at T_1 is known and when the values of the heat capacities of each of the reactants and products are known over the range of temperature T_1 to T_2. An equation similar to Equation 38 may be used when the value of ΔH is known at some other temperature within the given range T_1 to T_2, as at T_3:

$$\Delta H - \Delta H_{T_3} = (\Delta a)(T - T_3) + \tfrac{1}{2}(\Delta b)(T^2 - T_3{}^2) + \tfrac{1}{3}(\Delta c)(T^3 - T_3{}^3). \tag{39}$$

In Equation 39, T and T_3 have any values within the range of applicability of the equation, and T may be lower than T_3. Equation 37 may be integrated without specific limits of temperature to give the relation

$$\Delta H = \Delta H_* + (\Delta a)T + \tfrac{1}{2}(\Delta b)T^2 + \tfrac{1}{3}(\Delta c)T^3, \qquad (40)$$

where ΔH_* is the constant of integration required to make the equation valid over the range of applicability. In Equation 40, the values of the constants Δa, Δb, and Δc are obtained from the equations for the heat capacity of each of the reactants and products, and ΔH_* is evaluated from the foregoing constants and the value of ΔH at a known temperature in the range T_1 to T_2. Although the substitution of $T = 0$ in Equation 40 makes ΔH_* appear formally to be the value for 0°K, it must be remembered that Equation 40 is valid only over the range of temperature for which heat capacities, as given by Equations 31 and 32, are known, and within which range of temperature the actual value of ΔH is known at some one temperature.

The heat capacity of each of the products and reactants in the given reaction may frequently be expressed as a function of temperature over the range T_1 to T_2 by means of an equation of the form (*21*)

$$C_P = a + bT + \frac{c}{T^2}. \qquad (41)$$

In such case, the equations corresponding to Equations 37, 39, and 40 are, respectively, as follows:

$$\frac{\mathrm{d}(\Delta H)}{\mathrm{d}T} = (\Delta a) + (\Delta b)T + \frac{(\Delta c)}{T^2}; \qquad (42)$$

$$\Delta H - \Delta H_{T_3} = (\Delta a)(T - T_3) + \frac{1}{2}(\Delta b)(T^2 - T_3{}^2) - \frac{(\Delta c)}{T - T_3}; \qquad (43)$$

$$\Delta H = \Delta H_* + (\Delta a)T + \frac{1}{2}(\Delta b)T^2 - \frac{(\Delta c)}{T}. \qquad (44)$$

As in Equations 39 and 40, Equations 43 and 44 may be used only over the range of temperature for which the corresponding equations for heat capacity are valid, and the value of the constant of integration, ΔH_*, must be evaluated from a known value of ΔH at a given temperature within the range of applicability of the equations for heat capacity. Equation 44 is of a form that does not permit substitution of $T = 0$.

Frequently, there are known, for each of the reactants and products of a given reaction, values at various temperatures of the heat content, $H - H_0$, which is the heat content at a given temperature referred to the heat content at 0°K. Then the value of ΔH for other temperatures may be readily calculated from the value of ΔH at one temperature. Suppose that the value of ΔH at 25°C is known. Then the actual value of ΔH at 0°K is equal to

$$\Delta H_0 = \Delta H_{298.16} - \Delta(H_{298.16} - H_0), \tag{45}$$

where

$$\Delta(H_{298.16} - H_0) = \sum(H_{298.16} - H_0)_{\text{products}} - \sum(H_{298.16} - H_0)_{\text{reactants}}. \tag{46}$$

The value of ΔH at any other temperature may be obtained from the relation

$$\Delta H = \Delta H_0 + \Delta(H - H_0), \tag{47}$$

where, as before,

$$\Delta(H - H_0) = \sum(H - H_0)_{\text{products}} - \sum(H - H_0)_{\text{reactants}}. \tag{48}$$

Equations 45 and 47 may be readily proved by considering the symbol Δ as an operator and multiplying it into each term inside the parentheses.

If there is need for them, equations corresponding to all the foregoing may be derived for the energy, E, the heat capacity at constant volume, C_V, and the energy content referred to 0°K, $E - E_0$.

4. Thermochemical method. The modern thermochemical method aims to determine as directly as possible the quantity of energy associated with unit amount of a given reaction or process. The thermochemical investigation consists of a calorimetric part, involving the measurement of energy, and a chemical part, involving the measurement of the amount of the given reaction or process. The desired result is the ratio, in appropriate units, of the quantity of energy to the amount of the reaction or process.

5. Calorimetric part of the thermochemical investigation. For a chemical reaction or process that is exothermal, that is, evolves heat energy as it takes place, the method is schematically illustrated in Figure 1. Here, A represents a fixed calorimeter system at the "standard" initial temperature, T_A, and B represents the same fixed calorimeter system at the "standard" final higher temperature, T_B. In one kind of experiment, the heat evolved by a measured amount of the given chemical reaction or process is used to take the calorimeter system from its initial state A and temperature, T_A, to its final state B and temperature, T_B. In another kind of experiment, with the same calorimeter system at the same initial state, the heat evolved by a measured amount of electrical energy is used to take the calorimeter system from the same initial state A and temperature, T_A, to the same final state B and temperature, T_B. In this manner, there is obtained a direct equivalence between the measured amount of chemical reaction and the measured amount of electrical energy, using the fixed calorimeter system as the absorber and comparator of the two kinds of energy.

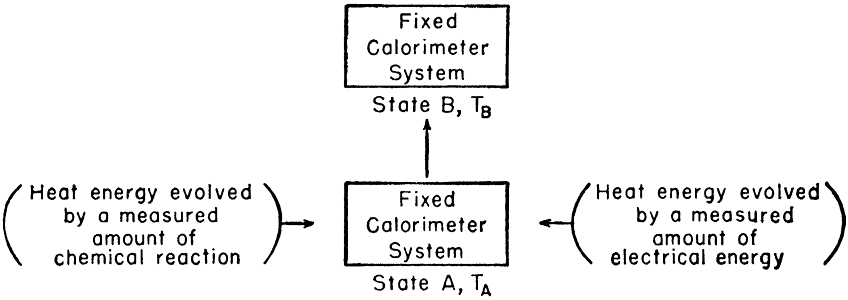


FIGURE 1. Schematic diagram of the thermochemical method of determining the heats of exothermal reactions.

In actual practice it is easy to use a fixed calorimeter system but impracticable to try to obtain exactly the same rise of temperature in all experiments. Instead, with the fixed calorimeter system, the rise of temperature is made substantially the same in all experiments, and the small differences from one experiment to another are measured in order to effect the correction to the common or standard value of the rise of temperature. In most cases, the amount of electrical or chemical energy added to the calorimeter can be so regulated that the differences in the rise of temperature in the various experiments will be less than several percent of the total rise. Since the small differences can be measured as precisely as necessary, the advantage of the substitutional nature of the method is retained, and the experimenter gains some needed flexibility in operation.

For the given calorimeter system it is convenient to determine a quantity called its energy equivalent,* which is the amount of electrical energy added to the fixed calorimeter system divided by the rise of temperature, the amount of energy added being regulated so that the actual rise of temperature differs little from the "standard" rise of temperature. The simple relation used in computing the energy equivalent of the calorimeter is

$$(\text{energy equivalent}) = \frac{(\text{electrical energy})}{\Delta t_e}, \tag{49}$$

where Δt_e is the rise of temperature in the experiment with electrical energy. From a series of such experiments, an average value of the energy equivalent is determined.

In a series of calorimetric reaction experiments, there is measured the amount of chemical reaction that produces, in the calorimeter, a rise of temperature substantially equal to the selected "standard" rise of temperature. The relation used to evaluate the "reaction equivalent" is

$$(\text{reaction equivalent}) = \frac{\Delta t_r}{n}, \tag{50}$$

where Δt_r is the rise of temperature in the experiment with chemical energy (measured with the same thermometer over substantially the same range), and n is the number of moles of reaction measured by the mass and molecular weights of the substance that is used to determine the amount of reaction. From a series of such experiments, an average value of the reaction equivalent is determined.

The experimental value of the change in energy or heat content for the given reaction, per mole, is then evaluated by the product of Equations 49 and 50:

$$-q = \left(\frac{\text{electrical energy}}{n}\right)\left(\frac{\Delta t_r}{\Delta t_e}\right). \tag{51}$$

---

* The energy equivalent is substantially the same as that which in the early days was called the heat capacity of the calorimeter, but the latter designation is not recommended because it implies that the investigator has a knowledge of the actual physical boundaries of the material system to which the heat capacity is ascribed, and that the heat-capacity of the calorimeter may be evaluated by a summation of the heat capacities of its component parts.

It will be noted from Equation 51 that the rises of temperature in the two kinds of experiments substantially cancel. It follows that the temperature need be known in an accurate sense, as distinguished from precision of differences, only to the extent required to specify the temperature to which the measured thermodynamic property is to be assigned.

Examples of exothermal reactions for which the decrease in energy or heat content may be measured in the above way are those of the following kinds: Combustion of a gaseous, liquid, or solid substance in oxygen, as the combustion of gaseous methane, or liquid normal octane, or solid normal octadecane, in oxygen to form gaseous carbon dioxide and liquid water; solution of a gaseous, liquid, or solid substance in a liquid solvent, as the solution of hydrogen chloride in water to form aqueous hydrochloric acid, or the solution of liquid sulfuric acid in water to form aqueous sulfuric acid, or the solution of solid potassium hydroxide in water to form aqueous potassium hydroxide; neutralization, in the liquid phase, of an acid with a base, as the neutralization of aqueous nitric acid with aqueous sodium hydroxide to form aqueous sodium nitrate; reaction of a gaseous, liquid, or solid substance with a liquid to form an aqueous solution, with or without a gaseous product or solid product, as the reaction of solid sodium with liquid water to form aqueous sodium hydroxide and gaseous hydrogen; reaction of two gaseous substances to form a gaseous product, as in the hydrogenation or chlorination of ethylene; formation of a gaseous, liquid, or solid product from its elements, gaseous, liquid, or solid, as in the formation of liquid water from gaseous hydrogen and oxygen, or the formation of gaseous sulfur dioxide from solid sulfur and gaseous oxygen, or the formation of solid sodium chloride from solid sodium and gaseous chlorine, or the formation of gaseous hydrogen chloride from gaseous hydrogen and chlorine.

If the reaction or process is an endothermal one, that is, absorbs heat energy as it takes place, then, in principle, the method is simplified. In this case, a measured quantity of electrical energy is added to the calorimeter system in an amount that is just sufficient to maintain the temperature constant, balancing the energy absorbed by the reaction or process as it proceeds. This is illustrated schematically in Figure 2. For this experiment, the initial and final states of the calorimeter system are the same and the calorimeter neither absorbs nor gives up energy. In this way, a direct equivalence (except for sign) is obtained between the measured amount of electrical energy and the measured amount of the given reaction or process.

Examples of endothermal reactions or processes for which the increase in energy or heat content may be measured isothermally in the above way include any reactions of the kinds mentioned earlier which may be endothermal, together with endothermal reactions of the following types: decomposition of a gaseous substance into gaseous, liquid, or solid products, as the decomposition of gaseous lead tetramethyl into solid lead and gaseous ethane; vaporization of a liquid substance to the gaseous state, as the vaporization of liquid water to gaseous water; sublimation of a solid substance to the gaseous state, as the sublimation of the solid octane, 2,2,3,3-tetramethylbutane; melting or fusion of a solid substance to the liquid state, as the melting or fusion of water ice to liquid water; transition of a solid substance from one stable crystalline form to another, as the transition of carbon tetrachloride from crystalline form II to crystalline form I.

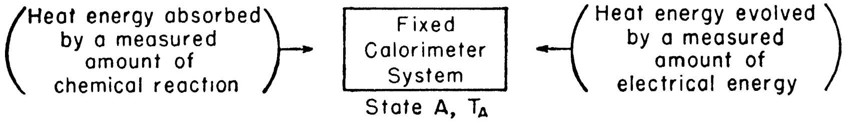


FIGURE 2. Schematic diagram of the thermochemical method of determining the heats of endothermal reactions.

When exothermal reactions are to be measured, and the investigator does not have available apparatus for measuring the electrical energy with adequate accuracy, there may be substituted for the experiments with electrical energy calibrating experiments with a similar chemical reaction the decrease in energy or heat content of which has previously been determined accurately in another laboratory. It is preferable that such calibrating reactions be ones which have been agreed upon by the leading investigators in the field.

Examples of the use of such calibrating reactions are the following: evaluation of the "energy equivalent" of a calorimeter system in which the reaction vessel is a closed bomb, using the combustion of standard benzoic acid under certain standardized conditions; evaluation of the "energy equivalent" of a calorimeter system in which the reaction vessel is one designed to burn gases in a flame at constant pressure, using the combustion of hydrogen in oxygen to form water; evaluation of the "energy equivalent" of a calorimeter system for measuring heats of solution of solids in water to form aqueous solutions, using the solution of a solid the heat of solution of which has been previously accurately determined.

Similarly, for endothermal reactions, if the investigator does not have available apparatus for measuring electrical energy with adequate accuracy, it is possible to determine the ratio of the amount of the given reaction or process to the amount of a calibrating reaction or process associated with the same quantity of energy. This may be done either by ascertaining what amount of the calibrating reaction is needed to produce the same change (decrease) in the temperature of the calorimeter system, as is produced by a known amount of the given reaction, or by ascertaining what amount of the given reaction is brought about by identically the same, but not accurately measured, amount of electrical energy as is needed to bring about a known amount of the calibrating reaction.

In processes involving no chemical reaction as such, and where the substance under investigation does not change its state, as in the determination of the heat capacity of a liquid or a solid substance, the experiment involves measurement of the energy required to produce a measured change of temperature for the substance and the container. In such cases, the "energy equivalent" or heat capacity of the containing vessel must be accounted for. The most reliable way of doing this is to perform two sets of experiments, in one of which the calorimetric container is full of the substance under investigation and in the other of which the container contains only a small amount of the given substance. The difference in the two sets of experiments serves, in effect, to determine the heat capacity of that amount of the given substance corresponding to the difference in mass of the two charges. With such a procedure, the container is under more nearly identical conditions than would exist if the container were measured actually empty in the second set of experiments.

For any of the cases where a calibrating reaction or process is used, for energy either evolved or absorbed, it is possible, in principle, to devise a twin calorimeter arrangement, wherein the values of the "energy equivalent" of the two calorimeters are the same or have a known ratio one to the other. With such an apparatus, the given reaction and the calibrating reaction are run simultaneously, and the experiment serves, in effect, to determine the ratio of the amounts of the two reactions with which equal amounts of energy or heat content are associated.

6. Chemical part of the thermochemical investigation. In the chemical part of the thermochemical investigation, it is necessary first to establish that the actual reaction or process that occurs is the specified one, and second to measure with the necessary accuracy the amount of the given reaction or process that occurs in each experiment for which the heat energy has been evaluated.

In the examination of the purity of the chemical reaction being studied, the investigator should demonstrate with reasonable certainty, by means of appropriate chemical or physical tests, that the reaction which actually occurs in the calorimetric reaction vessel is one that does not differ significantly from the theoretically pure reaction. Or, if there is a side reaction, the amount and effect of it must be evaluated with the necessary accuracy.

Having first decided that the reaction being studied is reasonably complete and clear cut, one can investigate the purity of the reaction as it actually occurs in the reaction vessel in the calorimeter, first by establishing the purity of the reacting substances, and second by examining the products of the reaction for the presence of possible foreign substances. The permissible amounts of impurities in the reacting substances, and the permissible amounts of side reactions, depend to a large extent upon the method by which the amount of the reaction is determined and upon the amount of heat energy contributed by the side reactions involved.

One of the vital points in any thermochemical investigation is the method of determining the amount of chemical reaction that occurs in any given experiment. The method selected should be precise and accurate with respect to true mass, and the amount should be accurately expressible in terms of moles. This latter requirement involves an accurate knowledge of the molecular weight of the substance whose mass determines the amount of reaction. Suppose, for example, the reaction being studied is

$$C_6H_{14}\ (\text{liq}) + 9\tfrac{1}{2}O_2\ (\text{g}) = 6CO_2\ (\text{g}) + 7H_2O\ (\text{liq}). \qquad (52)$$

In such a case, the amount of the reaction may be measured from the mass of hexane consumed, the mass of carbon dioxide formed, or the mass of water formed. For each mole of hexane consumed, the corresponding masses are hexane, 86.172 g; carbon dioxide, 264.060 g; and water, 126.112 g. If the atomic weight of each element involved is known without significant uncertainty, and if the true mass in grams is capable of being determined with about the same absolute uncertainty in each case, it is obvious that the substance whose mass should determine the amount of reaction in moles is, in order of preference, carbon dioxide, water, and hexane. If the mass of hexane is used, correction must be made for the small amount of water and air that may be dissolved in the sample.

Another point which needs consideration is that the determination of the amount of reaction from the mass of one substance, rather than that of another, may make permissible a greater amount of certain impurities in one of the reacting substances. An example of this situation is in the combustion of ethanol in oxygen,

$$C_2H_5OH\ (\text{liq}) + 3\tfrac{1}{2}O_2\ (\text{g}) = 2CO_2\ (\text{g}) + 3H_2O\ (\text{liq}). \qquad (53)$$

In this case, it would be unwise to determine the amount of reaction from the mass of the ethanol itself, or from the mass of water formed, without first establishing beyond reasonable doubt that the sample contained no water.

On the other hand, the determination of the amount of reaction from the mass of carbon dioxide produced would make permissible the presence, in the ethanol, of a relatively large amount of water without introducing a significant error other than that of the heat of solution of the impurity of liquid water in the ethanol, which can be corrected for.

From the foregoing discussion, it is clear that the correction of values of molal heats of reaction by reason of changes in molecular weights must be done in each case with regard to the change in the molecular weights of the particular substance whose mass was used to determine the amount of reaction. If the molecular weight of this "determining" substance has not changed, no change in the value of the molal heat of reaction is necessary.

7. Corrections to reference or standard states. For purposes of intercomparison and tabulation of data on the energies or heats of reactions and processes, it is desirable that each substance participating in the given reaction or process be corrected to an appropriate reference or standard state. For example, with regard to energy or heat content, it is convenient and desirable to select for the reference state at the given temperature, say 25°C, the pure liquid or solid substance at an actual pressure of 1 atmosphere and the gas in the ideal state at 1 atmosphere. Appropriate other reference states are required for aqueous and other solutions.

For every reaction or process that takes place in a calorimeter, it is imperative that significant data be recorded as to the phase, pressure, temperature, and concentration of each of the substances at the beginning and at the end of the reaction. A study of each reaction will indicate with what significance the various properties must be known and recorded.

Consider, for example, the reaction that actually takes place in the calorimeter during the combustion of pure liquid normal heptane in oxygen in a closed bomb. In this experiment, a small amount of water is initially placed in the bottom of the bomb; the sample of hydrocarbon, usually about 1 gram, is contained in a suitable ampoule in a dish held near the lower center of the bomb; the temperature will usually be near 25°C, with a rise of several degrees; and the pressure will usually be near 30 atmospheres, with a change of several atmospheres. The reaction that actually occurs in the calorimetric bomb may be described by the following equation:

$$\begin{aligned} &\mathrm{C_7H_{16}}\ (\mathrm{liq}, P_A) + [(a - y)\mathrm{O_2} + x\mathrm{H_2O}]\ (\mathrm{g}, P_A) \\ &\qquad\qquad + [(b - x)\mathrm{H_2O} + y\mathrm{O_2}]\ (\mathrm{liq}, P_A) = \\ &\quad [(7 - w)\mathrm{CO_2} + (a - 11 - z)\mathrm{O_2} + v\mathrm{H_2O}]\ (\mathrm{g}, P_B) \\ &\qquad + [(8 + b - v)\mathrm{H_2O} + z\mathrm{O_2} + w\mathrm{CO_2}]\ (\mathrm{liq}, P_B). \qquad (54) \end{aligned}$$

The calorimetrically determined value of the heat energy associated with this process is a measure of ΔE for the actual reaction represented by Equation 54. This complex reaction is to be compared with the simple reaction for which the change in energy is required:

$$\begin{aligned} &\mathrm{C_7H_{16}}\ (\mathrm{liq, 1\ atm}) + 11\mathrm{O_2}\ (\mathrm{g, ideal, 1\ atm}) \\ &\qquad = 7\mathrm{CO_2}\ (\mathrm{g, ideal, 1\ atm}) + 8\mathrm{H_2O}\ (\mathrm{liq, 1\ atm}). \qquad (55) \end{aligned}$$

To pass from the complex reaction of Equation 54 to the simple one of Equation 55, it is necessary to correct each reactant and product from the state in which it occurs in Equation 54 to the reference state which it has in Equation 55. Such corrections will include the changes in energy with pressure for the various substances involved, the energy of solution of oxygen and carbon dioxide in water, and the energy of vaporization of water.

8. Assignment of the temperature for the reaction or process. For every reaction or process which is carried out in a calorimeter and for which a value of the change in energy or heat content is determined, it is important to assign with adequate accuracy the value of temperature to which the given thermodynamic property is to be ascribed. In those experiments where each reactant enters the calorimeter, and each product leaves the calorimeter, on the average, at the mean temperature of the experiment, the value of the given thermodynamic property may usually be assigned to the mean of the initial and final temperatures of the calorimeter in the given experiment.

On the other hand, if the reaction takes place in a system such that all the reactant material is in the calorimeter at the beginning of the experiment at the initial temperature, T_A, and all the product material is in the calorimeter at the end of the experiment at the final temperature, T_B, one has a choice of using as the assigned temperature of the given property the initial temperature, T_A, the final temperature, T_B, or the mean temperature, $(T_A + T_B)/2$. If the energy equivalent of the calorimeter is taken as that of the final system, then the assigned temperature is the initial temperature. If the energy equivalent of the calorimeter is taken as that of the initial system, then the assigned temperature is the final temperature. If the energy equivalent of the calorimeter is taken as the mean of the initial and final systems, then the assigned temperature is the mean of the initial and final temperatures. Actually, also, the assigned temperature may be any intermediate temperature provided the appropriate fractions of the initial and final systems are used to evaluate the energy equivalent of the calorimeter.

An example of a reaction in which the foregoing points are important is as follows: Given the reaction of neutralization of aqueous sodium hydroxide with aqueous hydrochloric acid to form aqueous sodium chloride, with the reaction occurring at constant pressure in a calorimeter, with an initial temperature of 20°C and a rise of 5°C to give a final temperature of 25°C. The reaction may be written as follows:

$$(NaOH \cdot 100H_2O)(liq, 20°C) + (HCl \cdot 100H_2O)(liq, 20°C) = (NaCl \cdot 201H_2O)(liq, 25°C). \quad (56)$$

One can proceed from the initial state to the final state in two simple ways.

The first way is given by the following two equations:

$$(NaOH \cdot 100H_2O)(liq, 20°C) + (HCl \cdot 100H_2O)(liq, 20°C) = (NaOH \cdot 100H_2O)(liq, 25°C) + HCl \cdot 100H_2O)(liq, 25°C); \quad (57)$$

$$(NaOH \cdot 100H_2O)(liq, 25°C) + (HCl \cdot 100H_2O)(liq, 25°C) = (NaCl \cdot 201H_2O)(liq, 25°C). \quad (58)$$

It is clear that, if the measured heat of the reaction is to be assigned to the final temperature, 25°C, the energy equivalent of the calorimeter must be determined in a separate experiment, on the initial system, before reaction occurs, over the range of temperature 20° to 25°C.

The second way is given by the following two equations:

$$(NaOH \cdot 100H_2O)(liq, 20°C) + (HCl \cdot 100H_2O)(liq, 20°C) = (NaCl \cdot 201H_2O)(liq, 20°C); \quad (59)$$

$$(NaCl \cdot 201H_2O)(liq, 20°C) = (NaCl \cdot 201H_2O)(liq, 25°C). \quad (60)$$

In this case, the heat of the reaction is to be ascribed to the initial temperature, 20°C, and the energy equivalent of the calorimeter must be determined in a separate experiment, on the final system, after reaction occurs, over the range of temperature, 20° to 25°C.

A third way of going from the initial to the final state for the reaction under discussion is given by the following three equations:

$$(NaOH \cdot 100H_2O)(liq, 20°C) + (HCl \cdot 100H_2O)(liq, 20°C) = (NaOH \cdot 100H_2O)(liq, 22.5°C) + (HCl \cdot 100H_2O)(liq, 22.5°C); \quad (61)$$

$$(NaOH \cdot 100H_2O)(liq, 22.5°C) + (HCl \cdot 100H_2O)(liq, 22.5°C) = (NaCl \cdot 201H_2O)(liq, 22.5°C); \quad (62)$$

$$(NaCl \cdot 201H_2O)(liq, 22.5°C) = (NaCl \cdot 201H_2O)(liq, 25°C). \quad (63)$$

In this last case, the heat of the reaction is to be ascribed to the mean temperature, 22.5°C, and the energy equivalent of the calorimeter system must be determined in two separate experiments, one on the initial system over the range of temperature 20° to 22.5°C, and one on the final system over the range of temperature 22.5° to 25°C.

9. Heats of formation. The ideal table of heats of reaction is one which will permit calculation of the heat of every possible chemical reaction. Obviously it would be impractical to list in a table every chemical reaction and its corresponding change in heat content, but the same end is accomplished by listing for each chemical substance its heat of formation from its elements in selected reference states. It is evident that, by proper selection, the number of chemical reactions whose heats must be measured will be about the same as the number of substances listed in the table. Some saving in the number of reactions to be measured will occur because of the correlations of energy with molecular structure which are possible among certain organic compounds, particularly hydrocarbons.

The value of the heat of formation of a given substance from its elements may be the result of the determination of the heat of one reaction, as for the heat of formation of liquid water:

$$H_2\ (g) + \tfrac{1}{2}O_2\ (g) = H_2O\ (liq). \tag{64}$$

For many other substances, however, the value will result from the measurement of the heats of a number of reactions, as for the heat of formation of crystalline sodium hydroxide:

$$Na\ (c) + H_2O\ (liq) = NaOH\ (aq) + \tfrac{1}{2}H_2\ (g); \tag{65}$$

$$H_2\ (g) + \tfrac{1}{2}O_2\ (g) = H_2O\ (liq); \tag{66}$$

$$NaOH\ (c) = NaOH\ (aq). \tag{67}$$

Addition of Equations 65 and 66 and subtraction of Equation 67 give the desired result:

$$Na\ (c) + \tfrac{1}{2}O_2\ (g) + \tfrac{1}{2}H_2\ (g) = NaOH\ (c). \tag{68}$$

Similarly the heat of formation of carbon monoxide is evaluated from data on the following reactions:

$$CO\ (g) + \tfrac{1}{2}O_2\ (g) = CO_2\ (g); \tag{69}$$

$$C\ (c, \text{graphite}) + O_2\ (g) = CO_2\ (g). \tag{70}$$

Subtraction of Equation 69 from Equation 70 gives

$$\text{C (c, graphite)} + \tfrac{1}{2}\text{O}_2\ \text{(g)} = \text{CO (g)}, \tag{71}$$

which is the desired result. In every case the reactions selected for measurement must be ones that can be made to proceed adequately and handled quantitatively in a calorimeter.

There are certain basic values in the table which will be used very frequently in the derivation of other values. These basic values, which should preferably be known with the highest accuracy, include the heats of formation of water, carbon dioxide, nitric acid, sulfuric acid, hydrogen chloride, hydrogen sulfide, etc. Because of this interdependence of many of the values of heats of formation, it is desirable that the basic values be carefully selected, and, when any change is made in any one of them, corresponding changes should be made in all the values which depend upon it. It is for this same reason that the addition or subtraction of values of heats of formation from different tables is a procedure fraught with uncertainty.

For the primary table of heats of formation of the chemical compounds, it is necessary to have a selected temperature and a reference state for each substance. For each element, the heat of formation is given as zero for that phase in which it naturally exists at the selected temperature, when it is in the reference state. As previously mentioned, for liquid and solid substances, the reference state is taken as the real state at a pressure of 1 atmosphere, while for gases the reference state is taken as the ideal gaseous state at 1 atmosphere.

10. Collateral reading. For further discussion of heats and energies of reaction and formation, their variation with temperature, and their experimental determination, see Lewis and Randall (*1*), Washburn (*2*), Sturtevant (*3*), Eckman and Rossini (*4*), Rossini (*5,6,7,8*), Prosen and Rossini (*9,10,11,12*), Prosen, Johnson, and Rossini (*13,14*), Bichowsky and Rossini (*15*), Rossini and Deming (*16*), Huffman and Ellis (*17*), Richards (*18*), Jessup (*19*), and Dickinson (*20*).

REFERENCES

1. G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill Book Company, New York, 1923.

2. E. W. Washburn, *J. Research Natl. Bur. Standards* **9**, 521 (1932).

3. J. M. Sturtevant, "Calorimetry," in *Physical Methods of Organic Chemistry*, Interscience Publishers, New York, 1945.

4. J. R. Eckman and F. D. Rossini, *J. Research Natl. Bur. Standards* **3**, 597 (1929).

5. F. D. Rossini, *J. Research Natl. Bur. Standards* **6**, 1 (1931); **7**, 329 (1931).

6. F. D. Rossini, *J. Research Natl. Bur. Standards* **9**, 679 (1932).

7. F. D. Rossini, *J. Research Natl. Bur. Standards* **12**, 735 (1934).

8. F. D. Rossini, *Chem. Revs.* **18**, 233 (1936).

9. E. J. Prosen and F. D. Rossini, *J. Research Natl. Bur. Standards* **27**, 289 (1941).

10. E. J. Prosen and F. D. Rossini, *J. Research Natl. Bur. Standards* **33**, 255 (1944).

11. E. J. Prosen and F. D. Rossini, *J. Research Natl. Bur. Standards* **34**, 263 (1945).

12. E. J. Prosen and F. D. Rossini, *J. Research Natl. Bur. Standards* **36**, 269 (1946).

13. E. J. Prosen, W. H. Johnson, and F. D. Rossini, *J. Research Natl. Bur. Standards* **36**, 455 (1946).

14. E. J. Prosen, W. H. Johnson, and F. D. Rossini, *J. Research Natl. Bur. Standards* **37**, 51 (1946).

15. F. R. Bichowsky and F. D. Rossini, *Thermochemistry of the Chemical Substances*, Reinhold Publishing Corporation, New York, 1936.

16. F. D. Rossini and W. E. Deming, *J. Wash. Acad. Sci.* **29**, 416 (1939).

17. H. M. Huffman and E. L. Ellis, *J. Am. Chem. Soc.* **57**, 41 (1935).

18. T. W. Richards, *J. Am. Chem. Soc.* **25**, 209 (1903).

19. R. S. Jessup, *J. Research Natl. Bur. Standards* **29**, 247 (1942).

20. H. C. Dickinson, *Bur. Standards Bull.* **11**, 189 (1915).

21. K. K. Kelley, *U. S. Bur. Mines Bull.* **371** (1934).

PROBLEMS

1. Write the chemical equation for a reaction in which 1 mole of solid sodium, at a pressure of 0.1 atm and a temperature of 0°C, reacts with 50 moles of liquid water, at a pressure of 1 atm and a temperature of 25°C, to form the resulting aqueous solution of sodium hydroxide, at a pressure of 1 atm and a temperature of 30°C, and gaseous hydrogen, at a pressure of 0.5 atm and a temperature of 30°C.

2. Specify the thermodynamic properties, and reactions, if any, measured in the following experiments and give the values in units of calories, degrees, and moles.

a. One mole of a gas MX is contained in a closed vessel. Electrical energy in the amount of 100 watt-seconds is introduced into the gas calorimetrically, with a resultant change in temperature of 2.00°C.

b. A given gas flows at a constant rate of 10 moles per hour through a long tube appropriately maintained in a calorimeter. The gas enters the tube at a pressure of 1.01 atm and a temperature of 24.50°C. Within the tube, electrical energy is introduced into the gas at the rate of $\frac{1}{6}$ watt. The gas leaves the calorimeter at a pressure of 0.99 atm and a temperature of 25.50°C. Assume no interchange of energy between the gas and its container and surroundings.

c. One mole of gaseous hydrogen and $\frac{1}{2}$ mole of gaseous oxygen are contained in a calorimeter in a closed bomb having a volume of 1000 cm^3. Under the influence of contact with a suitable catalyst, reaction occurs, and the heat energy evolved is determined calorimetrically to be *a* cal at the final temperature of the experiment, 25°C. The vapor pressure of liquid water at 25°C is 0.031222 atm.

d. A calorimeter is arranged with a suitable vessel for reaction in a flame at constant pressure. During the experiment, gaseous hydrogen and gaseous oxygen enter the system, each at a pressure of 1 atm and at a substantially constant rate, and gaseous water leaves the system at a pressure of 1 atm and at a substantially constant rate. The initial temperature of the calorimeter system is 102°C, and the final temperature is 104°C. The calorimetrically determined value of the heat energy associated with this reaction is *b* cal for each mole of water produced.

3. Given the following values:

$$\mathrm{H_2O\ (g) + CH_4\ (g) = CO\ (g) + 3H_2\ (g)},\ \Delta H^\circ_{400} = 50.354\ \mathrm{kcal/mole};$$

$$\mathrm{H_2O\ (g)},\ H^\circ_{400} - H_0^\circ = 3190.0,\ H^\circ_{1000} - H_0^\circ = 8580.0,\ \mathrm{cal/mole};$$

$$\mathrm{CH_4\ (g)},\ H^\circ_{400} - H_0^\circ = 3323,\quad H^\circ_{1000} - H_0^\circ = 11{,}560,\ \mathrm{cal/mole};$$

$$\mathrm{CO\ (g)},\ H^\circ_{400} - H_0^\circ = 2783.8,\ H^\circ_{1000} - H_0^\circ = 7256.5,\ \mathrm{cal/mole};$$

$$\mathrm{H_2\ (g)},\ H^\circ_{400} - H_0^\circ = 2731.0,\ H^\circ_{1000} - H_0^\circ = 6965.8,\ \mathrm{cal/mole}.$$

Calculate the value of ΔH_0° and ΔH°_{1000} for the given reaction.

4. Given the following values:

$$\mathrm{CO_2\ (g) + H_2\ (g) = CO\ (g) + H_2O\ (g)},\ \Delta H^\circ_{400} = 9.710\ \mathrm{kcal/mole};$$

$$\mathrm{CO_2\ (g)},\ C_P = 6.3957 + 0.0101933T - 0.0000035333T^2\ \mathrm{cal/deg\ mole};$$

$$\mathrm{H_2\ (g)},\ C_P = 6.9469 - 0.0001999T + 0.0000004808T^2\ \mathrm{cal/deg\ mole};$$

$$\mathrm{CO\ (g)},\ C_P = 6.3424 + 0.0018363T - 0.00000028017T^2\ \mathrm{cal/deg\ mole};$$

$$\mathrm{H_2O\ (g)},\ C_P = 7.1873 + 0.0023733T + 0.0000002084T^2\ \mathrm{cal/deg\ mole}.$$

Assuming the equations for heat capacity to be valid over the range 290° to 1000°K within the desired limits of uncertainty, derive a general equation giving the value of ΔH° for any temperature in the range 290° to 1000°K and calculate the value of ΔH° for 298.16°K.

5. Is it ever necessary now to know the actual heat capacity of water itself at any given temperature and pressure in order to measure the change in energy or heat content associated with a reaction or process?

6. State the principle of determining calorimetrically the energy or heat of a given reaction or process.

7. To what extent is it necessary to have calibrated, according to the

International Scale of Temperature, a platinum resistance thermometer which is to be used in a calorimeter for measuring heats of reaction?

8. Upon what depends the accuracy of the calorimetric part of a thermochemical investigation?

9. Upon what depends the accuracy of the chemical part of a thermochemical investigation?

10. Measurement is to be made, at a constant pressure of 1 atm, of the heat of solution of a solid, MX, in water to form the resulting aqueous solution, according to the reaction,

$$\text{MX (c)} + 50\text{H}_2\text{O (liq)} = (\text{MX} \cdot 50\text{H}_2\text{O})\text{(liq)}.$$

For the experiment in which the reaction occurs, the initial temperature of the calorimeter is 20°C and the final temperature is 25°C. In separate experiments, the investigator determines the "energy equivalent" of the calorimeter system for the initial state over the range 20° to 25°C. Write the specified reaction and property which have been determined in this investigation.

11. Starting from scratch, in each case, what series of reactions could be measured calorimetrically to evaluate the heat of formation of the following compounds from the elements, at 25°C: $CaCl_2 \cdot 6H_2O$ (c); C_2H_5OH (liq); CO (g); N_2O (g); C_6H_5Cl (chlorobenzene)(liq)?

12. In an investigation to determine the heat of formation of carbon dioxide from graphite and oxygen, the following observations were made with a closed bomb in a calorimeter in experiments in which both the average temperature and the range of temperature were substantially the same from experiment to experiment:

a. As the average value from a series of six experiments, the rise of temperature was such as to be equivalent to an increase of 0.0649920 ohm in the resistance of the particular platinum thermometer for each 1.00000 g of carbon dioxide formed in the combustion.

b. As the average value from a series of seven experiments, the ratio of the quantity of electrical energy (required to produce the standard change in temperature of the calorimeter system) to the corrected change in temperature of the calorimeter system was 137,740.1 joules per ohm increase in resistance of the platinum thermometer, when the calorimeter system was in its initial state.

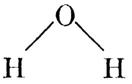
The initial and final temperatures of the experiments were 23.5° and 26.5°C, respectively. Calculate the value of ΔE, in kilocalories per mole of carbon dioxide formed, for the reaction as it occurred in the bomb calorimeter, and specify the temperature to which it applies.

19

Thermodynamic Functions from Statistical Calculations

1. General method. Theoretical and experimental investigations in physics and chemistry have yielded relatively simple pictures of the structure of individual molecules in the ideal gaseous state, that is, for the molecules at pressures sufficiently low that interactions between the molecules are negligible.

Consider, for example, the water molecule, H_2O, in the ideal gaseous state. The picture is one of a triangular shaped molecule



with the oxygen atom between and bonded to the two hydrogen atoms. The angle formed by the three atoms is 104°27′, and the centers of the hydrogen atoms are 0.958×10^{-8} cm from the center of the oxygen atom (*1*). The molecule has a total of 9 degrees of ordinary freedom, 3 times the total number of atoms in the molecule (see Chapter 15). Of these degrees of freedom, 3 are translational, 3 are rotational, and 3 are vibrational. (For a triatomic linear molecule, there would be only 2 degrees of freedom for rotation, and, since the total number of degrees of freedom and the number of degrees of freedom for translation are unchanged, there would be 4 degrees of freedom for vibration.)

In the simple case, we may consider that there is a complete set of discrete quantum levels of energy associated with each degree of freedom. Each set of levels of energy may be represented schematically by the diagram in Figure 1. The levels of energy are numbered as indicated, beginning with zero at the bottom, lowest, or ground level. The energy of each level is represented by $\epsilon_0, \epsilon_1, \epsilon_2, \epsilon_3, \cdots, \epsilon_i$. The multiplicity, or number of individual states of virtually the same energy existing at each level of energy, is given by $g_0, g_1, g_2, g_3, \cdots, g_i$. Although the individual states labeled for the same level actually have extremely small differences in energy, these differences become important only at extremely low temperatures, near 0°K. At any given temperature, the distribution of molecules among the possible states of energy is given by the Boltzmann distribution law:

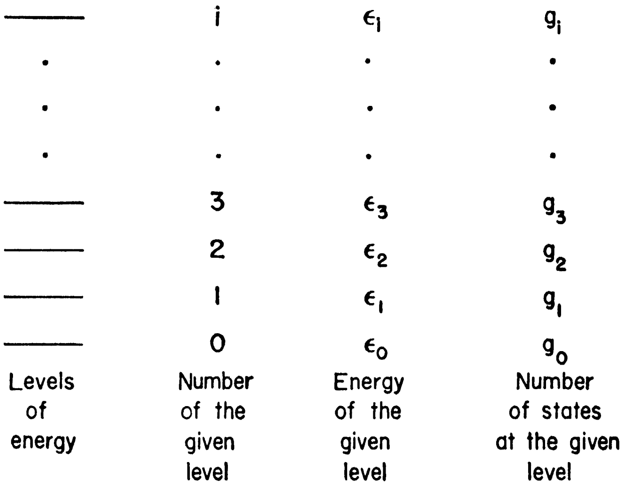


FIGURE 1. Schematic diagram of a set of levels of energy in a molecule.

$$n_i = n_0 e^{-(\epsilon_i - \epsilon_0)/kT}. \tag{1}$$

In this equation, n_i is the average number of molecules in each quantum state of energy ϵ_i, n_0 is the average number of molecules in each state at the ground level of energy ϵ_0, e is the base of the natural logarithms, k is the Boltzmann constant, and T is the absolute temperature.

Equation 1 gives the average of the population of each state of energy ϵ_i in terms of the population of a state at the ground level having an energy ϵ_0. The calculation requires only the specification of the temperature, T, and a knowledge of the difference in energy between the given level and the ground level, $\epsilon_i - \epsilon_0$. Simple application of Equation 1 indicates that as the temperature approaches the absolute zero the population tends to converge at the ground level, and that as the temperature becomes very large, in comparison with the value of

$(\epsilon_i - \epsilon_0)/k$, the population tends to become equally distributed over all the possible states of energy. When the value of T is very large in comparison to $(\epsilon_i - \epsilon_0)/k$, the degree of freedom giving rise to the particular set of energy levels is said to be fully "excited" to its classical value.

The order of magnitude of the spacing of the levels of energy near the ground level for the sets of levels of energy arising from the ordinary degrees of freedom is approximately as follows, in calories per mole: translational, 10^{-21}; rotational, 10 to 100; vibrational, 1000 to 10,000. From the foregoing, it may be readily seen that the translational degrees of freedom will be fully "excited" to their classical values even at extremely low temperatures, and that the rotational degrees of freedom will tend to be fully excited near room temperature, where most of the molecules will be in the ground state of vibrational energy.

At sufficiently high temperatures, we need to consider, in addition to translation, rotation, and vibration, also the degrees of freedom arising from the excitation of the valence electrons in the molecule, which gives rise to a set of levels of electronic energy. It may be readily calculated that the population of molecules in an electronic state having an energy of 10 kcal/mole, referred to the ground level, will usually be entirely negligible at ordinary temperatures.

In Figure 2 is shown a representative diagram of levels of energy, taken from Johnston and Chapman (*2*), showing for the diatomic molecule, NO, the levels of rotational energy, vibrational energy, and electronic energy. The two low-lying electronic states are to be noted.

An example of the shift in population among the vibrational levels of energy of a gaseous diatomic molecule in the ideal state as a function of temperature is given in Table 1, which presents the results of some calculations made by Johnston and Chapman (*2*) on nitric oxide. In this molecule, the first vibrational level is near 5350 cal/mole above the ground level, and the calculations show that, at room temperature, the population of the first vibrational is only 1 in 10,000 of that in the ground level. Table 1 shows how, with increasing temperature, the population shifts to the higher levels.

The entire method of calculating the thermodynamic properties of a given molecule statistically is based on the fact that it is possible to calculate the energy of one mole of molecules at any given temperature in the ideal gaseous state. This calculation may be repeated for all temperatures of interest. Once the energy is known as a function of the temperature, the other basic thermodynamic properties may be evaluated through the regular thermodynamic relations:

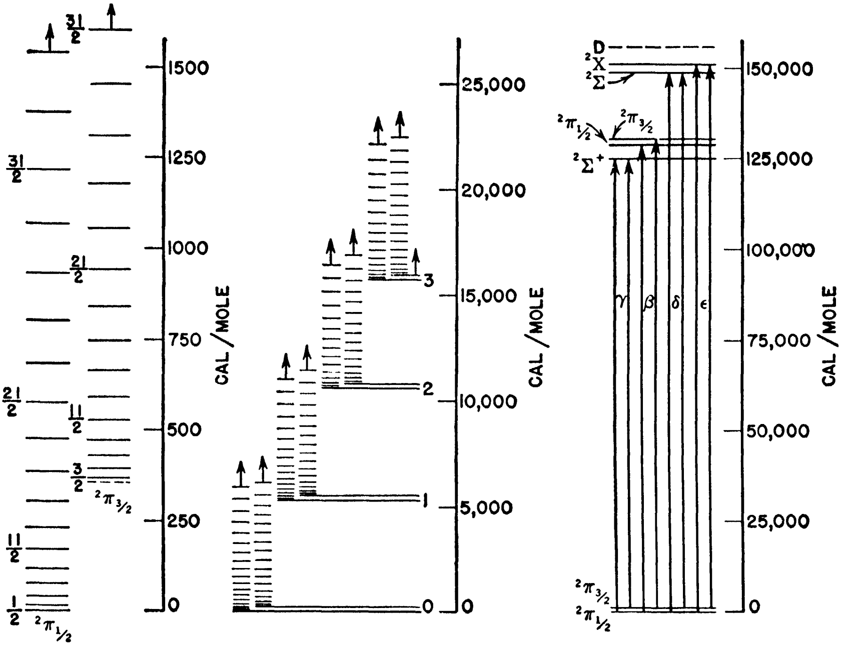


FIGURE 2. Diagram showing the levels of rotational, vibrational, and electronic energy for the molecule, nitric oxide, NO. From Johnston and Chapman (2).

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V; \tag{2}$$

$$S = \int \left(\frac{\partial E}{\partial T}\right)_V \mathrm{d} \ln T. \tag{3}$$

From Table 1, it may be seen how the total vibrational energy possessed by one mole of nitric oxide in the ideal gaseous state may be summed. The calculation requires first the calculation, for each temperature, of the fractional population at each level, covering as many vibrational levels, beginning with the ground

TABLE 1. POPULATION OF THE VIBRATIONAL LEVELS OF ENERGY OF THE DIATOMIC MOLECULE, NITRIC OXIDE, NO, IN THE IDEAL GASEOUS STATE, AS A FUNCTION OF TEMPERATURE

From Johnston and Chapman (*2*)

Number of the Vibrational Level	Temperature, °K									
	300	400	500	600	800	1000	2000	3000	4000	5000
	Mole Fraction									
0	0.9999	0.9988	0.9953	0.9886	0.9647	0.9311	0.7344	0.5832	0.4777	0.4020
1	.0001	.0012	.0047	.0113	.0339	.0640	.1936	.2406	.2466	.2373
2	.0000	.0000	.0000	.0001	.0013	.0046	.0521	.1007	.1286	.1413
3				.0000	.0001	.0003	.0143	.0427	.0677	.0848
4					.0000	.0000	.0040	.0183	.0361	.0513
>4							.0016	.0145	.0433	.0833

level, as have any significant population. Then there is summed the product of the population times the energy at each level, referred to the ground level, counted for each state at each level.

For our calculation, we take the total number of molecules as one mole, N. Then at a given temperature

$$N = \sum n_i g_i. \tag{4}$$

Substituting the value of n_i from Equation 1 gives

$$N = \sum n_0 g_i e^{-(\epsilon_i - \epsilon_0)/kT}, \tag{5}$$

or, since, at the given temperature n_0 is constant, Equation 5 may be solved for n_0 to give

$$n_0 = \frac{N}{\sum g_i e^{-(\epsilon_i - \epsilon_0)/kT}}. \tag{6}$$

The population of each state at the ground level at any temperature is thus given in terms of known factors, namely, N, g_i, $\epsilon_i - \epsilon_0$, k, and T.

Combination of Equations 1 and 6 permits calculation of the population of each state at the level, i, in terms of known factors:

$$n_i = \frac{N(e^{-(\epsilon_i - \epsilon_0)/kT})}{\sum g_i e^{-(\epsilon_i - \epsilon_0)/kT}}. \tag{7}$$

The total energy of one mole of molecules, referred to the ground level, is then at the given temperature:

$$E - E_0 = \sum n_i g_i (\epsilon_i - \epsilon_0). \tag{8}$$

Substituting into Equation 8 the value for n_i given by Equation 7 yields for the energy at the given temperature

$$E - E_0 = \frac{N[\sum g_i (\epsilon_i - \epsilon_0) e^{-(\epsilon_i - \epsilon_0)/kT}]}{\sum g_i e^{-(\epsilon_i - \epsilon_0)/kT}}. \tag{9}$$

In order to simplify the writing of Equation 9 and the other equations that may be derived from it, we may use the following abbreviations (*2*):

$$A_i = g_i e^{-(\epsilon_i - \epsilon_0)/kT}; \tag{10}$$

$$B_i = (\epsilon_i - \epsilon_0) A_i; \tag{11}$$

$$D_i = (\epsilon_i - \epsilon_0) B_i = (\epsilon_i - \epsilon_0)^2 A_i. \tag{12}$$

It may be noted that

$$\frac{dA_i}{dT} = \frac{B_i}{kT^2}, \tag{13}$$

and

$$\frac{dB_i}{dT} = \frac{D_i}{kT^2}. \tag{14}$$

The sum of the A_i terms over all levels is called the partition function, and, for any temperature, is equal to the series

$$\sum A_i = A_0 + A_1 + A_2 + A_3 + \cdots, \tag{15}$$

or

$$\sum A_i = g_0 + g_1 e^{-(\epsilon_1 - \epsilon_0)/kT} + g_2 e^{-(\epsilon_2 - \epsilon_0)/kT} + \cdots. \tag{16}$$

With these abbreviations, the energy of one mole of molecules, in the given set of levels of energy, at the temperature T, as given by Equation 9, is

$$E - E_0 = N \frac{\sum B_i}{\sum A_i}. \tag{17}$$

Since the calculation is being made for the molecules in the ideal gaseous state, and, for simplicity, at unit pressure, we can indicate this by the appropriate superscript on the symbol for the energy, so that Equation 17 may be written as

$$E^\circ - E_0^\circ = N \frac{\sum B_i}{\sum A_i}. \tag{18}$$

2. Thermodynamic properties and functions calculated. Once the energy of one mole of molecules is known as a function of the temperature, then the other thermodynamic functions may be evaluated from the regular thermodynamic relations. As will become evident later, it is convenient to evaluate the following five thermodynamic properties or functions of the given substance in the ideal gaseous state of unit pressure:

$\dfrac{H^\circ - H_0^\circ}{T}$, the heat content (or enthalpy) function; (19)

$\dfrac{F^\circ - H_0^\circ}{T}$, the free energy function; (20)

$S°$, the entropy; (21)

$H° - H_0°$, the heat content (or enthalpy); (22)

$C_P°$, the heat capacity at constant pressure. (23)

In the foregoing symbols, the superscript ° denotes the ideal gaseous reference state and the subscript 0 denotes the absolute zero of temperature.

For one mole of molecules in the ideal gaseous state, the following relations hold:

$$PV = RT; \tag{24}$$

$$H° = E° + (PV)° = E° + RT; \tag{25}$$

$$F° = E° + (PV)° - TS° = E° + RT - TS°; \tag{26}$$

$$C_P° = C_V° + R = \left(\frac{\partial E°}{\partial T}\right)_V + R. \tag{27}$$

At 0°K, Equation 25 reduces to

$$H_0° = E_0°. \tag{28}$$

Subtracting Equation 28 from Equation 25 and dividing by T, we obtain

$$\frac{H° - H_0°}{T} = \frac{E° - E_0°}{T} + R, \tag{29}$$

which, in terms of the statistically evaluated quantities is, for each set of levels of energy or each degree of freedom,

$$\frac{H° - H_0°}{T} = R + \left(\frac{N}{T}\right)\left(\frac{\sum B_i}{\sum A_i}\right). \tag{30}$$

The heat content is obtained by multiplying the heat content function by the temperature:

$$H° - H_0° = RT + N\frac{\sum B_i}{\sum A_i}. \tag{31}$$

The heat capacity, $C_V°$, is obtained by differentiating Equation 18 with temperature,

$$C_V° = \left[\frac{\partial(E° - E_0°)}{\partial T}\right]_V, \tag{32}$$

or

$$C_V{}^\circ = N\left[\sum A_i\frac{\mathrm{d}(\sum B_i)}{\mathrm{d}T} - \sum B_i\frac{\mathrm{d}(\sum A_i)}{\mathrm{d}T}\right]\frac{1}{(\sum A_i)^2}$$

$$= \left(\frac{N}{kT^2}\right)\left[\frac{\sum D_i}{\sum A_i} - \left(\frac{\sum B_i}{\sum A_i}\right)^2\right]. \qquad (33)$$

The heat capacity, $C_P{}^\circ$, is then

$$C_P{}^\circ = R + \left(\frac{N}{kT^2}\right)\left[\frac{\sum D_i}{\sum A_i} - \left(\frac{\sum B_i}{\sum A_i}\right)^2\right]. \qquad (34)$$

From the definition of the free energy, we can write, for one mole of our molecules in the ideal gaseous standard state,

$$F^\circ = E^\circ + (PV)^\circ - TS^\circ = H^\circ - TS^\circ. \qquad (35)$$

Subtracting $H_0{}^\circ$ from both sides and dividing by T gives the free energy function as

$$\frac{F^\circ - H_0{}^\circ}{T} = \frac{H^\circ - H_0{}^\circ}{T} - S^\circ. \qquad (36)$$

Substituting for the terms on the right side their equivalents from Equations 3 and 29, and taking the entropy at the absolute zero of temperature equal to zero (see next section), we obtain

$$\frac{F^\circ - H_0{}^\circ}{T} = R + \frac{E^\circ - E_0{}^\circ}{T} - \int_0^T \left[\partial\left(\frac{E^\circ - E_0{}^\circ}{\partial T}\right)\right]_V \mathrm{d}\ln T. \qquad (37)$$

But the last term on the right side may, for an ideal gas, be simplified to

$$\int_0^T \frac{1}{T}\,\mathrm{d}(E^\circ - E_0{}^\circ), \qquad (38)$$

and we may write Equation 37 as

$$\frac{F^\circ - H_0{}^\circ}{T} = R + \frac{1}{T}(E^\circ - E_0{}^\circ) - \int_0^T \frac{1}{T}\,\mathrm{d}(E^\circ - E_0{}^\circ). \qquad (39)$$

But the last two terms on the right side may be combined in accordance with the mathematical relation*

$$xy - \int y \, \mathrm{d}x = \int x \, \mathrm{d}y. \tag{40}$$

Then

$$\frac{F^\circ - H_0^\circ}{T} = R + \int_0^T (E^\circ - E_0^\circ) \, \mathrm{d}\left(\frac{1}{T}\right). \tag{41}$$

But from Equation 18

$$E^\circ - E_0^\circ = N \frac{\sum B_i}{\sum A_i}, \tag{42}$$

and from Equation 13,

$$\sum B_i = kT^2 \frac{\mathrm{d}(\sum A_i)}{\mathrm{d}T}. \tag{43}$$

Combination of Equations 42 and 43 gives

$$E^\circ - E_0^\circ = (NkT^2)\left(\frac{1}{\sum A_i}\right)\frac{\mathrm{d}(\sum A_i)}{\mathrm{d}T}, \tag{44}$$

or

$$E^\circ - E_0^\circ = RT^2 \frac{\mathrm{d} \ln \sum A_i}{\mathrm{d}T}, \tag{45}$$

or

$$E^\circ - E_0^\circ = -R \frac{\mathrm{d} \ln \sum A_i}{\mathrm{d}\left(\frac{1}{T}\right)}. \tag{46}$$

Hence

$$(E^\circ - E_0^\circ) \, \mathrm{d}\left(\frac{1}{T}\right) = -R \, \mathrm{d} \ln \sum A_i, \tag{47}$$

---

* Differentiation of the product xy gives

$$\mathrm{d}(xy) = x \, \mathrm{d}y + y \, \mathrm{d}x.$$

Integration of each term gives

$$xy = \int x \, \mathrm{d}y + \int y \, \mathrm{d}x.$$

Transposition gives the desired result

$$\int x \, \mathrm{d}y = xy - \int y \, \mathrm{d}x.$$

and

$$\int_0^T (E^\circ - E_0^\circ)\, \mathrm{d}\left(\frac{1}{T}\right) = -R\int_0^T \mathrm{d} \ln \textstyle\sum A_i. \tag{48}$$

But

$$\int_0^T \mathrm{d} \ln \textstyle\sum A_i = [\ln \sum A_i]_T - [\ln \sum A_i]_{T=0}. \tag{49}$$

From Equations 15 and 16, the value of $\sum A_i$ for $T = 0$ would appear to be equal to the multiplicity of the ground level:

$$\textstyle\sum A_i = A_0 = g_0. \tag{50}$$

But at a temperature sufficiently near the absolute zero, when g_0 is greater than unity, cognizance must be taken of the fact that the several states at the ground level actually have small differences in energy, which become significant in comparison with kT as T approaches zero. Therefore, as T approaches zero, the ground level may be treated as a series of levels of energy, g_0 in number, with one of them being lowest in energy. Giving this last one the number 00 and the others numbers 01, 02, etc., up to $0g_0$, the value of the partition function at the absolute zero reduces to

$$\textstyle\sum A_i = A_{00} = g_{00} = 1. \tag{51}$$

Therefore

$$[\ln \textstyle\sum A_i]_{T=0} = 0, \tag{52}$$

and Equation 48 becomes

$$\int_0^T (E^\circ - E_0^\circ)\, \mathrm{d}\left(\frac{1}{T}\right) = -R\int_0^T \mathrm{d} \ln \textstyle\sum A_i = -R \ln \sum A_i. \tag{53}$$

Then Equation 41 becomes

$$\frac{F^\circ - H_0^\circ}{T} = R - R \ln \textstyle\sum A_i. \tag{54}$$

From Equation 36, the entropy may be written as the heat content function less the free energy function,

$$S^\circ = \frac{H^\circ - H_0^\circ}{T} - \frac{F^\circ - H_0^\circ}{T}, \tag{55}$$

and may be evaluated from these latter functions if their values have already been calculated. In terms of the components of the statistical calculations,

$$S^\circ = \left(\frac{N}{T}\right)\left(\frac{\sum B_i}{\sum A_i}\right) + R \ln \sum A_i. \tag{56}$$

From Equations 30, 34, 42, 54, and 55, it may be seen that the free energy function, as given by Equation 54, is the thermodynamic property most easily calculated statistically because it involves only the simple summation of the series of terms of A_i.

From the foregoing, it is seen that when the complete diagram of levels of energy is known for each degree of freedom for a given molecule in the ideal gaseous state, the value of each thermodynamic function may be calculated in a straightforward manner for each set of levels of energy and summed for all the different sets of levels of energy, one for each degree of freedom in the molecule. That is, the overall value of a given thermodynamic property, G, is, for example,

$$\begin{aligned} G = G \text{ (translation)} &+ G \text{ (rotation)} \\ &+ G \text{ (vibration)} + G \text{ (electronic)}. \end{aligned} \tag{57}$$

In summing the several contributions to obtain the overall value of the given thermodynamic property, it is important to note that, in the case of the heat content function, $(H^\circ - H_0^\circ)/T$, and the free energy function, $(F^\circ - H_0^\circ)/T$, the value of the gas constant R, which arises from the substitution of PV by RT and subsequent division by T, is counted for the entire molecule in the contribution from the translational degrees of freedom and is not to be included again with any of the other contributions. That is to say, for the contributions following translation, the heat content function would be given by the term $(N/T)(\sum B_i/\sum A_i)$, from Equation 30, and the free energy function would be given by the term $-R \ln \sum A_i$, from Equation 54.

It is important to note that the thermodynamic properties evaluated statistically are values of the several given thermodynamic properties for a given substance in the ideal gaseous state, with reference to the value of that given property at the absolute zero of temperature, except for the property of the heat capacity. For the properties of the entropy and the free energy function, the reference values at the absolute zero of temperature are zero. For the heat capacity, which is the temperature coefficient of the energy, the differentiation eliminates the constant of reference. For the energy, $E^\circ - E_0^\circ$, or the heat content, $H^\circ - H_0^\circ$, the reference value is of course the absolute energy content, $E_0^\circ = H_0^\circ$, of the given substance in the ideal gaseous state at the absolute zero of temperature. Statistical calculations do not evaluate the difference in energy content of different molecules, which difference, if known, would permit the calculation of the heat of any reaction involving the given molecules.

3. Entropy at the absolute zero of temperature. From Equation 56, we have the entropy given as

$$S^\circ = \left(\frac{N}{T}\right)\left(\frac{\sum B_i}{\sum A_i}\right) + R \ln \sum A_i, \tag{58}$$

with the assumption having been made in deriving Equation 37 that

$$S_0^\circ = 0. \tag{59}$$

As the temperature approaches the absolute zero of temperature, both the terms on the right side of Equation 58 approach zero. In the simple picture presented above, the given pure substance is in the ideal gaseous state and the molecules are distributed among the various states of the given set of levels of energy at the given temperature according to the Boltzmann distribution law. By this simple picture, we would have, at the absolute zero of temperature, all the molecules in the lowest state at the ground level. From Chapter 11, we have seen that the entropy may also be defined as

$$S = k \ln W, \tag{60}$$

where W is the probability of existence and corresponds to the number of states of existence available to the system. If there is only one state available, as at the absolute zero of temperature according to the simple picture presented above, then W is unity, its logarithm is zero, and, as before,

$$S_0^\circ = 0. \tag{61}$$

Each of the possible sets of levels of energy or degrees of freedom would be treated in the same way, and the entropy at the absolute zero of temperature would be the sum of the several contributions, each of which, according to the simple picture, would have the value zero.

At this point, it is necessary to point out that actually at very low temperatures the Boltzmann distribution law must be replaced by that of the Einstein-Bose statistics or the Fermi-Dirac statistics, in accordance with the requirements of the given system (*3*). However, the net result is the same as far as the entropy at the absolute zero is concerned, in that, in each case, the ideal gaseous molecules at the absolute zero of temperature have only one state of existence available to them and the entropy has the value zero.

4. Contributions from the translational degrees of freedom. The levels of energy associated with the 3 translational degrees of freedom, for a particle of mass m in the ideal gaseous state in a cubic space of volume V, are given by the expression (*3*).

$$(\epsilon_i - \epsilon_0)(\text{translation}) = (n_x^2 + n_y^2 + n_z^2)\frac{h^2}{8mV^{2/3}}, \tag{62}$$

where h is the Planck constant, and n_x, n_y, and n_z are integral positive quantum numbers associated with the 3 coordinates of the system, x, y, and z, and have values running from 0 to infinity.

For convenience, we let

$$s^2 = \frac{h^2}{8mV^{2/3}}, \tag{63}$$

so that Equation 62 becomes

$$(\epsilon_i - \epsilon_0)(\text{translation}) = (n_x^2 + n_y^2 + n_z^2)s^2. \tag{64}$$

Then, for the 3 degrees of translational freedom, the partition function is

$$\begin{aligned}\sum A_i(\text{translation}) &= \sum_0^\infty e^{-(n_x^2+n_y^2+n_z^2)\,s^2/kT}\\ &= \left(\sum_0^\infty e^{-n_x^2s^2/kT}\right)\left(\sum_0^\infty e^{-n_y^2s^2/kT}\right)\left(\sum_0^\infty e^{-n_z^2s^2/kT}\right).\end{aligned} \tag{65}$$

For ordinary values of V and T, and masses corresponding to that of the hydrogen atom or greater, the successive terms in each series change very slowly with n and each summation may be replaced by an integration. Thus

$$\sum_0^\infty e^{-n^2 s^2/kT} = \int_0^\infty e^{-n^2 s^2/kT}\,dn. \tag{66}$$

But, mathematically,

$$\int_0^\infty e^{-a^2 u^2}\,du = \frac{\sqrt{\pi}}{2a}. \tag{67}$$

Therefore, taking

$$a^2 = \frac{n^2}{kT} \tag{68}$$

we have

$$\begin{aligned}\sum_0^\infty e^{-n^2 s^2/kT} = \int_0^\infty e^{-n^2 s^2/kT}\,dn &= \frac{\sqrt{\pi}}{2(s^2/kT)^{1/2}} \\ &= (2\pi mkT)^{1/2}\frac{V^{1/3}}{h}.\end{aligned} \tag{69}$$

The partition function for the 3 degrees of translational freedom is then, from Equations 65 and 69,

$$\sum A_i(\text{translation}) = \left[\frac{(2\pi mkT)^{1/2}V^{1/3}}{h}\right]^3, \tag{70}$$

or

$$\sum A_i(\text{translation}) = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V. \tag{71}$$

Substituting the value of $\sum A_i$ (translation) into Equations 13 and 18, or directly into Equation 45, one obtains for the 3 degrees of translational freedom

$$(E^\circ - E_0^\circ)(\text{translation}) = \tfrac{3}{2}RT. \tag{72}$$

Then, directly from Equations 2 and 72,

$$C_V{}^\circ(\text{translation}) = \tfrac{3}{2}R. \tag{73}$$

The free energy function for translation is obtained by substituting the value of $\sum A_i$ (translation) into Equation 54, so that

$$\left(\frac{F^\circ - H_0{}^\circ}{T}\right)(\text{translation}) = R - R\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} V\right]. \tag{74}$$

The heat content function for translation is obtained from Equations 29 and 72:

$$\left(\frac{H^\circ - H_0^\circ}{T}\right)(\text{translation}) = \tfrac{5}{2}R. \tag{75}$$

The entropy for translation is obtained from Equations 55, 74, and 75:

$$S^\circ(\text{translation}) = \tfrac{3}{2}R + R \ln \left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} V\right]. \tag{76}$$

5. Contributions from the rotational degrees of freedom. In the case of the contributions to the thermodynamic functions arising from the rotational degrees of freedom, the most accurate procedure is to use the actual levels of rotational energy as determined from appropriate spectral data. The value of the partition function, $\sum A_i$, may be obtained by summation over the actual levels of rotational energy, term by term. Or the energy of the various levels may be expressed in terms of an appropriate series, and the value of $\sum A_i$ obtained by analytical summation.

An example of an analytical expression for the levels of rotational energy of a diatomic molecule is the following for a diatomic molecule:

$$(\epsilon_i - \epsilon_0)(\text{rotation}) = A(m^2 + am^4 + bm^6 + \cdots). \tag{77}$$

Here m is $j + \frac{1}{2}$, where j is the rotational quantum number, and A, a, and b are constants.

Whenever the actual diagram of the levels of rotational energy is not known for a given molecule, a very good approximation for ordinary temperatures may be obtained by using the levels of rotational energy deduced theoretically for an ideal rigid rotator. The calculation requires that there be known the value of the moment of inertia for each degree of rotational freedom.

For a diatomic molecule, which has effectively only 2 degrees of rotational freedom, the levels of rotational energy for a rigid rotator are given by the following relation (*3*):

$$(\epsilon_i - \epsilon_0)(\text{rotation}) = \frac{j(j+1)h^2}{8\pi^2 I}. \tag{78}$$

In this equation, I is the moment of inertia about the axis of rotation and j is the rotational quantum number. For a diatomic molecule, composed of atoms of masses m_1 and m_2, and with the equilibrium distance between the atoms equal to r_0, the moment of inertia is calculated from the following relations, in which μ represents the "reduced mass" of the molecule or the mass on which the moment of inertia depends:

$$\mu = \frac{m_i m_2}{m_i + m_2}; \tag{79}$$

$$I = \mu r_0^2. \tag{80}$$

For the levels of rotational energy, the multiplicity, g_i, is given in terms of the rotational quantum number:

$$g_i = 2j + 1. \tag{81}$$

For convenience, we let

$$\frac{h^2}{8\pi^2 I} = b, \tag{82}$$

so that

$$(\epsilon_i - \epsilon_0)(\text{rotation}) = j(j+1)b. \tag{83}$$

Therefore, for the diatomic molecule, taken as a rigid rotator, the partition function for rotation is

$$\sum A_i\ (\text{rotation}) = \sum (2j+1)e^{-j(j+1)b/kT}. \tag{84}$$

Whenever $h^2/8\pi^2 IkT$, or b/kT, is small in comparison with unity, as it is for most molecules at ordinary and high temperatures, the summation on the right side of Equation 84 may be replaced by an integration:

$$\sum A_i\ (\text{rotation}) = \int_0^\infty (2j+1)e^{-j(j+1)b/kT}\, \mathrm{d}j \tag{85}$$

The term on the right side of Equation 85 may be written as

$$\int_0^\infty e^{-(j^2+j)b/kT}[(2j+1)\,\mathrm{d}j] = \int_0^\infty e^{-(j^2+j)b/kT}\,\mathrm{d}(j^2+j). \tag{86}$$

Since the integration is being performed at constant temperature, we may then write

$$\sum A_i\ (\text{rotation}) = \frac{kT}{b}\int_0^\infty e^{-(j^2+j)b/kT}\,\mathrm{d}\left[\frac{(j^2+j)b}{kT}\right]. \tag{87}$$

The integral in Equation 87 may be easily evaluated in the form

$$\int_0^\infty e^{-u}\,du = -[e^{-u}]_0^\infty = -[0 - 1] = 1. \tag{88}$$

Therefore, the partition function for the diatomic molecule becomes

$$\sum A_i \text{ (rotation)} = \frac{kT}{b}, \tag{89}$$

or

$$\sum A_i \text{ (rotation)} = \frac{8\pi^2 IkT}{h^2}. \tag{90}$$

For any linear polyatomic molecule, taken as a rigid rotator, and composed of n atoms of masses $m_1, m_2, \cdots, m_i$, there are only 2 degrees of rotational freedom, as in the case of the diatomic molecule, and the same equations hold as above except that the moment of inertia, I, is calculated by the relation,

$$I = \sum_{i=1}^{i=n} m_i x_i^2. \tag{91}$$

Here x_i is the vector distance of the ith atom of mass m_i from the center of mass, with the center of mass being taken so that

$$\sum_{i=1}^{i=n} m_i x_i = 0. \tag{92}$$

For any polyatomic non-linear molecule, which will have 3 degrees of rotational freedom, similar equations may be derived (*3*). For small values of the quantity $h^2/8\pi^2 IkT$, or b/kT, the partition function for rotation for a polyatomic non-linear molecule, taken as a rigid rotator, reduces to (*3*)

$$\sum A_i \text{ (rotation)} = \left(\frac{8\pi^2 kT}{h^2}\right)^{3/2} (\pi I_x I_y I_z)^{1/2}. \tag{93}$$

Here I_x, I_y, and I_z, are the moments of inertia about the three axes of the polyatomic non-linear molecule.

It is shown theoretically that, whenever the diatomic molecule is composed of identical atoms, the number of states of rotational energy is only half that given for the diatomic molecule composed of dissimilar atoms (*3*). The effect of this is to introduce the factor $\frac{1}{2}$ into the value of the partition function for rotation as given by Equation 85 to obtain the proper value for the partition function for rotation to be used for a diatomic molecule composed of identical atoms. Similarly, it is shown that, for any polyatomic molecule having two or more identical atoms, the allowable number of states of rotational energy is only $1/\sigma$ times the number for polyatomic molecules composed of dissimilar atoms, where σ is the symmetry number, a small integer, evaluated as the number of ways the molecule may be superimposed upon itself by rotation of the entire molecule (*3*). The effect of this is to introduce the factor $1/\sigma$ into the value of the partition function for rotation for the polyatomic molecule. Examples of the value of the symmetry number for several polyatomic molecules are: OCO, carbon dioxide, 2; CH_4, methane, 12; NH_3, ammonia, 3; NNO, nitrous oxide, 1; HCCH, acetylene, 2; H_2CCH_2, ethylene, 4.

With the symmetry number, σ, the partition function for rotation for any molecule taken as a rigid rotator has the following values:

$$\sum A_i \text{ (rotation, linear molecule)} = \frac{8\pi^2 IkT}{h^2\sigma}; \tag{94}$$

$$\sum A_i \text{ (rotation, non-linear molecule)} = \left(\frac{8\pi^2 kT}{h^2}\right)^{3/2} \frac{(\pi I_x I_y I_z)^{1/2}}{\sigma}. \tag{95}$$

Substituting the value of the partition function from Equations 94 and 95 into the appropriate preceding equations of this chapter, we obtain the following rotational contributions to the thermodynamic properties for molecules taken as rigid rotators:

For any linear molecule:

$$(E^\circ - E_0^\circ)\text{(rotation)} = RT; \tag{96}$$

$$C_V^\circ \text{ (rotation)} = R;$$

$$\left(\frac{F^\circ - H_0^\circ}{T}\right) \text{(rotation)} = -R \ln \left(\frac{8\pi^2 IkT}{h^2\sigma}\right); \tag{97}$$

$$\left(\frac{H^\circ - H_0^\circ}{T}\right) \text{(rotation)} = R; \tag{98}$$

$$S^\circ \text{ (rotation)} = R + R \ln \left(\frac{8\pi^2 IkT}{h^2\sigma}\right). \tag{99}$$

For any non-linear molecule:

$$(E^\circ - E_0^\circ)(\text{rotation}) = \tfrac{3}{2}RT; \tag{100}$$

$$C_V^\circ(\text{rotation}) = \tfrac{3}{2}R; \tag{101}$$

$$\left(\frac{F^\circ - H_0^\circ}{T}\right)(\text{rotation}) = -R \ln \left[\left(\frac{8\pi^2 kT}{h^2}\right)^{3/2} \frac{(\pi I_x I_y I_z)^{1/2}}{\sigma}\right]; \tag{102}$$

$$\left(\frac{H^\circ - H_0^\circ}{T}\right)(\text{rotation}) = \tfrac{3}{2}R; \tag{103}$$

$$S^\circ(\text{rotation}) = \tfrac{3}{2}R + R \ln \left[\left(\frac{8\pi^2 kT}{h^2}\right)^{3/2} \frac{(\pi I_x I_y I_z)^{1/2}}{\sigma}\right]. \tag{104}$$

As previously indicated, the foregoing equations for the rigid rotator give a good approximation for the rotational contributions to the thermodynamic properties at ordinary temperatures.

At temperatures such that for the given molecule the value of $h^2/8\pi^2IkT$, or b/kT, is not sufficiently small compared to unity, the replacement of the summation by integration in evaluating the partition function, $\sum A_i$, is not permissible, and calculations must be made in a more refined and extended manner (*3*). For high temperatures, where the value of $h^2/8\pi^2IkT$, or b/kT, is quite small compared to unity, the substitution of the integration for the summation in evaluating the partition function, $\sum A_i$, becomes more and more exact. But, unfortunately, the actual molecule is such that in the states of higher rotational energy, which will have a significant population at high temperatures, the equilibrium distance between the atoms in the molecule increases and a correction for the effect of this "stretching" on the moment of inertia of the molecule is necessary to improve the calculation.

Corrections to the equations for the rigid rotator to account for the "stretching" of the molecule in the states of higher rotational energy have been derived and may be applied whenever the population of molecules in such states is large enough (*3*, *5*).

It is important to note that all the uncertainties encountered in the application of the approximate equations given above for the contributions from the rotationl degrees of freedom, whether arising from the need for values at extremely low or extremely high temperatures, may be avoided if the actual levels of rotational energy for the given molecule are known, from which the exact calculations may be made. For calculations for high temperatures, a knowledge of the states of higher rotational energy is required, which is not needed for the calculations for low temperatures.

6. Contributions from the vibrational degrees of freedom. For the contributions to the thermodynamic functions arising from the vibrational degrees of freedom, the most accurate procedure is to use the actual levels of vibrational energy as determined from appropriate spectral data. As in the rotational contributions, the value of the partition function, $\sum A_i$, for vibration may be obtained by summation over the actual levels of vibrational energy, term by term. Or the energy of the various levels may be expressed in terms of an appropriate series, and the value of $\sum A_i$ obtained by analytical summation.

An example of an analytical expression for the levels of vibrational energy of a diatomic molecule is the following for nitric oxide (*2*), NO:

$$(\epsilon_i - \epsilon_0)(\text{vibration}) = Av_i(1 - 0.00762336v_i + 0.000021251v_i^2 - 0.000000714v_i^3). \quad (105)$$

Here A is a constant and v_i is the vibrational quantum number, having values from 0 to infinity.

Whenever the actual diagram of the levels of vibrational energy is not known for a given molecule, a very good approximation for ordinary temperatures may be obtained by using the levels of vibrational energy deduced theoretically for a harmonic oscillator. The calculation requires that there be known the value of the fundamental frequency of vibration for each of the degrees of vibrational freedom in the molecule, which, for a molecule of n atoms, are $3n - 5$ in number for a linear molecule and $3n - 6$ in number for a non-linear molecule.

For a diatomic molecule, which has only 1 degree of vibrational freedom, the levels of vibrational energy for the harmonic oscillator are given by the following expression (*3*):

$$(\epsilon_i - \epsilon_0)(\text{vibration}) = v_i h\nu. \quad (106)$$

In this equation, ν is the fundamental frequency of vibration and v_i is the vibrational quantum number, having values from 0 to infinity.

For the vibrational levels, the multiplicity is unity, and the partition function for vibration for a diatomic molecule taken as a harmonic oscillator becomes

$$\sum A_i \text{ (vibration)} = \sum e^{-v_i h\nu/kT}. \tag{107}$$

But, mathematically,

$$\sum e^{-v_i x} = \frac{1}{1 - e^{-x}}\cdot \tag{108}$$

Letting

$$\frac{h\nu}{kT} = x, \tag{109}$$

the partition function is given by

$$\sum A_i \text{ (vibration)} = \frac{1}{1 - e^{-x}}\cdot \tag{110}$$

For any molecule, taken as a harmonic oscillator, the value of the partition function for each of the degrees of vibrational freedom is given by Equation 110, where x is evaluated from the frequency of vibration of the given degree of vibrational freedom.

Substituting the value of the partition function from Equation 110 into the appropriate preceding equations of this chapter, we obtain the following vibrational contributions to the thermodynamic properties for molecules taken as harmonic oscillators, for each degree of vibrational freedom:

$$(E^\circ - E_0^\circ)\text{(vibration)} = \frac{RTx}{e^x - 1}; \tag{111}$$

$$C_V^\circ \text{ (vibration)} = \frac{Rx^2e^x}{(e^x - 1)^2}; \tag{112}$$

$$\left(\frac{F^\circ - H_0^\circ}{T}\right) \text{(vibration)} = R \ln (1 - e^{-x}); \tag{113}$$

$$\left(\frac{H^\circ - H_0^\circ}{T}\right) \text{(vibration)} = \frac{Rx}{e^x - 1}; \tag{114}$$

$$S^\circ \text{ (vibration)} = R\left[\frac{x}{(e^x - 1)} - \ln (1 - e^{-x})\right]\cdot \tag{115}$$

No significant error occurs in the use of the foregoing equations to calculate the vibrational contributions to the thermodynamic properties for low temperatures, and very little uncertainty occurs in the calculations for ordinary temperatures. For extremely high temperatures, however, the population of the higher levels of vibrational energy becomes large and the approximation of a uniform spacing of the levels of vibrational energy brings significant errors into the calculations. Corrections to the simple equations for the harmonic oscillator may be made to take cognizance of the fact that the spacing of the vibrational levels of energy actually decreases slowly with increase in the vibrational quantum number (*3*).

The total vibrational contribution is obtained by adding the contribution from each degree of vibrational freedom. The labor of such calculation is greatly lessened by making use of published tables (*6*) which give values of the functions in Equations 111, 112, 113, 114, and 115. In connection with the specification of the frequencies of vibration, it should be noted that these are usually given in terms of wave numbers, such that the wave number, ω, is related to the frequency, ν, as follows:

$$\omega = \frac{c}{\nu}. \tag{116}$$

Here c is the velocity of light.

Whenever the diagram of the actual levels of vibrational energy is known for each of the degrees of vibrational freedom in a given molecule, exact calculation of the vibrational contributions to the thermodynamic properties may be made without resort to the equations involving the harmonic oscillator.

7. Contributions from electronic states of energy. The contributions to the thermodynamic functions arising from electronic states of energy must be calculated using values of the energies of the electronic states of the molecule as determined from appropriate spectral data.

In certain cases, the electronic levels are ones of low energy, such as those constituting multiple states of a ground level, with the difference in energy of the states being small but significant, as in nitric oxide, in which the difference in energy of the two states is 354 cal/mole (see Figure 2). Table 2 shows, as a function of temperature, the fraction of molecules of nitric oxide in the

TABLE 2. RELATIVE POPULATION OF THE TWO STATES OF THE GROUND ELECTRONIC LEVEL OF THE DIATOMIC MOLECULE, NITRIC OXIDE, NO, IN THE IDEAL GASEOUS STATE, AS A FUNCTION OF TEMPERATURE

From Johnston and Chapman (*2*)

State	Relative Energy, cal/mole	Temperature, °K										
		30	50	100	200	400	700	1000	2000	3000	4000	5000
		Mole Fraction										
$^2\pi_{3/2}$	0	0.9978	0.9756	0.8651	0.7196	0.6188	0.5714	0.5519	0.5285	0.520	0.516	0.514
$^2\pi_{1/2}$	354	.0022	.0244	.1349	.2804	.3812	.4286	.4481	.4715	.480	.484	.486

two electronic states of the ground level, as calculated by Johnston and Chapman (*2*).

When a molecule undergoes electronic excitation to a new electronic level, the increase in energy is usually very high and the population of molecules in such an electronic level of high energy is usually insignificant except at very high temperatures. Whenever the population of such levels of high electronic energy does become significant, the contribution must be calculated in the usual way. An actual example is the oxygen molecule, O_2, which has an electronic level of energy, termed $^1\Delta$, with a multiplicity of 2, 22.63 kcal/mole above the ground level, with a multiplicity of 3. It may be readily calculated that at 5000°K the fraction 0.064 of the molecules will be in the $^1\Delta$ level of electronic energy, while at 1000°K only the fraction 0.0000075 of them will be in this level.

The contributions to the thermodynamic properties arising from the electronic states of energy are given by the following equations, in which ϵ_1, ϵ_2, ϵ_3, etc., represent the first, second, third, etc., levels of electronic energy above the ground level of energy, ϵ_0, and g_0, g_1, g_2, g_3, etc., represent the multiplicities:

$$\sum A_i(\text{electronic}) = g_0 + g_1 e^{-(\epsilon_1-\epsilon_0)/kT} + g_2 e^{-(\epsilon_2-\epsilon_0)/kT} + g_3 e^{-(\epsilon_3-\epsilon_0)/kT} + \cdots; \tag{117}$$

$$\sum B_i = \sum (\epsilon_i - \epsilon_0) A_i; \tag{118}$$

$$\sum D_i = \sum (\epsilon_i - \epsilon_0)^2 A_i; \tag{119}$$

$$(E^\circ - E_0^\circ)(\text{electronic}) = N \frac{\sum B_i}{\sum A_i}; \tag{120}$$

$$C_V^\circ\ (\text{electronic}) = \left(\frac{N}{kT^2}\right)\left[\frac{\sum D_i}{\sum A_i} - \left(\frac{\sum B_i}{\sum A_i}\right)^2\right]; \tag{121}$$

$$\left(\frac{H^\circ - H_0^\circ}{T}\right)(\text{electronic}) = \left(\frac{N}{T}\right)\left(\frac{\sum B_i}{\sum A_i}\right); \tag{122}$$

$$\left(\frac{F^\circ - H_0^\circ}{T}\right)(\text{electronic}) = -R \ln \sum A_i; \tag{123}$$

$$S^\circ\ (\text{electronic}) = \left(\frac{N}{T}\right)\left(\frac{\sum B_i}{\sum A_i}\right) + R \ln \sum A_i. \tag{124}$$

8. Contributions from restricted internal rotation. For polyatomic molecules having a group of atoms bonded to another group of atoms, one of the vibrational degrees of freedom of the molecule will be associated with the oscillation, about the bond joining the two groups, of one of the groups with respect to the other. Such oscillation may be highly restricted and of small amplitude, corresponding nearly to pure vibrational motion, or it may be little restricted and of large amplitude, approaching nearly free rotation about the given bond. Ascertaining the proper set of levels of energy to be associated with such a degree of freedom is considerably more complicated than for essentially pure rotation or pure vibration. When the restriction to rotation is extremely large, the levels of energy approach those of a simple harmonic oscillator, while, when the restriction to rotation is very small, the levels of energy approach those of a simple rotator.

For the degree of freedom involving such restricted internal rotation, it is assumed (*7*,*8*) that the potential energy of the rotating group may be expressed as a function involving the cosine of the angle of rotation. Specifically, for the molecule ethane, in which one methyl group may oscillate, with respect to the second methyl group, about the carbon—carbon bond joining the two groups, the potential energy for the restricted internal rotational degree of freedom is taken as follows:

$$U = U_{\max} \frac{1 - \cos 3\alpha}{2}. \tag{125}$$

Here $U_{\max}$ is the maximum value of the potential energy, α is the angle of rotation, and 3 is the number of maxima in the potential energy occurring in a complete rotation of the methyl group. Figure 3, taken from Mayer and Mayer (*3*), gives a schematic diagram of the situation existing in the restricted internal rotational degree of freedom in ethane.

Pitzer (*7*) and Pitzer and Gwinn (*8*) have calculated the levels of energy associated with a restricted internal rotational degree of freedom and have prepared extensive tables giving the contribution to the thermodynamic properties of energy, free energy function, entropy, and heat capacity arising from such a degree of freedom. The tabulated values cover, in suitable combination, an appropriate range of values of the maximum of the potential energy, the temperature, and the reduced moment of inertia for the given rotation.

For evaluating the contributions to the thermodynamic properties arising from a given restricted internal rotational degree of freedom, it is necessary to know the value of the reduced moment of inertia for the given rotation and the maximum of the potential energy (sometimes called the height of the potential barrier). The value of the reduced moment of inertia, I, for the given rotation of group A with respect to group B is given by the relation,

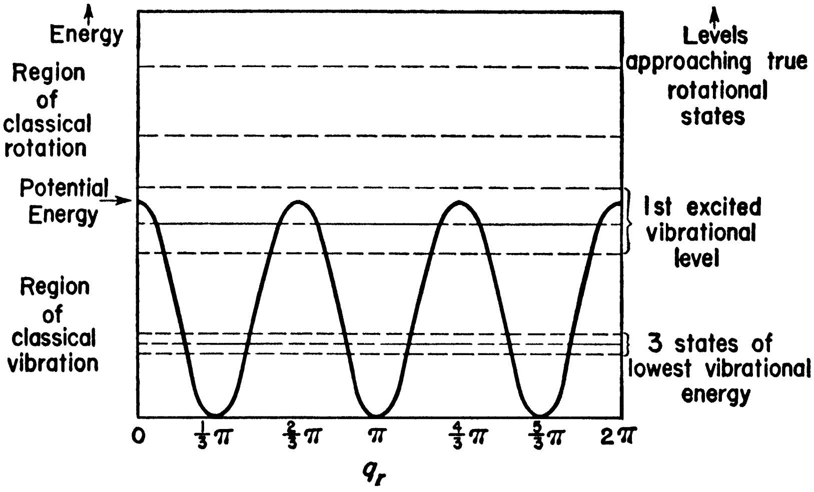


FIGURE 3. Schematic diagram showing the potential energy and quantum states of energy associated with the restricted internal rotational degree of freedom in the molecule, ethane, H_3CCH_3. From Mayer and Mayer (*3*).

$$I = \frac{I_A I_B}{I_A + I_B}, \tag{126}$$

where I_A and I_B are the moments of inertia of groups A and B, respectively, about the bond joining the two groups. The values of I_A and I_B may be calculated from a knowledge of the masses of the atoms and their position (distance and angles) with respect to an appropriate point on the axis of rotation.

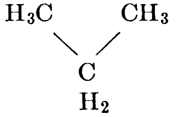
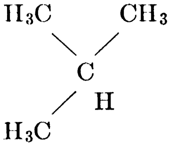
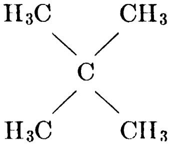
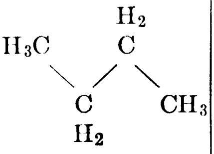
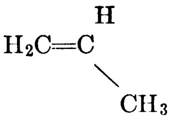
The manner of evaluating the maximum of potential energy may be illustrated by considering the molecule ethane, H_3CCH_3, which has a total of 24 degrees of freedom. Of these, 3 are of translation and 3 are of rotation (of the molecule as a whole about its 3 axes of rotation), leaving 18 degrees of freedom. These would normally be of ordinary vibration, but one is required for the oscillation of the two methyl groups with respect to each other (restricted internal rotation), so that 17 are for ordinary vibration. By appropriate analysis and calculation, the contribution to the thermodynamic properties arising from the 3 + 3 + 17, or 23, "known" degrees of freedom may be calculated. A given property, most conveniently the heat capacity or the entropy (referred to the entropy at 0°K), at one or more temperatures, or preferably both properties at several temperatures, is measured experimentally. The difference between the measured value and the value calculated for the 23 "known" degrees of freedom serves to yield, for the given temperatures, the contribution arising from the restricted internal rotational degree of freedom. The uncertainty of the resulting value will depend upon the uncertainties of the experimental measurements and the calculations. For ethane, the maximum of the potential energy for internal rotation has been evaluated from measurements both of the heat capacity and the entropy, and the results of both methods are in good accord.

Table 3 gives, as an example, the value of the maximum of the potential energy for internal rotation for a number of representative hydrocarbon molecules.

9. Contributions from nuclear spin. In connection with the statistical calculation of thermodynamic properties, cognizance must be taken of the fact that each atom may have a nuclear spin of zero or a small integral or half-integral number of units of $h/2\pi$. This nuclear spin is fixed for a given isotope of a given element, in the sense that a change in it can be brought about only by means of a large amount of energy. The nuclear spin, s, is an integer if the mass number of the isotope is even and is a half-odd integer if the mass number is odd. A nuclear spin of magnitude s results in $2s + 1$ different states of the atom. This is independent of the temperature, and the result is that every molecule would have its free energy function increased by the amount, $-R \ln (2s + 1)$, and its entropy increased by the amount, $R \ln (2s + 1)$, for every atom in the molecule having a nuclear spin s. The nuclear spin would not change the energy (relative to 0°K), the heat content function, or the heat capacity.

Except in those reactions of very high energy in which atoms

TABLE 3. MAXIMUM OF POTENTIAL ENERGY FOR INTERNAL ROTATION FOR SOME REPRESENTATIVE HYDROCARBON MOLECULES

Molecule			Number of the Given Kind of Restricted Rotation	Maximum of the Potential Energy, kcal/mole	References
Name	Formula	Structure			
Ethane	C_2H_6	$H_3C—CH_3$	1	2.8	*7,9,10,11*
Propane	C_3H_8		2	3.3	*7,9,12,13*
Isobutane	C_4H_{10}		3	3.9	*7,9,14*
Tetra-methyl-methane	C_5H_{12}		4	4.7	*7,9,15*
n-Butane	C_4H_{10}		2 1	3.3 3.7	*7,9,16*
Propylene	C_3H_6		1	2	*7,8,9,13,17*
Dimethyl-acetylene	C_4H_6	$H_3C—C\equiv C—CH_3$	2	0	*18,19*

are transformed, the number of atoms in a chemical reaction remains constant with the same nuclear spin, independent of the molecular combination of atoms. Therefore the sum of all the nuclear spin terms, $2s + 1$, for each of the atoms in the products is equal to the sum of all the nuclear spin terms, $2s + 1$, for each of the atoms in the reactants, so that the contributions of nuclear spin to the change in the free energy function and entropy cancels. It is doubly fortunate that the contributions from nuclear spin cancel in ordinary chemical reactions because accurate values of nuclear spin are known for relatively few atoms.

In those cases where it is desired to evaluate the contributions to the thermodynamic properties arising from nuclear spin, the following equations, applicable to all molecules at temperatures where the rotational degrees of freedom are substantially fully excited, may be used:

$$(E^\circ - E_0{}^\circ)(\text{nuclear spin}) = 0; \tag{127}$$

$$C_V{}^\circ\,(\text{nuclear spin}) = 0; \tag{128}$$

$$\left(\frac{H^\circ - H_0{}^\circ}{T}\right)(\text{nuclear spin}) = 0; \tag{129}$$

$$\left(\frac{F^\circ - H_0{}^\circ}{T}\right)(\text{nuclear spin}) = -R\sum_j \ln\,(2s_j + 1) \tag{130}$$

$$S^\circ\,(\text{nuclear spin}) = R\sum_j \ln\,(2s_j + 1) \tag{131}$$

These contributions are expressed per mole and are to be summed over all the atoms in the molecule, j in number. The foregoing equations will in general be applicable to all molecules except hydrogen, and some of its derivatives, at low temperatures.

10. Contributions from mixing of isotopes. Briefly stated, the existence of isotopes in the composition of a chemical element introduces no significant effect in the calculation of the thermodynamic properties. This is due to the fact that, if we wish to distinguish the isotopes, and have a knowledge of the amounts of the several isotopes present, the entropy of mixing the isotopes is readily calculable and may be added to the entropy previously calculated. However, it may be readily shown that, in all ordinary chemical reactions, the entropy of mixing isotopes will be constant for each mole of atoms whether in the products or in the reactants. Therefore, the entropy of mixing isotopes will be the same for the products as for the reactants, and will cancel. The same result holds true for the free energy function. As in nuclear spin, the energy (relative to 0°K), heat content function,

TABLE 4. SUMMARY OF USEFUL EQUATIONS, WITH NUMERICAL CONSTANTS, FOR CALCULATING THERMODYNAMIC PROPERTIES AND FUNCTIONS FOR MOLECULES IN THE IDEAL GASEOUS STATE AT A PRESSURE OF 1 ATMOSPHERE

Kind of Molecule	Thermodynamic Property*	Contribution,† cal/deg mole			
		Translational (exact)‡	Rotational (approximate)§	Vibrational (approximate)‖	Electronic (exact)¶
Monatomic	$\frac{H^\circ - H_0^\circ}{T}$	4.9680	......	......	$\left(\frac{N}{T}\right)\left(\frac{\Sigma B_i}{\Sigma A_i}\right)$
	$\frac{F^\circ - H_0^\circ}{T}$	$-6.8635 \log_{10} M$ $-11.4392 \log_{10} T + 7.2820$	......	......	$-1.9872 \ln \Sigma A_i$
	C_P°	4.9680	......	......	$\left(\frac{N}{kT^2}\right)\left[\frac{\Sigma D_i}{\Sigma A_i} - \left(\frac{\Sigma B_i}{\Sigma A_i}\right)^2\right]$
Linear polyatomic**	$\frac{H^\circ - H_0^\circ}{T}$	4.9680	1.9872	$1.9872 \sum_j \left[\frac{x_j}{e^{x_j} - 1}\right]$	$\left(\frac{N}{T}\right)\left(\frac{\Sigma B_i}{\Sigma A_i}\right)$
	$\frac{F^\circ - H_0^\circ}{T}$	$-6.8635 \log_{10} M$ $-11.4392 \log_{10} T + 7.2820$	$-4.5757 \log_{10} (I \times 10^{39})$ $-4.5757 \log_{10} T$ $+4.5757 \log_{10} \sigma + 2.7676$	$1.9872 \sum_j [\ln (1 - e^{-x_j})]$	$-1.9872 \ln \Sigma A_i$
	C_P°	4.9680	1.9872	$1.9872 \sum_j \left[\frac{x_j^2 e^{x_j}}{(e^{x_j} - 1)^2}\right]$	$\left(\frac{N}{kT^2}\right)\left[\frac{\Sigma D_i}{\Sigma A_i} - \left(\frac{\Sigma B_i}{\Sigma A_i}\right)^2\right]$
Non-linear polyatomic	$\frac{H^\circ - H_0^\circ}{T}$	4.9680	2.9808	$1.9872 \sum_j \left[\frac{x_j}{e^{x_j} - 1}\right]$	$\left(\frac{N}{T}\right)\left(\frac{\Sigma B_i}{\Sigma A_i}\right)$
	$\frac{F^\circ - H_0^\circ}{T}$	$-6.8635 \log_{10} M$ $-11.4392 \log_{10} T + 7.2820$	$-2.2878 \log_{10} (I_A I_B I_C \times 10^{117})$ $-6.8635 \log_{10} T$ $+4.5757 \log_{10} \sigma + 3.0140$	$1.9872 \sum_j [\ln (1 - e^{-x_j})]$	$-1.9872 \ln \Sigma A_i$
	C_P°	4.9680	2.9808	$1.9872 \sum_j \left[\frac{x_j^2 e^{x_j}}{(e^{x_j} - 1)^2}\right]$	$\left(\frac{N}{kT^2}\right)\left[\frac{\Sigma D_i}{\Sigma A_i} - \left(\frac{\Sigma B_i}{\Sigma A_i}\right)^2\right]$

* The value of the entropy may be obtained by subtracting the free energy function from the heat content function, as

$$S^\circ = \frac{H^\circ - H_0^\circ}{T} - \frac{F^\circ - H_0^\circ}{T}.$$

† In addition to the contributions from translation, rotation, ordinary vibration, and electronic excitation, which are given here, there must be included the contributions from the restricted internal rotational degrees of freedom, as from the tables of Pitzer and Gwinn (*8*).

‡ M is the molecular weight in grams per mole. T is the temperature in °K. The pressure has been taken in atmospheres.

§ Calculated for a rigid rotator. I, in grams per square centimeter, is the value of each of the two equal moments of inertia of a linear molecule about axes perpendicular to the axis of the molecule. I_A, I_B, and I_C, each in grams per square centimeter, are the three principal moments of inertia of a non-linear molecule. σ is the symmetry number.

‖ Calculated for a harmonic oscillator. The sums are to be taken over each of the ordinary fundamental frequencies of vibration, ν_1, ν_2, ν_3, etc. If the molecule of n atoms has no degrees of freedom associated with restricted internal rotation, the number of degrees of ordinary vibrational freedom is $3n - 5$ for linear, and $3n - 6$ for non-linear molecules. The number of degrees of freedom for ordinary vibration is reduced by one for each degree of freedom for restricted internal rotation. The contributions for restricted internal rotation may be evaluated from the tables of Pitzer and Gwinn (*8*). If the frequency of vibration is given in wave numbers, ω, in reciprocal centimeters, then

$$x_j = h\nu_j/kT = \frac{hc}{k}\,\omega_j/T.$$

For rapid evaluation of the contributions from ordinary vibration, see the tables of Johnston, Savedoff, and Belzer (*6*).

¶ The partition function for the levels of electronic energy is

$$\Sigma A_i = g_0 + g_1 e^{-(\epsilon_1-\epsilon_0)/kT} + g_2 e^{-(\epsilon_2-\epsilon_0)/kT} + g_3 e^{-(\epsilon_3-\epsilon_0)/kT} + \cdots. \qquad \Sigma B_i = \Sigma(\epsilon_i - \epsilon_0)A_i. \qquad \Sigma D_i = \Sigma(\epsilon_i - \epsilon_0)^2 A_i.$$

The multiplicity, g_i, and energy (referred to the ground level) must be known for each level of electronic energy.

** Includes all linear molecules with two or more atoms.

and heat capacity are not affected by the mixing of the isotopes.

Where a fractionation of the isotopes is produced in a given process or reaction and it is desired to evaluate the contributions to the thermodynamic functions arising from the mixing of isotopes, the following equations may be used:

$$(E^\circ - E_0^\circ)(\text{mixing of isotopes}) = 0; \tag{132}$$

$$C_V^\circ\ (\text{mixing of isotopes}) = 0; \tag{133}$$

$$\left(\frac{H^\circ - H_0^\circ}{T}\right)(\text{mixing of isotopes}) = 0; \tag{134}$$

$$\left(\frac{F^\circ - H_0^\circ}{T}\right)(\text{mixing of isotopes}) = R\sum_j \mathrm{N}_j \ln \mathrm{N}_j; \tag{135}$$

$$S^\circ\ (\text{mixing of isotopes}) = -R\sum_j \mathrm{N}_j \ln \mathrm{N}_j. \tag{136}$$

In the foregoing equations, the values of the properties are per mole, N_j is the mole fraction of the jth isotope, and the summation is to be carried over all the different isotopes. The thermodynamic properties of mixing isotopes are of course independent of temperature unless the process or reaction is one which produces a separation of the isotopes.

However, it should be pointed out that, for the contributions arising from the mixing of isotopes to be neglected, the values of the thermodynamic properties for the separate isotopic species must be calculated separately if the sets of levels of energy for the rotational and vibrational degrees of freedom are significantly different. Fortunately, the sets of levels of energy for the rotational and vibrational degrees may be taken without significant error as being those corresponding to the atoms of average mass, except for hydrogen. In the latter case, happily, complete information is available for the calculation of the thermodynamic properties of the several isotopic species.

11. Summary of useful equations. In Table 4 is given a summary of useful equations, with numerical constants, for calculating thermodynamic properties and functions for molecules in the ideal gaseous state.

12. Collateral reading. In the foregoing sections, only a skeleton outline has been given of the methods for calculating thermodynamic properties and functions statistically from spectroscopic and other molecular data. For detailed discussions of these methods, the reader is referred to Tolman (*23*), Mayer and Mayer (*3*), Pitzer (*7,9*), Johnston and Chapman (*2*), Giauque (*20*), Wilson (*21*), Crawford (*22*), Herzberg (*1,4*), and Rushbrooke (*24*).

REFERENCES

1. G. Herzberg, *Molecular Spectra and Molecular Structure*, Volume II, D. Van Nostrand Company, New York, 1945.
2. H. L. Johnston and A. T. Chapman, *J. Am. Chem. Soc.* **55**, 153 (1933).
3. J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, John Wiley & Sons, New York, 1940.
4. G. Herzberg, *Molecular Spectra and Molecular Structure*, Volume I, Prentice-Hall, New York, 1939.
5. E. B. Wilson, Jr., *J. Chem. Phys.* **4**, 526 (1936).
6. H. L. Johnston, L. Savedoff, and J. Belzer, *Contributions to the Thermodynamic Functions for a Planck-Einstein Oscillator in One Degree of Freedom*, U.S. Office of Naval Research Publication, U.S. Government Printing Office, 1949.
7. K. S. Pitzer, *J. Chem. Phys.* **5**, 469, 473 (1937).
8. K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.* **10**, 428 (1942).
9. K. S. Pitzer, *Chem. Revs.* **27**, 39 (1941).
10. J. D. Kemp and K. S. Pitzer, *J. Am. Chem. Soc.* **59**, 276 (1937).
11. G. B. Kistiakowsky, J. R. Lacher, and F. Stitt, *J. Chem. Phys.* **7**, 289 (1939).
12. J. D. Kemp and C. J. Egan, *J. Am. Chem. Soc.* **60**, 1521 (1938).
13. G. B. Kistiakowsky, J. R. Lacher, and W. W. Ransom, *J. Chem. Phys.* **6**, 900 (1938).
14. J. G. Aston, R. M. Kennedy, and S. C. Schumann, *J. Am. Chem. Soc.* **62**, 2059 (1940).
15. J. G. Aston and G. H. Messerly, *J. Am. Chem. Soc.* **58**, 2354 (1936).
16. J. G. Aston and G. H. Messerly, *J. Am. Chem. Soc.* **62**, 1917 (1940).
17. B. L. Crawford, Jr., G. B. Kistiakowsky, W. W. Rice, A. J. Wells, and E. B. Wilson, Jr., *J. Am. Chem. Soc.* **61**, 2980 (1939).
18. D. W. Osborne, C. S. Garner, and D. M. Yost, *J. Chem. Phys.* **7**, 131 (1939).
19. B. L. Crawford, Jr., and W. W. Rice, *J. Chem. Phys.* **7**, 437 (1939).
20. W. F. Giauque, *J. Am. Chem. Soc.* **52**, 4808 (1930).
21. E. B. Wilson, Jr., *Chem. Revs.* **27**, 17 (1941).
22. B. L. Crawford, Jr., *J. Chem. Phys.* **8**, 273 (1940).
23. R. C. Tolman, *The Principles of Statistical Mechanics*, Oxford University Press, New York, 1938.
24. G. S. Rushbrooke, *Introduction to Statistical Mechanics*, Oxford University Press, Oxford, 1949.

PROBLEMS

1. The ground level of energy of the chlorine atom, designated $^2P_{3/2}$, has a multiplicity of 4, and the next higher level of energy, designated $^2P_{1/2}$, has a multiplicity of 2 and lies 881 wave numbers (cm^{-1}) above the ground level. Taking the atomic mass to be 35.457 g/mole, calculate the following:

a. The ratio of the number of atoms in the $^2P_{1/2}$ state to the number in the $^2P_{3/2}$ state at the following temperatures: 0°, 100°, 500°, 1000°, 2000°, 3000°, 4000°, and 5000°K.

b. The value of the heat content function, free energy function, entropy, heat content, and heat capacity, at 300°, 1000°, 3000°, and 5000°K.

2. The gaseous diatomic molecule, NaH, has the following characteristics: energy of the first electronic state above the ground level, 23, 283 wave numbers (cm^{-1}); fundamental frequency of vibration, 1133 wave numbers (cm^{-1}); equilibrium distance, r_0, between the atoms, 1.88×10^{-8} cm. Taking the atomic masses to be 22.997 and 1.008 g/mole, assuming the molecule to be a rigid rotator and a harmonic oscillator, and taking the multiplicity of each level as one, calculate the following:

a. The fraction of molecules in the first electronic energy state above the ground level at 5000°K.

b. Heat content function, free energy function, entropy, heat content, and heat capacity, at 300°, 1000°, 3000°, and 5000°K.

3. The molecule carbon dioxide, OCO, is symmetrically linear and has the following characteristics: fundamental vibrational frequencies, 667.3, 667.3, 1388.3, and 2439.3 wave numbers (cm^{-1}); moment of inertia, 71.67×10^{-40} g cm^2; molecular weight, 44.010 g/mole. Calculate the following, assuming a rigid rotator and a harmonic oscillator: heat content function, free energy function, entropy, heat content, and heat capacity, at 300°, 1000°, and 2000°K.

4. The oxygen molecule, O_2, has its first electronic level of energy, a $^1\Delta_g$ state, with a multiplicity of 2, at 7918 wave numbers (cm^{-1}), above the ground level, $^3\Sigma_g^-$ state, with a multiplicity of 3. Assuming negligible population at other levels, calculate the mole fraction of oxygen molecules at those two levels, at 300°, 2000°, 4000°, and 6000°K.

20

Entropy and the Third Law of Thermodynamics

1. The third law of thermodynamics. When a substance participates in a reversible process, its increase in entropy is equal to the heat energy it absorbs divided by the absolute temperature:

$$\mathrm{d}S = \frac{\delta q}{T}. \qquad (1)$$

If the quantity of heat absorbed is known as a function of the temperature, down to the absolute zero, Equation 1 can be integrated to give the entropy of the given substance at the temperature T:

$$S = S_0 + \int_0^T \frac{\delta q}{T}. \qquad (2)$$

In Equation 2, S_0 is the entropy of the given substance at the absolute zero of temperature. From the discussion in Section 3 of Chapter 19, it is clear that, when the given substance is taken down to the absolute zero of temperature, the ensemble of molecules constituting the given substance will end up in a single lowest permitted state of energy, provided opportunity is given for the free passage of each of the molecules among all the permitted states of energy in accordance with the appropriate distribution law, Boltzmann, Fermi-Dirac, or Bose-Einstein. If the given ensemble of molecules is in a single quantum state at the absolute zero of temperature, the entropy of the ensemble is zero. This is the third law of thermodynamics, a formal statement of which is the following:

The entropy of any substance of which all component parts are in complete internal equilibrium becomes zero at the absolute zero of temperature.

By internal equilibrium in a given substance is meant that each of the atoms or molecules comprising the given substance has free access to all the permitted states in accordance with the given distribution law. Examples of gaseous substances have already been discussed in Chapter 19. In the case of a solid, for example, the entropy of crystalline carbon in the form of graphite, which is in internal equilibrium among all the states permitted for graphite, will be zero at 0°K. Similarly, the entropy of crystalline carbon in the form of diamond, which is in internal equilibrium among all the states permitted for diamond, will be zero at 0°K. Although, at ordinary pressures, diamond is thermodynamically unstable with respect to graphite, the carbon atoms may remain in the diamond configuration indefinitely. This persistence of a metastable crystalline state is not uncommon. Such metastable phases are in internal equilibrium, in the sense that each slight deviation due to fluctuations finds the system returning to its original state, with all near neighbor states being thermodynamically less stable. Each atom of carbon in the crystal of diamond lies in a potential energy trough, and the entire ensemble of atoms lies in a free energy trough, though neither is the lowest possible trough of its kind, the corresponding ones for graphite being lower, at ordinary pressures.

Returning now to Equation 2, we can say that actually, of course, calorimetric measurements can never be carried to the absolute zero of temperature. The investigator begins his observations at T_*, the lowest temperature of measurement, and the value of the integral below T_* is obtained by extrapolation, from T_* to 0°K, of the measurements made above T_*. Indicating this fact, we may write

$$S = S_0 + \left(\int_0^{T_*} \frac{\delta q}{T}\right)_{\text{extrap.}} + \int_{T_*}^{T} \frac{\delta q}{T}. \tag{3}$$

In Equation 3, the last term is derived completely from the experimental measurements (of heat capacity, heat of transition, heat of fusion, and heat of vaporization, as appropriate), and the second term on the right side is evaluated by extrapolating from T_* to 0°K the measurements of heat capacity made above T_*, in conjunction with an appropriate theoretical equation, usually the Debye equation for the heat capacity of solids. The extrapolation from T_* to 0°K in this way accounts for the ordinary thermal entropy resident in the substance at T_*, the lowest temperature of measurement. The term S_0 represents, therefore, the entropy of the substance at 0°K as determined essentially by its quantum condition at T_*. (See Chapter 19.)

A schematic plot of C_P/T as a function of T is given in Figure 1, to show the nature of the extrapolation from the lowest temperature of measurement, T_*, to 0°K. In the case of solid substances, the extrapolation from T_* to 0°K is usually made with the aid of the Debye equation for heat capacity, or some appropriate modification of it.

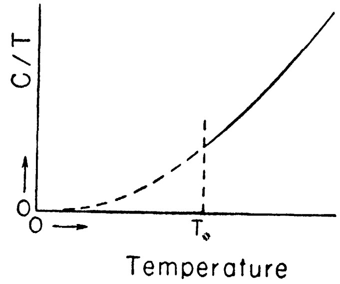


FIGURE 1. Schematic diagram of the relation between the temperature and the heat capacity divided by the temperature, C/T, near the absolute zero of temperature, to show the nature of the extrapolation to 0°K from T_*, the lowest temperature of measurement.

A simple statement of the application of the third law is the following:

If at the lowest temperature of measurement, T_*, a substance is in a single pure quantum state of energy, except for the ordinary thermal energy characteristic of T_* which is accounted for by the extrapolation from T_* to 0°K, then S_0, its entropy at 0°K, may be placed equal to zero.

When this condition holds, then Equation 3 reduces to

$$S = \left(\int_0^{T_*} \frac{\delta q}{T}\right)_{\text{extrap.}} + \int_{T_*}^{T} \frac{\delta q}{T}, \tag{4}$$

and the entropy of the given substance is determined substantially completely from the experimental observations. It is clear that, for such experiments, T_* should be made as low as practicable in order that the extrapolation shall introduce as little error as possible. It is important to note that the above statement of the application of the third law places no limitation on the physical state of the substance, as solid, liquid, or gas, although actually practically all substances investigated down to near 10°K will be in the solid state. In the application of the third law, the only requirement that needs to be fulfilled is that at the lowest temperature of measurement, T_*, the given substance, solid, liquid, or gas, shall be in a substantially single quantum state of energy except for that energy which will be accounted for by the extrapolation, from T_* to 0°K, of the measurements made above T_*. That is to say, the situation is such that the extrapolation, from T_* to 0°K, of the observations above T_* has the effect of reducing all the molecules of the given substance to a single quantum state of energy (usually but not necessarily the ground level) at 0°K in the same physical state, solid, liquid, or gas, in which it existed at T_*. However, if the given substance is in the liquid or gaseous state at T_*, and a change of state occurs below T_*, as from liquid to solid or gas to liquid, accompanied by a finite change in energy, it is obvious that the extrapolation, from T_* to 0°K, of the observations above T_* will not properly account for the term $\int_0^{T_*} \delta q/T$, and the system will not conform to the requirements for the application of the third law. In general, we may say that the requirements for the application of the third law are that, for some range of temperature above the lowest temperature of measurement, T_*, the molecules of the given substance are distributed among the available quantum states in accordance with the normal distribution law, and that, as the temperature is lowered, the distribution of the molecules among the available levels of energy changes progressively in such a way that in the limit, at 0°K, the molecules will have available only one state of existence.

We have already seen from Chapter 19 that the entropy of a mole of molecules in the ideal gaseous state at the absolute zero of temperature becomes zero when the mole of molecules has available only one state of existence. The third law is essentially, then, a statement of this fact applied to the evaluation of entropy from experimental measurements of energy as a function of temperature.

It is important to note also, in this connection, that the third law does not limit the given substance to existence in only one of two or more possible crystalline forms. The given substance may at the lowest temperature of measurement be in any one of several possible crystalline forms, and each of the different crystalline forms, pure in itself, may conform to the requirements for the application of the third law.

In extrapolating, from T_* to 0°K, the observations made above T_*, it is convenient to utilize a suitable theoretical relation between energy and temperature. In the case of crystalline solids, there is usually used the Debye relation (Chapter 15) or some appropriate modification of it.

For a substance that conforms to the requirements for the application of the third law and has two stable crystalline forms, similar to the substance referred to in Figure 1 of Chapter 10 and Figure 1 of Chapter 15, the entropy of the gas at the given pressure at the temperature T is given by the following relation:

$$\begin{aligned} S\,(\mathrm{g}) = \left(\int_0^{T_*} \frac{\delta q}{T}\right)_{\text{extrap.}} &+ \int_{T_*}^{Ttr} C_P\,(\mathrm{c, II})\,\mathrm{d}\ln T + \frac{\Delta Htr}{Ttr} \\ &+ \int_{Ttr}^{Tm} C_P\,(\mathrm{c, I})\,\mathrm{d}\ln T + \frac{\Delta Hm}{Tm} \\ &+ \int_{Tm}^{Tv} C_P(\mathrm{liq})\,\mathrm{d}\ln T + \frac{\Delta Hv}{Tv} \\ &+ \int_{Tv}^{T} C_P\,(\mathrm{g})\,\mathrm{d}\ln T. \end{aligned} \tag{5}$$

The terms on the right side of Equation 5 represent, respectively, the extrapolated entropy of crystalline form II from 0°K to T_*, the increase in entropy of crystalline form II from T_* to the temperature of transition, the entropy of transition of crystalline form II to crystalline form I, the increase in entropy of crystalline form I from the temperature of transition to the temperature of melting, the entropy of melting of crystalline form I, the increase in entropy of the liquid from the temperature of melting to the temperature of vaporization, the entropy of vaporization of the liquid, and the increase in entropy of the gas from the temperature of vaporization to the given temperature, T.

2. Cases of conformity and non-conformity with the requirements for the application of the third law. In the practical application of the third law, it is necessary to consider the problem of what substances are likely to conform, and what substances are likely not to conform, to the requirements for the application of the third law. Chronologically the evolution of this law preceded the evolution of the method of calculating thermodynamic properties statistically. Now, however, it is possible to take advantage of the knowledge resulting from such statistical calculations to assist in the formulation of a more elegant statement of the third law than was possible in the early days, and, what is equally important, to assist in determining what general types of substances may or may not conform to the requirements for the application of the third law.

By comparison of the values of entropy calculated for the ideal gas state in an accurate way statistically according to the method outlined in Chapter 19, with the values of entropy evaluated from experimental measurements of energy as a function of temperature, according to Equation 5, appropriately corrected by a small amount to the ideal gas state, it has been found that the following substances, among others, conform to the requirements for the application of the third law: O_2, N_2, Cl_2, HCl, HBr, HI, H_2S, SCO, CO_2, NH_3, CS_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6 (propylene), C_6H_6 (benzene), plus a large number of other hydrocarbons.

From the information that is now available, it appears that, without exception, all the many hydrocarbons for which the entropy has been evaluated by measurements, down to low temperatures, of energy as a function of temperature conform to the requirements of the third law. In all the foregoing cases, the accord of the two values of entropy at 25°C, from the third law and from statistical calculations, has been within the limits of uncertainty of the experimental measurements, usually ±0.1 to 0.2 cal/deg mole. The uncertainty of the values of entropy calculated statistically, for molecules for which substantially complete spectroscopic and other molecular data are available, is usually less than 0.01 to 0.02 cal/deg mole, and frequently only a few thousandths of a cal/deg mole.

The following values indicate the degree of accord between values of the entropy at 25°C for the given substance in the ideal gaseous state at 1 atmosphere obtained (1) by application of the third law, from Giauque and collaborators, and (2) by the method of statistical calculations, the values being given in that order in calories per degree mole and having respective uncertainties as indicated above: O_2, 49.1, 49.003; N_2, 45.9, 45.767; HCl, 44.5, 44.617; HBr, 47.6, 47.437; HI, 49.5, 49.314; H_2S, 49.1, 49.15; SCO, 55.3, 55.34; CO_2, 51.1, 51.061; NH_3, 45.9, 46.01.

Actually, it appears that, except for certain small molecules of the types discussed below, any substance obtainable in a pure crystalline form is likely to conform to the requirements for the application of the third law.

Possible causes of non-conformity with the requirements for the application of the third law, that is, causes which would result in the given substance not being in a single pure quantum state at T_* (except for those states which will become normally depopulated as the observations above T_* are extrapolated from T_* to 0°K), are the following: existence of nuclear spin; existence of isotopes; existence of randomness in the structure of the crystal; existence of a non-equilibrium distribution of molecules among the quantum states of energy; existence of a solution or mixture of different molecules; existence of the substance in a glassy instead of a crystalline form. Examples of these cases are discussed in the following sections.

3. Entropy of nuclear spin. With regard to the existence of nuclear spin in the atoms composing the molecules of the given substance, we have seen in Chapter 19 that the contribution to the thermodynamic properties arising from nuclear spin may ordinarily be neglected. The value of $\int_0^T \delta q/T$ obtained by application of the third law will not include the entropy of mixing the atoms in the $2s + 1$ different states arising from the existence of a nuclear spin of magnitude s. Since the number and population of the different states of nuclear spin are unaffected by ordinary reactions or processes, the entropy of nuclear spin will be the same for the reactants and products and hence will cancel. However, if the process or reaction is a "nuclear" one in which certain atoms disappear and others are formed, cognizance of the entropy of nuclear spin may be taken through the relation,

$$S \text{ (nuclear spin)} = R \sum \ln (2s_j + 1), \tag{6}$$

where the summation is to be made over all the j atoms in the molecule, each atom having a nuclear spin of magnitude s_j.

In certain molecules like ordinary hydrogen and "heavy" hydrogen or deuterium, the small moment of inertia and the similarity of the atoms in the molecule give effects arising from the existence of nuclear spin which are observable experimentally. These cases are discussed in a later section in this chapter.

4. Entropy of mixing isotopes. With regard to the existence of isotopes, the value of the $\int_0^T \delta q/T$, obtained by application of the third law, will not include the entropy of mixing the isotopes, except in an unusual case. In general, for ordinary purposes, the existence of the isotopes can be neglected, as discussed in Chapter 19, since the contribution of the entropy of mixing isotopes will be the same for the products as the reactants in any process and hence will cancel. However, if it is desired to take cognizance of the entropy of mixing isotopes, as in connection with a process or reaction which results in a fractionation of the isotopes, this can be done by the usual relation,

$$S \text{ (mixing isotopes)} = -R \sum \mathrm{N}_j \ln \mathrm{N}_j, \tag{7}$$

in which the summation is carried over all the different j isotopes, each of mole fraction N_j. The entropy of mixing isotopes is of course independent of the temperature.

5. Entropy associated with randomness in the structure of crystals at the absolute zero of temperature. For the molecules, nitric oxide, NO, carbon monoxide, CO, and nitrous oxide, NNO, each of which is a linear molecule having dissimilar atoms at the ends, Giauque and collaborators (*6*, *7*, *8*) have found that, in the relation

$$S^{\circ}_{298.16} = S_0{}^{\circ} + \int_0^{298.16} \frac{\delta q}{T}, \tag{8}$$

$S_0{}^{\circ}$ is significantly greater than zero. This indicates that these molecules do not conform to the requirements for the application of the third law. The explanation is the presence of a certain amount of randomness in the structure of the crystals as they exist at the lowest temperature of measurement, T_*. This randomness of arrangement is manifested by an end-for-end displacement of the molecules, such that all the molecules are not lined up with the same atom in the forward direction, as, for example, the random arrangement, NO, NO, ON, NO, ON, ON, NO, etc., as contrasted with the non-random arrangement, NO, NO, NO, NO, NO, NO, NO, etc.

In the completely random arrangement, each molecule has two positions available, whereas in the orderly arrangement each molecule has only one position available. The state of more orderly arrangement will have an energy less than that of the state of random arrangement. This difference in energy will approach zero as the two end atoms of the linear molecule become more and more alike. If the two end atoms are quite dissimilar, with a correspondingly larger difference in energy between the two states, then, as the temperature of the substance in the condensed state is lowered, the molecules will tend to go over to the state of lower energy and may be all lined up before they are "frozen" in the crystal, without opportunity to rotate and change position, end for end. However, if the two end atoms are almost alike, with a correspondingly very small difference in energy between the two states, the population of both states will, as the temperature is lowered, continue to be quite appreciable, and, when a temperature is reached at which the molecules are "frozen" in the crystal without opportunity to rotate, many molecules will exist in each state. The situation will remain down to the lowest temperature of measurement, T_*, so that the substance will possess an entropy associated with the randomness of arrangement of the molecules in the crystal.

If the arrangement of the molecules in the crystal at T_* is fully random, with p states available for each molecule, then the total number of available configurations for one mole of molecules is

$$W = p^N. \tag{9}$$

The entropy arising from such randomness is

$$S \text{ (randomness)} = k \ln W = k \ln p^N = Nk \ln p = R \ln p. \tag{10}$$

For the linear molecules mentioned above, with two positions available, $p = 2$, and

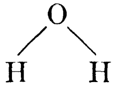
$$S \text{ (randomness)} = R \ln 2 = 1.38 \text{ cal/deg mole}. \tag{11}$$

For the three substances, NO, CO, and NNO, Giauque and collaborators (*6,7,8*) evaluated, by means of Equation 8, the entropy due to the randomness of arrangement in the crystal to be, respectively, 0.66, 1.10, and 1.14 cal/deg mole, with an uncertainty of about ±0.10 cal/deg mole. From these data, it appears that some movement away from complete randomness has occurred in each case, with the molecule NO having moved closer to the orderly arrangement than the others.

For the linear molecules, SCO and HCN, which have dissimilar atoms of greatly different mass at the ends, and hence would have a greater tendency to be aligned in an orderly way in the crystal;

the experimental data indicate no significant amount of randomness of arrangement in the crystals at low temperatures (*23,24*).

Another example of entropy associated with randomness in the structure of crystals at the absolute zero of temperature occurs in the case of the substance water, both as the naturally occurring mixture of isotopes, H_2O, or as deuterium oxide, D_2O or ^2H_2O. For these substances, the measurements of Giauque and Stout (*9*) and of Long and Kemp (*10*) give values of $\int_0^{298.16} \delta q/T$. When these values are compared with the accurate values of the entropy calculated statistically, it is found that the value of the entropy associated with randomness of arrangement of the molecules in the crystal at the absolute zero, according to Equation 8, is, for H_2O and D_2O, respectively, 0.83 and 0.69 cal/deg mole, with an uncertainty near ±0.10 cal/deg mole.

The explanation for this randomness of arrangement has been given by Pauling (*11*) [see also Wollan, Davidson, and Shull (*31*)] in terms of the randomness of arrangement of "hydrogen" bonds in the crystal of water ice, as follows: The structure of the crystal of water ice is governed by the following conditions: (1) The water molecule exists in ice with substantially the same distance between the hydrogen atoms and the oxygen atom to which they are strongly bonded, and with the same angle,  $\mathrm{H}\overset{\mathrm{O}}{\diagup\ \diagdown}\mathrm{H}$, as in the water molecule in the gaseous state; (2) each water molecule is oriented so that its two hydrogen atoms are directed approximately toward two of the four oxygen atoms which surround it tetrahedrally, forming "hydrogen" bonds, with the oxygen atoms forming six-membered puckered rings; (3) the orientations of adjacent water molecules are such that only one hydrogen atom lies approximately along each oxygen-oxygen axis; (4) under ordinary conditions, the interaction of non-adjacent molecules is not such as to stabilize appreciably any one of the many possible configurations satisfying the preceding conditions, that is to say, the available configurations have nearly the same energy. The crystal can change from one to another of the many available configurations by rotation of some of the water molecules, or by motion of some of the hydrogen nuclei, each a distance of about 0.86×10^{-8} cm from a potential minimum 0.95×10^{-8} cm from one oxygen atom to a potential minimum the same distance, 0.95×10^{-8} cm, from an adjacent oxygen atom. It is known from measurements of the dielectric constant that the molecules in water ice can, down to near 200°K, orient themselves in the crystal with considerable freedom. On cooling the crystal to still lower temperatures, however, each molecule is "frozen" in one of its available positions, with the entire crystal being frozen in one of its many possible configurations.

At this "frozen in" condition, the crystal does not in any reasonable time change toward a more orderly arrangement and so essentially retains at very low temperatures the entropy associated with the above described randomness of arrangement, which will be measured according to Equation 10 by the number of configurations available to each molecule in the crystal. A given molecule can orient itself in any one of six ways. However, the chance that the adjacent molecules will permit a given orientation is $\frac{1}{4}$; because each adjacent molecule has two of its tetrahedral directions vacant and two occupied by hydrogen atoms, making the chance that a given direction is available for each hydrogen of the original molecule $\frac{1}{2}$, and the chance that both can be located in accordance with the given orientation $\frac{1}{4}$. The number of configurations available for each molecule is, therefore, $p = \frac{6}{4} = \frac{3}{2}$, so that, for water ice,

$$S_0 \text{ (randomness)} = R \ln p = R \ln \tfrac{3}{2} = 0.81 \quad \text{cal/deg mole.} \qquad (12)$$

It is seen that, within the limits of uncertainty of the experimental observations, the molecules in the crystal of water ice at very low temperatures, for both H_2O and D_2O, have an essentially complete randomness of arrangement with respect to the "hydrogen" bonds in the crystal.

It is to be expected that entropy associated with randomness of arrangement of the molecules in the crystal at low temperatures will exist for other pure substances similar to those mentioned above, for corresponding reasons. See, for example, Giauque and Jones (*32*).

6. Entropy associated with a non-equilibrium distribution of molecules among the rotational states of energy. Certain molecules containing identical atoms, as hydrogen, H_2, or deuterium, D_2, have successive rotational states of energy which are alternately symmetrical and antisymmetrical with respect to nuclear spin. At temperatures at which the value of $h^2/8\pi^2IkT$ (see Chapter 19) is not small in comparison with unity, the transition of molecules between the even and odd rotational levels is extremely slow. The result is a sort of freezing of the molecules in their respective even or odd rotational levels, with transitions occurring freely among the even rotational levels and among the odd rotational levels but not between the two kinds of levels. In such case, the system behaves as though it were composed of two independent sets of levels of rotational energy, one set consisting of the rotational levels numbered, 0, 2, 4, 6, 8, 10, etc., and the other set consisting of the rotational levels numbered 1, 3, 5, 7, 9, 11, etc.

At high temperatures, the ratio of the number of molecules in the odd rotational levels to the number in the even rotational levels will be given by the ratio of the multiplicity arising from nuclear spin in the two sets of levels. The ratio of the number of molecules in the states of symmetrical spin to that in the states of antisymmetrical spin is, at high temperatures, $(s + 1)/s$, where s is the nuclear spin of the atom. As the temperature is lowered, and no transitions occur between the even and the odd rotational levels, this ratio remains constant and, in the limit, will represent the relative number of molecules in the rotational levels numbered 0 and 1, since with lowering of temperature the population will converge on the lowest level in each of the two series of levels, even and odd.

Because the hydrogen molecule has a small moment of inertia, and the separation of the levels of rotational energy is correspondingly great, the foregoing phenomenon is easily observed experimentally for this molecule. For the hydrogen atom of mass 1, the nuclear spin is $s = \frac{1}{2}$. The even rotational states are antisymmetric (called *para*) and the odd rotational states are symmetric (called *ortho*). At high temperatures the ratio of the number of molecules in the symmetric or odd rotational states to the number in the antisymmetric or even rotational states is calculated from the nuclear spin to be $(s + 1)/s = 3$.

As the temperature is lowered, this ratio of the number of molecules in the two sets of rotational levels remains substantially unchanged, and, in the limit of lowering temperature, will represent the ratio of the number of molecules in the rotational level numbered $j = 1$ to that in the rotational level numbered $j = 0$. But the ordinary multiplicity, g_i, of the rotational levels is $2j_i + 1$, so that for $j = 0$, $g_0 = 1$, and for $j = 1$, $g_1 = 3$. The multiplicity arising from the nuclear spin is $(s + 1)(2s + 1)$ for the symmetric or odd rotational levels and $s(2s + 1)$ for the antisymmetric or even rotational levels, the ratio being $(s + 1)/s$. For $s = \frac{1}{2}$, the multiplicity arising from nuclear spin becomes 1 for the even rotational levels and 3 for the odd rotational levels. Therefore, the total multiplicity for the rotational level $j = 0$ is $g_0 = 1$, and for the rotational level $j = 1$ is $g_1 = 3 \times 3 = 9$. Near 0°K, the mole fraction of molecules in the single state at the ground level, $j = 0$, is $\frac{1}{4}$, and the mole fraction of molecules in each of the 9 states at the first rotational level, $j = 1$, is $\frac{1}{9} \times \frac{3}{4} = \frac{1}{12}$. For such a system, the entropy will be greater than it would be if all the molecules were in a single state by just the entropy of mixing 1 mole of molecules such that $\frac{1}{4}$ mole is in the single state at the zero rotational level, $j = 0$, and $\frac{1}{12}$ mole is in each of the 9 states at the first rotational level, $j = 1$.

This entropy of mixing, arising from the effect of nuclear spin at low temperatures, is

$$S \text{ (mixing, effect of nuclear spin at low temperatures)} =$$
$$-R\sum \mathrm{N}_i \ln \mathrm{N}_i = -R[\tfrac{1}{4} \ln \tfrac{1}{4} + 9(\tfrac{1}{12} \ln \tfrac{1}{12})]$$
$$= R[\ln 4 + (\tfrac{3}{4}) \ln 3] = 4.392 \text{ cal/deg mole.} \quad (13)$$

Suppose that we have 1 mole of ordinary hydrogen at room temperature, such that it has the high-temperature distribution of numbers of molecules in the odd and even rotational states, 3 to 1, and subject this hydrogen to calorimetric measurements down to low temperatures (near 10°K), with no catalyst to permit transitions between the even and odd rotational levels in any significant amount. Then, retaining the convention that the entropy $S°$ written without qualification does not include the contribution arising from the effect of nuclear spin at high temperatures, which is $R \ln (2s + 1)$ for each atom in the molecule, we can write, for 1 mole of hydrogen,

$$S^\circ_{298.16} = S_0^\circ + \left(\int_0^{10} \frac{\delta q}{T}\right)_{\text{extrap.}} + \int_{10}^{298.16} \frac{\delta q}{T}. \quad (14)$$

For this 1 mole of hydrogen, the value of $S_0°$ should be equal to the entropy of mixing arising from the effect of nuclear spin at low temperatures, as given by Equation 13, less the entropy of mixing arising from the effect of nuclear spin at high temperatures, which is

$$S \text{ (mixing, effect of nuclear spin at high temperatures)} = \\ 2R \ln (2s + 1) = 2R \ln 2 = 2.755 \text{ cal/deg mole.} \quad (15)$$

Therefore, for 1 mole of this actual hydrogen, which has been subjected to measurement with the molecules "frozen" in the even and odd rotational states according to the relative populations at high temperatures,

$$\begin{aligned} S_0{}^\circ &= S \text{ (mixing, effect of nuclear spin at low temperatures)} \\ &\quad - S \text{ (mixing, effect of nuclear spin at high temperatures)} \\ &= 1.637 \text{ cal/deg mole.} \end{aligned} \quad (16)$$

Giauque (*12*) has reviewed the calorimetric data (*13,14*) on hydrogen down to low temperatures, and evaluated, in accordance with Equation 14, $S_0{}^\circ$ to be 1.57 cal/deg mole. Within the limits of uncertainty of the experimental data, this value is identical with the value given by Equation 16.

In the case of the diatomic molecule composed of hydrogen atoms of mass 2, deuterium, a similar situation exists, as follows: For the deuterium atom, the nuclear spin is $s = 1$. The value of the contribution from the effect of nuclear spin at high temperatures is

$$S \text{ (mixing, effect of nuclear spin at high temperatures)} = \\ 2R \ln (2s + 1) = 2R \ln 3 = 4.366 \text{ cal/deg mole.} \quad (17)$$

At high temperatures, the relative number of molecules in the symmetric to the number in the antisymmetric levels is $(s + 1)/s$, or 2. With a distribution of molecules "frozen" according to that at high temperatures, the deuterium will, in the limit at 0°K, have $\frac{2}{3}$ of the molecules in the lowest symmetric level and $\frac{1}{3}$ of the molecules in the lowest antisymmetric level. The even rotational levels of deuterium $j = 0, 2, 4, 6, 8, 10$, etc., are symmetric, and the odd rotational levels, $j = 1, 3, 5, 7, 9, 11$, etc., are antisymmetric. The ordinary multiplicity, $2j + 1$, of the 0 and 1 rotational levels is 1 and 3, respectively. The multiplicity arising from the effect of nuclear spin is $(s + 1)(2s + 1)$, or 6, for the symmetric or even rotational levels, and is $s(2s + 1)$, or 3, for the antisymmetric or odd rotational levels. Then the total multiplicity for the lowest symmetric, even, rotational level, $j = 0$, is $(2j + 1)(s + 1)(2s + 1)$, or 6, and the total multiplicity for the lowest antisymmetric, odd, rotational level, $j = 1$, is $(2j + 1)(s)(2s + 1)$, or 9.

At 0°K, the mole fraction of molecules in each of the 6 states at the ground level, $j = 0$, is $\frac{2}{3} \times \frac{1}{6}$, or $\frac{1}{9}$, and the mole fraction in each of the 9 states at first rotational level, $j = 1$, is $\frac{1}{3} \times \frac{1}{9}$, or $\frac{1}{27}$. Therefore, the entropy of mixing arising from the effect of nuclear spin at low temperatures is

S (mixing, effect of nuclear spin at low temperatures) =

$$-R\sum \text{N}_i \ln \text{N}_i = -R[6(\tfrac{1}{9} \ln \tfrac{1}{9}) + 9(\tfrac{1}{27} \ln \tfrac{1}{27})]$$

$$= \tfrac{7}{3} R \ln 3 = 5.094 \text{ cal/deg mole.} \qquad (18)$$

Consider a sample of deuterium gas obtained at room temperature, in which $\frac{2}{3}$ of the molecules are in the even or *ortho* rotational levels and $\frac{1}{3}$ are in the odd or *para* rotational levels. Suppose that calorimetric measurements are made on this deuterium down to low temperatures, near 10°K, in such a way that no significant number of transitions occur between the even and the odd rotational levels. Then the molecules are "frozen" in their respective sets of rotational levels, and, in the limit of low temperature, will be in the zero and first rotational levels in $\frac{2}{3}$ and $\frac{1}{3}$ mole fractions, respectively. With the convention that $S_0°$ is not to include the contribution arising from the effect of nuclear spin at high temperatures, we may write for the value of $S_0°$ for deuterium measured as above, in accordance with Equation 16:

$S_0°$ = S (mixing, effect of nuclear spin at low temperatures) −

S (mixing, effect of nuclear spin at high temperatures) =

$$0.728 \text{ cal/deg mole.} \qquad (19)$$

From the appropriate experimental data on deuterium down to low temperatures, the value of $S_0°$ from Equation 14 is calculated to be 0.68 cal/deg mole (*15,16*). Within the limits of the experimental data, this value is in accord with that given in Equation 19.

It should be emphasized that, if the calorimetric measurements down to low temperatures on hydrogen or deuterium are made in the presence of a catalyst which would permit substantially free transitions between the odd rotational levels and the even rotational levels, so that, as the temperature is lowered, in the limit, all the hydrogen or deuterium molecules would be in the zero rotational level, then such measurements would conform to the requirements for the application of the third law and the value of $S_0°$ in Equation 14 would be found to be zero.

7. Entropy of solutions at the absolute zero of temperature. Consider a substance, solid, liquid, or gas, that is composed of two different kinds of molecules, MX and NY. If, at the lowest temperature of measurement, T_*, the observations on this substance are such that the extrapolation of them from T_* to 0°K effectively places all of each of the two kinds of molecules in their respective zero levels of energy, then the entropy remaining in this substance at 0°K would be the entropy of mixing the two kinds of molecules to form the given solution. In such case, the value of $S_0°$ for this substance is given by the relation (Chapters 13 and 25)

$$S_0° = -R\sum \text{N}_i \ln \text{N}_i. \tag{20}$$

That is to say, the entropy of such a substance at 298.16°K would be equal to the value of the integral $\int_0^{298.16} \delta q/T$ plus the value of the entropy of mixing, $-R\sum \text{N}_i \ln \text{N}_i$.

An excellent illustration of the foregoing phenomenon is given by the work of Eastman and Milner (*17*), who determined the value of $\int_0^{298.16} \delta q/T$ for solid silver chloride, pure solid silver bromide, and a solid solution of silver chloride and silver bromide containing 0.272 mole fraction of silver chloride, and, from appropriate thermodynamic measurements at 298.16°K, determined the value of $\Delta S^\circ_{298.16}$ for the reaction of forming the solid solutions from the pure compounds. Letting A represent 1 mole of AgCl (c), B represent 1 mole of AgBr (c), and D represent 1 mole of the solid solution, we may write the quantities determined experimentally by Eastman and Milner (*17*) as follows:

$$(S^\circ_{298.16} - S_0°)(\text{A}) = \int_0^{298.16} \frac{\delta q}{T}\,(\text{A})$$
$$= 22.97 \pm 0.10 \text{ cal/deg mole}; \tag{21}$$

$$(S^\circ_{298.16} - S_0{}^\circ)(\mathrm{B}) = \int_0^{298.16} \frac{\delta q}{T}\,(\mathrm{B})$$

$$= 25.62 \pm 0.10 \text{ cal/deg mole}; \tag{22}$$

$$(S^\circ_{298.16} - S_0{}^\circ)(\mathrm{D}) = \int_0^{298.16} \frac{\delta q}{T}\,(\mathrm{D})$$

$$= 24.99 \pm 0.10 \text{ cal/deg mole}; \tag{23}$$

$$\Delta S^\circ_{298.16} = 1.12 \pm 0.06 \text{ cal/deg mole}. \tag{24}$$

Equation 24 applies to the reaction of forming the solid solution from its pure component compounds:

$$0.272\mathrm{AgCl}\ (\mathrm{c}) + 0.728\mathrm{AgBr}\ (\mathrm{c}) = (0.272\mathrm{AgCl} + 0.728\mathrm{AgBr})\ (\text{solid soln.}) \tag{25}$$

or, in the foregoing notation

$$0.272\mathrm{A} + 0.728\mathrm{B} = \mathrm{D}. \tag{26}$$

For this reaction, we may write

$$\begin{aligned}\Delta S^\circ_{298.16} - \Delta S_0{}^\circ &= \Delta(S^\circ_{298.16} - S_0{}^\circ) \\ &= (S^\circ_{298.16} - S_0{}^\circ)(\mathrm{D}) - 0.272(S^\circ_{298.16} - S_0{}^\circ)(\mathrm{A}) \\ &\quad - 0.728(S^\circ_{298.16} - S_0{}^\circ)(\mathrm{B}).\end{aligned} \tag{27}$$

Therefore,

$$\begin{aligned}\Delta S_0{}^\circ = \Delta S^\circ_{298.16} &- (S^\circ_{298.16} - S_0{}^\circ)(\mathrm{D}) \\ &+ 0.272(S^\circ_{298.16} - S_0{}^\circ)(\mathrm{A}) \\ &+ 0.728(S^\circ_{298.16} - S_0{}^\circ)(\mathrm{B}).\end{aligned} \tag{28}$$

Substituting the values given by Equations 21, 22, 23, and 24, we have for the experimentally determined value of $\Delta S_0{}^\circ$ for the reaction given by Equations 25 and 26,

$$\begin{aligned}\Delta S_0{}^\circ &= 1.12 - 24.99 + 6.248 + 18.653 \\ &= 1.03 \pm 0.15 \text{ cal/deg mole}.\end{aligned} \tag{29}$$

If our understanding of the application of the third law to solutions is correct, the value of $\Delta S_0{}^\circ$ should be calculated by Equation 20.

Calculating the entropy of mixing by Equation 20, we have,

$$\begin{aligned}\Delta S_0^\circ \text{ (mixing)} &= -R\sum \text{N}_i \ln \text{N}_i \\ &= -R(0.272 \ln 0.272 + 0.728 \ln 0.728) \\ &= 1.16 \text{ cal/deg mole.} \qquad (30)\end{aligned}$$

Within the limits of uncertainty of the experimentally determined value, the two values for ΔS_0° are in accord.

8. Entropy of glasses at the absolute zero of temperature. With lowering of temperature, some liquid substances may become glass-like solids instead of crystalline solids. In certain cases, the given liquid substance may become either a glass-like solid or a crystalline solid depending upon the rate and manner of cooling. In a glass-like solid, the molecules obviously exhibit a considerable randomness of arrangement. It is to be expected that on further cooling this radomness of arrangement will be "frozen" in the glass-like solid and, in the limit, the glass will possess, at 0°K, an entropy associated with this randomness of arrangement of the molecules. That is to say, when such glass-like substances are measured down to low temperatures, the value of S_0°, in Equation 3, will be greater than zero.

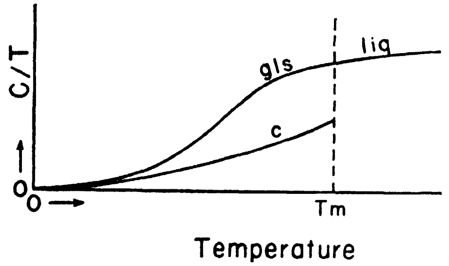


FIGURE 2. Schematic diagram of the relation between the temperature and heat capacity divided by the temperature, C/T, for both the crystalline and glass-like form of the same substance.

Figure 2 gives a schematic plot of the heat capacity divided by the temperature as a function of the temperature for a substance which may be obtained, below its normal melting point, either as a crystalline solid or as a glass. It will be noted that, when the substance goes completely to the glass form below the melting point, there is no discontinuity in the curve of heat capacity at the melting point, but the heat capacity decreases gradually until at some low temperature it approaches smoothly the curve of heat capacity for the crystalline solid.

The following general relation holds:

$$S_{Tm}^\circ \text{ (liq)} = S_0^\circ + \int_0^{Tm} \frac{\delta q}{T}. \qquad (31)$$

For the path involving the heat capacity of the crystalline solid form 0°K to the melting point, Tm, with melting of the crystalline solid at Tm, Equation 31 becomes

$$S^{\circ}_{Tm}\ (\text{liq}) = S_0{}^{\circ}\ (\text{c}) + \int_0^{Tm} \frac{C_P\ (\text{c})}{T}\, \mathrm{d}T + \frac{\Delta Hm\ (\text{c})}{Tm}. \tag{32}$$

For the path involving the heat capacity of the glass from 0°K to the melting point, Tm, Equation 31 becomes

$$S^{\circ}_{Tm}\ (\text{liq}) = S_0{}^{\circ}\ (\text{gls}) + \int_0^{Tm} \frac{C_P\ (\text{gls})}{T}\, \mathrm{d}T. \tag{33}$$

Equating the two values of the entropy of the liquid at the melting point, as given by Equations 32 and 33, we obtain

$$S_0{}^{\circ}\ (\text{gls}) - S_0{}^{\circ}\ (\text{c}) = -\int_0^{Tm} \frac{C_P\,(\text{gls})}{T}\, \mathrm{d}T + \int_0^{Tm} \frac{C_P\,(\text{c})}{T}\, \mathrm{d}T + \frac{\Delta Hm\ (\text{c})}{Tm}, \tag{34}$$

or

$$S_0{}^{\circ}\ (\text{gls}) - S_0{}^{\circ}\ (\text{c}) = \frac{\Delta Hm\ (\text{c})}{Tm} - \int_0^{Tm} \frac{C_P\,(\text{gls}) - C_P\,(\text{c})}{T}\, \mathrm{d}T. \tag{35}$$

Unless there are complicating factors of the kind described in the preceding sections of this chapter, the entropy of the crystal at 0°K may be placed equal to zero, so that the value of the entropy of the glass at 0°K is given by the relation

$$S_0{}^{\circ}\ (\text{gls}) = \frac{\Delta Hm\ (\text{c})}{Tm} - \int_0^{Tm} \frac{C_P\,(\text{gls}) - C_P\,(\text{c})}{T}\, \mathrm{d}T. \tag{36}$$

Since the entropy of the glass at 0°K will be greater than zero, the foregoing relation shows that the entropy of fusion of the crystalline solid at the melting point, $\Delta Sm = \Delta Hm/Tm$, will be greater than the value of the last term in Equation 36. Referring to Figure 2, this means that the entropy of fusion of the crystalline solid at the melting point is greater than the area between the two curves of C_P/T from 0° to Tm°K.

Examples of the foregoing phenomenon have been observed experimentally for glycerol and ethanol, both of which substances may be obtained as a glass or as a crystalline solid by appropriate cooling. In the case of glycerol, Gibson and Giauque (*18*) calculated that the glassy glycerol which was formed in their calorimeter had an entropy at 0°K equal to 5.6 cal/deg mole. Similar observations made on glycerol by Simon and Lange (*19*) yielded a value of 4.6 cal/deg mole for the entropy at 0°K of the glassy glycerol formed in their calorimeter. For ethanol, Kelley (*20*) calculated the entropy at 0°K of the glassy ethanol formed in his calorimeter to be 2.6 cal/deg mole. For further discussion of the significance of such measurements in relation to the third law, the reader is referred to Nelson and Newton (*34*) and Jones and Simon (*35*).

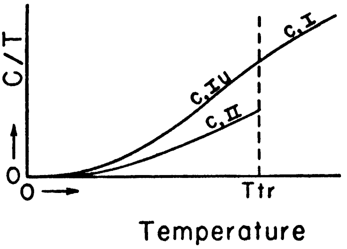


FIGURE 3. Schematic diagram of the relation between the temperature and heat capacity divided by the temperature, C/T, for a substance that has two stable crystalline forms, II from 0° to *Ttr*, and I from *Ttr* to *Tm*, with crystalline form I being obtainable in a metastable state, I*u*, below *Ttr*.

9. Entropy of different crystalline forms of the same pure substance at the absolute zero of temperature. It was earlier mentioned that the application of the third law was not limited to just one crystalline form of a given substance but might be applied to two or more different crystalline forms of the same substance, provided these forms could be obtained pure in a stable or metastable state at the lowest temperature of measurement, T_*, and provided the extrapolation from T_* to 0°K effectively reduced all the molecules of the given crystal to a common single state of energy.

This phenomenon is illustrated schematically in Figure 3, in which is plotted C_P/T as a function of T for a substance that has two stable crystalline forms. In this example, crystalline form I may be carried below *Ttr* to T_* in a metastable condition, denoted as (*u*), without transition to crystalline form II. Ordinarily, though, crystalline form I will have a transition to crystalline form II at the temperature of transition, *Ttr*.

The following relations hold:

$$S^\circ_{Ttr}\,(\text{c, I}) = S_0{}^\circ\,(\text{c, I}u) + \int_0^{Ttr} \frac{\delta q}{T}\,(\text{c, I}u)$$

$$= S_0{}^\circ\,(\text{c, I}u) + \int_0^{Ttr} \frac{C_P\,(\text{c, I}u)}{T}\,dT; \qquad (37)$$

$$S^\circ_{Ttr}\ (\text{c, I}) = S_0{}^\circ\ (\text{c, II}) + \int_0^{Ttr} \frac{\delta q}{T}\ (\text{c, II}) + \frac{\Delta Htr}{Ttr}\ (\text{II} \rightarrow \text{I})$$

$$= S_0{}^\circ\ (\text{c, II}) + \int_0^{Ttr} \frac{C_P\ (\text{c, II})}{T}\, \mathrm{d}T + \frac{\Delta Htr}{Ttr}\ (\text{II} \rightarrow \text{I}). \quad (38)$$

Now, if each crystalline form is in a single quantum state at the absolute zero of temperature, arrived at by extrapolation from T_* to 0°K, then, for each crystalline form, in this example the forms labeled c, I*u* and c, II, $S_0{}^\circ$ may be placed equal to zero. Equations 37 and 38 become, therefore, as follows:

$$S^\circ_{Ttr}\ (\text{c, I}) = \int_0^{Ttr} \frac{C_P\ (\text{c, I}u)}{T}\, \mathrm{d}T; \quad (39)$$

$$S^\circ_{Ttr}\ (\text{c, I}) = \int_0^{Ttr} \frac{C_P\ (\text{c, II})}{T}\, \mathrm{d}T + \frac{\Delta Htr}{Ttr}\cdot \quad (40)$$

Equating these two values of the entropy of crystalline form I at the temperature of transition, we obtain the relation

$$\frac{\Delta Htr}{Ttr} = \int_0^{Ttr} \frac{C_P\ (\text{c, I}u) - C_P\ (\text{c, II})}{T}\, \mathrm{d}T. \quad (41)$$

That is to say, if experimental measurements are made on two different crystalline forms of the same substance from the normal temperature of transition down to near 0°K, it will be found that the entropy of transition, $\Delta Str = \Delta Htr/Ttr$, is equal to the integral, from 0° to *Ttr*°K, of the difference in the heat capacity of the two crystalline forms divided by the temperature. Referring to Figure 3, we can say that the entropy of transition is equal to the area between the two curves of heat capacity from 0° to *Ttr*°K.

Examples of the foregoing phenomenon have been completely reported for sulfur in its rhombic and monoclinic forms, and for phosphine in the lower two of its three stable crystalline forms.

For sulfur, Eastman and McGavock (*21*) obtained the following results:

$$Ttr\ (\text{rhombic} \rightarrow \text{monoclinic}) = 368.6°\text{K}; \quad (42)$$

$$\int_0^{368.6} \frac{C_P\ (\text{c, monoclinic})}{T}\, \mathrm{d}T = 9.040 \pm 0.050\ \text{cal/deg mole}; \quad (43)$$

$$\int_0^{368.6} \frac{C_P\ (\text{c, rhombic})}{T}\, dT = 8.827 \pm 0.050 \text{ cal/deg mole;} \tag{44}$$

$$\Delta Str = \frac{\Delta Htr}{Ttr} = 0.258 \pm 0.010 \text{ cal/deg mole.} \tag{45}$$

According to Equation 41, the difference in the values given for Equations 43 and 44, namely, 0.213 ± 0.070 cal/deg mole, should be equal to the value of the heat of transition, 0.258 ± 0.010 cal/deg mole. Within the limits of uncertainty, the values are the same.

For phosphine, the data of Stephenson and Giauque (*22*) give the following results:

$$Ttr\ (\text{III} \rightarrow \text{II}) = 49.43^\circ \text{ K;} \tag{46}$$

$$\int_0^{49.43} \frac{\delta q}{T}\ (\text{c, II}u) = 8.127 \text{ cal/deg mole;} \tag{47}$$

$$\int_0^{49.43} \frac{\delta q}{T}\ (\text{c, III}) = 4.379 \text{ cal/deg mole;} \tag{48}$$

$$\begin{aligned} \Delta Str\ (\text{III} \rightarrow \text{II}) &= \frac{\Delta Htr(\text{III} \rightarrow \text{II})}{49.43} \\ &= 3.757 \text{ cal/deg mole.} \end{aligned} \tag{49}$$

It is seen that the difference between the values from Equations 47 and 48, namely, 3.748 cal/deg mole, is identical with the value of the entropy of transition given by Equation 49, namely, 3.757 cal/deg mole, within the limits of uncertainty of the measurements.

Kelley (*20*) has reported similar results on cyclohexanol.

10. History of the development of the third law of thermodynamics. The milestones in the development of the third law may be summarized as follows:

In 1902, Richards (*25*) reported on the results of an experimental study of the variation, with temperature, of the increment in free energy of certain reactions occurring in electrolytic cells. He found that, with lowering of temperature, the increment in entropy, ΔS, for each reaction approached zero, and the increment in heat capacity, ΔC_P, also approached zero. If the value of ΔS became zero at 0°K, the sum of the entropies at 0°K for the products of the given reaction would be equal to the sum of the entropies at 0°K for the reactants. This result would occur if the entropy of each reactant or product were equal to zero at 0°K, or if, at 0°K, the entropy of each atom had a constant value irrespective of its molecular combination.

In 1906, Nernst (*26*) pronounced his famous heat theorem, that for all reactions involving substances in the condensed state, liquid or solid, the increment in entropy would be zero at 0°K.

In 1912, Planck (*27*) amplified the Nernst heat theorem by suggesting that the entropy at 0°K be taken as zero for all condensed substances at 0°K, and pointed out that solutions at 0°K would have an entropy equal to the entropy of mixing.

In 1917, Lewis and Gibson (*28*) reported the results of extensive tests of the validity and applicability of the third law and in 1920 formulated their rigorous statement of the third law in non-quantum mechanical terms. Lewis and Gibson emphasized that it is necessary to specify an orderly arrangement of the molecules in the condensed phase to which the third law is to be applied, that, in general, the third law would be applicable only to "perfect" crystals, and that solutions and glasses are excluded from applications of the third law.

Under the inspiration of G. N. Lewis, many contributions bearing on the third law and its proper application to chemical substances were made by W. F. Giauque, E. D. Eastman, W. M. Latimer, and their associates at the University of California. Some of these contributions have been mentioned earlier in this chapter. Eastman (*2*) reviewed the status of the development of the third law as it existed in 1936, and Pauling and Eastman (*3*) and Rodebush (*30*) discussed the significance of the third law in terms of quantum mechanics.

11. Collateral reading. For detailed discussions of the third law of thermodynamics and its application to chemical substances, the reader is referred to the many references given in the preceding sections of this chapter together with the following: Lewis and Randall (*1*), Tolman (*4*), Mayer and Mayer (*5*), Pauling and Eastman (*3*), and Simon (*33*).

REFERENCES

1. G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill Book Company, New York, 1923.
2. E. D. Eastman, *Chem. Revs.* **18**, 257 (1936).
3. L. Pauling and E. D. Eastman, *J. Chem. Phys.* **4**, 393 (1936).
4. R. C. Tolman, *The Principles of Statistical Mechanics*, Oxford University Press, Oxford, 1938.
5. J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, John Wiley & Sons, New York, 1940.
6. H. L. Johnston and W. F. Giauque, *J. Am. Chem. Soc.* **51**, 3194 (1929).
7. J. O. Clayton and W. F. Giauque, *J. Am. Chem. Soc.* **54**, 2610 (1932).
8. R. W. Blue and W. F. Giauque, *J. Am. Chem. Soc.* **57**, 991 (1935).
9. W. F. Giauque and J. W. Stout, *J. Am. Chem. Soc.* **58**, 1144 (1936).
10. E. A. Long and J. D. Kemp, *J. Am. Chem. Soc.* **58**, 1829 (1936).
11. L. Pauling, *J. Am. Chem. Soc.* **57**, 2680 (1935).
12. W. F. Giauque, *J. Am. Chem. Soc.* **52**, 4816 (1930).
13. F. Simon and E. Lange, *Z. Physik.* **15**, 312 (1923).
14. R. E. Cornish and E. D. Eastman, *J. Am. Chem. Soc.* **50**, 627 (1928).
15. H. L. Johnston and E. A. Long, *J. Chem. Phys.* **2**, 389 (1934).
16. K. Clusius and E. Bartholomi, *Z. Physik. Chem.* **B30**, 258 (1935).
17. E. D. Eastman and R. T. Milner, *J. Chem. Phys.* **1**, 444 (1933).
18. G. E. Gibson and W. F. Giauque, *J. Am. Chem. Soc.* **45**, 93 (1923).
19. F. Simon and E. Lange, *Z. Physik.* **38**, 227 (1926).
20. K. K. Kelley, *J. Am. Chem. Soc.* **51**, 1400 (1929).
21. E. D. Eastman and W. C. McGavock, *J. Am. Chem. Soc.* **59**, 145 (1937).
22. C. C. Stephenson and W. F. Giauque, *J. Chem. Phys.* **5**, 149 (1937).
23. J. D. Kemp and W. F. Giauque, *J. Am. Chem. Soc.* **59**, 79 (1937).
24. W. F. Giauque and R. A. Ruehrwein, *J. Am. Chem. Soc.* **61**, 2626 (1939).
25. T. W. Richards, *Z. Physik. Chem.* **42**, 129 (1902).
26. W. Nernst, *Nachr. kgl. Ges. Wiss. Göttingen. Math.-physik. Klasse* 1, 1906.
27. M. Planck, *Ber.* **45**, 5 (1912).
28. G. N. Lewis and G. E. Gibson, *J. Am. Chem. Soc.* **39**, 2554 (1917).
29. G. N. Lewis and G. E. Gibson, *J. Am. Chem. Soc.* **42**, 1529 (1920).
30. W. H. Rodebush, *J. Chem. Phys.* **2**, 669 (1934).
31. E. O. Wollan, W. L. Davidson, and C. G. Shull, *Phys. Rev.* **75**, 1348 (1949).
32. W. F. Giauque and W. M. Jones, *J. Am. Chem. Soc.* **70**, 120 (1948).
33. F. E. Simon, *Physica* **4**, 1089 (1937).
34. E. W. Nelson and R. F. Newton, *J. Am. Chem. Soc.* **63**, 2178 (1941).
35. G. O. Jones and F. E. Simon, *Endeavour* **8**, 175 (1949).

PROBLEMS

1. The following data are given for the substance MX:

MX (c), $C_P = 0.040T + 0.00020T^2$ cal/deg mole, from 0° to Tm°K;

MX (liq), $C_P = 7.00 + 0.0050T$ cal/deg mole, from Tm° to Tv°K;

$$MX\ (g),\ C_P = 8.00 + 0.0030T + 0.00010T^2 \text{ cal/deg mole, from } Tv^\circ \text{ to } 400^\circ\text{K};$$

$$Tm = 100^\circ\text{K};$$

$$Tv = 200^\circ\text{K};$$

$$\Delta Hm = 1200 \text{ cal/mole at } Tm^\circ\text{K};$$

$$\Delta Hv = 4800 \text{ cal/mole at } Tv^\circ\text{K and 1 atm.}$$

Calculate the value of H°_{400} (g) $-$ $H_0{}^\circ$ (c). Assuming the substance to conform to the requirements of the third law, calculate the value of the entropy of MX (g) at 400°K and 1 atm.

2. Calculate the entropy of mixing the isotopes of mercury to form 1 mole of the naturally occurring mixture of the isotopes, assumed as follows, in mole fraction: ^{196}Hg, 0.001; ^{198}Hg, 0.101; ^{199}Hg, 0.170; ^{200}Hg, 0.233; ^{201}Hg, 0.132; ^{202}Hg, 0.296; ^{204}Hg, 0.067.

3. Assuming no other complications, calculate the entropy at 0°K of a solid solution of MX and NY containing 0.40 mole fraction of MX and 0.60 mole fraction of NY.

4. For the substance MX, which has two stable crystalline forms, the following experimental data are given:

$$\int_0^{Ttr} \frac{C_P\ (\text{c, I})}{T}\, dT = 25.00 \text{ cal/deg mole;}$$

$$\int_0^{Ttr} \frac{C_P\ (\text{c, II})}{T}\, dT = 20.00 \text{ cal/deg mole;} \qquad Ttr = 100^\circ\text{K.}$$

Calculate the heat of transition of crystalline form II to crystalline form I at 100°K.

5. By experimental measurement in the range 10° to 300°K, and extrapolation from 10° to 0°K by means of the Debye equation for the heat capacity of solids, values of $\int_0^{298.16} \delta q/T$ are obtained for several substances, as follows, in calories per degree mole: Ag, 10.15; AgCl, 22.97; HgCl, 22.80; Hg, 17.80. The physical state of each of these substances at 298.16°K is solid except for Hg, which is liquid. Calculate the value of ΔS at 298.16°K for the reaction

$$\text{Ag (c)} + \text{HgCl (c)} = \text{AgCl (c)} + \text{Hg (liq).}$$

21

Equilibrium Constant and the Change in Free Energy for Reactions of Ideal Gases

1. Free energy of an ideal gas as a function of pressure at constant temperature. When a given system participates in a reversible process in which only heat energy and PV work energy occur, we have seen (Chapter 17) that, at constant temperature,

$$dF = V\,dP. \tag{1}$$

Substituting, for an ideal gas,

$$V = \frac{RT}{P} \tag{2}$$

we obtain

$$dF = \frac{RT}{P}\,dP = RT\,d\ln P. \tag{3}$$

Equation 3 gives the variation of the free energy of an ideal gas with pressure at constant temperature. On integrating between states of different pressure, A and B, at constant temperature, we obtain the relation

$$F_B - F_A = RT\ln\frac{P_B}{P_A}\cdot \tag{4}$$

2. Free energy of mixing ideal gases. In Chapter 13, we derived the relation giving the change in entropy on mixing different ideal gases. For the case of bringing together gases initially at identical pressures to form a mixture at the same pressure, the change in entropy, calculated per mole of the mixture, was found to be

$$\Delta S\ (\text{mixing}) = -R\sum \mathrm{N}_i \ln \mathrm{N}_i, \tag{5}$$

where N_i is the mole fraction of component i in the mixture and the summation is carried over all the components. The number of moles in the entire mixture is $\sum n_i$, so that the entropy of mixing for the entire mixture is the value given by Equation 5 multiplied by $\sum n_i$.

From the definition of the ideal gas, we can write, for constant temperature,

$$\Delta E \text{ (mixing)} = \Delta H \text{ (mixing)} = 0. \tag{6}$$

But by definition of the free energy for a given substance (Chapter 16),

$$F = H - TS. \tag{7}$$

Applied to a process or reaction at constant temperature, Equation 7 becomes

$$(F_B - F_A) = (H_B - H_A) - T(S_B - S_A), \tag{8}$$

or

$$\Delta F = \Delta H - T\,\Delta S. \tag{9}$$

Applying Equation 9 to the above process of mixing ideal gases, and substituting from Equations 5 and 6, we obtain, at constant temperature,

$$\Delta F \text{ (mixing)} = RT \sum N_i \ln N_i. \tag{10}$$

Equation 10 gives the change in free energy, per mole of mixture, on mixing different ideal gases brought together in different amounts from initially identical pressures to form a mixture at the same pressure. For the entire mixture, the corresponding value is that given by Equation 10 multiplied by $\sum n_i$, the number of moles in the entire mixture.

The change in free energy on mixing ideal gases originally at different pressures is readily calculated by first taking account of the change in free energy on bringing each gas separately to the common pressure before mixing. The change in free energy with pressure at constant temperature for the mixture of ideal gases is given by Equation 4, assuming the mixture to remain fixed in composition.

By proceeding as mentioned in the foregoing paragraph, it may be shown that the free energy of an ideal gas at constant temperature is fixed by the volume it occupies, and is independent of the presence of other gases. That is to say, if two ideal gases are mixed so that the volume of the mixture is the same as the volume of each gas before mixing, then the change in free energy (as also the change in entropy) is zero.

3. Definition of the proper quotient of pressures and the equilibrium constant. At this point in our discussion, it is convenient to define what we may term the "proper quotient of pressures," as well as the equilibrium constant, for reactions of ideal gases.

Given the following reaction in which each reactant and product is an ideal gas:

$$b\mathrm{B}\ (\mathrm{g}) + c\mathrm{C}\ (\mathrm{g}) = m\mathrm{M}\ (\mathrm{g}) + n\mathrm{N}\ (\mathrm{g}). \tag{11}$$

Equation 11 states that b moles of the gas B react with c moles of the gas C to form m moles of the gas M and n moles of the gas N. For any such reaction, the "proper quotient of pressures" is here defined as

$$Q_P = \frac{(P_\mathrm{M})^m (P_\mathrm{N})^n}{(P_\mathrm{B})^b (P_\mathrm{C})^c}. \tag{12}$$

That is to say, the numerator is the product of the pressure of each of the product gases with each pressure raised to a power equal to the stoichiometrical number of moles of the given gas, and the denominator is the product of the pressure of each of the reactant gases, with each pressure raised to a power equal to the stoichiometrical number of moles of the given gas.

The proper quotient of pressures, Q_P, may be written for any reaction of gases in any states. When, however, the pressure of each reactant and each product gas is that which it has at thermodynamic equilibrium for the given reaction, the proper quotient of pressures is then specified for the equilibrium states, as Q_P (equilibrium), or $Q_P{}^e$, and it is convenient to write this as the equilibrium constant, K. For the reaction of ideal gases given by Equation 11, the equilibrium constant is

$$K = Q_P{}^e = \frac{(P_\mathrm{M}{}^e)^m (P_\mathrm{N}{}^e)^n}{(P_\mathrm{B}{}^e)^b (P_\mathrm{C}{}^e)^c}. \tag{13}$$

4. Relation between the change in free energy and the equilibrium constant. Consider the reaction given by Equation 11 as occurring at some constant temperature, T. We may write for the change in free energy for the given reaction, for any specified set of conditions,

$$\Delta F = mF_{\mathrm{M}} + nF_{\mathrm{N}} - bF_{\mathrm{B}} - cF_{\mathrm{C}}. \tag{14}$$

In Equation 14, F_{M}, F_{N}, F_{B}, and F_{C} are the free energies, per mole, for the gases M, N, B, and C, respectively, and m, n, b, and c are, respectively, the number of moles of the given gases participating in the reaction.

Suppose that we consider this reaction taking place under two different sets of conditions, one in which the participating gases are in certain states s, and the other in which the participating gases are in certain states e, and let us be concerned with the difference in the change in free energy for the given reaction under the two sets of conditions.

For the states s, we write

$$\Delta F^s = m(F_{\mathrm{M}}{}^s) + n(F_{\mathrm{N}}{}^s) - b(F_{\mathrm{B}}{}^s) - c(F_{\mathrm{C}}{}^s). \tag{15}$$

And for the states e, we write

$$\Delta F^e = m(F_{\mathrm{M}}{}^e) + n(F_{\mathrm{N}}{}^e) - b(F_{\mathrm{B}}{}^e) - c(F_{\mathrm{C}}{}^e). \tag{16}$$

Subtraction of Equation 16 from Equation 15 gives

$$\begin{aligned}\Delta F^s - \Delta F^e = m(F_{\mathrm{M}}{}^s - F_{\mathrm{M}}{}^e) + n(F_{\mathrm{N}}{}^s - F_{\mathrm{N}}{}^e)\\ - b(F_{\mathrm{B}}{}^s - F_{\mathrm{B}}{}^e) - c(F_{\mathrm{C}}{}^s - F_{\mathrm{C}}{}^e).\end{aligned} \tag{17}$$

But from Equation 4, for the gas M,

$$F_{\mathrm{M}}{}^s - F_{\mathrm{M}}{}^e = RT \ln \frac{P_{\mathrm{M}}{}^s}{P_{\mathrm{M}}{}^e}, \tag{18}$$

and

$$m(F_{\mathrm{M}}{}^s - F_{\mathrm{M}}{}^e) = mRT \ln \frac{P_{\mathrm{M}}{}^s}{P_{\mathrm{M}}{}^e} = RT \ln \left(\frac{P_{\mathrm{M}}{}^s}{P_{\mathrm{M}}{}^e}\right)^m. \tag{19}$$

Similar relations hold for the other gases.

Substitution into Equation 17 gives

$$\begin{aligned}\Delta F^s - \Delta F^e = RT \ln \left(\frac{P_{\mathrm{M}}{}^s}{P_{\mathrm{M}}{}^e}\right)^m + RT \ln \left(\frac{P_{\mathrm{N}}{}^s}{P_{\mathrm{N}}{}^e}\right)^n\\ - RT \ln \left(\frac{P_{\mathrm{B}}{}^s}{P_{\mathrm{B}}{}^e}\right)^b - RT \ln \left(\frac{P_{\mathrm{C}}{}^s}{P_{\mathrm{C}}{}^e}\right)^c.\end{aligned} \tag{20}$$

The terms on the right side of Equation 20 may be rearranged to bring together the factors involving the same states rather than the same molecules, as follows:

$$\Delta F^s - \Delta F^e = RT \ln \frac{(P_{\mathrm{M}}{}^s)^m (P_{\mathrm{N}}{}^s)^n}{(P_{\mathrm{B}}{}^s)^b (P_{\mathrm{C}}{}^s)^c} - RT \ln \frac{(P_{\mathrm{M}}{}^e)^m (P_{\mathrm{N}}{}^e)^n}{(P_{\mathrm{B}}{}^e)^b (P_{\mathrm{C}}{}^e)^c}, \tag{21}$$

or

$$\Delta F^s - \Delta F^e = RT \ln Q_P{}^s - RT \ln Q_P{}^e. \tag{22}$$

Now we may for convenience identify the states s as the reference or standard states in which each of the ideal gases has a pressure of unity, so that

$$(P_{\mathrm{M}}{}^s) = (P_{\mathrm{N}}{}^s) = (P_{\mathrm{B}}{}^s) = (P_{\mathrm{C}}{}^s) = 1. \tag{23}$$

Then

$$Q_P{}^s = 1, \quad \text{and} \quad \ln Q_P{}^s = 0. \tag{24}$$

Following the usual nomenclature, the reference or standard state may be indicated by the superscript °, so that the change in free energy for the s states becomes the standard change in free energy:

$$\Delta F^s = \Delta F^\circ. \tag{25}$$

Since we are interested in the states of the participating gases at thermodynamic equilibrium, we identify the e states as those of thermodynamic equilibrium for the given reaction at the given temperature. In such case, the proper quotient of pressures is the equilibrium constant,

$$Q_P{}^e = K. \tag{26}$$

But we have seen (Chapter 16) that, at constant temperature and constant pressure, the change in free energy at thermodynamic equilibrium is equal to zero, so that

$$\Delta F^e = 0. \tag{27}$$

On appropriate substitution of the foregoing into Equation 22, the latter reduces to

$$\Delta F^\circ = -RT \ln K. \tag{28}$$

It should be noted that, of the two pairs of corresponding terms in Equation 22, one term applying to the standard states and one term applying to the equilibrium states have been eliminated, so that in Equation 28 there remain two non-corresponding terms, one relating to the standard states, ΔF°, and one to the equilibrium states, $RT \ln K$.

Equation 28, which has been derived for any reaction of ideal gases at a given temperature, is one of the most powerful relations in the practical application of chemical thermodynamics. With this relation, the equilibrium constant may be evaluated from a knowledge of the standard change in free energy, and vice versa. Later on, it will be seen how the powerful simplicity of Equation 28 can be retained for use in reactions of any substances in any state, solid, liquid, or gas.

5. Relation between the equilibrium constant and the change in heat content and in entropy. From the definition of free energy (Chapter 16), we can write for any given substance

$$F = H - TS. \tag{29}$$

Equation 29 can be applied to the reactants and products of a given reaction, so that

$$\Delta F = \Delta H - \Delta(TS). \tag{30}$$

At constant temperature, Equation 30 becomes

$$\Delta F = \Delta H - T\,\Delta S. \tag{31}$$

If each of the reactants and products of the given reaction is in its respective standard reference state (see Equations 23, 24, and 25), then Equation 31 may be written as

$$\Delta F^\circ = \Delta H^\circ - T\,\Delta S^\circ, \tag{32}$$

where each of the thermodynamic properties applies to each reactant and product in its standard reference state.

But, from Equation 28,

$$\Delta F^\circ = -RT \ln K. \tag{33}$$

Combination of Equations 32 and 33 gives

$$\Delta H^\circ - T\,\Delta S^\circ = -RT \ln K, \tag{34}$$

or

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}. \tag{35}$$

From Equation 35, it is seen how one may calculate the equilibrium constant for a given reaction at a given temperature, if there are known the value of the heat of the reaction, ΔH°, and the value of the standard change in entropy for the reaction, ΔS°. We have seen (Chapter 18) how the value of the heat of the given reaction, ΔH°, may be determined. The value of ΔS° for the given reaction is obtained simply as the sum of the entropies of the products less the sum of the entropies of the reactants, each in its standard reference state:

$$\Delta S^\circ = \sum S^\circ \text{ (products)} - \sum S^\circ \text{ (reactants)}. \tag{36}$$

We have seen (Chapters 19 and 20) how the value of the entropy of a given substance may be determined from statistical calculations utilizing spectroscopic and other molecular data, or from application of the third law to calorimetric measurements of heats of vaporization, fusion, and transition and heat capacities, down to low temperatures.

6. Significance of the change in energy for a reaction. When two free neutral gaseous hydrogen atoms combine to form a gaseous hydrogen molecule,

$$\mathrm{H\ (g) + H\ (g) = H_2\ (g)}, \tag{37}$$

there is a decrease in the energy of the system of more than 100 kcal/mole. This means that the hydrogen molecule, with one H—H bond, has a lower energy than two separated hydrogen atoms not bonded together. Whenever the atoms in a given system rearrange themselves so that they are more securely bound one to another, the energy of the system is lowered.

Consider now the reaction of isomerization of cyclopropane to propylene:

$$\mathrm{C_3H_6\ (g, cyclopropane) = C_3H_6\ (g, propylene)}. \tag{38}$$

In the cyclopropane molecule, the three carbon atoms are bound one to another to form a ring, with two hydrogen atoms attached to each carbon atom, producing, in the molecule, three C—C bonds and six C—H bonds. In the propylene molecule, the three carbons are arranged in an open chain, with the center carbon being singly bound, C—C, to one end carbon and doubly bound, C═C, to the other end carbon, and with two hydrogen atoms on the doubly bound end carbon, one hydrogen atom on the center carbon, and three hydrogen atoms on the singly bound end carbon, producing, in the molecule, one C—C bond, one C═C bond, and six C—H bonds. When cyclopropane isomerizes to propylene, about 8 kcal/mole of energy are evolved, so that the energy of propylene is that much less than the energy of cyclopropane. In the isomerization to form propylene, the carbon and hydrogen atoms have rearranged themselves in such a way as to be more securely bound one to another, with consequent lower energy for the system.

In general, then, we may say that the change in energy of a reaction, ΔE [and for a simple approximation this may be taken as not significantly different from the value of ΔH, since the two differ only by the term $\Delta(PV)$], is a measure of the security of binding of the atoms in the molecules, the lower the energy the greater the security of binding. We may consider the decrease in energy (or approximately the heat content) of a system to be a measure of the security of existence possessed by the given system.

7. Significance of the change in entropy for a reaction. As we have already seen from the discussions in Chapters 11, 19, and 20, the entropy of a system is a measure of the total number of states of existence available to it. If a given assembly of atoms has a greater number of states of existence in one molecular configuration than in a second, its entropy is greater in the first configuration than in the second. Usually the entropy of a given number of atoms will be greater the greater the number of separate molecules formed by the given atoms.

For example, in the case mentioned in the preceding section on the combination of two hydrogen atoms to form the hydrogen molecule, the two atoms enjoy a greater freedom of existence as separate atoms than they do combined in the molecule. Actually, at room temperature, the entropy of the hydrogen molecule is less than the entropy of two separate hydrogen atoms by about 24 cal/deg mole.

Similarly, consider two isomeric paraffin hydrocarbons, the straight-chain normal octane and the highly branched hexamethylethane. One can visualize the eight carbon and eighteen hydrogen atoms having a greater freedom of existence in the straight-chain isomer than in the more compact branched-chain isomer. At room temperature, the entropy of gaseous *n*-octane is greater than that of its isomer hexamethylethane by about 16 cal/deg mole.

In a similar way, one can say that usually the entropy of a given polymer is less than the sum of the entropies of any component parts into which it may be subdivided.

In general, then, we may say that the change in entropy accompanying a given reaction is a corresponding measure of the increase or decrease in the total number of states of existence available to the system in the form of the products over the number of states of existence available in the form of the reactants. We may consider the total number of states of existence available to a given system or assembly of atoms to be a measure of the freedom enjoyed by the given system.

8. General statement regarding the behavior of atoms in a chemical reaction. Equation 35 may be written explicitly in terms of the equilibrium constant, K, as follows:

$$K = (e^{\Delta S^\circ/R})(e^{-\Delta H^\circ/RT}). \tag{39}$$

Given any reaction, as for example,

$$\mathrm{CO\ (g) + H_2O\ (g) = CO_2\ (g) + H_2\ (g)}, \tag{40}$$

when the value of the equilibrium constant is large, greater than unity, the component atoms, at equilibrium, tend to go preferentially into forming the products, and when the equilibrium constant is small, less than unity, the component atoms tend to go preferentially into forming the reactants. When the equilibrium constant is small for the reaction as first written, the reaction may be written in the reverse direction so that the equilibrium constant will be large for the reaction as now written. In general, the equilibrium constant will be large for the reaction written in such a way that the product molecules are the ones predominating at equilibrium.

That is to say, the participating atoms will tend to go into those molecular configurations which are products for the reaction written to have the largest value of the equilibrium constant. But, according to Equation 39, the equilibrium constant will be greatest for the reaction written with products having a maximum value of the change in entropy, ΔS°, and a minimum value of the change in heat content, ΔH°. Therefore, we may say that the atoms constituting the molecules involved in the reaction will tend to go preferentially into those molecular configurations in which the entropy is greatest and in which the heat content (approximately the energy) is lowest (algebraically). The greatest entropy is in general associated with those molecular configurations having the largest number of states of existence, that is, those molecular configurations in which the atoms will have the greatest freedom of existence. On the other hand, the lowest heat content (approximately the energy) is, in general, associated with those molecular configurations in which the atoms are bound most securely one to another, that is, those molecular configurations in which the atoms will have the greatest security of existence. The final state of equilibrium, then, is a compromise between these two opposing tendencies, toward maximum freedom on the one hand and maximum security on the other.

Further examination of Equation 39 shows also that, in general, the equilibrium constant at high temperatures is determined largely by the value of $\Delta S°$, the "freedom" factor, whereas at low temperatures the equilibrium constant is determined largely by the value of $\Delta H°$, the "security" factor. In general, we may say that, at thermodynamic equilibrium in a given process, the atoms involved prefer a secure molecular configuration at low temperatures and a loose or free molecular configuration at high temperatures.

It is to be emphasized that the foregoing statements regarding the behavior of atoms in chemical processes or reactions apply only to those states between which the path is sufficiently open to permit the establishment of thermodynamic equilibrium.

PROBLEMS

1. Given the statement that among paraffin hydrocarbons the more compact isomers usually have lower energy and lower entropy than the less compact ones. For the reaction of isomerization,

$$C_5H_{12}\ (\text{g, } n\text{-pentane}) = C_5H_{12}\ (\text{g, 2,2-dimethylpropane}),$$

decide how the equilibrium constant for the reaction as written will vary in going from low to high temperatures.

2. Calculate the change in free energy of 1 mole of an ideal gas in passing from 1 to 100 atm at 25°C.

3. Calculate the free energy of mixing, at 25°C, $\frac{1}{2}$ mole of ideal gas A, occupying a volume of 10 liters, with $\frac{1}{2}$ mole of ideal gas B, occupying a volume of 10 liters, to form 1 mole of an equimolal mixture of A and B, occupying a volume of 10 liters.

4. Given a reaction in which the atoms involved constitute 2 molecules in the reactants and 8 molecules in the products. What would you normally expect concerning the change of the equilibrium constant for this reaction in going from low to high temperatures?

5. Given a reaction in which at room temperature the energy of the products is much lower than the energy of the reactants. What can you estimate concerning the magnitude of the equilibrium constant for this reaction at low temperatures?

6. One mole of ideal gas A at a pressure of 0.1 atm, 2 moles of ideal gas B at a pressure of 0.3 atm, and 3 moles of ideal gas C at a pressure of 0.4 atm, each at 25°C, are mixed and brought to a final pressure of 1.0 atm at 25°C. Calculate the change in free energy for the process.

22

Equilibrium between Different Phases of One Pure Substance

1. Escaping tendency. We have seen that the temperature of a system may be considered a measure of the tendency for energy to escape from that system in the form of heat. We say that a system is in thermal equilibrium when the temperature is the same throughout all parts of the given system. Similarly, any combination of systems is in thermal equilibrium when the temperature is the same throughout all the systems involved. That is to say, thermal equilibrium exists in any combination of systems when all the systems involved have the same tendency to lose energy in the form of heat.

In a similar way, we can think of the thermodynamic equilibrium involving the molecules of a given substance capable of existing in more than one phase under given conditions. Such molecules will have a tendency to escape from the phase in which they exist. Unless this escaping tendency is exactly balanced by the tendency of the molecules to return to the given phase by escaping from another coexisting phase, the phase in which the escaping tendency is greater will disappear in favor of the phase of smaller escaping tendency. We can say that thermodynamic equilibrium exists between two or more different phases of one pure substance when the given molecular species has the same escaping tendency in each of the phases.

Consider the simple equilibrium of water molecules in the liquid and gaseous phases at a fixed pressure of 1 atmosphere:

$$\mathrm{H_2O\ (liq)} = \mathrm{H_2O\ (g)}. \tag{1}$$

At the fixed pressure of 1 atmosphere and a temperature of 100°C, the water molecules will have the same escaping tendency in each of the phases. If, at the fixed pressure, the temperature is decreased, the escaping tendency of the water molecules will be greater in the gaseous phase than in the liquid phase, and the gaseous phase will disappear in favor of the liquid phase. Likewise, if, at the same fixed pressure of 1 atmosphere, the temperature is raised above 100°C, the water molecules will have a greater tendency to escape from the liquid phase, and the latter will disappear in favor of the gaseous phase.

Under an external pressure of 1 atmosphere, water molecules can exist in thermodynamic equilibrium between the solid and liquid phases at a temperature of 0.0025°C, in a closed system with no other molecules present.

$$H_2O\ (c) = H_2O\ (liq). \tag{2}$$

If, at this pressure, the temperature is decreased, the water molecules will have a greater tendency to escape from the liquid phase, and the latter will disappear in favor of the solid phase. Similarly, if, at the given pressure, the temperature is raised above 0.0025°C, the water molecules in the solid phase will have a greater escaping tendency, and the solid phase will disappear in favor of the liquid phase.

If a mixture of solid and liquid water is placed in a closed system having a volume appreciably larger than that of the water in the solid and liquid phases, so that a vapor phase may exist, and if the temperature is held at 0.0100°C, the water molecules will be found to be in thermodynamic equilibrium in three phases:

$$H_2O\ (c) = H_2O\ (liq) = H_2O\ (g). \tag{3}$$

At this temperature, the pressure of the water molecules in the gaseous phase, and hence the pressure in the system, will be 0.00603 atmosphere. Under these conditions, the water molecules have the same escaping tendency in all three phases.

2. Free energy as a measure of the escaping tendency. We have seen (Chapter 16) that thermodynamic equilibrium exists in any process at constant temperature and pressure when

$$dF = 0. \tag{4}$$

For a finite change, Equation 4 becomes

$$\Delta F = 0. \tag{5}$$

If a given assembly of atoms or molecular species has an open path leading to a state in which the value of the free energy,

$F = E + PV - TS$, per mole, is lower (algebraically), they will pass to the state of lower free energy. If the second state has a value of the free energy, per mole, equal to that of the first state, the two states will be in thermodynamic equilibrium.

For the equilibrium between water in the liquid and gaseous phases, we can write that, at 100°C and 1 atmosphere, the change in free energy, per mole, is zero:

$$\mathrm{H_2O}\ (\text{liq, 1 atm, 100°C}) = \mathrm{H_2O}\ (\text{g, 1 atm, 100°C});\ \Delta F = 0. \quad (6)$$

Equation 6 also means that the molal free energy of water in the two phases is equal:

$$F[\mathrm{H_2O}\ (\text{liq, 1 atm, 100°C})] = F[\mathrm{H_2O}\ (\text{g, 1 atm, 100°C})]. \quad (7)$$

If the temperature is increased above 100°C, say 101°C, and the pressure is kept fixed at 1 atmosphere, the molal free energy of water in the liquid phase will be greater than that in the gas phase,

$$F[\mathrm{H_2O}\ (\text{liq, 1 atm, 101°C})] > F[\mathrm{H_2O}\ (\text{g, 1 atm, 101°C})], \quad (8)$$

and, the path being open, the water will disappear from the liquid phase in favor of the gaseous phase.

Equation 8 may also be written as follows:

$$\mathrm{H_2O}\ (\text{liq, 1 atm, 101°C}) = \mathrm{H_2O}\ (\text{g, 1 atm, 101°C});\ \Delta F < 0. \quad (9)$$

Similarly, if the temperature is decreased below 100°C, say 99°C, and the pressure is kept fixed at 1 atmosphere, the molal free energy of the water will be greater in the gaseous phase than in the liquid phase, and the gaseous phase will disappear in favor of the liquid state. This may be written as

$$F[\mathrm{H_2O}\ (\text{liq, 1 atm, 99°C})] < F[\mathrm{H_2O}\ (\text{g, 1 atm, 99°C})], \quad (10)$$

or

$$\mathrm{H_2O}\ (\text{liq, 1 atm, 99°C}) = \mathrm{H_2O}\ (\text{g, 1 atm, 99°C});\ \Delta F > 0. \quad (11)$$

In general, we may say that, if the molal free energy of any substance is greater in one state than it is in another state, with the path between the states open, the given substance will pass from the former state to the latter state. Or, in other words, any given substance has, thermodynamically, a tendency to pass from a state of higher free energy, per mole, to one of lower free energy, per mole, and will do so whenever the path between the two states is open.

3. Phase rule. A system is said to possess f degrees of freedom when at least f data are required to fix the system completely. A system composed of one component in one phase, solid, liquid, or gas, can be completely fixed by specifying the temperature and the pressure, if all other conditions such as the gravitational field and magnetic field are constant. That is, under these conditions, a system of one component in one phase has two degrees of freedom, while, if two phases of the one component exist together at equilibrium, the system has only one degree of freedom. In the latter case, the specification of either the temperature or the pressure fixes the system completely. If the given component exists in three phases together at equilibrium, then, under these conditions, the system has no degrees of freedom and is invariant, meaning that the three phases of the one component can exist together only at one temperature and pressure. The foregoing statements are summarized in the phase rule of Gibbs (*1*), that, whatever the number of variables, the number of degrees of freedom of the complete system is equal to the number of variables needed to fix the state of the individual phases less the number of phases beyond the first. That is, for a system of one component in one or more phases,

$$f = r - (p - 1) = r + 1 - p, \tag{12}$$

where f is the number of degrees of freedom, p is the number of phases, and r is the number of all the variables needed to fix the states of the individual phases.

If, as is usually the case, the variables of temperature and pressure are adequate to fix the state of the individual phases, then $r = 2$ and Equation 12 becomes

$$f = 3 - p. \tag{13}$$

Figure 1 gives a diagram showing the equilibrium among the phases of the substance water as a function of pressure and temperature, at low pressures, from −10 to 10°C. The point B represents the "triple point" at which the system has no degrees of freedom, where the solid, liquid, and gaseous phases are in equilibrium. The line AB represents the equilibrium between solid and gaseous water, the line BD between liquid and gaseous water, and the line BC between solid and liquid water. The line EB represents metastable equilibrium between the undercooled liquid and the gaseous phase.

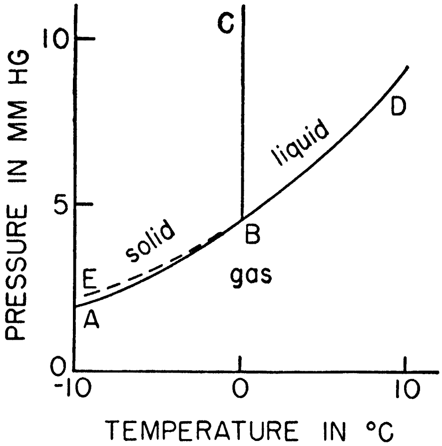


FIGURE 1. Diagram showing the equilibrium among the phases of water at low pressures, from −10° to 10°C.

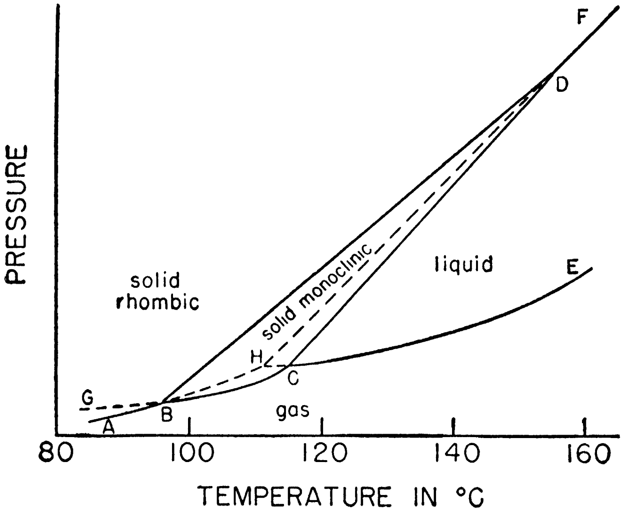


FIGURE 2. Schematic diagram showing the equilibrium among the several phases of sulfur as a function of pressure and temperature, up to high pressures. (The scale of ordinates is purely schematic, the pressures at the points *B*, *C*, and *D* being, respectively, approximately 0.000001, 0.000004, and 1400 atm.)

Figure 2 gives a schematic diagram showing the equilibrium among the several phases of the substance sulfur as a function of pressure and temperature, up to high pressures. The line AB represents the equilibrium between the rhombic solid phase and the gaseous phase, the line BC between the monoclinic solid phase and the gaseous phase, the line CE between the liquid and gaseous phases, the line CD between the monoclinic solid phase and the liquid phase, the line BD between the rhombic solid phase and the monoclinic solid phase, and the line DF between the rhombic solid phase and the liquid phase.

The line GB represents metastable equilibrium between the monoclinic solid phase and the gas phase, the line BH represents metastable equilibrium between the rhombic solid phase and the gaseous phase, and the line HD represents metastable equilibrium between the rhombic solid phase and the liquid phase. The stable triple points are represented as follows: by the point B, at which the rhombic solid phase, the monoclinic solid phase, and the gas phase are in equilibrium; by the point C, at which the monoclinic solid phase, the liquid phase and the gaseous phase are in equilibrium; by the point D, at which the rhombic solid phase, the monoclinic solid phase, and the liquid phase are in equilibrium. The point H represents a metastable triple point at which the rhombic solid phase, the liquid phase, and the gaseous phase are in metastable equilibrium.

4. Change of pressure with temperature for the equilibrium between two phases. Consider the thermodynamic equilibrium between two different phases, *a* and *b*, of the same pure substance, MX:

$$\mathrm{MX}\ (a) = \mathrm{MX}\ (b). \tag{14}$$

At equilibrium

$$F_a = F_b. \tag{15}$$

Moreover, if equilibrium is to be maintained when a small change in temperature, $\mathrm{d}T$, or a small change in pressure, $\mathrm{d}P$, occurs, then

$$F_a + \mathrm{d}F_a = F_b + \mathrm{d}F_b, \tag{16}$$

or

$$\mathrm{d}F_a = \mathrm{d}F_b. \tag{17}$$

But the free energy may be expressed as a function of pressure and temperature:

$$F = f(P,T). \tag{18}$$

Therefore,

$$\mathrm{d}F_a = \left(\frac{\partial F_a}{\partial P}\right)_T \mathrm{d}P + \left(\frac{\partial F_a}{\partial T}\right)_P \mathrm{d}T \tag{19}$$

and

$$\mathrm{d}F_b = \left(\frac{\partial F_b}{\partial P}\right)_T \mathrm{d}P + \left(\frac{\partial F_b}{\partial T}\right)_P \mathrm{d}T. \tag{20}$$

But

$$\left(\frac{\partial F}{\partial P}\right)_T = V, \tag{21}$$

and

$$\left(\frac{\partial F}{\partial T}\right)_P = -S. \tag{22}$$

Therefore, Equations 19 and 20 become

$$\mathrm{d}F_a = V_a\,\mathrm{d}P - S_a\,\mathrm{d}T \tag{23}$$

and

$$\mathrm{d}F_b = V_b\,\mathrm{d}P - S_b\,\mathrm{d}T. \tag{24}$$

Combination of Equations 17, 23, and 24 gives

$$(V_b - V_a)\,\mathrm{d}P = (S_b - S_a)\,\mathrm{d}T, \tag{25}$$

or

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{S_b - S_a}{V_b - V_a}. \tag{26}$$

For the process represented by Equation 14, Equation 26 may be written as

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta S}{\Delta V}. \tag{27}$$

But at thermodynamic equilibrium,

$$\Delta S = \frac{\Delta H}{T}, \tag{28}$$

so that Equation 27 becomes

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta H}{T\,\Delta V}. \tag{29}$$

Equation 29, commonly called the Clapeyron equation, gives, for the equilibrium between two different phases of the same pure substance, the ratio of the change in the equilibrium pressure to the change in temperature in terms of the absolute temperature and the difference in heat content and the difference in volume of the substance in the two phases.

Equation 29 can be recast to give either the value of the increment in heat content or the increment in volume explicitly, as

$$\Delta H = T\,\Delta V \frac{\mathrm{d}P}{\mathrm{d}T}, \tag{30}$$

and

$$\Delta V = \frac{\Delta H}{T} \frac{\mathrm{d}T}{\mathrm{d}P}. \tag{31}$$

That is, for the given process involving the equilibrium between phase *a* and phase *b*, the increment in heat content can be evaluated if the increment in volume and the change of pressure with temperature are known. Similarly, the increment in volume can be calculated if the increment in heat content and the change of temperature with pressure are known.

5. Equilibrium between the liquid and gaseous phases. If the equilibrium under consideration is that between the liquid and gaseous phases of the same pure substance, as

$$\mathrm{MX\ (liq)} = \mathrm{MX\ (g)}, \tag{32}$$

then Equation 29 may be written as

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{H\ (\mathrm{g}) - H\ (\mathrm{liq})}{T[V\ (\mathrm{g}) - V\ (\mathrm{liq})]}, \tag{33}$$

or

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta Hv}{T[V\ (\mathrm{g}) - V\ (\mathrm{liq})]} = \frac{\Delta Hv}{T\,\Delta Vv}, \tag{34}$$

where ΔHv and ΔVv represent, respectively, the increment in heat content and the increment in volume for the process of vaporization as given by Equation 32. ΔHv is the heat of vaporization. It is important to note that, in Equations 33 and 34, the increments in heat content and in volume apply to the given phases at the equilibrium pressure and temperature.

If, for the given substance MX in the gaseous state, the value of the compressibility factor, PV/RT, is known for the given temperature and pressure, we may write the following:

$$z = \frac{PV}{RT} \tag{35}$$

and

$$V\ (\mathrm{g}) = \frac{zRT}{P}. \tag{36}$$

Substitution into Equation 34 yields

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta Hv}{T\left[\frac{zRT}{P} - V\ (\mathrm{liq})\right]}. \tag{37}$$

At sufficiently low pressures the value of the compressibility factor approaches unity, and the volume of the liquid, per mole, is small in comparison with the value (in the same units) of RT/P. Under these conditions of sufficiently low pressures, then, Equation 37 becomes the following approximation

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{P\,\Delta Hv}{RT^2}, \tag{38}$$

or

$$\frac{\mathrm{d}\ln P}{\mathrm{d}T} = \frac{\Delta Hv}{RT^2}, \tag{39}$$

or

$$\frac{\mathrm{d}\ln P}{\mathrm{d}\left(\frac{1}{T}\right)} = \frac{-\Delta Hv}{R}. \tag{40}$$

Equation 40, commonly called the Clausius-Clapeyron equation, is an approximation good only at sufficiently low pressures.

6. Equilibrium between the solid and liquid phases. If the equilibrium is that between the solid and liquid phases of the same pure substance, as

$$\mathrm{MX\ (c) = MX\ (liq)}, \tag{41}$$

then Equation 29 may be written as

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{H\ (\mathrm{liq}) - H\ (\mathrm{c})}{T[V\ (\mathrm{liq}) - V\ (\mathrm{c})]}, \tag{42}$$

or

$$\frac{dP}{dT} = \frac{\Delta Hm}{T[V\ (\text{liq}) - V\ (\text{c})]} = \frac{\Delta Hm}{T\ \Delta Vm}, \tag{43}$$

where ΔHm and ΔVm represent, respectively, the increment in heat content and the increment in volume for the process of melting or fusion given by Equation 41. ΔHm is the heat of fusion. As before, it is to be noted that the increments in heat content and volume apply to the given phases at the equilibrium temperature and pressure.

Since the value of $T\ \Delta Vm$ is usually small compared to the value of ΔHm, Equation 43 shows that, in a plot of pressure as ordinate and temperature as abscissa, the curve will have a large slope and will be nearly vertical. The nearly vertical line will have a positive or negative slope according to whether the change in volume on melting is positive or negative. For most substances, ΔVm is positive, although for ordinary water it is negative.

7. Equilibrium between the solid and gaseous phases. If the equilibrium is that between the solid and gaseous phases of the same pure substance, as

$$\text{MX (c)} = \text{MX (g)}, \tag{44}$$

then Equation 29 may be written as

$$\frac{dP}{dT} = \frac{H\ (\text{g}) - H\ (\text{c})}{T[V\ (\text{g}) - V\ (\text{c})]}, \tag{45}$$

or

$$\frac{dP}{dT} = \frac{\Delta Hs}{T[V\ (\text{g}) - V\ (\text{c})]} = \frac{\Delta Hs}{T\ \Delta Vs}, \tag{46}$$

where ΔHs and ΔVs represent, respectively, the increment in heat content and the increment in volume for the process of sublimation given by Equation 44. ΔHs is the heat of sublimation. As previously noted, the increments in heat content and volume apply to the given phases at the equilibrium temperature and pressure.

As for the equilibrium between the liquid and gaseous phases, we may write for the gaseous phase,

$$V\ (\text{g}) = \frac{zRT}{P}, \tag{47}$$

where z represents the compressibility factor, PV/RT. Substitution into Equation 44 gives

$$\frac{dP}{dT} = \frac{\Delta Hs}{T\left[\frac{zRT}{P} - V\,(c)\right]}. \tag{48}$$

At sufficiently low pressures, as will frequently exist for the equilibrium between most ordinary solids and their vapors, the value of the compressibility factor approaches unity and the volume of the solid per mole is small in comparison with the value of RT/P. Then Equation 48 becomes the following approximation:

$$\frac{dP}{dT} = \frac{P\,\Delta Hs}{RT^2} \tag{49}$$

or

$$\frac{d\ln P}{dT\cdot} = \frac{\Delta Hs}{RT^2}, \tag{50}$$

or

$$\frac{d\ln P}{d\left(\frac{1}{T}\right)} = \frac{-\Delta Hs}{R}. \tag{51}$$

8. Equilibrium between two solid phases. If the equilibrium is that between two different solid phases of the same pure substance, as

$$\text{MX (c, II)} = \text{MX (c, I)}, \tag{52}$$

then Equation 29 may be written as

$$\frac{dP}{dT} = \frac{H\,(c,\text{I}) - H\,(c,\text{II})}{T[V\,(c,\text{I}) - V\,(c,\text{II})]}, \tag{53}$$

or

$$\frac{dP}{dT} = \frac{\Delta Htr}{T[V\,(c,\text{I}) - V\,(c,\text{II})]} = \frac{\Delta Htr}{T\,\Delta Vtr}, \tag{54}$$

where ΔHtr and ΔVtr represent, respectively, the increment in heat content and the increment in volume for the process of transition given by Equation 52. Since the value of ΔHtr (c, II → c, I) is always positive, the value of dP/dT will be positive or negative according to the value of ΔVtr, the change in volume for the transition.

9. Collateral reading. For further discussion of the topics discussed in this chapter, the reader is referred to Gibbs (*1*), Findlay (*2*), Bridgman (*3*), and Bowden (*4*).

REFERENCES

1. J. Willard Gibbs, *Collected Works*, Volume I, Longmans, Green, and Company, New York, 1928.

2. Alexander Findlay, *The Phase Rule and Its Applications*, Longmans, Green, and Company, New York, 1931.

3. P. W. Bridgman, *The Physics of High Pressure*, G. Bell and Sons, London, 1931.

4. S. T. Bowden, *The Phase Rule and Phase Reactions, Theoretical and Practical*, Macmillan Company, London, 1938.

PROBLEMS

1. State which of the following has the greater escaping tendency:

a. H_2O (liq, −5°C, 1 atm) or H_2O (c, −5°C, 1 atm);

b. H_2O (liq, 95°C, 1 atm) or H_2O (g, 95°C, 1 atm);

c. H_2O (liq, 100°C, 0.9 atm) or H_2O (g, 100°C, 0.9 atm).

2. Calculate the heat of vaporization at 300°K for a given liquid for which, at this temperature, the following data exist: vapor pressure, 1 atm; molal volume of the liquid, 150 cm^3/mole; for the gas at saturation pressure, $PV/RT = 0.95$; $dT/dP = 0.050$°C/mm Hg. What percentage of error is introduced (*a*) by assuming the gas to be ideal? (*b*) by assuming the volume of the liquid to be negligible? (*c*) by assuming both the gas to be ideal and the volume of the liquid to be negligible?

3. For the equilibrium between solid and liquid water at 0°C, the equilibrium pressure is 0.006027 atm. Calculate the temperature for an equilibrium pressure of 100 atm, assuming the heat of fusion to be 1436.3 cal/mole and the densities of the solid and liquid phases to be 0.917 and 1.000 g/cm^3, respectively.

4. Calculate the heat of vaporization of *n*-heptane at the normal boiling point (1 atm), given the following data: vapor pressure of the liquid, $\log_{10} p$ (in mm Hg) $= 6.90319 - 1268.586/(t + 216.954)$ (t in °C); density of the liquid, $d = 0.67947 - 0.0008\ (t - 25)$ g/ml; for the gas at the normal boiling point and 1 atm, $PV/RT = 0.9453$.

5. Given the equilibrium MX (c, II) = MX (c, I), at 400°K and 1 atm. Taking the heat of transition to be 1200 cal/mole, the change of the equilibrium pressure with temperature to be 20.0 atm/°C, the density of crystalline form I to be 1.25 g/ml at 400°K, and the molecular weight of MX to be 120.0 g/mole, calculate the density of crystalline form II at the same temperature.

6. At 1 atm, MX (c, II) is in equilibrium with MX (c, I) at 300°K. For MX (c, II) and MX (c, I), the values of $\int_0^{300} C_P \, d \ln T$ are 19.83 and 21.73 cal/deg mole, respectively. Calculate the value of ΔH_{300} for the transition MX (c, II) = MX (c, I). Which form is more stable at 290°K and 1 atm?

23

Fugacity; Standard States

1. Fugacity as a measure of the escaping tendency. In Chapter 22, we used the molal free energy as a measure of the escaping tendency of a given molecular species from a given phase. In the equilibrium involving one pure substance in several different phases, the given substance has a tendency to leave each phase in which it exists and to pass into every other phase which is open to it. At equilibrium, the escaping tendency has a constant value throughout every phase of the system, and similarly for the molal free energy.

When the phases under consideration are condensed ones, as liquid and solid, the molal free energy serves as a satisfactory quantitative measure of the escaping tendency. However, when the gaseous phase is involved, the molal free energy becomes a rather inconvenient measure of the escaping tendency because the value of the free energy of an ideal gas (Chapter 21) approaches minus infinity as the pressure approaches zero. Since any real gas approaches the ideal gas as the pressure is indefinitely reduced, it follows that the free energy of any real gas approaches minus infinity as the pressure approaches zero. It is obvious, then, that a more convenient measure of the escaping tendency than the free energy is needed in the case of gases, particularly for ordinary and low pressures.

For the ideal gas the pressure itself is a satisfactory measure of the escaping tendency, because, for the ideal gas, at constant temperature, the pressure is related to the molal free energy by a simple mathematical relation involving no unknown constants (see Chapter 21):

$$F_P - F_{P=1} = RT \ln P. \tag{1}$$

However, real gases depart significantly from the relations for an ideal gas, and the simple form of Equation 1 does not hold. Nevertheless, it is possible to retain the simplicity of Equation 1 for real gases by inventing a new thermodynamic function, called the fugacity (*1*), and labeled f, which will be evaluated in such a way that the substitution of values of the fugacity for pressure will make Equation 1 valid for real gases as well as for the ideal gas.

2. Definition of fugacity. The form in which the fugacity must be defined to achieve the foregoing end may be derived as follows:

For any gas at constant temperature (Chapter 17),

$$dF = V\,dP. \qquad (2)$$

For any gas in its real condition, we may write Equation 2 as

$$dF_{\text{real}} = V_{\text{real}}\,dP. \qquad (3)$$

Similarly, for the same gas in its hypothetical ideal condition, we may write

$$dF_{\text{ideal}} = V_{\text{ideal}}\,dP. \qquad (4)$$

Subtraction of Equation 4 from Equation 3 gives

$$d(F_{\text{real}} - F_{\text{ideal}}) = (V_{\text{real}} - V_{\text{ideal}})\,dP. \qquad (5)$$

For convenience in writing, we may let the experimentally observable quantity representing, at some given pressure, the difference in the molal volumes of the gas in the ideal and the real conditions be

$$\alpha = V_{\text{ideal}} - V_{\text{real}} = \frac{RT}{P} - V_{\text{real}}. \qquad (6)$$

Substituting α into Equation 5 and marking it for integration from zero pressure to a pressure P, we have

$$\int_0^P d(F_{\text{real}} - F_{\text{ideal}}) = -\int_0^P \alpha\,dP. \qquad (7)$$

This becomes

$$(F_{\text{real}} - F_{\text{ideal}})^P - (F_{\text{real}} - F_{\text{ideal}})^{P=0} = -\int_0^P \alpha\,dP. \qquad (8)$$

But the difference in free energy between the real and ideal conditions approaches zero at zero pressure, so that

$$(F_{\text{real}} - F_{\text{ideal}})^{P=0} = 0, \qquad (9)$$

and Equation 8 becomes, at constant temperature, for the pressure P,

$$F_{\text{real}} - F_{\text{ideal}} = -\int_0^P \alpha\, dP, \tag{10}$$

or

$$F_{\text{real}} = F_{\text{ideal}} - \int_0^P \alpha\, dP. \tag{11}$$

But the relation between free energy and pressure for an ideal gas at constant temperature and the pressure P is (Equation 1):

$$F_{\text{ideal}} = F_{\text{ideal}}^{P=1} + RT \ln P. \tag{12}$$

Combination of Equations 11 and 12 with elimination of F_{ideal} gives

$$F_{\text{real}} = F_{\text{ideal}}^{P=1} + RT \ln P - \int_0^P \alpha\, dP. \tag{13}$$

Our desire is to have for the real gas a function, f, which will permit us to use, for the real gas, the simple form of Equation 12,

$$F_{\text{real}} = F_{\text{ideal}}^{P=1} + RT \ln f. \tag{14}$$

Comparison of Equations 12, 13, and 14 shows that the fugacity must therefore be defined by the relation

$$RT \ln f = RT \ln P - \int_0^P \alpha\, dP, \tag{15}$$

or

$$\ln f = \ln P - \frac{1}{RT}\int_0^P \alpha\, dP, \tag{16}$$

or

$$\ln \frac{f}{P} = -\frac{1}{RT}\int_0^P \alpha\, dP, \tag{17}$$

or

$$\frac{f}{P} = e^{-(1/RT)\int_0^P \alpha\, dP}, \tag{18}$$

or

$$f = Pe^{-(1/RT)\int_0^P \alpha\, dP}. \tag{19}$$

3. Fugacity of gases. From the foregoing definition of fugacity, it is seen that for any gas at constant temperature the fugacity may be evaluated as a function of pressure from values of the molal volume of the actual gas at various pressures. If $\alpha = (RT/P) - V$ is plotted on the scale of ordinates for various pressures, the area under the curve from zero pressure to the pressure P, multiplied by the negative of the reciprocal of RT, is the value of the natural logarithm of the ratio of the fugacity to the pressure, at the given pressure (Equation 17).

If the P-V-T data for a given temperature are expressible by an equation of state that gives the volume explicitly in terms of the pressure, the foregoing operation may be performed analytically in a very simple way. If the P-V-T data for a given temperature are expressible by an equation of state that gives the pressure explicitly in terms of the volume, fugacity may still be calculated analytically, although the procedure (Section 10) is more complicated.

For the ideal gas,

$$\frac{RT}{P} = V, \tag{20}$$

and

$$\alpha = \frac{RT}{P} - V = 0, \tag{21}$$

so that, for every pressure,

$$f = P. \tag{22}$$

The fugacity may be looked upon as a sort of corrected pressure such that it permits the retention of the simplicity of the relation with free energy given by Equation 14. It will be seen later that this is important in the relations between the equilibrium constant and the free energy for reactions involving real gases.

4. Thermodynamic standard reference state for gases. In Equations 1, 12, 13, and 14, we found it convenient to use a reference state of unit pressure from which to measure changes in free energy. In the practical application of chemical thermodynamics, such reference states will be used quite frequently and it is desirable to define formally the thermodynamic standard reference state that is to be used for gases.

For gases, the thermodynamic standard reference state is taken to be the ideal gaseous state at unit pressure (in atmospheres unless otherwise specified) at each temperature. This standard state is designated by the usual superscript on the appropriate thermodynamic symbols, as F° or f°.

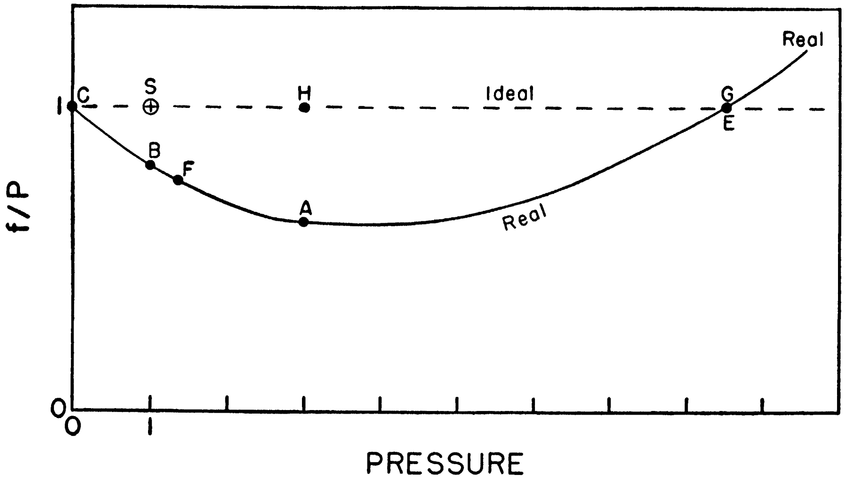


Figure 1. Schematic diagram of the ratio of the fugacity to pressure for a gas as a function of pressure.
See text for explanation.

Any real gas may be taken from its real state at the pressure P to the ideal state at unit pressure by proceeding along the path of the real gas from the pressure P to zero pressure and then passing from zero pressure to unit pressure along the path of the ideal gas. This may be easily seen from Figure 1, in which is plotted schematically the ratio of fugacity to pressure, f/P, as a function of pressure at constant temperature. The process just mentioned consists in taking (see Figure 1) the real gas from the state A along the path of the real gas through B to zero pressure at C and then along the path of the ideal gas to S, the ideal state at unit pressure, which is the thermodynamic standard reference state.

In Figure 1, point B represents the real gas at unit pressure, point E represents the real gas at some particular higher pressure at which its fugacity is equal to the pressure, and point F represents the real gas at a pressure where its fugacity is unity. These same relations may be seen in Figure 2, in which the fugacity is plotted as a function of the pressure, at constant temperature.

At constant temperature, the energy and heat content of a gas

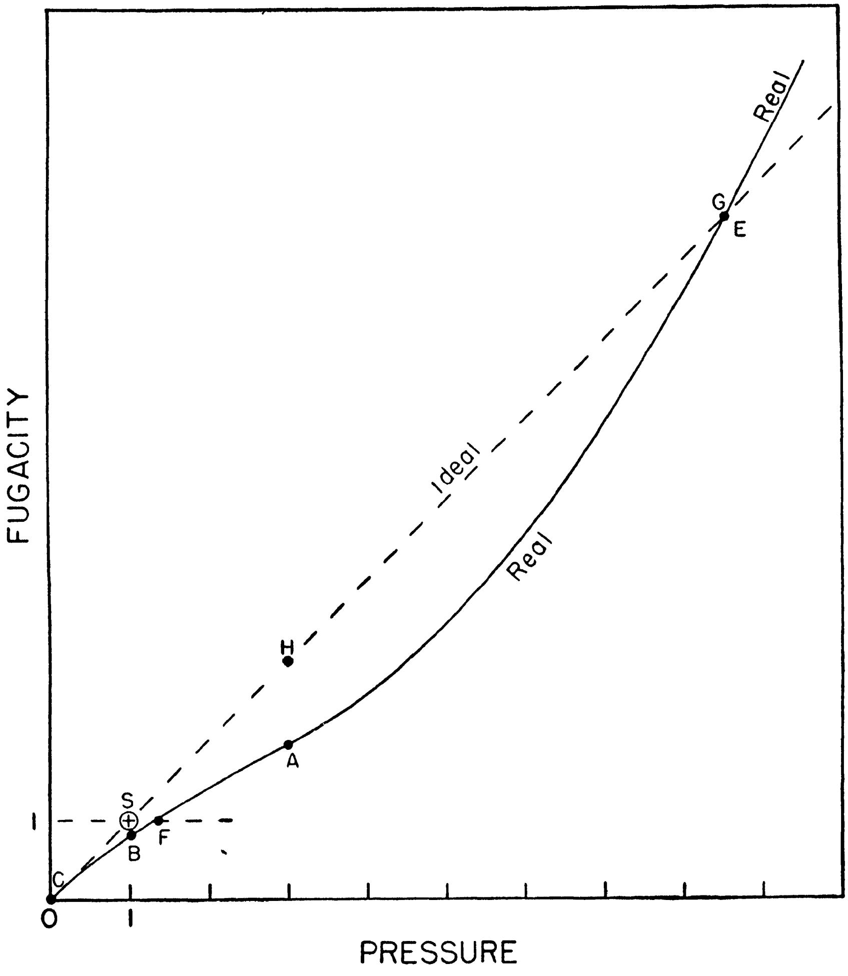


FIGURE 2. Schematic diagram of the fugacity of a gas as a function of pressure.

See text for explanation.

in the hypothetical ideal condition are constant. That is, as shown in Figure 3, for a gas in the ideal condition, the heat content at zero pressure, point *C*, is the same as the heat content at the standard state of unit pressure, point *S*, and as the heat content at any other pressure in the ideal condition, point *G*.

At constant temperature, the energy and heat content of a gas in its real condition vary with the pressure. The heat content of the real gas at a given pressure, as at point *A*, Figure 3, relative to its heat content at zero pressure, measures the difference in heat content of the gas at the given pressure, point *A*, relative to its heat content in the standard state, point *S*, or relative to its heat content in the ideal condition at the same pressure, point *H*. These statements are expressed mathematically as follows:

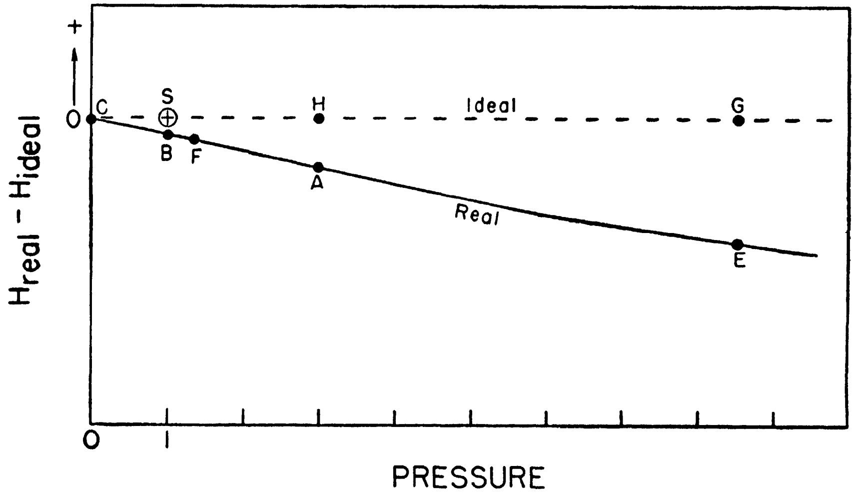


FIGURE 3. Schematic diagram of the difference in heat content of a gas between the real and ideal states as a function of pressure. See text for explanation.

$$H_{\text{real}}^{P=0} = H_{\text{ideal}}^{P=0} = H_{\text{ideal}}^{P} = H_{\text{ideal}}^{P=1} = H^\circ; \tag{23}$$

$$H_{\text{real}}^{P} - H_{\text{real}}^{P=0} = H_{\text{real}}^{P} - H_{\text{ideal}}^{P=1} = H_{\text{real}}^{P} - H^\circ; \tag{24}$$

$$(H_{\text{real}} - H_{\text{ideal}})^{P} = H_{\text{real}}^{P} - H_{\text{ideal}}^{P} = H_{\text{real}}^{P} - H_{\text{real}}^{P=0}. \tag{25}$$

Although at the pressure given by point *E*, the fugacity and pressure of the given gas have the same value, so that

$$(F_{\text{real}} - F_{\text{ideal}})^{P_E} = 0, \tag{26}$$

the real gas at the pressure P_E is not in the same thermodynamic state as the ideal gas at the pressure P_E because the heat content of the real gas at the pressure P_E has a value different from that for the ideal gas at the same pressure. That is, although at the pressure P_E the fugacity is the same in the two states, real and ideal, and likewise the free energy is the same in the two states, the heat content in the two states is different:

$$(H_{\text{real}} - H_{\text{ideal}})^{P_E} \neq 0. \tag{27}$$

Figure 3 gives a schematic diagram of the heat content of the gas in the real condition less that at zero pressure, as a function of the pressure.

With reference to the thermodynamic standard state, we can write for any real gas, at a given pressure at constant temperature,

$$F - F^\circ = RT \ln \frac{f}{f^\circ}, \tag{28}$$

or, since for the standard state,

$$f^\circ = 1, \tag{29}$$

$$F - F^\circ = RT \ln f. \tag{30}$$

5. Difference in properties of a gas between the real and ideal conditions. We have already derived (Equation 10) the relation giving the difference in the molal free energy of a gas between the real and ideal conditions at the same temperature at a given pressure, in terms of α:

$$\alpha = V_{\text{ideal}} - V_{\text{real}} = \frac{RT}{P} - V. \tag{31}$$

$$(F_{\text{real}} - F_{\text{ideal}})^P = -\int_0^P \alpha \, dP. \tag{32}$$

From Chapter 13, we have

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P. \tag{33}$$

At constant temperature, this becomes

$$dS = -\left(\frac{\partial V}{\partial T}\right)_P dP. \tag{34}$$

Equation 31 may be rewritten as

$$V = \frac{RT}{P} - \alpha. \tag{35}$$

Then

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} - \left(\frac{\partial \alpha}{\partial T}\right)_P. \tag{36}$$

For the ideal gas, α is zero at all temperatures, and

$$\left(\frac{\partial \alpha}{\partial T}\right)_P = 0. \tag{37}$$

We may then write

$$\mathrm{d}S_{\text{real}} = -\left[\frac{R}{P} - \left(\frac{\partial \alpha}{\partial T}\right)_P\right]\mathrm{d}P, \tag{38}$$

and

$$\mathrm{d}S_{\text{ideal}} = -\frac{R}{P}\,\mathrm{d}P. \tag{39}$$

Subtraction of Equation 39 from Equation 38 gives

$$\mathrm{d}(S_{\text{real}} - S_{\text{ideal}}) = \left(\frac{\partial \alpha}{\partial T}\right)_P \mathrm{d}P. \tag{40}$$

Integrating from zero pressure to a pressure P, we obtain

$$(S_{\text{real}} - S_{\text{ideal}})^P - (S_{\text{real}} - S_{\text{ideal}})^{P=0} = \int_0^P \left(\frac{\partial \alpha}{\partial T}\right)_P \mathrm{d}P. \tag{41}$$

Since the difference in entropy between the real and ideal conditions approaches zero at zero pressure, Equation 41 becomes

$$(S_{\text{real}} - S_{\text{ideal}})^P = \int_0^P \left(\frac{\partial \alpha}{\partial T}\right)_P \mathrm{d}P. \tag{42}$$

From the relation

$$F = H - TS, \tag{43}$$

we have, for constant temperature,

$$(F_{\text{real}} - F_{\text{ideal}})^P = (H_{\text{real}} - H_{\text{ideal}})^P - T(S_{\text{real}} - S_{\text{ideal}})^P. \tag{44}$$

Combination of Equations 32, 42, and 44 gives

$$(H_{\text{real}} - H_{\text{ideal}})^P = -\int_0^P \alpha\,\mathrm{d}P + T\int_0^P \left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_P \mathrm{d}P. \tag{45}$$

Equations 32, 42, and 45 permit the evaluation of the difference in the properties of free energy, entropy, and heat content of a gas between the real and ideal conditions at any pressure P at a given temperature.

If the volume of a gas can be expressed explicitly as a function of the pressure and temperature, it becomes a relatively simple matter to evaluate the difference in the properties of a gas between the real and ideal states.

For example, consider the Berthelot equation of state,

$$V = \frac{RT}{P} + \left(\frac{9}{128}\right)\left(\frac{RT_c}{P_c}\right)\left(1 - 6\frac{T_c^2}{T^2}\right), \tag{46}$$

where T_c and P_c represent the critical temperature and critical pressure, respectively. Then

$$\alpha = \frac{RT}{P} - V = -\left(\frac{9}{128}\right)\left(\frac{RT_c}{P_c}\right)\left(1 - 6\frac{T_c^2}{T^2}\right). \tag{47}$$

Substitution of this value of α into Equations 32, 42, and 45 gives

$$F_{\text{real}} - F_{\text{ideal}} = \left(\frac{9}{128}\right)\left(\frac{RT_c}{P_c}\right)\left(1 - 6\frac{T_c^2}{T^2}\right)P, \tag{48}$$

$$S_{\text{real}} - S_{\text{ideal}} = -\left(\frac{27}{32}\right)\left(\frac{R}{P_c}\right)\left(\frac{T_c}{T}\right)^3 P, \tag{49}$$

and

$$H_{\text{real}} - H_{\text{ideal}} = \left(\frac{9}{128}\right)\left(\frac{RT_c}{P_c}\right)\left(1 - 18\frac{T_c^2}{T^2}\right)P. \tag{50}$$

The foregoing equations, of course, are valid only over the range of applicability of the equation of state and within its limits of uncertainty.

Other equations of state may also be used to evaluate the above quantities. These include the van der Waals equation of state,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT, \tag{51}$$

in which a and b are constants; the Beattie-Bridgeman equation of state,

$$P = RT\left(1 - \frac{c}{VT^3}\right)\frac{\left(V + B_0 - \frac{bB_0}{V}\right)}{V^2} - \frac{A_0}{V^2} - \frac{aA_0}{V^3}, \tag{52}$$

in which A_0, B_0, a, b, and c are arbitrary constants; the general power series equation of state,

$$V = \frac{RT}{P} + a + bP + cP^2 + eP^3, \tag{53}$$

in which the factors a, b, c, and e are functions of the temperature only; and the generalized van der Waals equation of state,

$$\left(\frac{P}{P_c} + 3\frac{V_c^2}{V^2}\right)\left(\frac{V}{V_c} - \frac{1}{3}\right) = \frac{8}{3}\left(\frac{T}{T_c}\right), \tag{54}$$

in which P_c, V_c, and T_c are the critical pressure, volume, and temperature, respectively.

6. Fugacity of pure substances in the liquid and solid states. Although, as we have already indicated, the fugacity is more useful in connection with substances in the gaseous state than with substances in the liquid and solid states, it is sometimes desirable to evaluate the fugacity of a substance in a condensed phase. This may be done simply by evaluating the fugacity of the given substance in the gaseous phase that is in equilibrium with the substance in the liquid or solid phase.

Given, under certain conditions, the equilibrium,

$$\text{MX (liq)} = \text{MX (g)}, \tag{55}$$

then, for the given equilibrium,

$$f\text{ (liq)} = f\text{ (g)}. \tag{56}$$

Similarly, given the equilibrium,

$$\text{MX (c)} = \text{MX (g)}, \tag{57}$$

then

$$f\text{ (c)} = f\text{ (g)}. \tag{58}$$

It is to be noted that the vapor pressure of liquids and solids under ordinary conditions is usually low, under which circumstances the fugacity of the gaseous phase will not differ greatly from its pressure, so that the fugacity of ordinary pure liquid and solid substances may be taken approximately as equal to the vapor pressure.

7. Thermodynamic standard reference state for pure liquids and solids. In connection with pure liquids and solids, it is convenient to select a standard state to use for reference, just as in the case of gaseous substances. However, because the fugacity of a substance in the liquid or solid phase is usually very low, it is desirable to use a different reference state from that of the gaseous phase. A satisfactory thermodynamic standard reference state for pure liquids and solids at a given temperature is the real state of the liquid or solid substance at a pressure of 1 atmosphere. Just as for gases, we can write for any solid or liquid substance at a given pressure and temperature, with reference to the selected thermodynamic standard state,

$$F - F^\circ = RT \ln \frac{f}{f^\circ}. \tag{59}$$

It is to be noted that, whereas, for the gaseous phase, the fugacity of the standard state, f°, is unity, for the liquid and solid phases the fugacity of the standard state will be different from unity, except by coincidence, and will usually be less than unity.

8. Variation of fugacity with pressure at constant temperature. From the definition of fugacity, we may write

$$RT \ln \frac{f}{f^\circ} = F - F^\circ, \tag{60}$$

or

$$\ln f - \ln f^\circ = \frac{1}{RT}(F - F^\circ). \tag{61}$$

Differentiation with pressure at constant temperature gives

$$\left(\frac{\partial \ln f}{\partial P}\right)_T = \left(\frac{1}{RT}\right)\left(\frac{\partial F}{\partial P}\right)_T, \tag{62}$$

since f° and F° are constant at constant temperature. But

$$\left(\frac{\partial F}{\partial P}\right)_T = V. \tag{63}$$

Therefore,

$$\left(\frac{\partial \ln f}{\partial P}\right)_T = \frac{V}{RT}. \tag{64}$$

Equation 64 may be written, for constant temperature, as

$$d \ln f = \frac{V}{RT} dP, \tag{65}$$

or, between two specified pressures, P_A and P_B, at constant temperature, as

$$\ln \frac{f_B}{f_A} = \int_{P_A}^{P_B} \frac{V}{RT}\, \mathrm{d}P. \tag{66}$$

9. Variation of fugacity with temperature at constant pressure. From the definition of fugacity, we may write, as above,

$$\ln f - \ln f^\circ = \left(\frac{1}{R}\right)\left(\frac{F}{T} - \frac{F^\circ}{T}\right). \tag{67}$$

Differentiation with temperature at constant pressure gives

$$\left(\frac{\partial \ln f}{\partial T}\right)_P - \left(\frac{\partial \ln f^\circ}{\partial T}\right)_P = \left\{\left[\frac{\partial\left(\frac{F}{T}\right)}{\partial T}\right]_P - \left[\frac{\partial\left(\frac{F^\circ}{T}\right)}{\partial T}\right]_P\right\}\left(\frac{1}{R}\right). \tag{68}$$

But, at constant pressure,

$$\begin{aligned}\frac{\mathrm{d}\left(\frac{F}{T}\right)}{\mathrm{d}T} = \frac{T\left(\frac{\mathrm{d}F}{\mathrm{d}T}\right) - F}{T^2} &= -\frac{TS + F}{T^2} \\ &= -\frac{F + TS}{T^2} = -\frac{H}{T^2}.\end{aligned} \tag{69}$$

Therefore, Equation 68 becomes

$$\left(\frac{\partial \ln f}{\partial T}\right)_P - \left(\frac{\partial \ln f^\circ}{\partial T}\right)_P = -\frac{\left(\frac{H}{T^2} - \frac{H^\circ}{T^2}\right)}{R} = -\frac{H - H^\circ}{RT^2}. \tag{70}$$

For gases, f° is unity at all temperatures, so that

$$\left(\frac{\partial \ln f^\circ}{\partial T}\right)_P = 0. \tag{71}$$

Therefore, for gases,

$$\left(\frac{\partial \ln f}{\partial T}\right)_P = -\frac{H - H^\circ}{RT^2}. \tag{72}$$

For constant pressure, Equation 72 may be written as

$$\mathrm{d}\ln f = -\frac{H - H^\circ}{RT^2}\,\mathrm{d}T, \tag{73}$$

or, between two specified temperatures, T_A and T_B, at constant pressure, as

$$\ln\frac{f_A}{f_B} = -\frac{1}{R}\int_{T_A}^{T_B}\frac{H - H^\circ}{T^2}\,\mathrm{d}T = \frac{1}{R}\int_{T_A}^{T_B}(H - H^\circ)\,\mathrm{d}\left(\frac{1}{T}\right). \tag{74}$$

10. Evaluation of the fugacity of gases. From the manner of definition of fugacity, it is clear that, at any given temperature, a knowledge of

$$\alpha = V_{\text{ideal}} - V_{\text{real}} = \frac{RT}{P} - V, \tag{75}$$

over the range from zero pressure to the pressure, P, provides a complete evaluation of the fugacity. Since the operation is one at constant temperature, Equation 17 may be rewritten as

$$\ln\frac{f}{P} = -\int_0^P \frac{\alpha}{RT}\,\mathrm{d}P. \tag{76}$$

But from Equation 75,

$$\frac{\alpha}{RT} = \frac{1}{P} - \frac{V}{RT} = \left(\frac{1}{P}\right)\left(1 - \frac{PV}{RT}\right), \tag{77}$$

or

$$\frac{\alpha}{RT} = \frac{1 - z}{P}, \tag{78}$$

where z is the compressibility factor, PV/RT. If values of the compressibility factor are known as a function of the pressure, at constant temperature, then

$$\ln\frac{f}{P} = -\int_0^P \frac{1 - z}{P}\,\mathrm{d}P = -\int_0^P (1 - z)\,\mathrm{d}\ln P. \tag{79}$$

That is to say, the value of $-\ln(f/P)$ may be evaluated graphically in several ways:

From Equation 17 by plotting α as a function of pressure, integrating from zero pressure to the pressure P, and multiplying by $1/RT$;

From Equation 76, by plotting α/RT as a function of pressure, and integrating from zero pressure to the pressure P;

From Equation 79, by plotting $(1 - z)/P$ as a function of pressure and integrating from zero pressure to the pressure P;

From Equation 79, by plotting $1 - z$ as a function of the logarithm of the pressure, and integrating from zero pressure to the pressure P.

If the P-V-T data for the given gas can be fitted to an equation of state in which the volume can be expressed explicitly as a function of the pressure and temperature, the evaluation of $\ln (f/P)$ can be made analytically in a very simple manner by substituting in Equation 17.

For example, from the Berthelot equation of state, Equation 46, we obtain

$$\ln \frac{f}{P} = \left(\frac{9}{128}\right)\left(\frac{T_c}{P_c}\right)\left(1 - 6\frac{T_c^2}{T^2}\right)\left(\frac{P}{T}\right). \qquad (80)$$

Similarly, from the general power series equation of state, Equation 53, we can obtain

$$\alpha = -(a + bP + cP^2 + eP^3) \qquad (81)$$

and

$$\ln \frac{f}{P} = \left(aP + \frac{b}{2}P^2 + \frac{c}{3}P^3 + \frac{e}{4}P^4\right)\left(\frac{1}{RT}\right). \qquad (82)$$

In Equations 81 and 82, the factors a, b, c, and e are constant at constant temperature.

If the equation of state is one in which the pressure is expressed explicitly, then, instead of substituting the value of V into the expression for α, one may substitute the value of dP into the equation for evaluating the change of fugacity with pressure (Equation 66). Consider the van der Waals equation of state, Equation 51, which can be expressed explicitly in terms of the pressure:

$$P = \frac{RT}{V - b} - \frac{a}{V^2}. \qquad (83)$$

At constant temperature,

$$dP = \left[-\frac{RT}{(V - b)^2} + \frac{2a}{V^3}\right] dV. \qquad (84)$$

Substituting this value of dP into Equation 66 gives

$$\ln\frac{f_B}{f_A}=\int_{V_A}^{V_B}\left[-\frac{V}{(V-b)^2}+\frac{2a}{V^2RT}\right]\mathrm{d}V. \tag{85}$$

On integration* we obtain

$$\ln\frac{f_B}{f_A} = -\ln(V_B-b)+\ln(V_A-b)+\frac{b}{V_B-b}$$
$$-\frac{b}{V_A-b}-\frac{2a}{RTV_B}+\frac{2a}{RTV_A}. \tag{86}$$

Let state A be at a very low pressure. Then

$$f_A = P_A. \tag{87}$$

If the pressure is very low, then the volume is very large, and

$$\frac{V_A-b}{V_A}\cong 1, \tag{88}$$

$$\frac{1}{V_A}\cong 0, \tag{89}$$

and

$$V_A\cong\frac{RT}{P_A}. \tag{90}$$

Making the foregoing substitutions in Equation 86, and simplifying, we obtain

$$\ln f_B = \ln\left(\frac{RT}{V_B-b}\right)+\frac{b}{V_B-b}-\frac{2a}{RTV_B}. \tag{91}$$

Equation 91 serves to evaluate, at a given temperature, the fugacity of a gas at a pressure P_B from the values of the constants a and b of the van der Waals equation of state together with the volume, V_B, of the gas in the given state.

It is to be noted that expressions of the form of Equations 80, 82, 91, and others which may similarly be derived from appropriate equations of state are valid only over the range of pressure for which the given equations of state are valid.

Whenever P-V-T data on a given gas are not available or

---

* $\int\left[\frac{V}{(V-b)^2}\right]\mathrm{d}V = \ln(V-b)-\frac{b}{V-b}.$

not adequate for evaluating the fugacity, a reasonably good approximation can be made by reason of the fact that, for the same value of the reduced pressure, P/P_c, and the reduced temperature, T/T_c, the ratio of fugacity to pressure, f/P, has about the same value for nearly all gases.* Accordingly, if the available data on different gases are all placed on one plot of f/P against P/P_c, generalized curves are formed, one for each different value of the reduced temperature, from which values of f/P can be read for given values of P/P_c at given values of the reduced temperature, T/T_c, for any gas for which data do not exist.

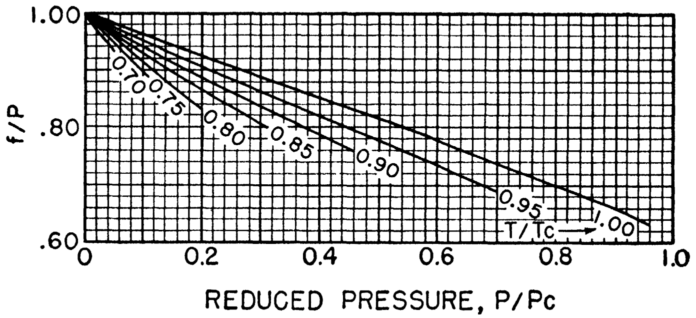


FIGURE 4. Generalized plot of values of the ratio of fugacity to pressure, f/P, as a function of the reduced pressure, P/P_c, for values of the reduced temperature, $T_R = T/T_c$, from 0.7 to 1.00. From Newton (*2*).

Figures 4, 5, and 6, taken from Newton (*2*), present generalized plots of values of f/P as a function of the reduced pressure, P/P_c. Figure 4 covers the range of low pressures and temperatures, Figure 5 covers the intermediate range, and Figure 6 goes to high pressures and temperatures with a less sensitive scale.

11. Equations of state for gases. Numerous equations have been proposed for representing in one mathematical equation the P-V-T relations for given gases. As may well be imagined, many constants are required in such equations, and the forms of the equations tend to become rather complex, as the range of pressure and temperature to be covered increases and as the

---

* Following the usual custom, the ratio of the given temperature to the critical temperature for the given gas is denoted the reduced temperature, T/T_c, the temperature being measured on the absolute thermodynamic scale. Similarly, the ratio of the given pressure to the critical pressure for the given gas is denoted the reduced pressure, P/P_c.

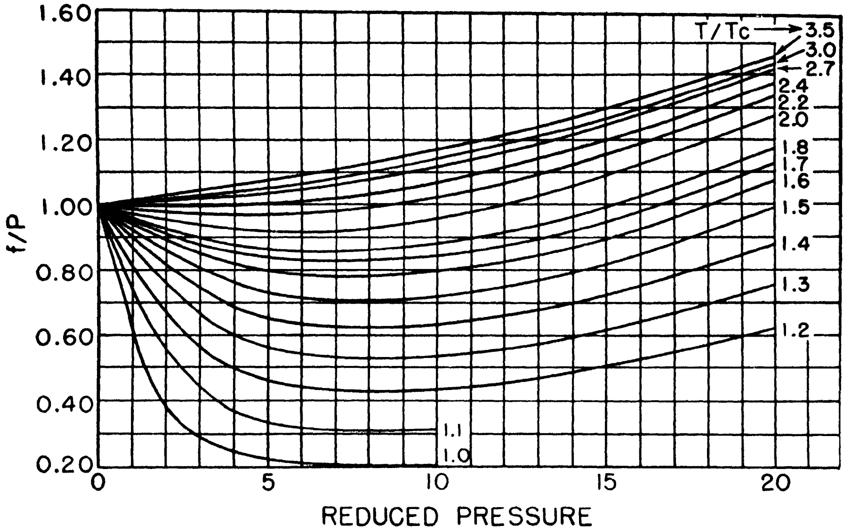


FIGURE 5. Generalized plot of values of the ratio of fugacity to pressure, f/P, as a function of the reduced pressure, P/P_c, for values of the reduced temperature, $T_R = T/T_c$, from 1.0 to 3.5. From Newton (*2*).

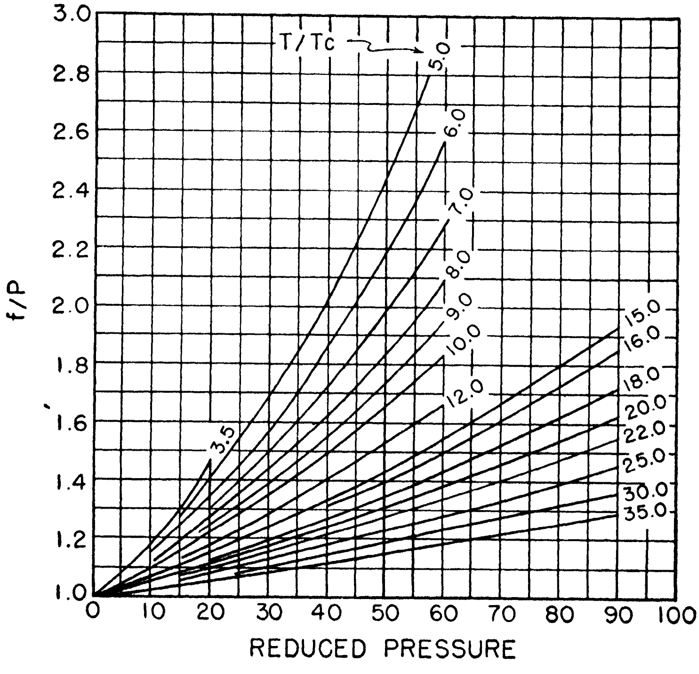


FIGURE 6. Generalized plot of values of the ratio of fugacity to pressure, f/P, as a function of the reduced pressure, P/P_c, for values of the reduced temperature, $T_R = T/T_c$, from 3.5 to 35. From Newton (*2*).

requirement of accuracy of the various first and second derivatives increases. Beattie (*9*) has reviewed and summarized the existing *P-V-T* equations from the standpoint of their usefulness in producing values of the thermodynamic properties. It appears that the most satisfactory equations of state for accurate thermodynamic calculations are those of Beattie and Bridgeman (*3*) and of Benedict, Webb, and Rubin (*12*).

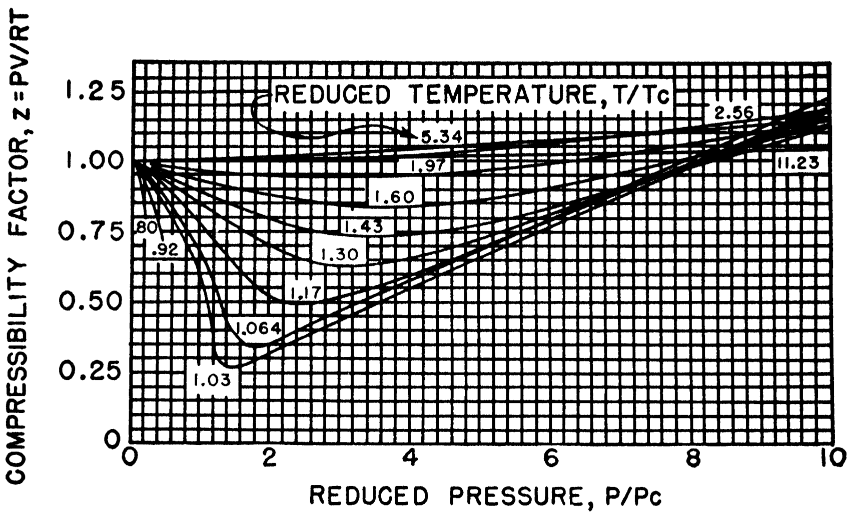


FIGURE 7. Generalized plot of values of the compressibility factor for gases as a function of the reduced pressure, at various values of the reduced temperature, for values of the reduced pressure from 0 to 10. From Dodge (*11*).

12. Compressibilities of gases. As has already been noted above, one of the useful functions to have evaluated for gases as a function of pressure at various temperatures is the compressibility factor, z, defined as

$$z = \frac{PV}{RT}. \tag{92}$$

At zero pressure at every temperature for every gas, the value of the compressibility factor is unity. It is to be noted also that, at constant temperature,

$$\left(\frac{\partial z}{\partial P}\right)_T = \left(\frac{1}{RT}\right)\left[\frac{\partial (PV)}{\partial P}\right]_T. \tag{93}$$

It has been found that, at the same value of the reduced temperature, T/T_c, most gases have nearly equal values of the compressibility factor for the same values of the reduced pressure. Figures 7 and 8, taken from Dodge (*11*), give generalized plots of the compressibility factor for gases as a function of the reduced pressure for various values of the reduced temperature.

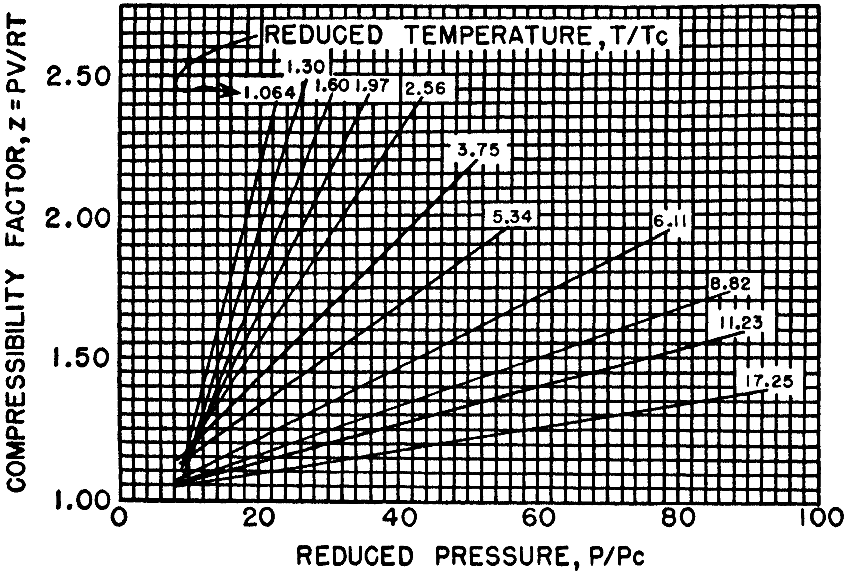


FIGURE 8. Generalized plot of values of the compressibility factor for gases as a function of the reduced pressure, at various values of the reduced temperature, for values of the reduced pressure from 10 to 90. From Dodge (*11*).

13. Collateral reading. For detailed discussion regarding the fugacities of gases and their evaluation, equations of state, compressibilities, and related properties, the reader is referred to Lewis (*1*), Lewis and Randall (*7*), Newton (*2*), Beattie and Bridgeman (*3*), Deming and Shupe (*4*), Tunell (*5*), Maron and Turnbull (*6*), Mayer and Mayer (*8*), Beattie (*9*), Redlich and Kwong (*10*), and Dodge (*11*).

REFERENCES

1. G. N. Lewis, *Proc. Am. Acad. Arts Sci.* **37**, 49 (1901).
2. R. H. Newton, *Ind. Eng. Chem.* **27**, 302 (1935).
3. J. A. Beattie and O. C. Bridgeman, *J. Am. Chem. Soc.* **49**, 1665 (1927).
4. W. E. Deming and L. E. Shupe, *J. Am. Chem. Soc.* **52**, 1382 (1930).

5. G. Tunell, *J. Phys. Chem.* **35**, 2885 (1931).

6. S. H. Maron and D. Turnbull, *J. Am. Chem. Soc.* **64**, 44 (1942).

7. G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill Book Company, New York, 1923.

8. J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, John Wiley & Sons, New York, 1940.

9. J. A. Beattie, *Chem. Revs.* **44**, 141 (1949).

10. O. Redlich and J. N. S. Kwong, *Chem. Revs.* **44**, 233 (1949).

11. B. F. Dodge, *Ind. Eng. Chem.* **24**, 1353 (1932).

12. M. Benedict, G. B. Webb, and L. C. Rubin, *J. Chem. Phys.* **8**, 334 (1940).

PROBLEMS

1. Given for a gas at 25°C, from 0 to 10 atm: $PV = RT(1 - 0.0052P)$; P in atmospheres. Calculate the ratio of fugacity to pressure at pressures of 1, 5, and 10 atm.

2. For a gas for which the critical temperature is 304.3°K and the critical pressure is 73.0 atm, assume the Berthelot equation of state and calculate, for 25°C, the value of $F_{\text{real}} - F_{\text{ideal}}$, $S_{\text{real}} - S_{\text{ideal}}$, $H_{\text{real}} - H_{\text{ideal}}$, and f/P, at pressures of 1, 10, and 50 atm.

3. For a gas at 0°C, $PV = RT(1 - 0.000993P + 0.00000219P^2)$. Calculate the fugacity at pressures of 1, 10, and 50 atm.

4. If the vapor pressure of liquid water at 0°C is 4.58 mm Hg, what is the fugacity, in atmospheres, of water ice at 0°C?

5. For water, the critical temperature and pressure are 647.3°K and 218.4 atm, respectively. Utilizing the relations given in Figure 4, 5, or 6, evaluate the following: (*a*) the fugacity of liquid water at 100°C and 1 atm; (*b*) the fugacity of water at the critical point.

6. For a given gas, the van der Waals constants have the following values: a, 5.46 atm liters^2/mole^2; b, 0.0647 liters/mole. Evaluate the following at 25°C and 10 atm: f/P; $F_{\text{real}} - F_{\text{ideal}}$; $S_{\text{real}} - S_{\text{ideal}}$; $H_{\text{real}} - H_{\text{ideal}}$.

24

Solutions; Partial Molal and Apparent Molal Properties

1. Specification of the composition of solutions. In our earlier discussions, we have seen that for systems consisting of one component, that is, pure substances, the thermodynamic state of the system under ordinary conditions can be adequately specified in terms of two variables, such as the pressure and temperature. With a system of two or more components comprising a solution, however, the thermodynamic state of the system is not adequately specified until the composition is given. For a solution, then, the thermodynamic state is, under ordinary conditions, adequately specified in terms of $2 + c - 1$ or $1 + c$ variables, c being the number of components.

The composition of a solution may be specified by giving the number of moles, n, of each of the components, 1, 2, 3, etc., as n_1, n_2, n_3, etc.* It is customary to use the subscript 1 to denote the component present in largest amount, so that in a binary solution, for example, the number of moles of solvent is n_1 and the number of moles of solute is n_2.

The foregoing method specifies both the composition and the quantity of the components, the latter an extensive property. It is usually more convenient to specify the composition separately as an intensive property. This may be done by means of the mole fraction,† N, which, for any given component i is the number of moles of component i, n_i, divided by the total number of moles of all the components $\sum n_i$. That is to say, our solution may consist of n_1 moles of substance X_1, n_2 moles of substance X_2, n_3 moles of substance X_3, and, in general, n_i moles of substance X_i. The

---

* Lower case n is used as the symbol for the number of moles.

† Roman small cap N is used as the symbol for the mole fraction.

total number of moles is

$$\sum n_i = n_1 + n_2 + n_3 + \cdots + n_i. \tag{1}$$

Then

$$\mathrm{N}_1 = \frac{n_1}{\sum n_i}; \quad \mathrm{N}_2 = \frac{n_2}{\sum n_i}; \quad \mathrm{N}_3 = \frac{n_3}{\sum n_i}; \quad \mathrm{N}_i = \frac{n_i}{\sum n_i}. \tag{2}$$

Further, the sum of the mole fractions of the components is unity:

$$\sum \mathrm{N}_i = \sum \frac{n_i}{\sum n_i} = \frac{\sum n_i}{\sum n_i} = 1. \tag{3}$$

The specification of the composition of a solution by means of the mole fractions of the components is simple and exact. However, in the case of aqueous solutions, there has grown up a system of expressing the composition in terms of the molarity, which is defined as the number of moles of solute per liter of the solution, or the molality, which is defined as the number of moles of solute per 1000 grams of the solvent, water. The expression of composition in terms of the number of moles per liter of solution is disadvantageous because, for a given solution, the volume changes with temperature, and, as the temperature changes, the concentration changes, without addition or removal of any components.

For this reason, the composition of aqueous solutions is usually more advantageously expressed in terms of the molality, or number of moles of solute per 1000 grams of water. The molality so defined is, for any given solution, independent of the temperature and provides a complete specification of the composition.

For any solute, i, the molality* is given by

$$m_i = \frac{1000}{(\text{mass of solvent})} \frac{(\text{mass of component } i)}{M_i}. \tag{4}$$

where M_i is the molecular weight of component i in g/mole.

2. Partial molal and apparent molal quantities. In scrutinizing a system of two or more components thermodynamically, it is important to decide what part of the total value of a given thermodynamic property of the solution is due to each component. For this purpose, it is convenient to define what is called

---

* Italic lower case m is the symbol used for molality. Where it is necessary, italic lower case c will be used for molarity or concentration in moles per liter of solution.

by Lewis (*1*) the partial molal quantity, for a component i, as*

$$\bar{\text{G}}_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_1,n_2,n_3,\cdots,n_j}. \tag{5}$$

That is, for any property, G, of the solution, the partial molal quantity for component i is denoted† by $\bar{\text{G}}_i$ and is defined as the rate of change of the property G of the solution with change in the number of moles of component i, with the number of moles of all other components being held constant, all at constant pressure and temperature. For example, if the property involved is the volume, then the partial molal volume of component i is the change in the volume of the solution, ΔV, which takes place on the addition of Δn_i moles of component i, divided by Δn_i, the number of moles of component i added, the ratio being taken in the limit as Δn_i approaches zero, all at constant pressure and temperature:

$$\bar{\text{V}}_i = \text{limit, as } \Delta n_i \rightarrow 0, \text{ of} \left(\frac{\Delta V}{\Delta n_i}\right)_{P,T}. \tag{6}$$

Similarly, the partial molal volume of component i would be the change in the volume occurring on the addition of one mole of component i to a quantity of solution so large that the addition of one mole of component i does not significantly change the composition, all at constant pressure and temperature.

The foregoing is illustrated in Figure 1, in which the volume, V, of a system composed of two components is plotted as a function of the number of moles of the solute, n_2. At point A is shown the volume of the pure solvent, or, what is the same thing, of a solution of components 1 and 2 infinitely dilute in component 2. At point B is shown the volume of a given solution containing the

---

* It is to be noted that the partial molal quantity defined by Equation 5 is specified for constant pressure and temperature because most reactions and processes involving solutions for which information regarding partial molal properties is needed occur at constant pressure and temperature. If it were needed, one could of course define a different partial molal quantity specified for constant volume and constant temperature, as

$$(\bar{\text{G}}_i)_{V,T} = \left(\frac{\partial G}{\partial n_i}\right)_{V,T,n_1,n_2,n_3,\cdots,n_j}.$$

† A roman small cap, with a bar overhead, as $\bar{\text{G}}$, is used to denote a partial molal quantity.

original amount of the solvent, component 1, plus a finite amount of the solute, component 2. The rate of change of the volume of the solution with change in the number of moles of component is given graphically by the slope of the line, *DE*, drawn tangent to the curve at *B*. That is,

$$\bar{v}_2 = \text{tangent} \angle EBF. \tag{7}$$

It is clear that the partial molal property is one which may not always be conveniently measurable experimentally with the required precision. For the purpose of providing a simpler means of evaluating the partial molal quantity, it is convenient to define what Lewis and Randall (*2*) term the apparent molal property of a solute. The apparent molal property of a given solute component, *j*, in a solution of two or more components is defined as the value of the property *G* of the given solution less the value of the property *G* for the same solution with all the given solute component, *j*, removed, divided by the number of moles of solute component, *j*, in the original solution.

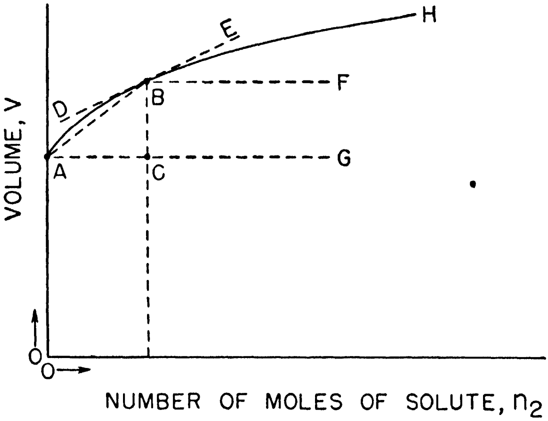


Figure 1. Schematic diagram showing the relation between the partial molal property (volume) and the apparent molal property (volume).
See text for details.

For example, the given solution contains $n_1, n_2, n_3, n_j, + \cdots + n_i$ moles of components, and its volume is V_B. With n_j moles of component *j* removed, the solution contains $n_1, n_2, n_3, + \cdots + n_i$ moles of components, and the volume is now V_A. The apparent molal volume of solute component j is then

$$\Phi \mathrm{v}_j = \frac{V_B - V_A}{n_j}. \tag{8}$$

Or, in general, for any property G, the apparent molal property for component j is

$$\Phi \mathrm{G}_j = \frac{(G)_{\text{given solution}} - (G)_{n_j=0}}{n_j}. \tag{9}$$

That is to say, the value of the apparent molal property $\Phi \mathrm{G}_j$ of a given component, j, is the change, ΔG, in the value of the given property, G, produced when the given solution is formed by adding the given number of moles n_j of component j to a solution already containing all the other components of the solution, the change in the value of G being divided by the number of moles of component j. The entire change, ΔG, is thus ascribed to n_j moles of component j, so that

$$\Phi \mathrm{G}_j = \frac{\Delta G}{n_j}, \tag{10}$$

the value of ΔG being counted between the solution containing zero moles of component j and n_j moles of component j.

The foregoing is a general definition of the apparent molal property for any one particular solute in a solution of two or more components. Practically, however, in working with the apparent molal property in a solution of more than two components, it may be useful to lump together all the different solute components as constituting a mean solute and all the different solvent components as constituting a mean solvent, and operating with the relations for a solution of two components. In such case, the values of the apparent molal property for the mean solute would be evaluated as a function of the mole fraction or molality of the mean solute, for a given composition of the mean solute and a given composition of the mean solvent (if composed of more than one component). Similar evaluations would be made for different compositions of the mean solute and, if necessary, for different compositions of the mean solvent. An example of such a system is a solution composed of sodium chloride and potassium bromide as solute components with water and dioxane as solvent components.

Usually, the apparent molal property is most used in connection with binary solutions in which water is the main component and the apparent molal property is applied to the solute. In such solutions, for example, the apparent molal property, Φ_{G_2}, of the solute is equal to the value of the property G for the solution containing n_1 moles of water and n_2 moles of the solute less the value of the property G for n_1 moles of water, all divided by the number of moles, n_2, of the solute. That is, for this solution, the apparent molal property of the solute is

$$\Phi_{G_2} = \frac{G_{(n_1+n_2)} - G_{n_1}}{n_2} = \frac{\Delta G}{n_2}. \tag{11}$$

Referring to Figure 1, in which is plotted the volume of a solution of two components, 1 and 2, as a function of the number of moles of the solute, component 2, it is seen that the apparent molal volume of the solute in the solution denoted by the point B is given by the slope of the chord drawn from the origin, A, to the point B. That is,

$$\Phi_{V_2} = \text{slope } AB = \frac{\overline{BC}}{\overline{AC}} = \text{tangent } \angle BAC. \tag{12}$$

In Figure 1, the line $\overline{BC}$ represents ΔV and the line $\overline{AC}$ represents n_2, in the relation

$$\Phi_{V_2} = \frac{V_{(n_1+n_2)} - V_{n_1}}{n_2} = \frac{\Delta V}{n_2}. \tag{13}$$

Referring to Figure 1, it is to be noted that, for the solution denoted by the point B, the value of the partial molal volume of the solute differs from the value of the apparent molal volume of the solute by the difference in the slopes of the lines DE and AB, the slope of the latter in this case being greater. Consider the solution denoted by the point A, which is pure solvent, or a solution infinitely dilute in component 2, or a solution containing a finite number of moles of solute in an infinite amount of solvent. Here, it is clear that the tangent to the curve at A is identical with the chord at A. Hence, in the infinitely dilute solution, the value of the apparent molal property of a solute is identical with the value of the partial molal property of the solute. That is, at infinite dilution,

$$(\Phi_{G_2})_{n_2=0} = (\bar{G}_2)_{n_2=0}. \tag{14}$$

3. Basic partial molal equations. The change in the value of any property G of any solution is, at constant pressure and temperature, a function of the composition only, and may be expressed mathematically as

$$dG = \sum \left(\frac{\partial G}{\partial n_i}\right)_{n_j} dn_i, \tag{15}$$

where j refers to all components except component i. That is. at constant temperature and pressure,

$$dG = \left(\frac{\partial G}{\partial n_1}\right)_{n_2, n_3, \cdots, n_i} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{n_1, n_3, \cdots, n_i} dn_2 + \left(\frac{\partial G}{\partial n_3}\right)_{n_1, n_2, \cdots, n_i} dn_3 + \cdots + \left(\frac{\partial G}{\partial n_i}\right)_{n_j} dn_i. \tag{16}$$

But we have defined the partial molal property of any component i, at constant pressure and temperature, as

$$\bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{n_j} dn_i. \tag{17}$$

Using the abbreviation provided by this equation, Equation 16 may be written as

$$dG = \bar{G}_1\, dn_1 + \bar{G}_2\, dn_2 + \bar{G}_3\, dn_3 + \cdots + \bar{G}_i\, dn_i = \sum \bar{G}_i\, dn_i. \tag{18}$$

But Equation 18 may be integrated at constant composition to give, with pressure and temperature constant, the first basic partial molal equation,*

$$G = \bar{G}_1 n_1 + \bar{G}_2 n_2 + \bar{G}_3 n_3 + \cdots + \bar{G}_i n_i = \sum \bar{G}_i n_i. \tag{19}$$

Now Equation 19 may be differentiated at constant temperature

---

* If the number of moles of the several components of the given final amount of the solution are n_1, n_2, $n_3, \cdots$, the integration of Equation 18 at constant relative composition may be thought of physically as adding increments of quantity of the given solution of fixed composition. Since the composition is fixed and only the quantity of solution is being integrated, the values of the partial molal properties of the components are constant and the integration is simply the following:

$$dG = \bar{G}_1 \int_0^{n_1} dn_1 + \bar{G}_2 \int_0^{n_2} dn_2 + \bar{G}_3 \int_0^{n_3} dn_3 + \cdots + \bar{G}_i \int_0^{n_i} dn_i.$$

and pressure, with all the components variable, to give

$$\begin{aligned} dG &= n_1\, d\bar{\mathrm{G}}_1 + \bar{\mathrm{G}}_1\, dn_1 + n_2\, d\bar{\mathrm{G}}_2 + \bar{\mathrm{G}}_2\, dn_2 + n_3\, d\mathrm{G}_3 \\ &\qquad + \bar{\mathrm{G}}_3\, dn_3 + \cdots + n_i\, d\bar{\mathrm{G}}_i + \bar{\mathrm{G}}_i\, dn_i \\ &= \textstyle\sum n_i\, d\bar{\mathrm{G}}_i + \sum \bar{\mathrm{G}}_i\, dn_i. \end{aligned} \tag{20}$$

Subtraction of Equation 18 from Equation 20 gives the second basic partial molal equation,

$$n_1\, d\bar{\mathrm{G}}_1 + n_2\, d\bar{\mathrm{G}}_2 + n_3\, d\bar{\mathrm{G}}_3 + \cdots + n_i\, d\bar{\mathrm{G}}_i = \textstyle\sum n_i\, d\bar{\mathrm{G}}_i = 0. \tag{21}$$

Equations 19 and 21 are the two basic partial molal equations.

If each term in Equations 19 and 21 is divided by the total number of moles in the solution, corresponding equations with the composition in terms of mole fraction are obtained:

$$\mathrm{G} = \bar{\mathrm{G}}_1\mathrm{N}_1 + \bar{\mathrm{G}}_2\mathrm{N}_2 + \bar{\mathrm{G}}_3\mathrm{N}_3 + \cdots + \bar{\mathrm{G}}_i\mathrm{N}_i = \textstyle\sum \bar{\mathrm{G}}_i\mathrm{N}_i; \tag{22}$$

$$\mathrm{N}_1\, d\bar{\mathrm{G}}_1 + \mathrm{N}_2\, d\bar{\mathrm{G}}_2 + \mathrm{N}_3\, d\bar{\mathrm{G}}_3 + \cdots + \mathrm{N}_i\, d\bar{\mathrm{G}}_i = \textstyle\sum \mathrm{N}_i\, d\bar{\mathrm{G}}_i = 0. \tag{23}$$

4. Relations holding for binary solutions. For a solution of two components, the basic partial molal equations, Equations 19, 21, 22, and 23, are respectively as follows:

$$G = \bar{\mathrm{G}}_1 n_1 + \bar{\mathrm{G}}_2 n_2, \tag{24}$$

$$n_1\, d\bar{\mathrm{G}}_1 + n_2\, d\bar{\mathrm{G}}_2 = 0, \tag{25}$$

$$\mathrm{G} = \bar{\mathrm{G}}_1\mathrm{N}_1 + \bar{\mathrm{G}}_2\mathrm{N}_2, \tag{26}$$

and

$$\mathrm{N}_1\, d\bar{\mathrm{G}}_1 + \mathrm{N}_2\, d\bar{\mathrm{G}}_2 = 0. \tag{27}$$

By dividing each term in Equation 27 by $d\mathrm{N}_2$, we obtain the relation

$$\mathrm{N}_1 \frac{d\bar{\mathrm{G}}_1}{d\mathrm{N}_2} + \mathrm{N}_2 \frac{d\bar{\mathrm{G}}_2}{d\mathrm{N}_2} = 0, \tag{28}$$

or

$$\frac{\dfrac{d\bar{\mathrm{G}}_1}{d\mathrm{N}_2}}{\dfrac{d\bar{\mathrm{G}}_2}{d\mathrm{N}_2}} = -\frac{\mathrm{N}_2}{\mathrm{N}_1}. \tag{29}$$

Equation 29 gives several important relations involving the slopes of curves of $\bar{\mathrm{G}}_1$ and $\bar{\mathrm{G}}_2$ plotted as a function of the mole fraction, N_1 or N_2.

When $N_1 = N_2 = 0.5$, Equation 29 becomes

$$\frac{d\bar{G}_1}{dN_2} = -\frac{d\bar{G}_2}{dN_2}. \tag{30}$$

That is, for the equimolal solution, the slopes of the two curves are equal but opposite in sign, as shown at *A*, *A′*, and *A″* in Figure 2.

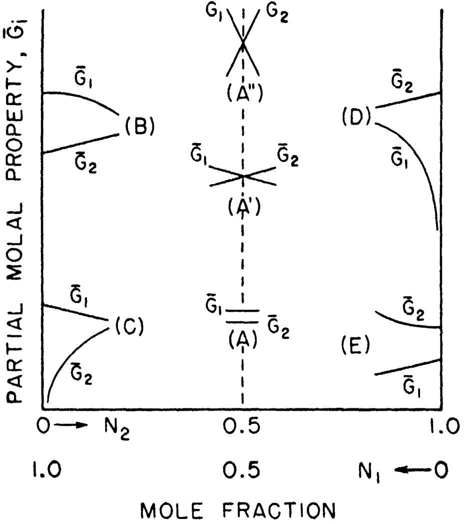


FIGURE 2. Diagram showing some relations holding for the slopes of the curves of the partial molal properties for the components of a binary solution, at 0, 0.5, and 1.0 mole fraction.
See text for details.

When $N_2 = 0$ and $N_1 = 1$, Equation 29 becomes

$$\frac{\dfrac{d\bar{G}_1}{dN_2}}{\dfrac{d\bar{G}_2}{dN_2}} = 0. \tag{31}$$

That is, when N_2 is zero, the ratio of the slope of the $\bar{G}_1$ curve to that of the $\bar{G}_2$ curve is zero. When the slope of the $\bar{G}_2$ curve is finite, the slope of the $\bar{G}_1$ curve must be zero, as shown at *B* in Figure 2. When the slope of the $\bar{G}_1$ curve is finite, the slope of the $\bar{G}_2$ curve must be infinite, as shown at *C* in Figure 2.

When $N_2 = 1$ and $N_1 = 0$, Equation 29 becomes

$$\frac{\frac{d\bar{G}_1}{dN_2}}{\frac{d\bar{G}_2}{dN_2}} = -\infty. \tag{32}$$

That is, when N_2 is unity, the ratio of the slope of the $\bar{G}_1$ curve to that of the $\bar{G}_2$ curve is infinity. When the slope of the $\bar{G}_2$ curve is finite, the slope of the $\bar{G}_1$ curve must be infinite, as at *D* in Figure 2. When the slope of the $\bar{G}_1$ curve is finite, the slope of the $\bar{G}_2$ curve must be zero, as at *E* in Figure 2.

The foregoing relations hold for all partial molal properties and serve as a convenient check on the reliability of the experimental data from which the partial molal properties are calculated.

5. Relations between apparent and partial molal quantities. For a binary solution consisting of n_1 moles of solvent and n_2 moles of solute, the value of a given property of the solution is

$$G = n_1\bar{G}_1 + n_2\bar{G}_2. \tag{33}$$

When n_2 is zero, as in the infinitely dilute solution or pure solvent, the value of the given property of the solution is the same as that of the pure solvent. Using a superscript asterisk to denote the pure solvent, we may write for zero moles of solute,

$$G^* = n_1\bar{G}_1^*. \tag{34}$$

By definition, the value of the apparent molal property of the solute in the given solution, containing n_1 moles of solvent and n_2 moles of solute, is

$$\Phi G_2 = \frac{G - G^*}{n_2}. \tag{35}$$

Substituting for G^* its value from Equation 34 gives

$$\Phi G_2 = \frac{G - n_1\bar{G}_1^*}{n_2}, \tag{36}$$

or

$$G = n_1\bar{G}_1^* + n_2\Phi G_2. \tag{37}$$

Equating Equations 33 and 37 and solving for the apparent molal property of the solute gives

$$\Phi G_2 = \bar{G}_2 + \frac{n_1}{n_2}(\bar{G}_1 - \bar{G}_1^*). \tag{38}$$

Equation 38 serves to evaluate either $\bar{G}_1$ or $\bar{G}_2$ when ΦG_2 and either $\bar{G}_2$ or $\bar{G}_1$ are known, as

$$\bar{G}_1 - \bar{G}_1^* = \frac{n_2}{n_1}(\Phi G_2 - \bar{G}_2), \tag{39}$$

or

$$\bar{G}_2 = \Phi G_2 - \frac{n_1}{n_2}(\bar{G}_1 - \bar{G}_1^*). \tag{40}$$

Differentiation of Equation 37 with respect to the number of moles of solute, at constant temperature, pressure, and moles of solvent, gives

$$\frac{dG}{dn_2} = n_2\frac{d(\Phi G_2)}{dn_2} + \Phi G_2. \tag{41}$$

But, at constant T, P, and n_1,

$$\frac{dG}{dn_2} = \bar{G}_2. \tag{42}$$

Hence Equation 41 may be written as

$$G_2 = \Phi G_2 + n_2\frac{d(\Phi G_2)}{dn_2}. \tag{43}$$

Equation 43 shows how the partial molal property of the solute, $\bar{G}_2$, may be calculated if the apparent molal property of the solute, ΦG_2, is known as a function of the number of moles of component 2. That is, on a plot of ΦG_2 against n_2, with n_1 constant, $\bar{G}_2$ is, for a given value of n_2, equal to the ordinate plus the product of the slope and the abscissa.

Combination of Equations 38 and 43 gives

$$\bar{G}_1 - \bar{G}_1^* = -\frac{n_2^2}{n_1}\frac{d(\Phi G_2)}{dn_2}. \tag{44}$$

Equation 44 shows how the partial molal property of the solvent, referred to pure solvent, may be evaluated if the apparent molal property is known as a function of the number of moles of solute, the number of moles of solvent being constant. That is, if ΦG_2 is plotted against n_2, $\bar{\text{G}}_1 - \bar{\text{G}}_1{}^*$ is, for any given value of n_2, equal to the slope of the curve multiplied by $-n_2{}^2/n_1$.

If the given binary solution is an aqueous one, consisting of 1000 grams or 55.506 moles of water and m moles of solute, then

$$n_1 = 55.506; \quad n_2 = m. \tag{45}$$

Then we may write

$$G = 55.506\bar{\text{G}}_1 + m\bar{\text{G}}_2, \tag{46}$$

and

$$G = 55.506\bar{\text{G}}_1{}^* + m\Phi\text{G}_2. \tag{47}$$

Subtraction of these two equations gives

$$\Phi\text{G}_2 = \bar{\text{G}}_2 + \frac{55.506}{m}(\bar{\text{G}}_1 - \bar{\text{G}}_1{}^*). \tag{48}$$

Differentiation of Equation 47 with m, at constant pressure and temperature, gives

$$\frac{\mathrm{d}G}{\mathrm{d}m} = m\frac{\mathrm{d}(\Phi\text{G}_2)}{\mathrm{d}m} + \Phi\text{G}_2, \tag{49}$$

or, since

$$\frac{\mathrm{d}G}{\mathrm{d}m} = \bar{\text{G}}_2, \tag{50}$$

$$\bar{\text{G}}_2 = \Phi\text{G}_2 + m\frac{\mathrm{d}(\Phi\text{G}_2)}{\mathrm{d}m}. \tag{51}$$

Combination of Equations 48 and 51 yields

$$\bar{\text{G}}_1 - \bar{\text{G}}_1{}^* = -\frac{m^2}{55.506}\frac{\mathrm{d}(\Phi\text{G}_2)}{\mathrm{d}m}. \tag{52}$$

6. Thermodynamic equations involving partial molal properties. All the thermodynamic relations given previously involving properties such as heat capacity, heat content, free energy, entropy, and volume, for one mole of substance, may be shown to hold for the corresponding partial molal properties.

Examples of such relations are the following:

$$\bar{F}_1 = \bar{H}_1 - T\bar{S}_1, \tag{53}$$

$$\left(\frac{\partial \bar{F}_1}{\partial T}\right)_P = -\bar{S}_1, \tag{54}$$

$$\left(\frac{\partial \bar{F}_1}{\partial P}\right)_T = \bar{V}_1, \tag{55}$$

$$\bar{C}_{P_1} = \left(\frac{\partial \bar{H}_1}{\partial T}\right)_P, \tag{56}$$

and

$$\left[\frac{\partial\left(\frac{\bar{F}_1}{T}\right)}{\partial T}\right]_P = -\frac{\bar{H}_1}{T^2}. \tag{57}$$

In each of the above relations, the partial molal property has been labeled for component 1 in the solution. The same relations hold for each of the other components of the solution.

7. Evaluation of partial molal properties. If the given property, G, of the solution is one which can be expressed analytically as a function of the composition, the evaluation of the partial molal property of the components is relatively simple. Suppose that for an aqueous binary solution the value of the property G for that amount of solution containing 1000 grams of water and m moles of solute is given by the relation,

$$G = f(m). \tag{58}$$

The value of the partial molal property of the solute is obtained by differentiating Equation 52 with respect to m:

$$\bar{G}_2 = \frac{d[f(m)]}{dm}. \tag{59}$$

But

$$G = 55.506\bar{G}_1 + m\bar{G}_2, \tag{60}$$

or

$$\bar{G}_1 = \frac{G - m\bar{G}_2}{55.506}. \tag{61}$$

That is,

$$\bar{G}_1 = \left\{f(m) - m\frac{d[f(m)]}{dm}\right\}\left(\frac{1}{55.506}\right). \tag{62}$$

Also, it is to be noted that, for zero molality,

$$G^* = 55.506\bar{G}_1^*, \tag{63}$$

and

$$G^* = f(m)_{m=0}. \tag{64}$$

If the value of G is expressible as a simple power series in m, over a given range of molality, then

$$G = f(m) = a + bm + cm^2 + em^3, \tag{65}$$

$$G^* = a, \tag{66}$$

$$\bar{G}_2 = b + 2cm + 3em^2, \tag{67}$$

$$\bar{G}_1 = \frac{a - cm^2 - 2em^3}{55.506}, \tag{68}$$

$$\bar{G}_1 - \bar{G}_1^* = -\frac{m^2}{55.506}(c + 2em). \tag{69}$$

If the property is expressible as a simpler function of m, as

$$G = f(m) = a + bm + cm^2, \tag{70}$$

the corresponding equations are the same as Equations 66 to 69, inclusive, with the constant e placed equal to zero.

Similarly, if the property is expressible as a linear function of m, over a given range of molality, the corresponding equations are the same as Equations 65 to 69, inclusive, with c and e placed equal to zero. In this case, both $\bar{G}_2$ and $\bar{G}_1$ are constant over the given range of molality, being equal to the constants b and $a/55.506$, respectively.

For aqueous solutions of strong electrolytes, it frequently happens that the apparent molal property is expressible as a linear function of the square root of the molality, over a given range of molality. That is, for the given range,

$$\Phi G_2 = a + bm^{1/2}. \tag{71}$$

In this case, from Equations 51 and 52, we find

$$\bar{G}_2 = a + \tfrac{3}{2}bm^{1/2}, \tag{72}$$

and

$$\bar{G}_1 - \bar{G}_1^* = -\frac{b}{2(55.506)}m^{3/2}. \tag{73}$$

For the foregoing case, of course, it turns out that the property G of the solution must be equal to (see Equation 47)

$$G = 55.506\bar{G}_1{}^* + am + bm^{3/2}, \tag{74}$$

where $55.506\bar{G}_1{}^*$ is a constant representing the value of G for 1000 grams of pure water at the given temperature.

Frequently, the experimental observations giving the value of a property G for a solution, or the value of the apparent molal property ΦG_2 for the solute, are not simply expressible analytically by any conveniently usable function. The same data may, however, be easily handled graphically by plotting the observations as an appropriate function of the composition in order to obtain curves which do not depart greatly from a simple function and which have slopes in the critical regions which are readily measured, the slopes not being nearly infinite in value.

The graphical method may be illustrated by the following simple procedure used by Randall and Rossini (*3*): Suppose that the property is one for which there can be readily measured the difference between G^*, the value of the property for 1000 grams of pure water, and G, the value of the property for a solution containing 1000 grams of pure water and m moles of solute. These observations give directly the value of the apparent molal property of the solute, as

$$\Phi G_2 = \frac{G - G^*}{m}. \tag{75}$$

Further, suppose it is found that the values of ΦG_2 so obtained may be plotted against the square root of the molality to obtain a curve having not too great a curvature over the given range. From Equation 51, the value of the partial molal property of the solute is given by

$$\bar{G}_2 = \Phi G_2 + m\,\frac{d(\Phi G_2)}{dm}. \tag{76}$$

Converting to the slope of ΦG_2 against $m^{1/2}$, by substituting $2m^{1/2}\,dm^{1/2}$ for dm, we have

$$\bar{G}_2 = \Phi G_2 + \frac{1}{2}\,m^{1/2}\,\frac{d(\Phi G_2)}{d(m^{1/2})}. \tag{77}$$

That is to say, from the plot of ΦG_2 against $m^{1/2}$, one obtains the value of $\bar{G}_2$ for a given value of $m^{1/2}$ as the value of the ordinate plus one-half the product of the value of the abscissa into the slope of the curve at that point. From Equation 52,

$$\bar{G}_1 - \bar{G}_1{}^* = -\frac{m^2}{55.506}\,\frac{d(\Phi G_2)}{dm}. \tag{78}$$

Substituting for dm as before, we obtain

$$\bar{G}_1 - \bar{G}_1{}^* = -\frac{m^{3/2}}{2(55.506)}\,\frac{d(\Phi G_2)}{d(m^{1/2})}. \tag{79}$$

That is, the value of $\bar{G}_1$, less the value for the pure solvent, $\bar{G}_1{}^*$, is equal to the slope of the curve at the given molality multiplied by the factor $-m^{3/2}/2(55.506)$.

Frequently, the available data to be used in evaluating partial molal properties are expressed per unit mass of substance, as data on volume given as specific volume in cubic centimeters per gram or density in grams per cubic centimeters or data on heat capacity given as specific heat in calories per gram degree. In such cases, it may be desirable first to calculate the apparent molal property before proceeding with the evaluation of the partial molal properties. The apparent molal property is related to the specific property as follows, for volume and heat capacity, in aqueous solutions:

$$\Phi V_2 = \frac{1}{\rho}\left[\left(\frac{1000}{m}\right)\left(\frac{\rho^* - \rho}{\rho^*}\right) + M\right]. \tag{80}$$

$$\Phi C_{P_2} = \left(\frac{1000}{m}\right)(s - s^*) + Ms. \tag{81}$$

In Equations 80 and 81, ρ is the density and s is the specific heat of the solution of molality m, ρ^* is the density and s^* is the specific heat of pure water, and M is the molecular weight of the solute.

Substantially all the practical possible combinations of ordinates and abscissas which may be utilized to obtain values of the partial molal properties from plots of experimentally determinable quantities have been summarized in excellent form by Young and Vogel (*4*). Among the 48 different combinations listed by these authors are included, for example:

a. A plot of the apparent molal property plus a constant,

ΦG_2 + constant, against the following functions of composition: (i) N_1; (ii) N_2; (iii) m; (iv) $m^{1/2}$; (v) m^k; (vi) $\log_{10} m^k$; (vii) N_2/N_1; (viii) N_1/N_2.

Similarly are given equations for calculating $\bar{G}_1$ and $\bar{G}_2$ from plots of the following additional quantities against the foregoing functions of composition:

b. G/n_2 + constant;
c. $G/(n_1 + n_2)$ + constant;
d. $(n_1 + n_2)/G$ + constant;
e. $G - (n_1\bar{G}_1^* + n_2\bar{G}_2^*)$;
f. G/(mass of solution).

Since the graphical methods discussed above involve the slope of curves drawn through certain experimental points, the evaluation of the slopes of such curves must be done carefully to preserve the full accuracy and precision of the data. Young and collaborators (*5,6,21*) have described improved methods for evaluating the slopes of curves of the apparent molal property.

8. Apparent and partial molal volume. For liquid solutions commonly termed nearly "ideal," in which the components 1 and 2 are such that the molecular interactions between them are not greatly different from the interactions between different molecules of component 1 and between different molecules of component 2, the partial molal volumes of the components have values nearly the same as those for the pure components. That is, approximately,

$$\bar{V}_1 \cong \bar{V}_1^*, \tag{82}$$

$$\bar{V}_2 \cong \bar{V}_2^*, \tag{83}$$

$$\Phi V_2 \cong \bar{V}_2 \cong \bar{V}_2^*, \tag{84}$$

and

$$\frac{V}{n_1 + n_2} \cong N_1\bar{V}_1^* + N_2\bar{V}_2^*. \tag{85}$$

These relations are illustrated in Figure 3.

In most solutions of non-electrolytes which are normally liquid, the values of the partial molal volumes do not change markedly from the values for the pure liquid components. The relations for such solutions are illustrated schematically in Figure 4.

In aqueous solutions of solutes, such as the alcohols, which interact markedly with water, the values of the partial molal volumes may change in an irregular manner with composition. This is illustrated in Figure 5, which gives a schematic plot of the values of $\bar{v}_1 - \bar{v}_1^*$ and $\bar{v}_2 - \bar{v}_2^*$ as a function of mole fraction for the system water plus methanol at 15°C. It should be noted how the curves in Figure 5 conform to the requirements of Equation 29, relating the slopes and the composition.

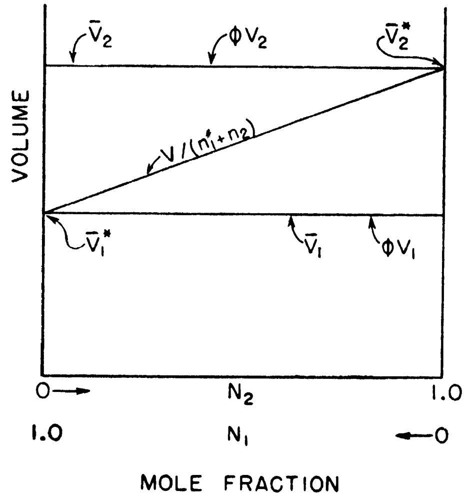


Figure 3. Schematic diagram giving the partial molal and apparent molal volumes of the components, and the molal volume of the solution, as a function of mole fraction, for an ideal solution of two components.

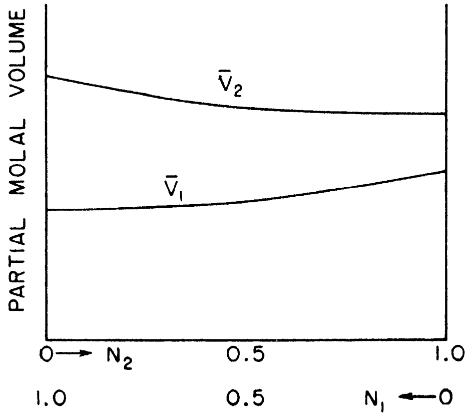


Figure 4. Schematic diagram giving the partial molal volumes as functions of mole fraction for a real solution of non-electrolytes.

In aqueous solutions of strong electrolytes, in the not too concentrated solutions, the apparent molal volume of the solute is

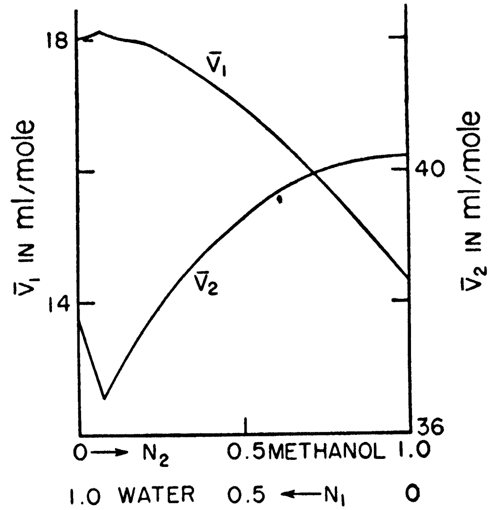


FIGURE 5. Partial molal volumes as functions of mole fraction for a solution of water and methanol.

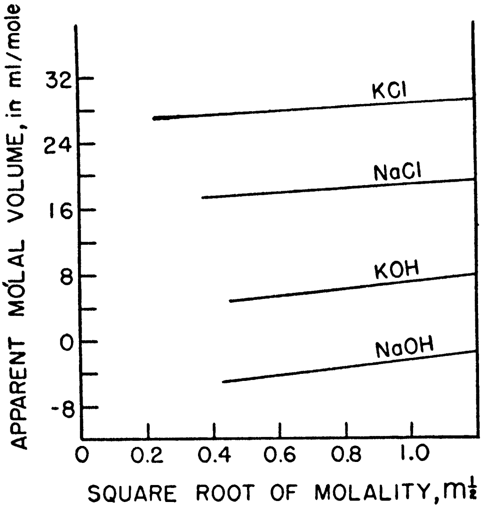


FIGURE 6. Plot of values of the apparent molal volume of the solute in aqueous solutions of NaCl, KCl, NaOH, and KOH. From Gucker (*13*).

found to be nearly linear with the square root of the molality. This is illustrated in Figure 6, which gives data for several strong electrolytes in aqueous solution. For strong electrolytes at infinite dilution in water, it is found that the values of $\bar{v}_2$ for individual ions are additive. In this connection, it is of interest to note that in very dilute aqueous solutions the apparent and partial molal volumes of certain strong electrolytes may be negative. A negative value of $\bar{v}_2$ at infinite dilution means that the introduction of a pair of ions in a large number of water molecules results in a decrease in the volume occupied by the respective near-neighbor water molecules in an amount greater than the volume occupied by the ions themselves.

Studies of data on apparent and partial molal volumes have been published by Masson (*7*), Scott (*8*), Geffcken (*9*), Redlich and Rosenfeld (*10*), Root (*11*), Geffcken and Price (*12*), and Redlich and collaborators (*22*,*23*,*24*).

9. Apparent and partial molal heat capacity. As in the case of volumes, the partial molal heat capacities of the components of nearly "ideal" liquid solutions have values nearly the same as those for the pure components:

$$\bar{c}_{P_1} \cong \bar{c}_{P_1}{}^*, \tag{86}$$

$$\bar{c}_{P_2} \cong \bar{c}_{P_2}{}^*, \tag{87}$$

$$\Phi c_{P_2} \cong \bar{c}_{P_2} \cong \bar{c}_{P_2}{}^*. \tag{88}$$

These relations are the same as the corresponding ones for volumes shown in Figure 3.

For solutions of non-electrolytes, the partial molal heat capacities of the components do not vary greatly with concentration. Schematically, these relations are the same as the corresponding ones for volumes shown in Figure 4.

For aqueous solutions of strong electrolytes, the apparent molal heat capacity of the solute is, like the apparent molal volume, roughly linear with the square root of the molality. This is illustrated in Figure 7, which gives data for several strong electrolytes in aqueous solution.

For strong electrolytes at infinite dilution in water, it is found that the values of $\bar{c}_{P_2}$ for individual ions are additive, as for volumes. Frequently, the values of $\bar{c}_{P_2}$ at infinite dilution are negative. Such negative values mean that the introduction of a pair of ions in a large number of water molecules results in a decrease in the heat capacity of the respective near-neighbor water molecules in an amount greater than the heat capacity of the ions themselves.

Studies of data on apparent and partial molal heat capacities have been published by Randall and Rossini (*3*), Rossini (*14*,*15*), and Gucker (*13*).

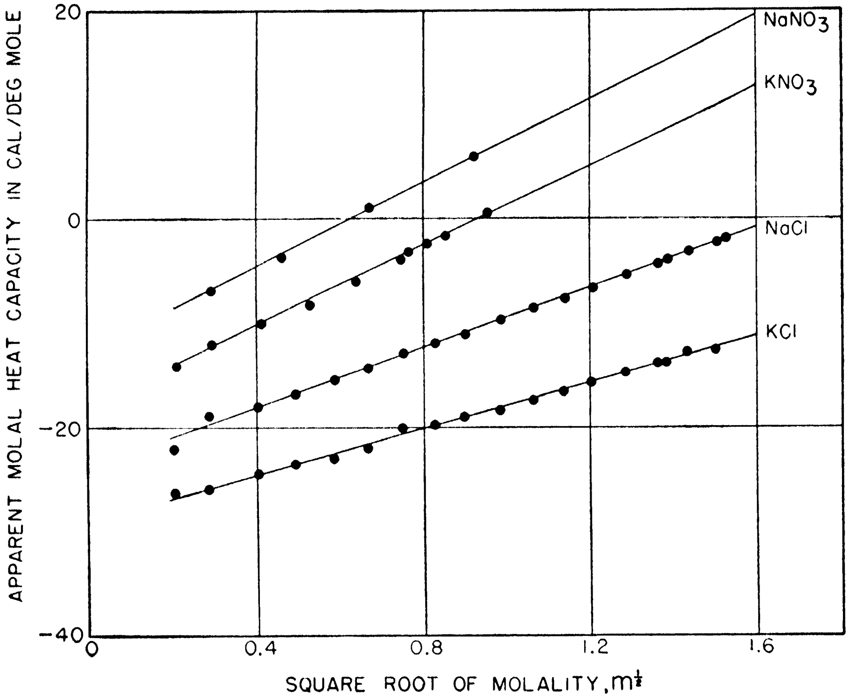


Figure 7. Plot of values of the apparent molal heat capacity of the solute in aqueous solutions of NaCl, KCl, $NaNO_3$, and KNO_3. From Rossini (*15*).

10. Apparent and partial molal heat content.

In the properties of volume and heat capacity, we have dealt with quantities that can be measured in an absolute sense. The heat content, however, can not be measured in an absolute sense, and it is necessary to use a reference state from which to make the evaluations.

For solutions that are nearly "ideal," or solutions of liquid nonelectrolytes in general, a convenient reference state for each component may be its own pure liquid state. The partial molal heat content of component 1 in such a solution, referred to the partial molal heat content of component 1 in the pure state, would be designated as $\bar{H}_1 - \bar{H}_1^*$. This is called the relative partial molal heat content. Similarly for component 2 in such a solution the relative partial molal heat content is $\bar{H}_2 - \bar{H}_2^*$.

For some solutions, however, in which the composition range to be covered is largely with component 1 in excess and with component 2 going from a small to zero concentration, it would be impracticable to use component 2 in the pure liquid state as the reference state for the heat content of component 2 in the dilute solution. A more useful reference state for such cases, which include aqueous solutions of electrolytes and non-electrolytes, is that of infinite dilution in the given component 1 as solvent. For the present, the state of infinite dilution will be denoted by a superscript zero on the appropriate thermodynamic symbol for component 2, as $\bar{H}_2^0$. That is, the relative partial molal heat content of the solute in an aqueous solution is denoted by $\bar{H}_2 - \bar{H}_2^0$.

For solutions that are nearly "ideal," the partial molal heat content of the solute will be nearly the same as for the solute in the pure liquid state, and similarly for the solvent. In such cases,

$$\bar{H}_1 - \bar{H}_1^* \cong 0, \tag{89}$$

$$\bar{H}_2 - \bar{H}_2^* \cong 0, \tag{90}$$

and

$$\Phi H_2 \cong \bar{H}_2 \cong \bar{H}_2^*. \tag{91}$$

The foregoing indicates zero heat of mixing the pure components to form a given solution. In general, for all solutions of nonelectrolytes, and to a certain extent for aqueous solutions of nonelectrolytes, the heat of mixing is not large.

With regard to aqueous solutions of strong electrolytes, however, the situation is quite different, because here the heats of dilution can be very large. The manner of evaluating the relative partial molal heat content of the components of aqueous solutions of electrolytes will be illustrated by utilizing data on heats of dilution and data on heats of solution.

Consider an aqueous solution consisting of 1000 grams of water and m moles of solute. Now, from Equation 46, we may write

$$H = 55.506\bar{H}_1 + m\bar{H}_2, \tag{92}$$

and from Equation 47

$$H = 55.506\bar{H}_1^* + m\Phi_{H_2}. \tag{93}$$

For zero concentration,

$$H^* = 55.506\bar{H}_1^*. \tag{94}$$

But from Equation 75,

$$\Phi_{H_2} = \frac{H - H^*}{m}. \tag{95}$$

Substituting for H and H^* in Equation 95 from Equations 92 and 94 gives

$$\Phi_{H_2} = \frac{m\bar{H}_2 + 55.506\bar{H}_1 - 55.506\bar{H}_1^*}{m}$$

$$= \bar{H}_2 + \frac{55.506}{m}(\bar{H}_1 - \bar{H}_1^*). \tag{96}$$

But

$$\Phi_{H_2}^0 = \bar{H}_2^0. \tag{97}$$

Subtraction of Equation 97 from Equation 96 gives

$$\Phi_{H_2} - \Phi_{H_2}^0 = \bar{H}_2 - \bar{H}_2^0 + \frac{55.506}{m}(\bar{H}_1 - \bar{H}_1^*), \tag{98}$$

or

$$\bar{H}_1 - \bar{H}_1^* = \frac{m}{55.506}[(\Phi_{H_2} - \Phi_{H_2}^0) - (\bar{H}_2 - \bar{H}_2^0)]. \tag{99}$$

The symbol $\Phi_{H_2} - \Phi_{H_2}^0$ denotes the relative apparent molal heat content and is the quantity most readily evaluated from calorimetric measurements of heats of dilution or heats of solution. While not linear with the square root of the molality, the relative apparent molal heat content for a strong electrolyte in aqueous solution may be plotted against the square root of the molality to yield a curve with a finite slope in the critical region. From Equation 77,

$$\bar{H}_2 = \Phi_{H_2} + \frac{1}{2}m^{1/2}\frac{d(\Phi_{H_2})}{d(m^{1/2})}. \tag{100}$$

But

$$\bar{H}_2^0 = \Phi_{H_2}^0 \tag{101}$$

and

$$\frac{d(\Phi_{H_2}^0)}{d(m^{1/2})} = 0, \tag{102}$$

so that

$$\bar{H}_2 - \bar{H}_2^0 = (\Phi H_2 - \Phi H_2^0) + \frac{1}{2} m^{1/2} \frac{d(\Phi H_2 - \Phi H_2^0)}{d(m^{1/2})}, \quad (103)$$

and

$$\bar{H}_1 - \bar{H}_1^* = - \frac{m^{3/2}}{2(55.506)} \frac{d(\Phi H_2 - \Phi H_2^0)}{d(m^{1/2})}. \quad (104)$$

If values of the relative apparent molal heat content can be determined experimentally, they may be utilized graphically to evaluate the relative partial molal heat content of the solute and solvent in accordance with Equations 103 and 104. Values of the relative apparent molal heat content may be obtained experimentally by measuring either heats of dilution or heats of solution.

For heats of dilution, the procedure may be illustrated as follows: Consider the reaction

$$(n_2MX \cdot n_1H_2O)(\text{liq}) + (\infty - n_1)H_2O\ (\text{liq}) = (n_2MX \cdot \infty H_2O)(\text{liq}). \quad (105)$$

For this reaction,

$$\Delta H = [n_2\bar{H}_2^0 + \infty \bar{H}_1^*] - [n_2\bar{H}_2 + n_1\bar{H}_1 + (\infty - n_1)\bar{H}_1^*], \quad (106)$$

or

$$\begin{aligned}\Delta H &= n_2(\bar{H}_2^0 - \bar{H}_2) + n_1(\bar{H}_1^* - \bar{H}_1) \\ &= -n_2(\bar{H}_2 - \bar{H}_2^0) - n_1(\bar{H}_1 - \bar{H}_1^*). \quad (107)\end{aligned}$$

In terms of the apparent molal heat content, for the same reaction,

$$\Delta H = [n_2\Phi H_2 + \infty \bar{H}_1^*] - [n_2\Phi H_2 + n_1\bar{H}_1^* + (\infty - n_1)\bar{H}_1^*], \quad (108)$$

or

$$\Delta H = n_2(\Phi H_2^0 - \Phi H_2) = -n_2(\Phi H_2 - \Phi H_2^0). \quad (109)$$

Equation 109 shows that, if a given solution is diluted to infinite dilution, the change in heat content, per mole, is the negative of the relative apparent molal heat content. Consider the following series of reactions of dilution:

$$(MX \cdot 25H_2O)(\text{liq}) + 25H_2O\ (\text{liq}) = (MX \cdot 50H_2O)(\text{liq}), \quad (110)$$

$$(MX \cdot 50H_2O)(\text{liq}) + 50H_2O\ (\text{liq}) = (MX \cdot 100H_2O)(\text{liq}), \quad (111)$$

$$(MX \cdot 100H_2O)(\text{liq}) + 100H_2O\ (\text{liq}) = (MX \cdot 200H_2O)(\text{liq}), \quad (112)$$

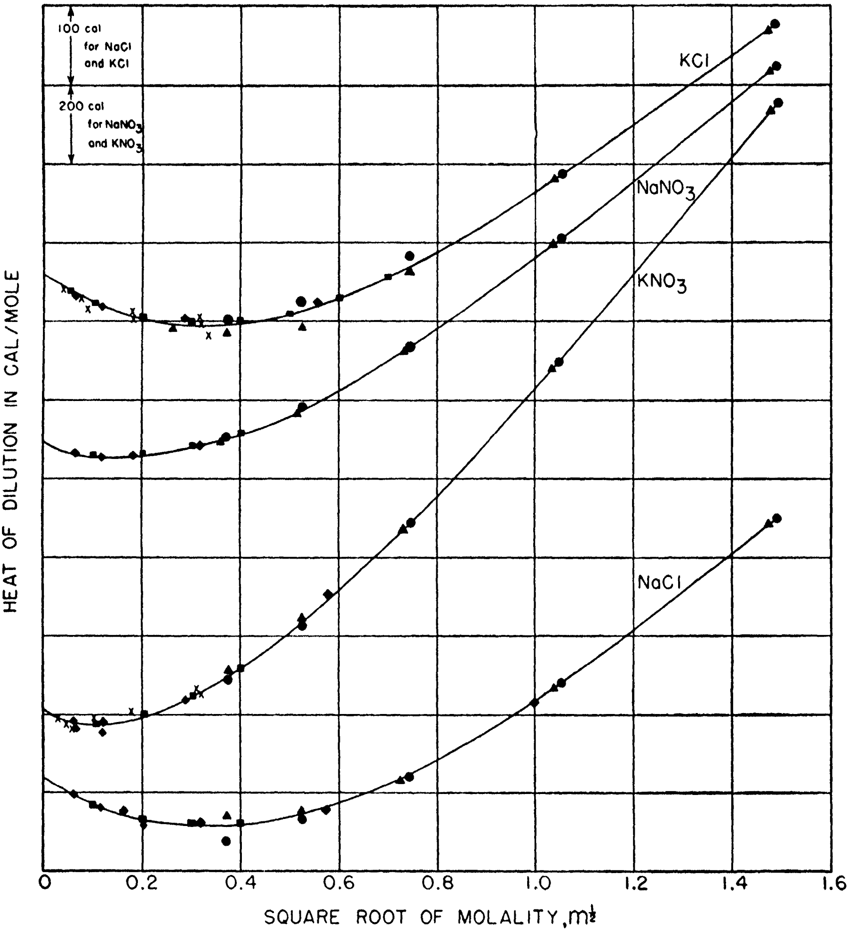


FIGURE 8. Plot of some experimental data on the heats of dilution of aqueous NaCl, KCl, $NaNO_3$, and KNO_3. From Rossini (*16*).

$$(MX\cdot 200H_2O)(liq) + 200H_2O\ (liq) = (MX\cdot 400H_2O)(liq). \quad (113)$$

For the successive dilutions, we may write the heats of the reactions as follows:

$$\Delta H\ (25 \rightarrow 50) = \Phi_{H_2}{}'' - \Phi_{H_2}{}', \quad (114)$$

$$\Delta H\ (50 \rightarrow 100) = \Phi_{H_2}{}''' - \Phi_{H_2}{}'', \quad (115)$$

$$\Delta H\ (100 \rightarrow 200) = \Phi_{H_2}{}'''' - \Phi_{H_2}{}''', \quad (116)$$

$$\Delta H\ (200 \rightarrow 400) = \Phi_{H_2}{}''''' - \Phi_{H_2}{}''''. \quad (117)$$

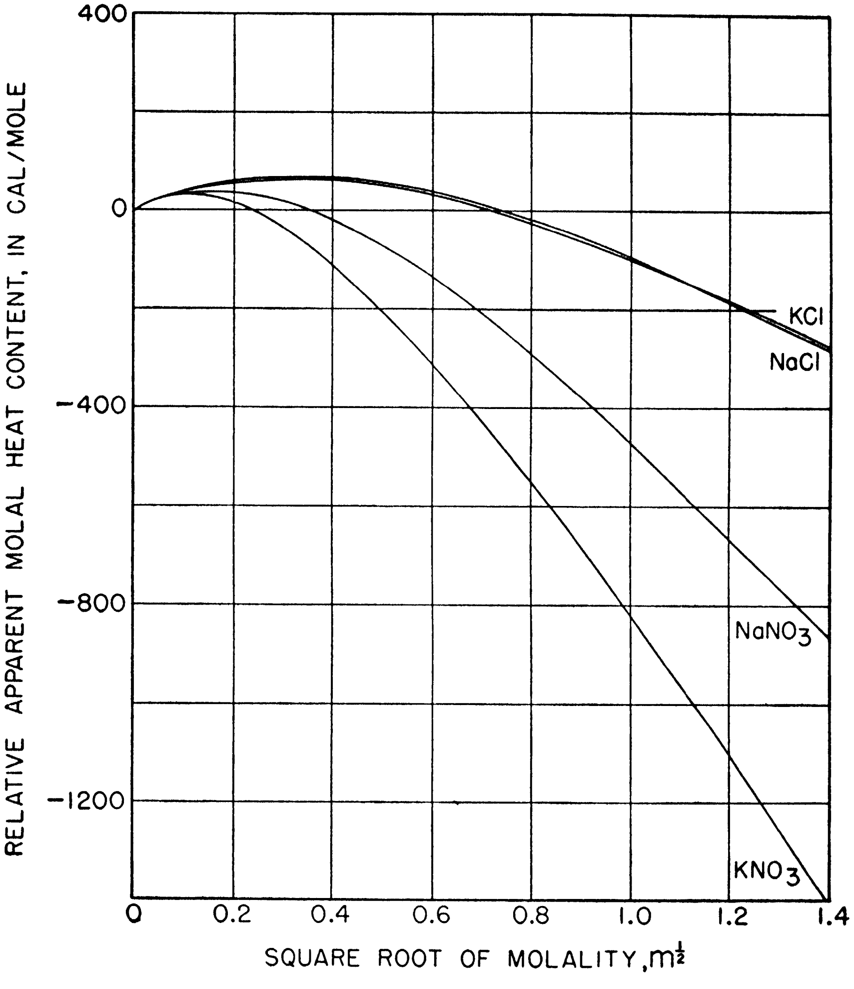


FIGURE 9. Plot of values of the relative apparent molal heat content of the solute in aqueous solutions of NaCl, KCl, $NaNO_3$, and KNO_3. From Rossini (*16*).

Appropriate combination of the foregoing yields values for the dilution from $MX \cdot 25H_2O$ to each of the subsequent solutions, $MX \cdot 50H_2O$, $MX \cdot 100H_2O$, etc. These values may be plotted against the square root of the molality, with the solution $MX \cdot 25H_2O$ as a temporary reference point. Then the curve is suitably extrapolated to infinite dilution. The point at which the curve reaches zero molality locates the desired reference point, $\Phi_{H_2}{}^0$. This is illustrated in Figure 8, which shows experimental results on the heats of dilution of several strong electrolytes in aqueous solution (*17*). With the new reference point, the curve is replotted as $\Phi_{H_2} - \Phi_{H_2}^0$ against $m^{1/2}$. This is shown in Figure 9. From the slopes and coordinates of the curves in Figure 9, the values of $\bar{H}_2 - \bar{H}_2^0$ and $\bar{H}_1 - \bar{H}_1^*$ may be calculated according to Equations 103 and 104.

For heats of solution, as of a solid in water to form an aqueous solution of a strong electrolyte, the procedure is not greatly different from the foregoing. Consider the following series of reactions of solution:

$$\text{MX (c)} + 25\text{H}_2\text{O (liq)} = (\text{MX}\cdot 25\text{H}_2\text{O})(\text{liq}), \tag{118}$$

$$\text{MX (c)} + 50\text{H}_2\text{O (liq)} = (\text{MX}\cdot 50\text{H}_2\text{O})(\text{liq}), \tag{119}$$

$$\text{MX (c)} + 100\text{H}_2\text{O (liq)} = (\text{MX}\cdot 100\text{H}_2\text{O})(\text{liq}), \tag{120}$$

$$\text{MX (c)} + 200\text{H}_2\text{O (liq)} = (\text{MX}\cdot 200\text{H}_2\text{O})(\text{liq}), \tag{121}$$

$$\text{MX (c)} + 400\text{H}_2\text{O (liq)} = (\text{MX}\cdot 400\text{H}_2\text{O})(\text{liq}). \tag{122}$$

The corresponding heats of these reactions are as follows:

$$\Delta H\ (\text{c} \rightarrow 25) = \Phi_{H_2}{}' - H_2\ (\text{c}), \tag{123}$$

$$\Delta H\ (\text{c} \rightarrow 50) = \Phi_{H_2}{}'' - H_2\ (\text{c}), \tag{124}$$

$$\Delta H\ (\text{c} \rightarrow 100) = \Phi_{H_2}{}''' - H_2\ (\text{c}), \tag{125}$$

$$\Delta H\ (\text{c} \rightarrow 200) = \Phi_{H_2}{}'''' - H_2\ (\text{c}), \tag{126}$$

$$\Delta H\ (\text{c} \rightarrow 400) = \Phi_{H_2}{}''''' - H_2\ (\text{c}). \tag{127}$$

It is to be noted that subtraction of Equation 118 from each of the following Equations 119, 120, 121, and 122, and the corresponding subtraction of Equation 123 from each of the following Equations 124, 125, 126, and 127, give values which yield a curve identical with that in Figure 8. As before, the extrapolation to infinite dilutions is made and the curves are replotted as $\Phi_{H_2} - \Phi_{H_2}^0$ against $m^{1/2}$. From these last curves, which will be the same as shown in Figure 9, the relative partial molal heat contents, $\bar{H}_2 - \bar{H}_2^0$ and $\bar{H}_1 - \bar{H}_1^*$, are calculated according to Equations 103 and 104.

It is to be noted that the usual relations involving the thermodynamic properties hold for the apparent molal properties, as for example, at constant pressure,

$$\frac{d(\Phi_{H_2} - \Phi_{H_2}^0)}{dT} = \Phi_{Cp_2} - \Phi_{Cp_2}^0. \qquad (128)$$

Studies relating to apparent and partial molal heat contents of strong electrolytes in aqueous solution have been published by Rossini (*16*), Young and collaborators (*5,6,17*), E. Lange and Robinson (*18*), Gulbransen and Robinson (*19*), and Gucker, Pickard, and Planck (*20*).

11. Partial molal free energy and entropy. The partial molal properties of free energy and entropy are not as simply evaluated as the partial molal properties of volume, heat capacity and heat content. The partial molal free energy and entropy vary greatly with composition. The evaluation of partial molal free energy and entropy in solutions will be discussed in subsequent chapters on the ideal and real solutions.

12. Collateral reading. For additional details regarding apparent and partial molal properties and their evaluation, the reader is referred to the references cited in the various sections in this chapter and to Lewis and Randall (*2*).

REFERENCES

1. G. N. Lewis, *Proc. Am. Acad. Arts Sci.* **43**, 259 (1907).
2. G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill Book Company, New York, 1923.
3. M. Randall and F. D. Rossini, *J. Am. Chem. Soc.* **51**, 323 (1929).
4. T. F. Young and O. G. Vogel, *J. Am. Chem. Soc.* **54**, 3025 (1932).
5. T. F. Young and O. G. Vogel, *J. Am. Chem. Soc.* **54**, 3030 (1932).
6. T. F. Young and W. L. Groenier, *J. Am. Chem. Soc.* **58**, 187 (1936).
7. D. O. Masson, *Phil. Mag.* **8**, 218 (1929).
8. A. F. Scott, *J. Phys. Chem.* **35**, 2315 (1931).
9. W. Geffcken, *Z. physik. Chem.* **A155**, 1 (1931).
10. O. Redlich and P. Rosenfeld, *Z. Elektrochem.* **37**, 705 (1931).
11. W. C. Root, *J. Am. Chem. Soc.* **55**, 850 (1933).
12. W. Geffcken and D. Price, *Z. physik. Chem.* **B26**, 81 (1934).
13. F. T. Gucker, Jr., *Chem. Revs.* **13**, 111 (1933).
14. F. D. Rossini, *J. Research Natl. Bur. Standards* **4**, 313 (1930).
15. F. D. Rossini, *J. Research Natl. Bur. Standards* **7**, 47 (1931).
16. F. D. Rossini, *J. Research Natl. Bur. Standards* **6**, 791 (1931).
17. T. F. Young and P. Seligmann, *J. Am. Chem. Soc.* **60**, 2379 (1938).
18. E. Lange and A. L. Robinson, *Chem. Revs.* **9**, 89 (1931).
19. E. A. Gulbransen and A. L. Robinson, *J. Am. Chem. Soc.* **56**, 2637 (1934).

20. F. T. Gucker, Jr., H. G. Pickard, and R. W. Planck, *J. Am. Chem. Soc.* **61**, 459 (1939).
21. T. F. Young and J. S. Machin, *J. Am. Chem. Soc.* **58**, 2254 (1936).
22. O. Redlich and J. Bigeleisen, *J. Am. Chem. Soc.* **64**, 758 (1942).
23. O. Redlich and J. Bigeleisen, *Chem. Revs.* **30**, 171 (1942).
24. O. Redlich, *J. Phys. Chem.* **44**, 619 (1940).

PROBLEMS

1. Given an aqueous solution made up of 1250 g of water and 125 g of a strong electrolyte, MX, whose molecular weight is 58.50 g/mole. The density of this solution at 25°C is 1.0705 g/cm^3. Calculate the following: the mole ratio, n_1/n_2; the mole fraction, N_2; the molality, m; the specific volume in centimeters^3 per gram; the volume of 1 mole of solution; the volume of that amount of solution containing 1000 g of water.

2. Given the following data at a given temperature for a 1 molal aqueous solution of $HC_2H_3O_2$ (acetic acid); the specific heat capacity is 0.9811 cal/deg g; for pure water, the specific heat capacity is 0.9980 cal/deg g. Calculate the apparent molal heat capacity of $HC_2H_3O_2$ in its 1 molal aqueous solution. If Φc_{P_2} is independent of the molality from $m = 0.04$ to $m = 2.0$, give the values of $\bar{c}_{P_2}$ and $\bar{c}_{P_1} - \bar{c}_{P_1}{}^*$ for this range of composition.

3. The following data were obtained for aqueous NaCl at 25°C:

m	0.000	0.255	0.511	1.030	2.560	5.140
V	1002.96	1007.45	1012.22	1022.11	1053.81	1112.36

(m is the molality in moles of solute per 1000 g H_2O, and V is the volume, in centimeters^3, of that amount of solution containing 1000 g H_2O and m moles of NaCl). Plot Φv_2 against $m^{1/2}$, draw best straight line, and give equations for Φv_2, $\bar{v}_2$, and $\bar{v}_1 - \bar{v}_1{}^*$.

4. The following data were obtained, at 25°C, for the heat capacity, in calories per degree, of that amount of solution containing 1000 g H_2O and m moles KCl:

m	0	0.01	0.04	0.09	0.16	0.25	0.49	1.00
C_P	998.00	997.72	996.94	995.69	994.09	992.14	987.66	980.20

Give the equations for Φc_{P_2}, $\bar{c}_{P_2}$, and $\bar{c}_{P_1}$, for this range of concentration. For what value of m would the addition of m moles of KCl to 1000 g of H_2O result in zero change in heat capacity between the water and the resulting solution? At what molality would the addition of 1 mole of KCl to an extremely large amount of aqueous KCl solution result in zero change in heat capacity?

5. Given $F = H - TS$; show that $\bar{F}_1 = \bar{H}_1 - T\bar{S}_1$.

6. Values of the apparent molal volume of a solute are plotted against the mole fraction of the solute. Derive the equations giving the value of $\bar{v}_2$ and $\bar{v}_1$ in terms of the coordinates and the slope of the curve.

7. Derive Equation 80 giving the apparent molal volume of the solute in terms of the density of the solution.

8. Derive Equation 81 giving the apparent molal heat capacity of the solute in terms of the specific heat capacity of the solution.

9. Given a liquid solution of two components. If the quantity $\mathrm{c}_P - (\mathrm{N}_1\bar{\mathrm{c}}_{P_1}{}^* + \mathrm{N}_2\bar{\mathrm{c}}_{P_2}{}^*)$ is plotted on the scale of ordinates as y, and N_2 on the scale of abscissas as x, show that

$$\bar{\mathrm{c}}_{P_2} = \bar{\mathrm{c}}_{P_2}{}^* + y + \mathrm{N}_1 \frac{dy}{dx},$$

and

$$\bar{\mathrm{c}}_{P_1} = \bar{\mathrm{c}}_{P_1}{}^* + y - \mathrm{N}_2 \frac{dy}{dx}.$$

(Here c_P represents the heat capacity of 1 mole of solution.)

10. Given a liquid solution of two components. If the specific volume (volume per gram), or the reciprocal of the density, is plotted on the scale of ordinates as y and N_2 on the scale of abscissas as x, show that

$$\bar{\mathrm{v}}_1 = M_1\left[y - \left(\frac{\mathrm{N}_1\mathrm{N}_2 + \mathrm{N}_2{}^2 M_2}{M_1}\right)\left(\frac{dy}{dx}\right)\right]$$

and

$$\bar{\mathrm{v}}_2 = M_2\left[y + \left(\frac{\mathrm{N}_1\mathrm{N}_2 + \mathrm{N}_1{}^2 M_1}{M_2}\right)\left(\frac{dy}{dx}\right)\right].$$

11. For the reaction,

$$\mathrm{NaCl}\ (c) + \frac{55.506}{m}\,\mathrm{H_2O}\ (\mathrm{liq}) = \left[\mathrm{NaCl}\cdot\frac{55.506}{m}\,\mathrm{H_2O}\right](\mathrm{liq}),$$

the following values were obtained, per mole of NaCl, at 18°C:

m	1.00	0.64	0.36	0.25	0.16	0.09	0.04	0.01
ΔH	1067	1141	1197	1212	1224	1226	1220	1202

(*a*) What is the heat of solution at 18°C of 1 mole of solid NaCl in an infinite amount of water? (*b*) Prepare a plot of the relative apparent molal heat content as a function of the square root of the molality. (*c*) Evaluate the relative partial molal heat content of the solute at a molality of 0.04 and of 0.25. (*d*) Evaluate the relative partial molal heat content of the solvent at a molality of 0.111. (*e*) Given, for aqueous NaCl, $\Phi\mathrm{c}_{P_2} = -24.8 + 14.4m^{1/2}$ cal/deg mole, and, for solid sodium chloride, $C_P = 12.0$ cal/deg mole. Calculate the heat of solution at 25°C of 1 mole of solid NaCl in an infinite amount of water.

25

The Ideal Solution

1. Definition of the ideal solution. It has been found that the properties of many real solutions have a nearly common pattern of behavior. In order to systematize our understanding of the properties of solutions and to focus our attention upon the important variables involved, it is desirable to define what is called an ideal solution. The ideal solution is a hypothetical solution having properties not possessed by any real solution. The properties of a given real solution may approach those of the ideal solution, according as the components of the solution become more nearly alike in their intermolecular properties.

The ideal solution, which may be gaseous, liquid, or solid, is defined as one in which the fugacity of each component is proportional to its mole fraction, over the entire range of composition, and at all temperatures and all pressures. That is,

$$f_i = k_i \text{N}_i. \tag{1}$$

The proportionality constant k_i is a constant for a given temperature and pressure, and holds for all concentrations at that temperature and pressure. Now, when the mole fraction of the given component becomes unity, then

$$\text{N}_i = 1; \quad f_i = k_i; \quad f_i = f_i^*. \tag{2}$$

Hence, k_i, the constant of proportionality in Equation 1, becomes identified as f_i^*, the fugacity of pure component i in the same state as the solution, gas, liquid, or solid, at the given temperature and pressure. Therefore,

$$k_i = f_i^*,$$

and Equation 1 may be written as

$$f_i = \text{N}_i f_i^*. \tag{3}$$

2. Partial molal properties of the components of ideal solution. Consider component i in a pure gas phase in equilibrium with component i in an ideal solution, gas, liquid, or solid. From the definition of fugacity, we may write for component i in the pure gas phase

$$\mathrm{F}_i\ (\mathrm{g}) = \mathrm{F}_i^\circ\ (\mathrm{g}) + RT \ln f_i\ (\mathrm{g}). \tag{4}$$

But if component i in the pure gas phase is in equilibrium with component i in the solution, we have

$$\mathrm{F}_i\ (\mathrm{g}) = \mathrm{F}_i\ (\mathrm{soln}), \tag{5}$$

and

$$f_i\ (\mathrm{g}) = f_i\ (\mathrm{soln}). \tag{6}$$

Therefore, Equation 4 becomes

$$\mathrm{F}_i = \mathrm{F}_i^\circ\ (\mathrm{g}) + RT \ln f_i\ (\mathrm{soln}). \tag{7}$$

Equation 7 applies to any mole fraction in the solution, so that, for $\mathrm{N}_i = 1$, we may write

$$\mathrm{F}_i^* = \mathrm{F}_i^\circ\ (\mathrm{g}) + RT \ln f_i^*. \tag{8}$$

Subtraction of Equation 8 from Equation 7 gives

$$\mathrm{F}_i - \mathrm{F}_i^* = RT \ln \frac{f_i}{f_i^*}\ (\mathrm{soln}). \tag{9}$$

But from Equation 3,

$$\frac{f_i}{f_i^*} = \mathrm{N}_i. \tag{10}$$

Therefore, for the ideal solution at a given temperature and pressure,

$$\mathrm{F}_i - \mathrm{F}_i^* = RT \ln \mathrm{N}_i. \tag{11}$$

That is, for component i in an ideal solution, the partial molal free energy, referred to its molal free energy in the pure state (gas, liquid, or solid, as in the solution), at the given temperature and pressure, is equal to RT multiplied by the natural logarithm of the mole fraction.

Since Equation 11 applies to constant temperature and pressure, we may also write,

$$\left(\frac{\partial \mathrm{F}_i}{\partial \mathrm{N}_i}\right)_{P,T} = \frac{RT}{\mathrm{N}_i}, \tag{12}$$

or

$$\left[\frac{\partial\left(\frac{\mathrm{F}_i}{T}\right)}{\partial \mathrm{N}_i}\right]_{P,T} = \frac{R}{\mathrm{N}_i}. \tag{13}$$

If Equation 11 is differentiated with pressure at constant temperature, we have

$$\left(\frac{\partial \mathrm{F}_i}{\partial P}\right)_T - \left(\frac{\partial \mathrm{F}_i^*}{\partial P}\right)_T = 0, \tag{14}$$

$$\bar{\mathrm{V}}_i = \bar{\mathrm{V}}_i^*. \tag{15}$$

That is to say, for the ideal solution at a given temperature and pressure, the partial molal volume of each component at every mole fraction is equal to its volume in the pure state (gas, liquid, or solid, as in the solution) at the same temperature and pressure. Or, in other words, there is zero change in volume on mixing components to form an ideal solution.

Equation 11 may be written as

$$\frac{\mathrm{F}_i}{T} - \frac{\mathrm{F}_i^*}{T} = R \ln \mathrm{N}_i. \tag{16}$$

Differentiating with temperature at constant pressure, we have

$$\left[\frac{\partial\left(\frac{\mathrm{F}_i}{T}\right)}{\partial T}\right]_P - \left[\frac{\partial\left(\frac{\mathrm{F}_i^*}{T}\right)}{\partial T}\right]_P = 0, \tag{17}$$

or

$$-\frac{\bar{\mathrm{H}}_i}{T^2} + \frac{\bar{\mathrm{H}}_i^*}{T^2} = 0, \tag{18}$$

or

$$\bar{\mathrm{H}}_i = \bar{\mathrm{H}}_i^*. \tag{19}$$

That is, for the ideal solution at a given temperature and pressure, the partial molal heat content of each component at every mole fraction is equal to its molal heat content in the pure state (gas, liquid, or solid, as in the solution) at the same temperature and pressure. In other words, the heat of mixing components to form an ideal solution is zero.

Since

$$\bar{\mathrm{H}}_i = \bar{\mathrm{H}}_i^*, \tag{20}$$

and

$$\bar{c}_{P_i} = \left(\frac{\partial \bar{H}_i}{\partial T}\right)_P; \quad \bar{c}_{P_i}{}^* = \left(\frac{\partial \bar{H}_i{}^*}{\partial T}\right)_P, \tag{21}$$

it follows that

$$\bar{c}_{P_i} = \bar{c}_{P_i}{}^*. \tag{22}$$

That is, for the ideal solution at a given temperature and pressure, the partial molal heat capacity of each component at every mole fraction is equal to its partial molal heat capacity in the pure state (gas, liquid, or solid, as in the solution) at the same temperature and pressure.

From the definition of the free energy, we may write

$$\bar{F}_i = \bar{H}_i - T\bar{S}_i, \tag{23}$$

and for $N_i = 1$,

$$\bar{F}_i{}^* = \bar{H}_i{}^* - T\bar{S}_i{}^*. \tag{24}$$

Subtracting, we obtain

$$(\bar{F}_i - \bar{F}_i{}^*) = (\bar{H}_i - \bar{H}_i{}^*) - T(\bar{S}_i - \bar{S}_i{}^*). \tag{25}$$

But from Equation 19,

$$\bar{H}_i - \bar{H}_i{}^* = 0, \tag{26}$$

so that

$$\bar{S}_i - \bar{S}_i{}^* = -\frac{\bar{F}_i - \bar{F}_i{}^*}{T}. \tag{27}$$

Combination with Equation 16 gives

$$\bar{S}_i - \bar{S}_i{}^* = -R \ln N_i. \tag{28}$$

That is, for component *i* in an ideal solution, gas, liquid, or solid, the partial molal entropy, referred to its molal entropy in the pure state, gas, liquid, or solid, at the given temperature and pressure, is equal to the negative of the gas constant *R* multiplied by the natural logarithm of the mole fraction.

All the foregoing relations of the partial molal properties, derived for the components of an ideal solution, apply to any solution, whether gaseous, liquid, or solid, that conforms to the definition of the ideal solution as given by Equation 3.

3. Entropy of mixing components to form an ideal solution. Equation 28 may be used to calculate the entropy of mixing N_1 moles of pure component 1, N_2 moles of pure component 2,

N_3 moles of pure component 3,· · ·, and N_i moles of pure component i, to form one mole of an ideal solution. The change in entropy for introducing each component into the solution is

$$\mathrm{N}_1(\bar{\mathrm{S}}_1 - \bar{\mathrm{S}}_1^*) = -\mathrm{N}_1 R \ln \mathrm{N}_1; \tag{29}$$

$$\mathrm{N}_2(\bar{\mathrm{S}}_2 - \bar{\mathrm{S}}_2^*) = -\mathrm{N}_2 R \ln \mathrm{N}_2; \tag{30}$$

$$\mathrm{N}_3(\bar{\mathrm{S}}_3 - \bar{\mathrm{S}}_3^*) = -\mathrm{N}_3 R \ln \mathrm{N}_3; \tag{31}$$

$$\mathrm{N}_i(\bar{\mathrm{S}}_i - \bar{\mathrm{S}}_i^*) = -\mathrm{N}_i R \ln \mathrm{N}_i. \tag{32}$$

The sum for all the components, which is the entropy of mixing all the components to form the ideal solution, is, per mole of solution,

$$\Delta \mathrm{S}\ (\text{mixing}) = -R \sum \mathrm{N}_i \ln \mathrm{N}_i. \tag{33}$$

Equation 33 gives the entropy of mixing components to form any solution, whether gaseous, liquid, or solid, which conforms to the definition of the ideal solution as given by Equation 3.

4. Equilibrium between a pure solid substance and an ideal liquid solution. Consider the thermodynamic equilibrium between a pure substance A in the solid state and an ideal liquid solution in which it is one of the components, as follows:

$$\text{A (c)} = \text{A (in ideal liq soln with B)}. \tag{34}$$

Here B represents one or more other components, which appear only in the liquid phase, not in the solid phase. At equilibrium,

$$\mathrm{F}_{\mathrm{A}}\ (\mathrm{c}) = \bar{\mathrm{F}}_{\mathrm{A}}. \tag{35}$$

For maintenance of equilibrium, the change in the molal free energy of A in the solid state must equal the change in the partial molal free energy of A in the solution,

$$d\mathrm{F}_{\mathrm{A}}\ (\mathrm{c}) = d\bar{\mathrm{F}}_{\mathrm{A}}. \tag{36}$$

The free energy of A in the solid state may be expressed as a function of pressure and temperature,

$$\mathrm{F}_{\mathrm{A}}\ (\mathrm{c}) = f(P,T). \tag{37}$$

Then

$$d\mathrm{F}_{\mathrm{A}}\ (\mathrm{c}) = \left(\frac{\partial \mathrm{F}_{\mathrm{A}}\ (\mathrm{c})}{\partial P}\right)_T dP + \left(\frac{\partial \mathrm{F}_{\mathrm{A}}\ (\mathrm{c})}{\partial T}\right)_P dT, \tag{38}$$

and

$$d\mathrm{F}_{\mathrm{A}}\ (\mathrm{c}) = \mathrm{V}_{\mathrm{A}}\ (\mathrm{c})\, dP - \mathrm{S}_{\mathrm{A}}\ (\mathrm{c})\, dT. \tag{39}$$

The free energy of A in the solution may be expressed as a function of pressure, temperature, and composition, as

$$\mathrm{F_A} = f(P,T,\mathrm{N_A}). \tag{40}$$

Then

$$d\mathrm{F_A} = \left(\frac{\partial \mathrm{F_A}}{\partial P}\right)_{T,\mathrm{N_A}} dP + \left(\frac{\partial \mathrm{F_A}}{\partial T}\right)_{P,\mathrm{N_A}} dT + \left(\frac{\partial \mathrm{F_A}}{\partial \mathrm{N_A}}\right)_{P,T} d\mathrm{N_A}, \tag{41}$$

and (see Equation 12)

$$d\mathrm{F_A} = \bar{\mathrm{v}}_\mathrm{A}\, dP - \bar{\mathrm{s}}_\mathrm{A}\, dT + \frac{RT}{\mathrm{N_A}}\, d\mathrm{N_A}, \tag{42}$$

or

$$d\mathrm{F_A} = \bar{\mathrm{v}}_\mathrm{A}\, dP - \bar{\mathrm{s}}_\mathrm{A}\, dT + RT d \ln \mathrm{N_A}. \tag{43}$$

Setting Equations 39 and 43 equal, in accordance with Equation 36, we have

$$\bar{\mathrm{v}}_\mathrm{A}\, dP - \bar{\mathrm{s}}_\mathrm{A}\, dT + RT d \ln \mathrm{N_A} = \mathrm{v_A}\ (\mathrm{c})\ dP - \mathrm{s_A}\ (\mathrm{c})\ dT. \tag{44}$$

At constant temperature, Equation 44 becomes

$$\bar{\mathrm{v}}_\mathrm{A}\, dP + RT d \ln \mathrm{N_A} = \mathrm{v_A}\ (\mathrm{c})\ dP, \tag{45}$$

or

$$\frac{d \ln \mathrm{N_A}}{dP} = -\frac{\bar{\mathrm{v}}_\mathrm{A} - \mathrm{v_A}\ (\mathrm{c})}{RT}. \tag{46}$$

But, for the ideal solution,

$$\bar{\mathrm{v}}_\mathrm{A} = \bar{\mathrm{v}}_\mathrm{A}^*, \tag{47}$$

so that, at constant temperature,

$$\frac{d \ln \mathrm{N_A}}{dP} = -\frac{\bar{\mathrm{v}}_\mathrm{A}^* - \mathrm{v_A}\ (\mathrm{c})}{RT}. \tag{48}$$

Equation 48 gives, for the equilibrium between a pure solid and an ideal solution in which it is one of the components, the change in mole fraction of the solution with pressure at constant temperature in terms of the change in volume on melting. If there is an increase in volume on melting, then $\bar{\mathrm{v}}_\mathrm{A}^* - \mathrm{v_A}\ (\mathrm{c})$ is positive and the mole fraction of A in the solution (which measures the solubility of the given solid A in the solution) decreases with increase in pressure. That is, with increasing pressure, the equilibrium is shifted in the direction of the state of lesser volume.

Equation 48 may be written, for constant temperature, as

$$d \ln N_A = -\frac{1}{RT}[\bar{v}_A{}^* - v_A\ (c)]\, dP. \tag{49}$$

This equation may be integrated between any two pressures and corresponding mole fractions if the change in volume of melting is known as a function of pressure. That is, for the mole fractions, $N_A{}'$ and N_A, and the corresponding pressures, P' and P, we have, for constant temperature,

$$\ln \frac{N_A}{N_A{}'} = -\frac{1}{RT}\int_{P'}^{P} [\bar{v}_A{}^* - v_A\ (c)]\, dP. \tag{50}$$

If the change in volume on mixing can be expressed as a simple power series of the pressure, as

$$\bar{v}_A{}^* - v_A\ (c) = a + bP + cP^2, \tag{51}$$

then

$$\ln \frac{N_A}{N_A{}'} = -\frac{1}{RT}\left\{a(P - P') + \frac{b}{2}[P^2 - (P')^2] + \frac{c}{3}[P^3 - (P')^3]\right\}. \tag{52}$$

In the simplest case where the change in volume on melting may be assumed constant over the given range of pressure, then,

$$\ln \frac{N_A}{N_A{}'} = -\frac{a(P - P')}{RT}. \tag{53}$$

The foregoing equations serve to evaluate the change in solubility, in terms of mole fraction, of a given pure solid, A, in an ideal solution in which it is one of the components. Conversely, if the solubility is known as a function of pressure, the foregoing equations would serve to evaluate the change in volume on melting of the pure solid, A.

At constant pressure, Equation 44 becomes

$$-\bar{s}_A\, dT + RT d \ln N_A = -s_A\ (c)\, dT, \tag{54}$$

or

$$\frac{d \ln N_A}{dT} = \frac{\bar{s}_A - s_A\ (c)}{RT}. \tag{55}$$

But at equilibrium,

$$F_A = F_A\ (c), \tag{56}$$

or

$$\bar{\text{H}}_\text{A} - T\bar{\text{S}}_\text{A} = \text{H}_\text{A}\ (\text{c}) - T\text{S}_\text{A}\ (\text{c}), \tag{57}$$

so that

$$\bar{\text{S}}_\text{A} - \text{S}_\text{A}\ (\text{c}) = \frac{\bar{\text{H}}_\text{A} - \text{H}_\text{A}\ (\text{c})}{T}. \tag{58}$$

Combination of Equations 55 and 58 gives

$$\frac{\text{d} \ln \text{N}_\text{A}}{\text{d}T} = \frac{\bar{\text{H}}_\text{A} - \text{H}_\text{A}\ (\text{c})}{RT^2}. \tag{59}$$

But, for the ideal solution,

$$\bar{\text{H}}_\text{A} = \bar{\text{H}}_\text{A}^*, \tag{60}$$

so that, at constant pressure,

$$\frac{\text{d} \ln \text{N}_\text{A}}{\text{d}T} = \frac{\bar{\text{H}}_\text{A}^* - \text{H}_\text{A}\ (\text{c})}{RT^2}. \tag{61}$$

Equation 61 gives, for the equilibrium between a pure solid and an ideal solution in which it is one of the components, the change in mole fraction of the solution with temperature at constant pressure in terms of the change in heat content on melting or the heat of fusion or melting. The heat of melting is always positive, so that, with increasing temperature, the mole fraction of A in the solution (which measures the solubility of the given solid A in the solution) increases with increase in temperature. That is, the equilibrium is shifted in the direction of that phase which has a greater heat content.

Equation 61 may be written, at constant pressure, as

$$\text{d} \ln \text{N}_\text{A} = \frac{\bar{\text{H}}_\text{A}^* - \text{H}_\text{A}\ (\text{c})}{RT^2}\, \text{d}T, \tag{62}$$

or

$$\text{d} \ln \text{N}_\text{A} = -\frac{\bar{\text{H}}_\text{A}^* - \text{H}_\text{A}\ (\text{c})}{R}\, \text{d}\left(\frac{1}{T}\right). \tag{63}$$

These equations may be integrated between the composition $\text{N}_\text{A} = 1$, at which the solution is pure component A and the temperature is T_A^*, to any other mole fraction N_A and corresponding temperature, T, as

$$\ln \text{N}_\text{A} = -\frac{1}{R}\int_{T_\text{A}^*}^{T} \frac{\bar{\text{H}}_\text{A}^* - \text{H}_\text{A}\ (\text{c})}{T^2}\, \text{d}T, \tag{64}$$

or

$$\ln \mathrm{N_A} = \frac{1}{R} \int_{T_A^*}^{T} \left[\bar{\mathrm{H}}_A^* - \mathrm{H_A}\ (\mathrm{c}) \right] d\left(\frac{1}{T}\right). \tag{65}$$

In the limit, as T approaches T_A^*, or $\mathrm{N_A}$ approaches 1, and if the heat of fusion can be taken as constant over the given range of temperature, and writing the heat of fusion of component A at T_A^* as

$$\bar{\mathrm{H}}_A^* - \mathrm{H_A}\ (\mathrm{c}) = \Delta \mathrm{H} m_A^*, \tag{66}$$

Equation 65 becomes

$$\ln \mathrm{N_A} \cong -\left(\frac{\Delta \mathrm{H} m_A^*}{R}\right)\left(\frac{T_A^* - T}{T T_A^*}\right). \tag{67}$$

Since B represents all other components in the solution,

$$\mathrm{N_A} = 1 - \mathrm{N_B}, \tag{68}$$

and, in the limit as $\mathrm{N_A}$ approaches unity or $\mathrm{N_B}$ approaches zero, we may write

$$\ln \mathrm{N_A} = \ln (1 - \mathrm{N_B}) \cong -\mathrm{N_B}, \tag{69}$$

and

$$T T_A^* \cong T_A^{*2}. \tag{70}$$

Therefore, in the aforesaid limit, we have

$$\mathrm{N_B} = A\ \Delta T, \tag{71}$$

where

$$A = \frac{\Delta \mathrm{H} m_A}{R (T_A^*)^2} \tag{72}$$

and

$$\Delta T = T_A^* - T. \tag{73}$$

Equation 71 shows that, when the liquid solution in equilibrium with the pure solid, A, approaches pure A in composition, the lowering of the temperature of equilibrium is proportional to the mole fraction of the other component or components, B.

The relation between the temperature and mole fraction of component A, at the given constant pressure, may be extended to a greater range of composition, as follows:

Take the difference in heat capacity of A in the ideal liquid solution and in the solid state to be constant over the given range of temperature, as

$$\bar{c}_{P_A}{}^* - c_{P_A}\,(c) = \Delta c_{P_A}{}^*. \tag{74}$$

Let

$$\Delta T = T_A{}^* - T. \tag{75}$$

Then the heat of fusion of component A over the given range of temperature may be expressed as

$$\Delta \mathrm{H}m_A = \Delta \mathrm{H}m_A{}^* - \Delta c_{P_A}{}^*\,\Delta T, \tag{76}$$

where $\Delta \mathrm{H}m_A{}^*$ is a constant representing the heat of fusion of A at the temperature, $T_A{}^*$.
But

$$T = T_A{}^*\left(1 - \frac{\Delta T}{T_A{}^*}\right). \tag{77}$$

and

$$\mathrm{d}T = -\,\mathrm{d}\,(\Delta T). \tag{78}$$

Then Equation 64 may be written as

$$\ln N_A = -\frac{1}{R}\int_0^{\Delta T}\frac{\Delta \mathrm{H}m_A{}^* - \Delta c_{P_A}{}^*\Delta T}{T^2}\,\mathrm{d}(\Delta T), \tag{79}$$

or, separating the terms on the right side,

$$\ln N_A = -\frac{\Delta \mathrm{H}m_A{}^*}{R}\int_0^{\Delta T}\frac{1}{T^2}\,\mathrm{d}(\Delta T) + \frac{\Delta c_{P_A}{}^*}{R}\int_0^{\Delta T}\frac{\Delta T}{T^2}\,\mathrm{d}(\Delta T). \tag{80}$$

Substituting for T from Equation 77, and changing to the variable $\Delta T/T_A{}^*$, since $\mathrm{d}(\Delta T/T_A{}^*)$ is equal to $(1/T_A{}^*)\,\mathrm{d}(\Delta T)$, we have

$$\ln N_A = -\frac{\Delta \mathrm{H}m_A{}^*}{RT_A{}^*}\int_0^{\frac{\Delta T}{T_A{}^*}}\frac{1}{\left(1 - \frac{\Delta T}{T_A{}^*}\right)^2}\,\mathrm{d}\left(\frac{\Delta T}{T_A{}^*}\right)$$

$$+ \frac{\Delta c_{P_A}{}^*}{R}\int_0^{\frac{\Delta T}{T_A{}^*}}\frac{\frac{\Delta T}{T_A{}^*}}{\left(1 - \frac{\Delta T}{T_A{}^*}\right)^2}\,\mathrm{d}\left(\frac{\Delta T}{T_A{}^*}\right). \tag{81}$$

Letting

$$x = \frac{\Delta T}{T_A{}^*}, \tag{82}$$

noting that

$$\frac{1}{(1-x)^2} = 1 + 2x + 3x^2 + 4x^3 + \cdots, \tag{83}$$

and substituting

$$A = \frac{\Delta \text{H}m_{\text{A}}{}^*}{R(T_{\text{A}}{}^*)^2}, \tag{84}$$

Equation 81 becomes

$$\ln \text{N}_{\text{A}} = -AT_{\text{A}}{}^* \int_0^x (1 + 2x + 3x^2 + 4x^3 + \cdots)\, dx + \frac{\Delta \text{C}p_{\text{A}}{}^*}{R} \int_0^x (x + 2x^2 + 3x^3 + 4x^4 + \cdots)\, dx. \tag{85}$$

This becomes

$$\ln \text{N}_{\text{A}} = -AT_{\text{A}}{}^*(x + x^2 + x^3 + x^4 + \cdots) + \frac{\Delta \text{C}p_{\text{A}}{}^*}{R} (\tfrac{1}{2}x^2 + \tfrac{2}{3}x^3 + \tfrac{3}{4}x^4 + \cdots), \tag{86}$$

or

$$\ln \text{N}_{\text{A}} = -AT_{\text{A}}{}^*x - \left(AT_{\text{A}}{}^* - \frac{\Delta \text{C}p_{\text{A}}{}^*}{2R}\right)x^2 + \left(AT_{\text{A}}{}^* - \frac{2\Delta \text{C}p_{\text{A}}{}^*}{3R}\right)x^3 - \left(AT_{\text{A}}{}^* - \frac{3\Delta \text{C}p_{\text{A}}{}^*}{4R}\right)x^4 + \cdots, \tag{87}$$

or

$$\ln \text{N}_{\text{A}} = -A(\Delta T)\left[1 + \left(1 - \frac{\Delta \text{C}p_{\text{A}}{}^* T_{\text{A}}{}^*}{2\Delta \text{H}m_{\text{A}}{}^*}\right)\left(\frac{\Delta T}{T_{\text{A}}{}^*}\right) + \left(1 - \frac{2\Delta \text{C}p_{\text{A}}{}^* T_{\text{A}}{}^*}{3\Delta \text{H}m_{\text{A}}{}^*}\right)\left(\frac{\Delta T}{T_{\text{A}}{}^*}\right)^2 + \left(1 - \frac{3\Delta \text{C}p_{\text{A}}{}^* T_{\text{A}}{}^*}{4\Delta \text{H}m_{\text{A}}{}^*}\right)\left(\frac{\Delta T}{T_{\text{A}}{}^*}\right)^3 + \cdots\right]. \tag{88}$$

Equation 88 may be written as

$$\ln \text{N}_{\text{A}} = -A(\Delta T)[1 + B(\Delta T) + C(\Delta T)^2 + D(\Delta T)^3 + \cdots], \tag{89}$$

where

$$B = \left(1 - \frac{\Delta \mathrm{C}p_{\mathrm{A}}{}^{*}T_{\mathrm{A}}{}^{*}}{2\Delta \mathrm{H}m_{\mathrm{A}}{}^{*}}\right)\left(\frac{1}{T_{\mathrm{A}}{}^{*}}\right), \tag{90}$$

$$C = \left(1 - \frac{2\Delta \mathrm{C}p_{\mathrm{A}}{}^{*}T_{\mathrm{A}}{}^{*}}{3\Delta \mathrm{H}m_{\mathrm{A}}{}^{*}}\right)\left(\frac{1}{T_{\mathrm{A}}{}^{*}}\right)^{2}, \tag{91}$$

and

$$D = \left(1 - \frac{3\Delta \mathrm{C}p_{\mathrm{A}}{}^{*}T_{\mathrm{A}}{}^{*}}{4\Delta \mathrm{H}m_{\mathrm{A}}{}^{*}}\right)\left(\frac{1}{T_{\mathrm{A}}{}^{*}}\right)^{3} \tag{92}$$

It may be seen that, for small values at ΔT, the values of the constants B, C, and D become increasingly negligible in that order. For many hydrocarbons, the constant B has a value near 0.003. Equation 89 is of course not applicable over the entire range of composition.

In order to obtain a relation between mole fraction and the temperature of equilibrium which is applicable over the entire range of composition, it is necessary to integrate Equation 81 without any mathematical approximations. It may be noted that

$$\int_0^x \frac{1}{(1-x)^2}\,dx = \left[\frac{1}{1-x}\right]_0^x = \frac{1}{1-x} - 1 = \frac{x}{1-x}, \tag{93}$$

and

$$\int_0^x \frac{x}{(1-x)^2}\,dx = \left[\ln(1-x) + \frac{1}{1-x}\right]_0^x$$

$$= \ln(1-x) + \frac{x}{1-x}. \tag{94}$$

Therefore, Equation 81 may be integrated to yield

$$\ln \mathrm{N}_{\mathrm{A}} = -\frac{\Delta \mathrm{H}m_{\mathrm{A}}{}^{*}}{RT_{\mathrm{A}}{}^{*}}\,\frac{\dfrac{\Delta T}{T_{\mathrm{A}}{}^{*}}}{1 - \dfrac{\Delta T}{T_{\mathrm{A}}{}^{*}}} + \frac{\Delta \mathrm{C}p_{\mathrm{A}}{}^{*}}{R}\left[\ln\left(1 - \frac{\Delta T}{T_{\mathrm{A}}{}^{*}}\right) + \frac{\dfrac{\Delta T}{T_{\mathrm{A}}{}^{*}}}{\left(1 - \dfrac{\Delta T}{T_{\mathrm{A}}{}^{*}}\right)}\right]. \tag{95}$$

Letting, as in Equation 84,

$$A = \frac{\Delta H m_{\mathrm{A}}^{*}}{R(T_{\mathrm{A}}^{*})^{2}}, \tag{96}$$

and

$$J = \frac{\Delta c_{P_{\mathrm{A}}}^{*}}{R}, \tag{97}$$

Equation 95 may be written as

$$\ln \mathrm{N_A} = -A(\Delta T)\left(1 - \frac{\Delta T}{T_{\mathrm{A}}^{*}}\right) + J\left[\ln\left(1 - \frac{\Delta T}{T_{\mathrm{A}}^{*}}\right) + \frac{\Delta T}{T_{\mathrm{A}}^{*} - \Delta T}\right]. \tag{98}$$

Equation 98 covers the entire range of composition since it has no mathematical approximations involving $\mathrm{N_A}$ or ΔT, but it does carry the assumption that the heat of fusion of pure A may be expressed as a linear function of the temperature, that is, that $\Delta c_{P_{\mathrm{A}}}^{*}$ is constant, as in Equation 76. If the heat of fusion is expressed by an equation having the second or higher power of ΔT, Equation 81 is still integrable without mathematical approximations, but the final equation, as Equation 98, will contain additional terms of a less important nature.

The form taken by Equation 98 is shown in Figure 1 by curves *A* and *B*. Curve *A* is based entirely on the values of the properties of pure A, and curve *B* is based entirely on the values of the properties of pure B. Curve *A* gives, according to Equation 98, the relation between the mole fraction of the pure substance A in an ideal liquid solution with any other components and the temperature at which this solution, at any given mole fraction of A, is in equilibrium with pure A in the solid phase. Similarly, curve B gives, according to Equation 98, the relation between the mole fraction of the pure substance B in an ideal liquid solution with any other components and the temperature at which this solution, at any given mole fraction of B, is in equilibrium with pure B in the solid phase. It is important to note well that, in each case, the given curve depends only on the properties of the component that is in both phases and not at all upon the properties of any other components.

Equation 98, or any of its equivalent or modified forms, properly applied, is one of the most important relations in thermodynamics, because it permits one to evaluate, under appropriate conditions, the purity of a given substance without knowing the identity of the components constituting the impurity in the given substance. Equation 98 is the basic equation for the lowering of the freezing point on the addition of a solute that is liquid-soluble and solid-insoluble.

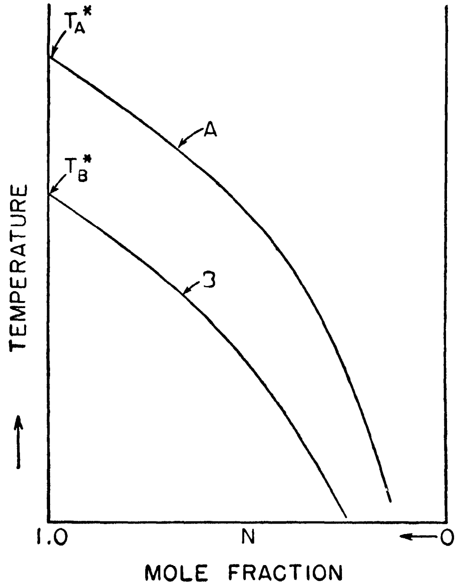


FIGURE 1. Schematic diagram showing the relation between temperature and composition of the solution for the equilibrium between a pure solid substance, A, and an ideal liquid solution in which A is one of the components, and similarly for the equilibrium between a pure solid substance, B, and an ideal liquid solution in which it is one of the components.

Figure 2 shows the two curves of Figure 1 combined to form the temperature-composition diagram for the liquid-solid equilibrium involving an ideal binary system. From $N_A = 1$ to the intersection of the two curves, the solid phase is pure A. From $N_B = 1$ to the intersection of the two curves, the solid phase is pure B. At the intersection of the two curves, which gives the eutectic temperature and composition, both pure solid phases, A and B, are in equilibrium with the solution of the eutectic composition. For any two substances that form a substantially ideal liquid solution, and that do not form a solid solution, it is possible to calculate the complete temperature-composition diagram, including the eutectic composition and temperature, entirely from the properties of the two pure components, in accordance with Equation 98 applied to each of the substances in turn.

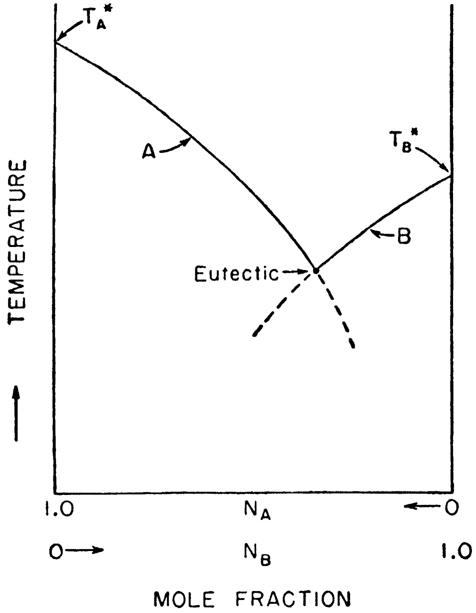


FIGURE 2. Schematic diagram showing the relation between temperature and composition of the solution for the liquid-solid equilibrium in a binary system of two components, A and B, which form an ideal liquid solution, but are not soluble in one another in the solid phase.

From $N_A = 1$ to the eutectic composition at the intersection of the two curves, the solid phase in equilibrium with the solution is pure A. From the eutectic composition to $N_B = 1$, the solid phase is pure B. The components A and B are the same ones represented in Figure 1.

5. Equilibrium between an ideal liquid solution and an ideal solid solution of the same components. Consider the thermodynamic equilibrium between the substance A in an ideal liquid solution with another component or components B, and substance A in an ideal solid solution with the same other component or components:

$$\text{A (in ideal solid soln with B, } n_A') = \text{A (in ideal liq soln with B, } n_A). \quad (99)$$

Using a prime mark to indicate the solid phase, we can write, at equilibrium,

$$\mathrm{F_A}' = \mathrm{F_A}. \tag{100}$$

For maintenance of equilibrium,

$$d\mathrm{F_A}' = d\mathrm{F_A}. \tag{101}$$

But

$$d\mathrm{F_A}' = \left(\frac{\partial \mathrm{F_A}'}{\partial P}\right)_{T,\mathrm{N_A}'} dP + \left(\frac{\partial \mathrm{F_A}'}{\partial T}\right)_{P,\mathrm{N_A}'} dT + \left(\frac{\partial \mathrm{F_A}'}{\partial \mathrm{N_A}'}\right)_{P,T} d\mathrm{N_A}', \tag{102}$$

and

$$d\mathrm{F_A} = \left(\frac{\partial \mathrm{F_A}}{\partial P}\right)_{T,\mathrm{N_A}} dP + \left(\frac{\partial \mathrm{F_A}}{\partial T}\right)_{P,\mathrm{N_A}} dT + \left(\frac{\partial \mathrm{F_A}}{\partial \mathrm{N_A}}\right)_{P,T} d\mathrm{N_A}. \tag{103}$$

Equations 102 and 103 become

$$d\mathrm{F_A}' = \bar{\mathrm{v}}_\mathrm{A}'\, dP - \bar{\mathrm{s}}_\mathrm{A}'\, dT + RT d \ln \mathrm{N_A}', \tag{104}$$

and

$$d\mathrm{F_A} = \bar{\mathrm{v}}_\mathrm{A}\, dP - \bar{\mathrm{s}}_\mathrm{A}\, dT + RT d \ln \mathrm{N_A}. \tag{105}$$

Equating and rearranging gives

$$RT d \ln \frac{\mathrm{N_A}}{\mathrm{N_A}'} = -(\bar{\mathrm{v}}_\mathrm{A} - \bar{\mathrm{v}}_\mathrm{A}')\, dP + (\bar{\mathrm{s}}_\mathrm{A} - \bar{\mathrm{s}}_\mathrm{A}')\, dT, \tag{106}$$

or

$$RT d \ln \frac{\mathrm{N_A}}{\mathrm{N_A}'} = -(\bar{\mathrm{v}}_\mathrm{A} - \bar{\mathrm{v}}_\mathrm{A}')\, dP + \frac{\bar{\mathrm{H}}_\mathrm{A} - \bar{\mathrm{H}}_\mathrm{A}'}{T}\, dT. \tag{107}$$

Since the solutions are ideal and the partial molal heat contents and volumes are independent of the compositions of the two phases, Equation 107 may be written as

$$RT d \ln \frac{\mathrm{N_A}}{\mathrm{N_A}'} = -(\bar{\mathrm{v}}_\mathrm{A}^* - \bar{\mathrm{v}}_\mathrm{A}^{*\prime})\, dP + \frac{\bar{\mathrm{H}}_\mathrm{A}^* - \bar{\mathrm{H}}_\mathrm{A}^{*\prime}}{T}\, dT, \tag{108}$$

where the terms in parentheses on the right side of the equation represent, respectively, for pure *M*, the increase in volume on melting and the increase in heat content on melting. The latter is, as before, the heat of fusion of pure A.

At constant temperature, Equation 108 becomes

$$\frac{d \ln \left(\dfrac{\mathrm{N_A}}{\mathrm{N_A}'}\right)}{dP} = -\frac{\bar{\mathrm{v}}_\mathrm{A}^* - \bar{\mathrm{v}}_\mathrm{A}^{*\prime}}{RT}. \tag{109}$$

Equation 109 gives the change, with pressure, of the ratio of the mole fractions of A in the liquid and solid phases, respectively, in terms of the change in volume of pure A on melting.

At constant pressure, Equation 108 becomes

$$\frac{d \ln \left(\frac{\mathrm{N_A}}{\mathrm{N_A}'}\right)}{dT} = \frac{\bar{\mathrm{H}}_{\mathrm{A}}^* - \bar{\mathrm{H}}_{\mathrm{A}}^{*\prime}}{RT^2}. \tag{110}$$

Equation 110 gives the change, with temperature, of the ratio of the mole fractions of A in the liquid and solid phases, respectively, in terms of the heat of fusion of pure A.

6. Equilibrium between a pure gaseous substance and an ideal liquid solution. Consider the thermodynamic equilibrium between a pure substance, A, in the gaseous state and an ideal liquid solution in which it is one of the components:

$$\mathrm{A\ (g) = A\ (in\ ideal\ liq\ soln\ with\ B,\ N_A)} \tag{111}$$

This system is one in which the other component or components represented by B are non-volatile.

Proceeding exactly as in the equilibrium between a pure solid substance and an ideal liquid solution, one may derive the corresponding equations, in which the gaseous state is substituted in each case for the solid state, as the following:

At constant temperature,

$$\frac{d \ln \mathrm{N_A}}{dP} = \frac{\mathrm{v_A\ (g)} - \bar{\mathrm{v}}_{\mathrm{A}}^*}{RT}. \tag{112}$$

At constant pressure,

$$\frac{d \ln \mathrm{N_A}}{dT} = -\frac{\mathrm{H_A\ (g)} - \bar{\mathrm{H}}_{\mathrm{A}}^*}{RT^2}. \tag{113}$$

Equation 113 gives the change in mole fraction of A with temperature in terms of the heat of vaporization of pure A, for the equilibrium between A in its ideal liquid solution with other non-volatile components and pure A in the gaseous phase. It is the basic equation for the elevation of the boiling point on the addition of a non-volatile solute.

7. Equilibrium between an ideal liquid solution and a gaseous solution of the same components. Consider the thermodynamic equilibrium between the substance A in an ideal liquid solution with another component or components B and substance A in an ideal gaseous solution with the same component or components:*

$$\text{A(in ideal gas. soln with B, } \mathrm{N_A}'\text{)} = \text{A(in ideal liq soln with B, } \mathrm{N_A}\text{)}. \quad (114)$$

Using a prime mark to indicate the gaseous phase, we can proceed as before to derive equations corresponding to those for the equilibrium between an ideal liquid solution and a solid solution of the same components, as the following:

$$RT \, \mathrm{d} \ln \frac{\mathrm{N_A}'}{\mathrm{N_A}} = -(\bar{\mathrm{V}}_{\mathrm{A}}^{*\prime} - \bar{\mathrm{V}}_{\mathrm{A}}^{*}) \, \mathrm{d}P + \frac{\bar{\mathrm{H}}_{\mathrm{A}}^{*\prime} - \bar{\mathrm{H}}_{\mathrm{A}}^{*}}{T} \, \mathrm{d}T. \quad (115)$$

At constant temperature, Equation 115 becomes

$$\frac{\mathrm{d} \ln \left(\frac{\mathrm{N_A}'}{\mathrm{N_A}}\right)}{\mathrm{d}P} = -(\bar{\mathrm{V}}_{\mathrm{A}}^{*\prime} - \bar{\mathrm{V}}_{\mathrm{A}}^{*}). \quad (116)$$

At constant pressure, Equation 115 becomes

$$\frac{\mathrm{d} \ln \left(\frac{\mathrm{N_A}'}{\mathrm{N_A}}\right)}{\mathrm{d}T} = \frac{\bar{\mathrm{H}}_{\mathrm{A}}^{*\prime} - \bar{\mathrm{H}}_{\mathrm{A}}^{*}}{RT^2}. \quad (117)$$

Equation 117 gives the change, with temperature, of the ratio of the mole fractions of A in the gaseous and liquid phases, respectively, in terms of the heat of vaporization of pure A.

From the definition of the ideal solution, we may write for the ideal liquid solution of A and B at a given temperature:

$$f_{\mathrm{A}} = \mathrm{N_A} f_{\mathrm{A}}^{*}, \quad (118)$$

$$f_{\mathrm{B}} = \mathrm{N_B} f_{\mathrm{B}}^{*}, \quad (119)$$

and

$$f_{\mathrm{A}} + f_{\mathrm{B}} = \mathrm{N_A} f_{\mathrm{A}}^{*} + \mathrm{N}_B f_B^{*} = \mathrm{N_A} f_{\mathrm{A}}^{*} + (1 - \mathrm{N_A}) f_{\mathrm{B}}^{*} = \mathrm{N_A}(f_{\mathrm{A}}^{*} - f_{\mathrm{B}}^{*}) + f_{\mathrm{B}}^{*}. \quad (120)$$

---

* It is important to note that an ideal solution of two or more gaseous components does not require the components to be ideal gases. It is necessary only that each component of the ideal gaseous solution satisfy the definition of the ideal solution as given by Equation 3.

The foregoing relations are shown graphically in Figure 3.

Using prime marks to indicate the gaseous phase, we may write

$$f_A = N_A'(f_A + f_B), \tag{121}$$

and

$$f_B = N_B'(f_A + f_B). \tag{122}$$

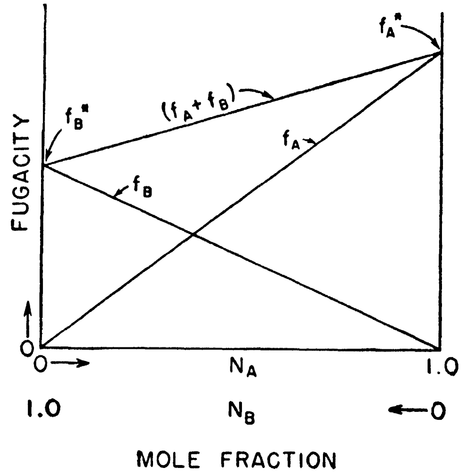


FIGURE 3. Plot of the relations between fugacity and composition, at constant temperature, for an ideal solution of two components.

The total fugacity is $f_A + f_B$.

Combination of Equations 118, 119, 121, and 122 yields the relation,

$$\frac{\dfrac{N_A'}{N_B'}}{\dfrac{N_A}{N_B}} = \frac{f_A^*}{f_B^*} = \alpha. \tag{123}$$

Equation 123 shows that the ratio of the mole fraction of A to that of B in the gaseous phase divided by the same ratio for the liquid phase is constant for an ideal solution and equal to the ratio of the fugacities (very nearly the vapor pressures) of pure A and pure B. The ratio f_A^*/f_B^* (or approximately P_A^*/P_B^*) is commonly termed the separation factor, α.

From the foregoing equations, it is possible to express the sum of the fugacities of A and B (which is very nearly the sum of the partial pressures of A and B or the total pressure), in terms of either the composition of the gaseous phase or the composition of the liquid phase.

Equation 120 gives directly

$$f_A + f_B = N_A(f_A^* - f_B^*) + f_B^*, \tag{124}$$

indicating the sum of the fugacities to be linear with the mole fraction of A in the liquid phase.

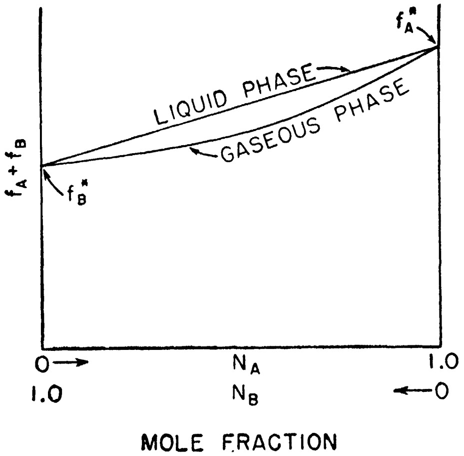


FIGURE 4. Schematic plot of the total fugacity, at constant temperature, as a function of the composition of the liquid phase and the gaseous phase for an ideal solution of two components.

Substituting $1 - N_A$ for N_B and $1 - N_A'$ for N_B', and eliminating N_A, one obtains from Equations 123 and 124

$$f_A + f_B = \frac{f_A^*}{\alpha - N_A'(\alpha - 1)}. \tag{125}$$

Equation 125 shows that the total fugacity, $f_A + f_B$, is not a linear function of the composition of the gaseous phase.

The relation between the mole fraction of A in the liquid phase, N_A, and the mole fraction of A in the gaseous phase, N_A', for any given value of the total fugacity, $f_A + f_B$, is given by the following equation, which is derived from Equations 124 and 125:

$$N_A = \frac{N_A'}{\alpha - N_A'(\alpha - 1)}. \tag{126}$$

In this equation, α is the ratio of the fugacities of pure A and pure

B as given by Equation 123. If A is taken as more volatile than B, then

$$(\alpha - 1) > 0, \tag{127}$$

and

$$[\alpha - N_A'(\alpha - 1)] > 1. \tag{128}$$

The foregoing relations given by Equations 124, 125, and 126 are illustrated in Figure 4.

8. Collateral reading. For additional material regarding the ideal solution, the reader is referred to Washburn (*1*), Lewis and Randall (*2*), Hildebrand and Scott (*3*), and Washburn and Read (*4*).

REFERENCES

1. E. W. Washburn, *J. Am. Chem. Soc.* **32**, 653 (1910).
2. G. W. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill Book Company, New York, 1923.
3. J. H. Hildebrand and R. L. Scott, *Solubility of Non-electrolytes*, Reinhold Publishing Corporation, New York, 1948.
4. E. W. Washburn and J. W. Read, *Proc. Natl. Acad. Sci. U.S.* **1**, 191 (1915).

PROBLEMS

1. Assuming an ideal liquid solution and ideal gases, calculate the fugacity of each component of a solution composed of 1 mole of component A and 155g of component B, if the molecular weight of B is 83.0 g/mole and the vapor pressures of pure A and pure B are 432 and 124 mm Hg, respectively.

2. Derive the equation giving the rise in boiling point of a solvent on the addition of an infinitesimal amount of a non-volatile solute.

3. Derive the value of $(\partial \bar{S}_1/\partial N_1)_{P,T}$ for an ideal solution.

4. Calculate, per mole of solution, the entropy of mixing the following components to form an ideal liquid solution: 0.45 mole A; 0.75 mole B; 0.45 mole C; 0.35 mole D; and 0.50 mole E.

5. What is the partial molal entropy and the partial molal free energy of the solute in an infinitely dilute solution?

26

The Dilute Real Solution

1. Definition of the dilute real solution. In the preceding chapter we discussed the relations holding for the ideal solution, which relations serve as a limiting description of the behavior of the components of many real solutions. There is another class of solutions the properties of which may be similarly described by a set of general thermodynamic relations, which, however, hold over only a limited range of composition. This additional class of solutions, not including electrolytes, is covered by the general name of the dilute real solution.

Consider a dilute solution of two components, N_1 being the mole fraction of the solvent and having a value near unity, and N_2 being the mole fraction of the solute and having a value near zero. The dilute real solution is defined as one for which, from $N_2 = 0$ to some small value of N_2, the fugacity of the solute is proportional to its mole fraction, as

$$f_2 = k_2 N_2. \tag{1}$$

It is important to note that the range of composition covered by different real solutions satisfying the foregoing definition may be quite different. For some solutions, the range of applicability of Equation 1 may be large, and for others it may be exceedingly small. It is also to be noted that the value of the constant of proportionality in Equation 1 is different for each solute and must be determined experimentally for each case. The experimental determination of k will also usually determine the range of composition over which the ratio f_2/N_2 is constant.

2. Fugacity of the solute. From the definition of the dilute real solution as given by Equation 1, the fugacity of the solute is given directly in terms of the mole fraction of the solute and the value of the constant k, over the range of composition from $N_2 = 0$ to that value of N_2 for which the relation is still applicable.

In the very dilute range, the molality is proportional to the mole fraction, so that, in this range, the relation may be written as

$$f_2 = \frac{k_2 m}{55.506}. \tag{2}$$

A similar linear relation holds in the dilute range between the fugacity of the solute and the concentration expressed in moles per liter of solution.

If the gaseous phase of component 2 in equilibrium with the solution may be taken as ideal, then the partial pressure of component 2 may be substituted for the fugacity in Equations 1 and 2, so that, as an approximation,

$$P_2 = k_2 \mathrm{N}_2, \tag{3}$$

and

$$P_2 = \frac{k_2 m}{55.506}. \tag{4}$$

Equations 3 and 4 are expressions of Henry's law for the vapor pressure of the solute in a dilute solution.

Since, in the foregoing relations, no limitation is placed on the identity of the solvent, the latter may in fact be a mixture of substances as well as one pure substance. That is, in a mixture of any number of components, if one of these components is present in very small amount, it may be considered the solute in a dilute real solution, and hence its fugacity will be proportional to its mole fraction over the given small range of composition.

3. Fugacity of the solvent. To our dilute real solution of two components, we can apply one of the basic partial molal equations from Chapter 24, at constant temperature and pressure:

$$\mathrm{N}_1\, d\mathrm{F}_1 + \mathrm{N}_2\, d\mathrm{F}_2 = 0. \tag{5}$$

Dividing by $d\mathrm{N}_1$, we obtain, for constant temperature and pressure,

$$\mathrm{N}_1 \frac{d\mathrm{F}_1}{d\mathrm{N}_1} + \mathrm{N}_2 \frac{d\mathrm{F}_2}{d\mathrm{N}_1} = 0. \tag{6}$$

But

$$d\mathrm{N}_1 = -d\mathrm{N}_2, \tag{7}$$

so that Equation 6 becomes

$$\mathrm{N}_1 \frac{d\mathrm{F}_1}{d\mathrm{N}_1} = \mathrm{N}_2 \frac{d\mathrm{F}_2}{d\mathrm{N}_2}, \tag{8}$$

or

$$\frac{d\mathrm{F}_1}{d \ln \mathrm{N}_1} = \frac{d\mathrm{F}_2}{d \ln \mathrm{N}_2}. \tag{9}$$

But, from Chapter 23 we have the following relation between the partial molal free energy and the fugacity of the solute:

$$\mathrm{F}_2 = \mathrm{F}_2^\circ\ (g) + RT \ln f_2. \tag{10}$$

Differentiating Equation 10 with respect to $\ln \mathrm{N}_2$ at constant temperature and pressure, and noting that F_2° (g) is a constant, we obtain, for constant temperature and pressure:

$$\frac{d\mathrm{F}_2}{d \ln \mathrm{N}_2} = RT \frac{d \ln f_2}{d \ln \mathrm{N}_2}. \tag{11}$$

But from Equation 1,

$$\ln f_2 = \ln k_2 + \ln \mathrm{N}_2, \tag{12}$$

and, hence, since k_2 is constant,

$$d \ln f_2 = d \ln \mathrm{N}_2, \tag{13}$$

so that, Equation 11 becomes

$$\frac{d\mathrm{F}_2}{d \ln \mathrm{N}_2} = RT, \tag{14}$$

and Equation 9 becomes

$$\frac{d\mathrm{F}_1}{d \ln \mathrm{N}_1} = RT, \tag{15}$$

or

$$d\mathrm{F}_1 = RT d \ln \mathrm{N}_1. \tag{16}$$

But the relation between the partial molal free energy and the fugacity of the solvent, is, from Chapter 23,

$$\mathrm{F}_1 = \mathrm{F}_1^\circ\ (g) + RT \ln f_1, \tag{17}$$

and, hence,

$$d\mathrm{F}_1 = RT d \ln f_1. \tag{18}$$

Combination of Equations 16 and 18 gives

$$d \ln f_1 = d \ln \mathrm{N}_1. \tag{19}$$

Since, in the dilute real solution, the range of applicability is from

$N_1 = 1$ to a value of N_1 near unity, Equation 19 may be integrated from $N_1 = 1$ to N_1, as

$$\int_{N_1=1}^{N_1} d \ln f_1 = \int_{N_1=1}^{N_1} d \ln N_1. \tag{20}$$

This gives

$$\ln \frac{f_1}{f_1^*} = \ln \frac{N_1}{1} \tag{21}$$

or

$$f_1 = N_1 f_1^*. \tag{22}$$

From the definition of the dilute real solution given by Equation 1 and the laws of thermodynamics, we have derived the important relation given by Equation 22, which states that in a dilute real solution the fugacity of the solvent is proportional to its mole fraction. It may be noted that, over the range of composition for which they are applicable, Equations 1 and 22 for the dilute real solution are identical with Equations 1 and 3 of Chapter 25 for the ideal solution. In fact over the range of concentration for which the fugacity of the solute is proportional to its mole fraction, the dilute real solution has all the properties of an ideal solution in which the solute is a hypothetical one whose fugacity up to $N_2 = 1$ is a continuation of the linear relationship between f_2 and N_2 in the dilute range. It follows that, within the foregoing limitations, in the dilute real solution, the partial molal volumes, heat contents, and heat capacities of the components are, as in the ideal solution, independent of the composition over the given range of composition near $N_1 = 1$.

If the gaseous phase of component 1 in equilibrium with the dilute solution may be taken as ideal, then Equation 22 becomes, as an approximation,

$$P_1 = N_1 P_1^*. \tag{23}$$

Equation 23 is a statement of Raoult's law of the lowering of the vapor pressure of the solvent.

4. Change of the freezing point with pressure and composition. In the preceding chapter, we derived the relations holding for the equilibrium between a pure solid substance and an ideal liquid solution. We now consider a similar case in which the range of composition is limited to the dilute region, with the solid phase being pure component 1, the solvent. Proceeding as before, we derive the following relation, applicable from $\mathrm{N}_1 = 1$ to a value of N_1 not far from unity:

$$\left(\frac{\partial \mathrm{F}_1}{\partial \mathrm{N}_1}\right)_{P,T} \mathrm{dN}_1 = -[\bar{\mathrm{v}}_1 - \mathrm{v}_1\,(\mathrm{c})]\,\mathrm{d}P + \frac{\bar{\mathrm{H}}_1 - \mathrm{H}_1\,(\mathrm{c})}{T}\,\mathrm{d}T. \qquad (24)$$

From Equations 17 and 22, we have

$$\mathrm{F}_1 = \mathrm{F}_1{}^\circ\,(\mathrm{g}) + RT \ln \mathrm{N}_1 + RT \ln f_1{}^*, \qquad (25)$$

so that

$$\left(\frac{\partial \mathrm{F}_1}{\partial \mathrm{N}_1}\right)_{P,T} = \frac{RT}{\mathrm{N}_1} \qquad (26)$$

Substituting into Equation 24 gives

$$RT\mathrm{d} \ln \mathrm{N}_1 = -[\bar{\mathrm{v}}_1 - \mathrm{v}_1\,(\mathrm{c})]\,\mathrm{d}P + \frac{\bar{\mathrm{H}}_1 - \mathrm{H}_1\,(\mathrm{c})}{T}\,\mathrm{d}T. \qquad (27)$$

Equation 27 and all the relations derivable thermodynamically and mathematically from it are applicable over the range of composition for which the given solution qualifies as a dilute real solution in accordance with Equation 1.

At constant temperature, Equation 27 reduces to

$$\frac{\mathrm{d} \ln \mathrm{N}_1}{\mathrm{d}P} = -\frac{\bar{\mathrm{v}}_1 - \mathrm{v}_1\,(\mathrm{c})}{RT}. \qquad (28)$$

Equation 28 is identical with Equation 46 of Chapter 25, relating to the ideal solution. In the dilute real solution, $\bar{\mathrm{v}}_1$ may be replaced by $\bar{\mathrm{v}}_1{}^*$, and Equation 28 becomes

$$\frac{\mathrm{d} \ln \mathrm{N}_1}{\mathrm{d}P} = -\frac{\bar{\mathrm{v}}_1{}^* - \mathrm{v}_1\,(\mathrm{c})}{RT}. \qquad (29)$$

Equations 28 and 29 give the change, with pressure at constant temperature, of the mole fraction of the solvent in the dilute real solution.

At constant pressure, Equation 27 reduces to

$$\frac{\mathrm{d} \ln \mathrm{N}_1}{\mathrm{d}T} = \frac{\bar{\mathrm{H}}_1 - \mathrm{H}_1\,(\mathrm{c})}{RT^2}. \qquad (30)$$

Equation 30 is identical with Equation 59 of Chapter 25, relating to the ideal solution. In the dilute real solution, $\bar{\mathrm{H}}_1$ may be replaced by $\bar{\mathrm{H}}_1^*$, and Equation 30 becomes

$$\frac{d \ln \mathrm{N}_1}{dT} = \frac{\bar{\mathrm{H}}_1^* - \mathrm{H}_1\ (\mathrm{c})}{RT^2}. \tag{31}$$

Equations 30 and 31 give the change, with temperature at constant pressure, of the mole fraction of the solvent in the dilute real solution. These equations also evaluate the lowering of the freezing point of the solvent on the addition of a given amount of solute.

Equation 31 may be integrated over the desired range of composition in the same manner as was Equation 61 of Chapter 25, to give

$$\ln \mathrm{N}_1 = -A\ (\Delta T)[1 + B\ (\Delta T) + C\ (\Delta T)^2 + \cdots], \tag{32}$$

where the constants A, B, and C are defined by Equations 84, 90, and 91 of Chapter 25, and ΔT is the difference between T_1^* and T.

If the temperature of a given substance in the liquid state is gradually lowered, the temperature at which an infinitesimal amount of crystals of the major component exists in thermodynamic equilibrium with the liquid phase may be defined as the freezing point. Similarly, if the temperature of the given substance in the solid state is gradually increased, the temperature at which the last infinitesimal amount of crystals in equilibrium with the liquid phase disappears is also the freezing point, identically the same temperature. Since, in each case, the quantity of the given sample in the crystal phase is infinitesimal, the composition of the liquid phase is identical with the composition of the original substance, and the freezing point may be used as a measure of the purity of the given substance in terms of the mole fraction of the main component, in accordance with Equation 32.

5. Elevation of the boiling point. Proceeding as in the preceding section, we may substitute the gaseous phase for the solid phase and obtain the following relation, analogous to Equation 27, for the equilibrium between the dilute real solution and a pure gaseous phase consisting of the major component only:

$$RT d \ln \mathrm{N}_1 = [\mathrm{v}_1\ (\mathrm{g}) - \bar{\mathrm{v}}_1]\, dP - \frac{\mathrm{H}_1\ (\mathrm{g}) - \bar{\mathrm{H}}_1}{T}\, dT. \tag{33}$$

Equation 33 is applicable over the entire range of composition for which the given solution qualifies as a dilute real solution in accordance with Equation 1. The equilibrium being considered is, of course, one in which the solute exists only in the liquid phase, with no measurable amount of it being in the gaseous phase.

At constant pressure, Equation 33 reduces to

$$\frac{d \ln \mathrm{N}_1}{dT} = -\frac{\mathrm{H}_1\ (g) - \bar{\mathrm{H}}_1}{RT^2}. \tag{34}$$

If, as before, $\bar{\mathrm{H}}_1$ may be replaced by $\bar{\mathrm{H}}_1{}^*$, Equation 36 becomes

$$\frac{d \ln \mathrm{N}_1}{dT} = -\frac{\mathrm{H}_1\ (g) - \bar{\mathrm{H}}_1{}^*}{RT^2}. \tag{35}$$

What was said about Equations 30 and 31 applies equally well to Equations 34 and 35.

6. Distribution of a solute between two solvents. Consider the equilibrium distribution of a given solute, C, between two solvents, A and B, which are in contact but not completely miscible with one another, as

$$\mathrm{C}\ (\text{soln in A}, \mathrm{N_C}^{\mathrm{A}}) = \mathrm{C}\ (\text{soln in B}, \mathrm{N_C}^{\mathrm{B}}). \tag{36}$$

At equilibrium,

$$(\mathrm{F_C})^{\mathrm{A}} = (\mathrm{F_C})^{\mathrm{B}}, \tag{37}$$

and

$$(f_{\mathrm{C}})^{\mathrm{A}} = (f_{\mathrm{C}})^{\mathrm{B}}. \tag{38}$$

But for the dilute real solution,

$$(f_{\mathrm{C}})^{\mathrm{A}} = (k_{\mathrm{C}})^{\mathrm{A}}(\mathrm{N_C})^{\mathrm{A}} \tag{39}$$

and

$$(f_{\mathrm{C}})^{\mathrm{B}} = (k_{\mathrm{C}})^{\mathrm{B}}(\mathrm{N_C})^{\mathrm{B}}. \tag{40}$$

Hence, from Equations 38, 39, and 40, we have

$$\frac{(\mathrm{N_C})^{\mathrm{A}}}{(\mathrm{N_C})^{\mathrm{B}}} = \frac{(k_{\mathrm{C}})^{\mathrm{B}}}{(k_{\mathrm{C}})^{\mathrm{A}}} = k'. \tag{41}$$

Equation 41, which is the Nernst law of the distribution of a solute between two solvents, shows that, over the range of composition where Equation 1 or Equations 39 and 40 are applicable, the ratio of the mole fractions of the solute in the two solvents remains constant.

7. Osmotic pressure. Consider, at constant temperature, the equilibrium between a pure liquid solvent, 1, under a pressure,

P^*, in equilibrium, through a membrane permeable only to this solvent, with a solution of the solvent and a solute, 2, the solution being under a pressure P and qualifying as a dilute real solution. This equilibrium is shown schematically in Figure 1. As the concentration of solute in the solution increases, the pressure P is required to be increased to maintain equilibrium. The value of $P - P^*$ for any given composition of the solution is defined as the osmotic pressure for that composition.

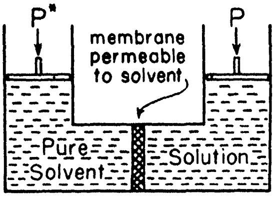


FIGURE 1. Schematic representation for osmotic pressure.

At equilibrium between the two phases,

$$(\mathrm{F}_1{}^*)^{P^*} = (\mathrm{F}_1)^P, \tag{42}$$

and

$$(f_1{}^*)^{P^*} = (f_1)^P. \tag{43}$$

But, at constant temperature,

$$d\mathrm{F}_1 = \bar{\mathrm{V}}_1\, dP. \tag{44}$$

Equation 44 may be integrated between the pressure P^* and the pressure P, assuming $\bar{\mathrm{V}}_1$ to be constant. Then

$$(\mathrm{F}_1)^P - (\mathrm{F}_1)^{P^*} = \bar{\mathrm{V}}_1(P - P^*). \tag{45}$$

Substituting from Equation 42, we obtain

$$(\mathrm{F}_1{}^*)^{P^*} - (\mathrm{F}_1)^{P^*} = \bar{\mathrm{V}}_1(P - P^*), \tag{46}$$

or

$$(\mathrm{F}_1{}^* - \mathrm{F}_1)^{P^*} = \bar{\mathrm{V}}_1(P - P^*), \tag{47}$$

or

$$(\mathrm{F}_1 - \mathrm{F}_1{}^*)^{P^*} = -\bar{\mathrm{V}}_1(P - P^*). \tag{48}$$

But

$$\mathrm{F}_1 - \mathrm{F}_1{}^* = RT \ln \frac{f_1}{f_1{}^*} = RT \ln \mathrm{N}_1. \tag{49}$$

Hence, from Equations 48 and 49,

$$P - P^* = -\frac{RT}{\bar{\mathrm{V}}_1} \ln \mathrm{N}_1. \tag{50}$$

But

$$\mathrm{N}_1 = 1 - \mathrm{N}_2, \tag{51}$$

and

$$\ln(1 - \text{N}_2) = -(\text{N}_2 + \tfrac{1}{2}\text{N}_2^2 + \tfrac{1}{3}\text{N}_2^3 + \cdots). \tag{52}$$

In the limit of the very dilute solution, as N_2 approaches zero,

$$\ln(1 - \text{N}_2) \cong -\text{N}_2, \tag{53}$$

and, in this limit, Equation 50 becomes

$$(P - P^*) = \text{N}_2 \frac{RT}{\bar{v}_1}. \tag{54}$$

Equations 50 and 54 are statements of the van't Hoff law of osmotic pressure. Equation 54 is seen to resemble in form the equation of state of the ideal gas.

8. Collateral reading. The reader is referred to Lewis and Randall (*1*) and Hildebrand and Scott (*2*) for additional discussion of the dilute real solution.

REFERENCES

1. G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill Book Company, New York, 1923.

2. J. H. Hildebrand and R. L. Scott, *Solubility of Non-electrolytes*, Reinhold Publishing Corporation, New York, 1948.

PROBLEMS

1. For the limiting case near infinite dilution, derive a quantitative expression in terms of the molality for (*a*) the lowering of the freezing point of water on the addition of a solid-insoluble solute, and (*b*) the elevation of the boiling point of water on the addition of a non-volatile solute. Take, for pure water, the heat of fusion to be 1.4363 kcal/mole at 0°C and 1 atm, and the heat of vaporization to be 9.717 kcal/mole at 100°C and 1 atm.

2. A small quantity of a given solute MX is dissolved in benzene and water. At equilibrium, the amount of MX dissolved in the two phases is 0.02 mole/mole of benzene and 0.08 mole/1000 g water. Calculate the distribution constant. What is the mole fraction of MX in benzene in equilibrium with a 0.05 molal solution of MX in water?

3. Given a 0.5 molal dilute real solution of MX in water at 25°C. Calculate the osmotic pressure, if

$$\bar{v}_1 = 18.0 \text{ cm}^3/\text{mole}.$$

27

Real Solutions; Activity and Activity Coefficient

1. Partial molal free energy and entropy and their variations with pressure and temperature. By definition,

$$F = H - TS. \tag{1}$$

If Equation 1 is applied to a solution containing n_1 moles of component 1, n_2 moles of component 2, n_3 moles of component 3, etc., we may differentiate Equation 1 with respect to n_i, keeping P, T, n_1, n_2, n_3, etc., constant. Then,

$$\left(\frac{\partial F}{\partial n_i}\right)_{P,T,n_1,n_2,n_3,\cdots} = \left(\frac{\partial H}{\partial n_i}\right)_{P,T,n_1,n_2,n_3,\cdots} - T\left(\frac{\partial S}{\partial n_i}\right)_{P,T,n_1,n_2,n_3,\cdots} \tag{2}$$

or

$$\bar{\mathrm{F}}_i = \bar{\mathrm{H}}_i - T\bar{\mathrm{S}}_i. \tag{3}$$

At 25°C, solid sodium chloride is in equilibrium with an aqueous solution of sodium chloride of 6.14 molality:

$$\mathrm{NaCl\ (c) = NaCl\ (aq,}\ m = 6.14). \tag{4}$$

At equilibrium, at constant temperature and pressure,

$$\Delta\mathrm{F} = 0 \tag{5}$$

or

$$\mathrm{F}_2\ (\mathrm{c}) = \bar{\mathrm{F}}_2, \tag{6}$$

and

$$\Delta\mathrm{H} = T\,\Delta\mathrm{S} \tag{7}$$

or

$$\bar{\mathrm{H}}_2 - \mathrm{H}_2\ (\mathrm{c}) = T[\bar{\mathrm{S}}_2 - \mathrm{S}_2\ (\mathrm{c})]. \tag{8}$$

According to Equation 6, one mole of solid sodium chloride could be added to a very large quantity of aqueous solution of sodium chloride of 6.14 molality with no change in free energy, at the given temperature. For such a transfer, the change in entropy is related to the change in heat content in accordance with Equation 8.

The variation of the partial molal free energy with pressure at constant temperature is derived simply as follows:

$$\left(\frac{\partial F}{\partial P}\right)_T = V. \tag{9}$$

If Equation 9 is applied to the solution described in the first paragraph above, and we differentiate with respect to n_i, keeping T, n_1, n_2, n_3, etc., constant, we obtain

$$\left(\frac{\partial^2 F}{\partial P\, \partial n_i}\right)_{T,n_1,n_2,n_3,\cdots} = \left(\frac{\partial V}{\partial n_i}\right)_{T,n_1,n_{,2}n_3,\cdots} \tag{10}$$

or

$$\left[\frac{\partial\left(\frac{\partial F}{\partial n_i}\right)}{\partial P}\right]_{T,n_1,n_2,n_3,\cdots} = \bar{\mathrm{v}}_i. \tag{11}$$

At constant temperature and constant composition, this is

$$d\mathrm{F}_i = \bar{\mathrm{v}}_i\, dP. \tag{12}$$

We have already seen that the partial molal volume of a component in solution may be negative. In such case, Equation 12 shows that the partial molal free energy may decrease with increase in pressure, whereas the molal free energy of pure substances always increases with increase in pressure.

Similarly, we can show that, at constant pressure and constant composition, the variation of the partial molal free energy with temperature is given by the relation,

$$d\mathrm{F}_i = -\bar{\mathrm{s}}_i\, dT. \tag{13}$$

2. Definition of activity. In considering the fugacity of gases, we found it convenient to use a standard reference state, for which the fugacity is unity and denoted by f°. In this case, we write the difference in free energy of the gas between a given state and the standard state, at constant temperature, as

$$\mathrm{F} - \mathrm{F}^\circ = RT \ln \frac{f}{f^\circ}. \tag{14}$$

For the ideal solution, we may write, at constant temperature and pressure, the partial molal free energy as

$$\mathrm{F}_i - \mathrm{F}_i^* = RT \ln \frac{f_i}{f_i^*}. \tag{15}$$

If the pure state of component i in the ideal solution is taken as its standard reference state at unit pressure, then Equation 15 may also be written as

$$\mathrm{F}_i - \mathrm{F}_i^\circ = RT \ln \frac{f_i}{f_i^\circ}. \tag{16}$$

For the ideal gas, $f = P$, and, since $f^\circ = 1$, Equation 14 becomes

$$\mathrm{F} - \mathrm{F}^\circ = RT \ln P. \tag{17}$$

For the ideal solution at unit pressure, we have for each component,

$$\mathrm{N}_i = \frac{f_i}{f_i^*} = \frac{f_i}{f_i^\circ}, \tag{18}$$

so that, for each component in the ideal solution at unit pressure,

$$\mathrm{F}_i - \mathrm{F}_i^\circ = RT \ln \mathrm{N}_i. \tag{19}$$

We thus see that for the ideal gas the molal free energy, referred to the standard state, is expressed simply in terms of the pressure. Similarly, for the ideal solution, the partial molal free energy, referred to the standard state, is expressed simply in terms of the mole fraction.

For most real solutions, the simple relation given by Equation 19 does not hold over the entire range of composition for all of the components. In order to retain the simplicity of the form of Equation 19, it becomes convenient to define a new thermodynamic function, called the activity, which may take the place of the mole fraction in Equation 19. From Equation 16, we can see that, to accomplish this purpose, it is necessary only to define the activity of any given component in any state as equal to the ratio of its fugacity in the given state to its fugacity in the standard state:

$$a_i = \frac{f_i}{f_i^\circ}. \tag{20}$$

It follows that, for any component i in a solution,

$$\mathrm{F}_i - \mathrm{F}_i^\circ = RT \ln a_i. \tag{21}$$

3. Thermodynamic standard reference states. In the systematic study and correlation of the thermodynamic properties of pure substances and solutions, it is convenient to agree formally upon a choice of standard states. In Chapter 23 on fugacity, we have already selected suitable thermodynamic standard reference states for pure substances in the gaseous, liquid, and solid states.

For a gas, the standard state, at each temperature, is taken as the hypothetical ideal state of unit fugacity. This standard state is illustrated in Figures 1 and 2 of Chapter 23. It should be noted again that, except for those properties which are primarily a function of the concentration of molecules, such as entropy and free energy, the properties, such as heat content and heat capacity, of a gas in the hypothetical thermodynamic standard reference state of unit fugacity are the same as those of the real gas at zero pressure. The foregoing standard state may be used not only for pure gases but also for the components of any gaseous solution.

Since

$$a = \frac{f}{f^\circ}, \tag{22}$$

and, for a gas,

$$f^\circ = 1, \tag{23}$$

it follows that for gases the activity is equal to the fugacity,

$$a = f. \tag{24}$$

Since the fugacity approaches the pressure in value as the pressure approaches zero, that is,

$$\frac{f}{P} \rightarrow 1, \tag{25}$$

then also

$$\frac{a}{P} \rightarrow 1. \tag{26}$$

For pure liquids and solids, we have already selected (Chapter 23) the thermodynamic standard reference state, at each temperature, as the pure liquid or solid at unit pressure. The activity of the pure liquid or solid at some other given pressure at the given temperature is then given by the ratio of the fugacity at the given pressure to the fugacity in the standard state, in accordance with the definition of activity:

$$a = \frac{f}{f^\circ}. \tag{27}$$

For a liquid or solid that may serve as a solvent, the standard state may be taken as the same as that for the pure liquid or solid, namely, the pure liquid or solid at unit pressure. As a solute is added to such a substance to form a liquid solution or a solid solution, the activity of the solvent for a given concentration is

$$a_1 = \frac{f_1}{f_1^\circ}. \tag{28}$$

It is to be noted here that, at unit pressure,

$$f_1^\circ = f_1^*. \tag{29}$$

We have seen that, for the dilute real solution,

$$f_2 = k_2\mathrm{N}_2, \tag{30}$$

so that, over the same range of composition, at unit pressure,

$$f_1 = \mathrm{N}_1 f_1^* = \mathrm{N}_1 f_1^\circ, \tag{31}$$

or

$$\mathrm{N}_1 = \frac{f_1}{f_1^\circ} \tag{32}$$

Therefore, for the solvent in the dilute real solution, at unit pressure, the activity is equal to the mole fraction:

$$a_1 = \mathrm{N}_1. \tag{33}$$

Equation 33 is valid for any infinitely dilute solution, and also valid over that range of composition for which Equation 30 is valid, all at unit pressure.

For a solute in any liquid or solid solution, the standard state is most conveniently selected as that hypothetical state in which the solute would exist if its fugacity, given in the dilute region by the relation,

$$f_2 = k_2\mathrm{N}_2, \tag{34}$$

continued along the same relation to a value of N_2 equal to unity, all at unit pressure. This is illustrated in Figure 1, in which f_2° indicates the hypothetical standard state of the solute. This hypothetical standard state is evaluated from measurements at unit pressure of the ratio of fugacity to mole fraction in the dilute range, where

$$f_2 = k_2 N_2, \tag{35}$$

or

$$N_2 = \frac{f_2}{k_2}. \tag{36}$$

It is seen that, at unit pressure,

$$f_2^\circ = k_2. \tag{37}$$

Over the range of composition for which the fugacity of the solute

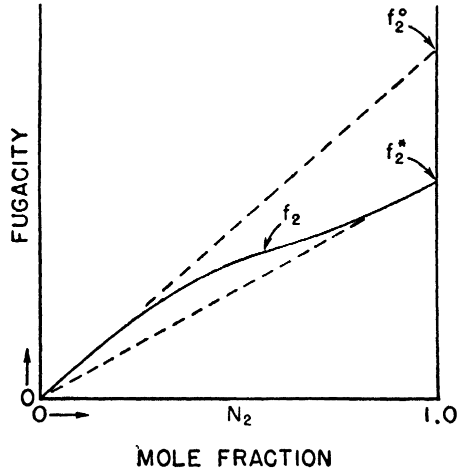


Figure 1. Schematic diagram showing the thermodynamic standard reference state for the solute in a real solution in which the composition is measured in mole fraction, at unit pressure.

is proportional to its mole fraction, in accordance with Equation 35, at unit pressure the activity is equal to the mole fraction,

$$a_2 = \frac{f_2}{f_2^\circ} = \frac{f_2}{k_2} = N_2. \tag{38}$$

It is to be noted (see Figure 1) that, at unit pressure, the fugacity of the pure solute, f_2^*, may differ appreciably from the fugacity in the hypothetical standard state, f_2°. It is also to be emphasized that, if component 2 is considered the solvent, a different standard state would be selected, namely, that of the pure substance, in which case f_2° and f_2^* would be identical, at unit pressure.

For a solute in aqueous solution, when the composition is expressed in terms of molality, it is convenient to select a different hypothetical standard from that where N_2 is unity, namely, one in which the molality is unity. This is illustrated in Figure 2, where the hypothetical standard state, $f_2{}^\circ$, is shown as that in which the solute would exist if the relation in the dilute range,

$$f_2 = k_m m, \tag{39}$$

were valid up to unit molality, at unit pressure. It follows that, for a solute in aqueous solution, at unit pressure,

$$f_2{}^\circ = k_m, \tag{40}$$

and

$$a_2 = \frac{f_2}{f_2{}^\circ} = \frac{f_2}{k_m} = m. \tag{41}$$

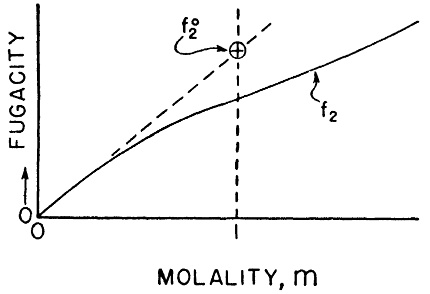


FIGURE 2. Schematic diagram showing the thermodynamic standard reference state for the solute in an aqueous real solution in which the composition is measured in molality, at unit pressure.

It is to be noted, in the case of the solute for which the standard state is a hypothetical one, where $N_2 = 1$ or $m = 1$, as shown in Figures 1 and 2, that, except for those properties such as entropy and free energy which are primarily a function of concentration, the properties, such as heat content, heat capacity, and volume, of the solute in the hypothetical standard state are the same as those of the solute at infinite dilution at unit pressure. That is to say, for such cases,

$$\bar{V}_2{}^0 = \bar{V}_2{}^\circ, \tag{42}$$

$$\bar{H}_2{}^0 = \bar{H}_2{}^\circ, \tag{43}$$

and

$$\bar{C}_{P_2}{}^0 = \bar{C}_{P_2}{}^\circ. \tag{44}$$

That is, the values of these properties in the hypothetical standard state are equal to the values for the real system at infinite dilution at unit pressure.

It is important to note that, where the standard state of a given component, i, of a solution has been selected to be the given component in a real or hypothetical system with $N_i = 1$, that is, the given component in a real or hypothetical pure condition, the standard state at a given temperature is taken as that of the given state at unit pressure (1 atmosphere, unless otherwise stated) in order to conform to the standard state that we have already agreed upon to use for pure liquids and pure solids. Where the standard state is not the given component, i, in a real or hypothetical pure condition with $\mathrm{N}_i = 1$, but at unit molality as in aqueous solutions, we likewise restrict the hypothetical standard state to the state at 1 atmosphere, in order to conform to the selection made for the standard states of the components of solutions having their composition measured in mole fraction. With this convention, we find that at a given temperature the thermodynamic properties of the standard state are independent of the pressure. For that component of any solution for which the standard state is taken as the real pure system of the given component, $\mathrm{N}_i = 1$, it follows that, at a given temperature, f_i^* at 1 atmosphere is equal to f_i°, but f_i^* at any other pressure is not equal to f_i°. Similarly, by this convention, for the solute in any aqueous solution, at a given temperature, the standard state is the solute in the hypothetical 1 molal solution at a pressure of 1 atmosphere, and the hypothetical 1 molal solution at any significantly different pressure does not give the properties of the solute in the standard state.

We have seen in Chapter 25 that in an ideal solution f_i is equal to $\mathrm{N}_i f_i^*$ at every temperature and every pressure. By reason of the particular way in which the standard state has been selected, namely, that at unit pressure, it follows that f_i^* is equal to f_i° only at 1 atmosphere at the given temperature. From the foregoing we see that the activity, a_i, of a component of an ideal solution, which is defined as f_i/f_i°, is equal to f_i/f_i^* only at 1 atmosphere, and, hence, while N_i is always equal to f_i/f_i^*, N_i is equal to f_i/f_i°, or a_i, only at 1 atmosphere.

4. Variation of activity with pressure and temperature. The variation of activity with pressure at constant temperature is derived as follows:

$$\mathrm{F}_i - \mathrm{F}_i^\circ = RT \ln a_i, \tag{45}$$

or

$$\ln a_i = \frac{1}{RT}(\mathrm{F}_i - \mathrm{F}_i^\circ). \tag{46}$$

Differentiating with pressure at constant temperature, we obtain

$$\left(\frac{\partial \ln a_i}{\partial P}\right)_T = \frac{1}{RT}(\bar{\mathrm{v}}_i - 0), \tag{47}$$

or, at constant temperature,

$$\frac{\mathrm{d} \ln a_i}{\mathrm{d}P} = \frac{\bar{\mathrm{v}}_i}{RT}. \tag{48}$$

That is, the rate of change of the activity with pressure at constant temperature of a given component of a solution is evaluated from a knowledge of its partial molal volume. If the activity is known at a given pressure, P_A, its value at a second pressure, P_B, may be readily calculated, at the same temperature, from a knowledge of the partial molal volume. Thus, at constant temperature,

$$\int_{P_A}^{P_B} \mathrm{d} \ln a_i = \frac{1}{RT}\int_{P_A}^{P_B} \bar{\mathrm{v}}_i \, \mathrm{d}P. \tag{49}$$

If $\bar{\mathrm{v}}_i$ can be taken as constant at its mean value over the given range of pressure, then Equation 49 leads to

$$\ln \frac{(a_i)_{P_B}}{(a_i)_{P_A}} = \frac{\bar{\mathrm{v}}_i(P_B - P_A)}{RT}. \tag{50}$$

To obtain the variation of the activity with temperature at constant pressure, Equation 45 is written as

$$\ln a_i = \frac{1}{R}\left(\frac{\bar{\mathrm{F}}_i}{T} - \frac{\bar{\mathrm{F}}_i{}^{\circ}}{T}\right), \tag{51}$$

whence, on differentiating with temperature at constant pressure, we have

$$\left(\frac{\partial \ln a_i}{\partial T}\right)_P = \frac{1}{R}\left(-\frac{\bar{\mathrm{H}}_i}{T^2} + \frac{\bar{\mathrm{H}}_i{}^{\circ}}{T^2}\right). \tag{52}$$

Or, at constant pressure,

$$\frac{\mathrm{d} \ln a_i}{\mathrm{d}T} = -\frac{\bar{\mathrm{H}}_i - \bar{\mathrm{H}}_i{}^{\circ}}{RT^2}. \tag{53}$$

If the partial molal heat content of component i at the given concentration is equal to the partial molal heat content in the standard state, the term on the right is zero and the activity of the given component does not change with temperature. For aqueous solutions of strong electrolytes, however, $\bar{H}_i - \bar{H}_i^\circ$ may be large and will change appreciably with temperature. In such cases, the activity at a second temperature, T_B, may be calculated from the activity at the first temperature, T_A, together with values of the relative partial molal heat content, $\bar{H}_i - \bar{H}_i^\circ$, and the relative partial molal heat capacity, $\bar{C}_{P_i} - \bar{C}_{P_i}^\circ$. Thus, at constant pressure,

$$\int_{T_A}^{T_B} d\ln a_i = -\frac{1}{R}\int_{T_A}^{T_B} \frac{\bar{H}_i - \bar{H}_i^\circ}{T^2}\, dT. \tag{54}$$

But

$$(\bar{H}_i - \bar{H}_i^\circ)_T = (\bar{H}_i - \bar{H}_i^\circ)_{T_A} + (\bar{C}_{P_i} - \bar{C}_{P_i}^\circ)(T - T_A), \tag{55}$$

where the relative partial molal heat capacity is taken as a constant having a value which is its mean for the given range of temperature. Hence, the relative partial molal heat content may be expressed as a simple linear function of the temperature, as

$$\bar{H}_i - \bar{H}_i^\circ = b + cT, \tag{56}$$

where

$$c = \bar{C}_{P_i} - \bar{C}_{P_i}^\circ \tag{57}$$

and

$$b = (\bar{H}_i - \bar{H}_i^\circ)_{T_A} - cT_A. \tag{58}$$

Hence, Equation 54 leads to

$$\begin{aligned}\ln\frac{(a_i)_{T_B}}{(a_i)_{T_A}} &= -\frac{1}{R}\int_{T_A}^{T_B}\left(\frac{b}{T^2} + \frac{c}{T}\right) dT \\ &= \frac{1}{R}\left[\frac{b(T_A - T_B)}{T_A T_B} - c\ln\frac{T_B}{T_A}\right].\end{aligned} \tag{59}$$

5. Activity in different phases at equilibrium. When a given substance, labeled component 2, is in equilibrium in three phases, A, B, and C, the partial molal free energies are equal and the fugacities are equal:

$$(\bar{F}_2)^A = (\bar{F}_2)^B = (\bar{F}_2)^C, \tag{60}$$

and

$$(f_2)^A = (f_2)^B = (f_2)^C. \tag{61}$$

But the activities are not equal unless the fugacities in the respective standard states are equal. Now

$$(a_2)^A = \left(\frac{f_2}{f_2^\circ}\right)^A; \quad (a_2)^B = \left(\frac{f_2}{f_2^\circ}\right)^B; \quad (a_2)^C = \left(\frac{f_2}{f_2^\circ}\right)^C. \tag{62}$$

Combination of the relations given by Equations 61 and 62 yields

$$(a_2 f_2^\circ)^A = (a_2 f_2^\circ)^B = (a_2 f_2^\circ)^C. \tag{63}$$

That is, the activities in two or more phases will be equal only if the fugacities in the corresponding standard states are equal.

6. Evaluation of a thermodynamic property of one component of a binary solution from the values for the other component. The basic partial molal equation given in Chapter 24 may be applied to a binary solution to give

$$\mathrm{N}_1\, d\bar{\mathrm{G}}_1 + \mathrm{N}_2\, d\bar{\mathrm{G}}_2 = 0, \tag{64}$$

or

$$d\bar{\mathrm{G}}_1 = -\frac{\mathrm{N}_2}{\mathrm{N}_1}\, d\bar{\mathrm{G}}_2\,. \tag{65}$$

Integration from $\mathrm{N}_1 = 1$ to any given value of N_1 yields

$$\int_{N_1=1}^{N_1} d\bar{\mathrm{G}}_1 = \bar{\mathrm{G}}_1 - \bar{\mathrm{G}}_1^* = -\int_{N_2=0}^{N_2} \frac{\mathrm{N}_2}{\mathrm{N}_1}\, d\bar{\mathrm{G}}_2. \tag{66}$$

Equation 66 shows that values of $\bar{\mathrm{G}}_1 - \bar{\mathrm{G}}_1^*$ may be obtained from a plot of $\mathrm{N}_2/\mathrm{N}_1$ against values of $\bar{\mathrm{G}}_2$.

If the given thermodynamic property is the partial molal free energy, Equation 66 will not be convenient because the partial molal free energy approaches negative infinity at infinite dilution. However, the activity may be introduced to simplify the problem. Since

$$\mathrm{F}_1 - \mathrm{F}_1^\circ = RT \ln a_1, \tag{67}$$

at constant temperature and pressure,

$$d\mathrm{F}_1 = RT d \ln a_1. \tag{68}$$

Hence, Equation 64 may be written as

$$\mathrm{N}_1 d \ln a_1 + \mathrm{N}_2 d \ln a_2 = 0, \tag{69}$$

so that

$$d \ln a_1 = -\frac{\mathrm{N}_2}{\mathrm{N}_1}\, d \ln a_2. \tag{70}$$

On integration between $\mathrm{N}_1 = 1$ and a given value of N_1, Equation 70 yields

$$\ln a_1 = -\int_{N_2=0}^{N_2} \frac{\mathrm{N}_2}{\mathrm{N}_1}\, d \ln a_2. \tag{71}$$

Equation 71 gives the general relation for evaluating the activity of one component of a binary solution when the values of the activity of the other component are known as a function of the composition, all at constant temperature and pressure.

Another form of equation for evaluating the activity of one component of a binary solution from values of the activity of the other component may be obtained as follows:

$$N_1 + N_2 = 1, \tag{72}$$

$$dN_1 = -dN_2, \tag{73}$$

$$N_1 \frac{dN_1}{N_1} = -N_2 \frac{dN_2}{N_2}, \tag{74}$$

so that

$$N_1 d \ln N_1 = -N_2 d \ln N_2. \tag{75}$$

Subtracting Equation 75 from Equation 69 gives

$$N_1 d \ln \frac{a_1}{N_1} = -N_2 d \ln \frac{a_2}{N_2} \cdot \tag{76}$$

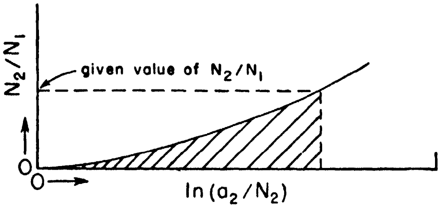


FIGURE 3. Schematic diagram showing the evaluation of activity of one component of a binary solution from values of the activity of the other component.

See text for details.

It is to be noted that, as N_1 approaches unity,

$$\frac{a_1}{N_1} = 1 \quad \text{and} \quad \frac{a_2}{N_2} = 1, \tag{77}$$

so that, on integration, Equation 76 yields

$$\ln \frac{a_1}{N_1} = -\int_{N_2=0}^{N_2} \frac{N_2}{N_1} d \ln \frac{a_2}{N_2}. \tag{78}$$

Figure 3 gives a schematic plot of N_2/N_1 against $\ln (a_2/N_2)$, where the area under the curve gives the value of $-\ln (a_1/N_1)$, in accordance with Equation 78.

Lewis and Randall (*1*) describe several more convenient relations by means of which the activity of one component of a binary solution may be evaluated from values of the activity of the other component. Each of these methods involves the definition and use of a function which rapidly approaches zero at infinite dilution, so that the graphical computation is simplified. For example, Lewis and Randall (*1*) define the function

$$h = \frac{\ln a_1}{r} + 1, \tag{79}$$

where

$$r = \frac{N_2}{N_1}. \tag{80}$$

Differentiation of Equation 79 gives

$$dh = \frac{1}{r}\, d \ln a_1 - \frac{\ln a_1}{r^2}\, dr. \tag{81}$$

Combination of Equations 70 and 81 gives

$$d \ln a_2 = -dh + (1 - h)\, d \ln r. \tag{82}$$

Subtraction of d ln r from both sides gives

$$d \ln \frac{a_2}{r} = -dh - h d \ln r. \tag{83}$$

Integration from $N_1 = 1$ to N_1 gives

$$\ln \frac{a_2}{r} = -h - \int_0^r \frac{h}{r}\, dr, \tag{84}$$

since, when $N_1 = 1$ or $N_2 = 0$,

$$\ln \frac{a_2}{r} = 0; \qquad h = 0. \tag{85}$$

If the composition is expressed in molality as for an aqueous solution,

$$r = \frac{N_2}{N_1} = \frac{m}{55.506}, \tag{86}$$

so that

$$h = \frac{55.506}{m} \ln a_1 + 1, \tag{87}$$

and

$$\ln \frac{a_2}{m} = -h - \int_0^m \frac{h}{m}\, dm. \tag{88}$$

Equations 84 and 88 permit relatively convenient evaluation of the activity of the solute when values of the activity of the solvent are known over the given range of composition, beginning with pure solvent. In all such problems, it is important to identify the proper standard state of the solute or value of $f_2°$ with the appropriate value of a_2. The standard states of the solute are different in Equations 84 and 88, for example.

7. Evaluation of activity from vapor pressures. Consider a binary solution in which the solvent is volatile and the solute is non-volatile. Here, measurements of the vapor pressure may be made as a function of the composition, yielding values of P_1/P_1^*. If the vapor may be considered an ideal gas, then the measurements yield values of f_1/f_1^* or $f_1/f_1°$. But this is by definition the activity of the solvent,

$$a_1 = \frac{f_1}{f_1°}, \tag{89}$$

so that the foregoing measurements give values of the activity of the solvent as a function of the composition. Then the activity of the solute may be evaluated from equations of the form of Equation 78.

If the binary solution is one in which the solute only is volatile and its partial pressure can be measured at various concentrations, then such measurements yield values of P_2/N_2. If the vapor can be considered an ideal gas, then the measurements give values of f_2/N_2. In the dilute range, the ratio f_2/N_2 is constant and equal to k_2 in the relation

$$f_2 = k_2\mathrm{N}_2. \tag{90}$$

That is, the experimental measurements in the dilute range evaluate k_2, which is $f_2°$, so that

$$a_2 = \frac{f_2}{f_2°} = \frac{f_2}{k_2}. \tag{91}$$

In this way, values of the activity of the solute are obtained as a function of the composition. Then, values of the activity of the solvent may be obtained by means of Equation 78 or a similar relation.

8. Evaluation of activity from the distribution of a solute between two solvents. When the activity of a solute in a given solvent is known as a function of the composition, the activity of the same solute in another solvent may be evaluated from measurements of the distribution of the solute between the two solvents. When a solute, labeled component 2, is in equilibrium between two solvents, A and B,

$$(f_2)^{\mathrm{A}} = (f_2)^{\mathrm{B}}. \tag{92}$$

Suppose that, in the solvent A, the concentration is in terms of molality; then

$$(f_2)^{\mathrm{A}} = (k_2)^{\mathrm{A}}(m)^{\mathrm{A}} \tag{93}$$

and

$$(a_2)^{\mathrm{A}} = \frac{(f_2)^{\mathrm{A}}}{(f_2{}^{\circ})^{\mathrm{A}}} = \frac{(f_2)^{\mathrm{A}}}{(k_2)^{\mathrm{A}}}. \tag{94}$$

Suppose that, in the solvent B, the concentration is measured in terms of mole fraction; then

$$(f_2)^{\mathrm{B}} = (k_2)^{\mathrm{B}}(N_2)^{\mathrm{B}} \tag{95}$$

and

$$(a_2)^{\mathrm{B}} = \frac{(f_2)^{\mathrm{B}}}{(f_2{}^{\circ})^{\mathrm{B}}} = \frac{(f_2)^{\mathrm{B}}}{(k_2)^{\mathrm{B}}}. \tag{96}$$

Combination of Equations 92, 94, and 96 gives

$$(a_2)^{\mathrm{A}} = (a_2)^{\mathrm{B}}\frac{(k_2)^{\mathrm{B}}}{(k_2)^{\mathrm{A}}}. \tag{97}$$

9. Evaluation of activity from the lowering of the freezing point. The activity of the solvent, in its solution with a solute that remains in the liquid phase during formation of crystals of the solvent, may be evaluated from measurements of the freezing point of the solution at various concentrations. Consider, as an example, the equilibrium

$$\mathrm{H_2O}\ (\mathrm{c},\ 1\ \mathrm{atm}) = \mathrm{H_2O}\ (\mathrm{soln\ with\ MX},\ m,\ 1\ \mathrm{atm}). \tag{98}$$

At the constant pressure of 1 atmosphere, measurements are made of the temperature at which an infinitesimal amount of crystals of water is in equilibrium with the liquid solution, for different values of the molality, beginning with $m = 0$. In air at 1 atmosphere, at 0°C or $T_1{}^*$, the molality of the solution is zero and the liquid phase is pure water. If the temperature is $-\Delta t$°C, or T, then the solution will have a certain molality, m.

At 0°C,

$$[\mathrm{F}_1\ (\mathrm{c})]_{T_1{}^*} = (\mathrm{F}_1{}^\circ)_{T_1{}^*} \tag{99}$$

and at $-\Delta t$°C,

$$[\mathrm{F}_1\ (\mathrm{c})]_T = (\mathrm{F}_1)_T. \tag{100}$$

Subtracting, we obtain

$$(\mathrm{F}_1)_T - (\mathrm{F}_1{}^\circ)_{T_1{}^*} = [\mathrm{F}_1\ (\mathrm{c})]_T - [\mathrm{F}_1\ (\mathrm{c})]_{T_1{}^*}. \tag{101}$$

Adding and subtracting $(\mathrm{F}_1)_{T_1{}^*}$, and rearranging, we obtain

$$(\mathrm{F}_1 - \mathrm{F}_1{}^\circ)_{T_1{}^*} = [\mathrm{F}_1\ (\mathrm{c}) - \mathrm{F}_1]_T - [\mathrm{F}_1\ (\mathrm{c}) - \mathrm{F}_1]_{T_1{}^*}. \tag{102}$$

But

$$[\mathrm{F}_1\ (\mathrm{c}) - \mathrm{F}_1]_T = 0, \tag{103}$$

so that, also

$$T_1{}^* \frac{[\mathrm{F}_1\ (\mathrm{c}) - \mathrm{F}_1]_T}{T} = 0. \tag{104}$$

Now

$$(\mathrm{F}_1 - \mathrm{F}_1{}^\circ)_{T_1{}^*} = (RT \ln a_1)_{T_1{}^*}. \tag{105}$$

Making the above substitutions into equation 102, we have

$$(RT \ln a_1)_{T_1*} = T_1{}^* \frac{[\mathrm{F}_1\ (\mathrm{c}) - \mathrm{F}_1]_T}{T} - T_1{}^* \frac{[\mathrm{F}_1\ (\mathrm{c}) - \mathrm{F}_1]_{T_1{}^*}}{T_1{}^*}, \tag{106}$$

or

$$R \ln\ (a_1)_{T_1*} = \left[\frac{\mathrm{F}_1\ (\mathrm{c}) - \mathrm{F}_1}{T}\right]_{T_1*}^{T} = \int_{T_1*}^{T_1} \mathrm{d}\left[\frac{\mathrm{F}_1\ (\mathrm{c}) - \mathrm{F}_1}{T}\right]. \tag{107}$$

But

$$\mathrm{d}\left(\frac{\mathrm{F}}{T}\right) = -\frac{\mathrm{H}}{T^2}, \tag{108}$$

so that

$$\begin{aligned} R \ln\ (a_1)_{T_1*} &= -\int_{T_1*}^{T} \frac{\mathrm{H}_1\ (\mathrm{c}) - \bar{\mathrm{H}}_1}{T^2}\, \mathrm{d}T \\ &= \int_{T_1*}^{T} \frac{\bar{\mathrm{H}}_1 - \mathrm{H}_1\ (\mathrm{c})}{T^2}\, \mathrm{d}T. \end{aligned} \tag{109}$$

Adding and subtracting $\bar{H}_1^\circ$ gives

$$\ln (a_1)_{T_1^*} = \frac{1}{R}\int_{T_1^*}^{T} \frac{\bar{H}_1 - \bar{H}_1^\circ}{T^2}\, dT + \frac{1}{R}\int_{T_1^*}^{T} \frac{\bar{H}_1^\circ - H_1\,(c)}{T^2}\, dT. \quad (110)$$

The relative partial molal heat content of the solvent, $\bar{H}_1 - \bar{H}_1^\circ$, can be expressed as a function of temperature, as

$$(\bar{H}_1 - \bar{H}_1^\circ)_T = (\bar{H}_1 - \bar{H}_1^\circ)_{T_1^*} - (T_1^* - T)(\bar{C}_{P_1} - \bar{C}_{P_1}^\circ), \quad (111)$$

where the relative partial molal heat capacity of the water, $\bar{C}_{P_1} - \bar{C}_{P_1}^\circ$, at the given concentration, is taken as the mean value between T_1^* and T, and $(\bar{H}_1 - \bar{H}_1^\circ)_{T_1^*}$ is a constant representing the value of the relative partial molal heat content of the water at 0°C. Equation 111 may also be written as

$$[\bar{H}_1 - \bar{H}_1^\circ]_T = b + cT, \quad (112)$$

where

$$c = \bar{C}_{P_1} - \bar{C}_{P_1}^\circ, \quad (113)$$

and

$$b = (\bar{H}_1 - \bar{H}_1^\circ)_{T_1^*} - T_1^* c. \quad (114)$$

Similarly, the heat of fusion of ice, $\bar{H}_1^\circ - H_1\,(c)$, may be expressed as a function of T as

$$[\bar{H}_1^\circ - H_1\,(c)]_T = d + eT, \quad (115)$$

where

$$e = \bar{C}_{P_1}^\circ - C_{P_1}\,(c), \quad (116)$$

and

$$d = [\bar{H}_1^\circ - H_1\,(c)]_{T_1^*} - T_1^* e. \quad (117)$$

Then

$$\ln (a_1)_{T_1^*} \doteq \frac{1}{R}\int_{T_1^*}^{T} \frac{b + cT + d + eT}{T^2}\, dT, \quad (118)$$

or

$$\ln (a_1)_{T_1^*} = \frac{1}{R}\int_{T_1^*}^{T} \left(\frac{d + b}{T^2} + \frac{e + c}{T}\right) dT, \quad (119)$$

and

$$\ln (a_1)_{T_1^*} = \frac{1}{R}\left[-\frac{d + b}{T} + (e + c)\ln T\right]_{T_1^*}^{T}, \quad (120)$$

or

$$\ln (a_1)_{T_1^*} = \frac{1}{R}\left[-(d + b)\left(\frac{1}{T} - \frac{1}{T_1^*}\right) + (e + c)\ln \frac{T}{T_1^*}\right]\cdot \quad (121)$$

Since

$$T_1^* - T = \Delta t, \tag{122}$$

Equation 121 may be written as

$$\ln (a_1)_{T_1^*} = \frac{1}{R}\left[- \frac{(d + b)\Delta t}{TT_1^*} + (e + c) \ln\left(1 - \frac{\Delta t}{T_1^*}\right)\right], \tag{123}$$

or

$$\ln (a_1)_{T_1^*} = \frac{1}{R}\left[- \frac{\Delta t}{(T_1^*)^2} \frac{(d + b)}{\left(1 - \dfrac{\Delta t}{T_1^*}\right)} + (e + c) \ln\left(1 - \frac{\Delta t}{T_1^*}\right)\right]\cdot \tag{124}$$

Equations 123 and 124 are the exact equations giving the value of the activity of the water at 0°C and take into account the relative partial molal heat content of the water and its variation with temperature, as well as the variation with temperature of the heat of fusion of water. The only assumptions involved in Equations 123 and 124 are that the relative partial molal heat capacity of the water and the difference in the heat capacity of liquid and solid water are constant over the given range of temperature, Δt.

Equation 124 may be simplified by certain assumptions. If the relative partial molal heat content can be taken as zero over the given range of temperature, then $b = c = 0$. Letting

$$[\bar{\text{H}}_1^\circ - \text{H}_1\ (\text{c})]_{T_1^*} = \Delta\text{H}m_1^*, \tag{125}$$

and

$$\bar{\text{C}}_{P_1}^\circ - \text{C}_{P_1}\ (\text{c}) = \Delta\text{C}_{P_1}^*, \tag{126}$$

with the foregoing substitutions, Equation 123 becomes

$$\ln (a_1)_{T_1^*} = \frac{1}{R}\left[- \left(\frac{\Delta\text{H}m_1^*}{T_1^*} - \Delta\text{C}_{P_1}^*\right)\left(\frac{\Delta t}{T_1^*}\right)\frac{1}{\left(1 - \dfrac{\Delta t}{T_1^*}\right)} + \Delta\text{C}_{P_1}^* \ln\left(1 - \frac{\Delta t}{T_1^*}\right)\right]\cdot \tag{127}$$

Substituting,

$$\frac{1}{1 - \dfrac{\Delta t}{T_1^*}} = 1 + \left(\frac{\Delta t}{T_1^*}\right) + \left(\frac{\Delta t}{T_1^*}\right)^2 + \cdots \tag{128}$$

and

$$\ln\left(1 - \frac{\Delta t}{T_1^*}\right) = -\left(\frac{\Delta t}{T_1^*}\right) - \frac{1}{2}\left(\frac{\Delta t}{T_1^*}\right)^2 - \cdots, \tag{129}$$

Equation 127 becomes, on rearrangement,

$$\ln (a_1)_{T_1^*} = \frac{1}{R}\frac{\Delta t}{(T_1^*)^2}\left[-\Delta \mathrm{H}m_1^* - \Delta \mathrm{H}m_1^*\left(\frac{\Delta t}{T_1^*}\right) + \frac{1}{2}\Delta \mathrm{C}_{P1}^*\,(\Delta t) + \cdots\right], \tag{130}$$

or, finally,

$$\ln (a_1)_{T_1^*} = -A(\Delta t)[1 + B(\Delta t) + \cdots], \tag{131}$$

where

$$A = \frac{\Delta \mathrm{H}m_1^*}{R(T_1^*)^2}, \tag{132}$$

and

$$B = \frac{1}{T_1^*} - \frac{1}{2}\frac{\Delta \mathrm{C}_{P1}^*}{\Delta \mathrm{H}m_1^*}. \tag{133}$$

Equation 131 may be seen to be identical in form with Equation 88 of Chapter 25. The succeeding terms of the series, Equation 131, are the same as those in Equation 88 of Chapter 25. For water as the solvent, in air at 1 atmosphere, the values of the freezing point, the heat of fusion, and the difference in heat capacity of the solid and liquid placed into Equation 131 yield

$$\ln (a_1)_{0^\circ\mathrm{C}} = -0.009687\Delta t\ (1 + 0.000558\Delta t). \tag{134}$$

Once the activity of the solvent is obtained in this way from the lowering of the freezing point, the activity of the solute may be evaluated by means of Equation 78 or a similar relation. Lewis and Randall (*1*) use a convenient function for evaluating the activity from measurements of the lowering of the freezing point, which is defined as

$$j = 1 - 55.506A\left(\frac{\Delta t}{m}\right), \tag{135}$$

where

$$A = \frac{\bar{\mathrm{H}}_1^\circ - \mathrm{H}_1\ (\mathrm{c})}{R(T_1^*)^2} = \frac{\Delta \mathrm{H}m_1^*}{R(T_1^*)^2}. \tag{136}$$

From Chapters 25 and 26, we see that

$$\frac{1}{55.506A} = \left(\frac{\Delta t}{m}\right)_{m=0}. \tag{137}$$

so that $j = 0$ when $m = 0$.
Differentiation of Equation 135 gives

$$dj = (55.506A)\left[\frac{1}{m}\,d(\Delta t) + (\Delta t)\,dm\right]. \tag{138}$$

Rearranging and substituting from Equation 135, we obtain

$$\frac{55.506A}{m}\,d(\Delta t) = (1 - j)\,d\ln m - dj. \tag{139}$$

But in the dilute region,

$$d\ln a_2 = -\frac{N_1}{N_2}\,d\ln a_1 \doteq -\frac{55.506}{m}\,d\ln a_1. \tag{140}$$

From Equation 133,

$$d\ln a_1 = -\left[A + \frac{\Delta c_{P_1}{}^*}{R(T_1{}^*)^2}\,\Delta t\right] d(\Delta t). \tag{141}$$

Combination of Equations 140 and 141 gives

$$d\ln a_2 = \frac{55.506}{m}\left[A + \frac{\Delta c_{P_1}{}^*}{R(T_1{}^*)^2}\,\Delta t\right] d(\Delta t). \tag{142}$$

Combination with Equation 139, with transposition of d ln m, gives

$$d\ln\left(\frac{a_2}{m}\right) = -j - \frac{j}{m}\,dm + 55.506\,\frac{\Delta c_{P_1}{}^*}{R(T_1{}^*)^2}\left(\frac{\Delta t}{m}\right) d(\Delta t). \tag{143}$$

Noting that when $m = 0$ all the terms on the right side of Equation 143 are zero, Equation 143 may be readily integrated from $m = 0$ to any given molality to yield

$$\ln\left(\frac{a_2}{m}\right) = -j - \int_0^m \frac{j}{m}\,dm + 55.506\,\frac{\Delta c_{P_1}{}^*}{R(T_1{}^*)^2}\int_0^m \left(\frac{\Delta t}{m}\right) d(\Delta t). \tag{144}$$

Of the terms on the right side of Equation 144, the first is the value of the function j itself, the second is the area under the curve on a plot of j/m against m, and the last term, which is rather small below unit molality, is a constant times the area under the curve on a plot of $\Delta t/m$ against m.

10. Evaluation of activity from the elevation of the boiling point. The activity of the solvent, in its solution with a non-volatile solute, may be evaluated from measurements of the boiling point of the solution at various concentrations of the solute, beginning with zero concentration or the pure solvent. Consider, as an example, the equilibrium,

$$H_2O \text{ (soln with MX, } m\text{, 1 atm)} = H_2O \text{ (g, 1 atm)}. \quad (145)$$

At the constant pressure of 1 atmosphere, measurements are made of the temperature at which the water vapor has a pressure of 1 atmosphere for different values of the molality of the solution, beginning with $m = 0$. Proceeding exactly as in the preceding section dealing with the lowering of the freezing point, except that H_2O (g) and F_1 (g) are substituted for H_2O (c) and F_1 (c), respectively, and the process is written in the reverse direction with the solution as the initial state rather than the final state, we obtain the following relation corresponding to Equation 110:

$$\ln (a_1)_{T_1^*} = -\frac{1}{R}\int_{T_1^*}^{T} \frac{\bar{\text{H}}_1 - \bar{\text{H}}_1^\circ}{T^2}\, dT + \frac{1}{R}\int_{T_1^*}^{T} \frac{\text{H}_1 \text{ (g)} - \bar{\text{H}}_1^\circ}{T^2}\, dT. \quad (146)$$

As before, the relative partial molal heat content of the water, $\bar{\text{H}}_1 - \bar{\text{H}}_1^\circ$, and the heat of vaporization of pure water, $\text{H}_1 \text{ (g)} - \bar{\text{H}}_1^\circ$, can be expressed as functions of the temperature, and the integration can be performed, yielding values of the activity of the water, in the solution of the given concentration, at the temperature, T_1^*, its boiling point at the given constant pressure of 1 atmosphere. Special functions, like the j function described above, may be used to expedite the calculation of activity from values of the elevation of the boiling point.

11. Activities of strong electrolytes in aqueous solution. In the case of strong electrolytes in aqueous solution, cognizance must be taken of the fact that, at infinite dilution, the value of an extensive property of the solute is the sum of the values of the property for the individual ions produced by the solute. We have seen that, for an aqueous solution of a non-electrolyte, the standard states for the components are selected in such a way that, in the very dilute region, the activity of the solute, a_2, approaches the molality, m, in value. It is possible to retain these same standard states, and, at the same time, let the activity of each ion be equal to its molality, by relating the activity, a_2, of the solute, MX, to the activity, a_+ and a_-, of its ions, M^+ and X^-, as follows:

$$a_2 = a_+a_-. \tag{147}$$

Near infinite dilution for MX, the molality of each ion is the same, and

$$a_+ = a_- = a_2^{1/2}. \tag{148}$$

In order not to make the assumption that this equality of activities extends to finite concentrations, it is possible to define the mean activity, $a_\pm$, as

$$a_\pm = (a_+a_-)^{1/2} = a_2^{1/2}, \tag{149}$$

which relation holds for all concentrations.

For any strong electrolyte, $M_{\nu_+}X_{\nu_-}$, the dissociation into ions may be represented as

$$M_{\nu_+}X_{\nu_-} = \nu_+M^{z+} + \nu_-X^{z-}, \tag{150}$$

where ν_+ and ν_- represent the number of ions of M and X, respectively, in the molecule, and z_+ and z_- represent the charges on the respective ions. It is to be noted that the sum of the positive charges must equal the sum of the negative charges:

$$\nu_+z_+ = \nu_-z_-. \tag{151}$$

From the conventions adopted above, it also follows that

$$a_2 = a_+^{\nu_+}a_-^{\nu_-}, \tag{152}$$

$$a_\pm = (a_+^{\nu_+}a_-^{\nu_-})^{1/(\nu_++\nu_-)}, \tag{153}$$

and

$$a_2 = a_\pm^{(\nu_++\nu_-)}. \tag{154}$$

In accordance with the foregoing relations, we write

$$\text{F}_2 - \text{F}_2^\circ = RT \ln a_2 = (\nu_+ + \nu_-)RT \ln a_\pm = \nu RT \ln a_\pm, \tag{155}$$

where ν is the sum of $\nu_+ + \nu_-$.

12. Definition of activity coefficient. At infinite dilution, the activity of each ion is equal to its molality, so that the ratio of the activity to the molality is unity. In order to study the actual behavior of the solute as a function of concentration as the concentration passes from infinite dilution to some finite concentration, it has been found convenient to define the ratio of the activity to the molality as the activity coefficient. For a non-electrolyte in aqueous solution,

$$\gamma = \frac{a_2}{m}. \tag{156}$$

For each ion of an electrolyte,

$$\gamma_+ = \frac{a_+}{m_+}, \tag{157}$$

and

$$\gamma_- = \frac{a_-}{m_-}. \tag{158}$$

The mean ion activity coefficient is

$$\gamma_\pm = \frac{a_\pm}{m_\pm}. \tag{159}$$

As for the mean ion activity, the mean ion molality, $m_\pm$, is defined as

$$m_\pm = (m_+^{\nu_+} m_-^{\nu_-})^{1/(\nu_+ + \nu_-)}. \tag{160}$$

It is also possible to define the activity coefficient for non-aqueous solutions in which the concentration is measured in terms of the mole fraction, in general, as

$$\gamma_i = \frac{a_i}{\mathrm{N}_i}. \tag{161}$$

In each of the above cases, the change in the value of the activity coefficient serves as a convenient measure for studying the behavior of the solute as the concentration increases from infinite dilution.

It is also convenient to use the activity coefficient in connection with gases. For any gaseous substance or component of any gaseous solution, the activity coefficient for component i is defined as

$$\gamma_i = \frac{a_i}{P_i}. \tag{162}$$

But, for gases, the activity is equal to the fugacity, so that also

$$\gamma_i = \frac{f_i}{P_i}. \tag{163}$$

In the foregoing equations, P_i is the partial pressure of the given component, defined as equal to the mole fraction of the given component multiplied into the total pressure,

$$P_i = \mathrm{N}_i \sum P_i = \mathrm{N}_i P, \tag{164}$$

where P is the total pressure. From the foregoing, it follows that

$$f_i = \gamma_i \mathrm{N}_i P. \tag{165}$$

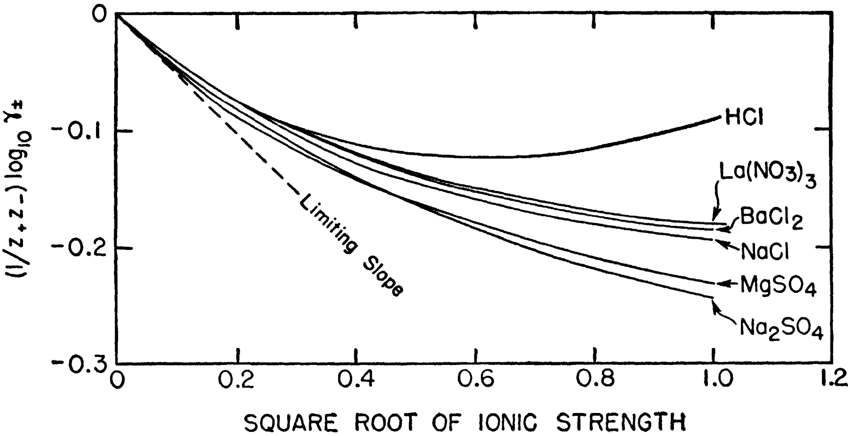


FIGURE 4. Plot of values of the logarithm of the activity coefficient as a function of the ionic strength for several strong electrolytes of different types, in aqueous solution at 25°C.

The scale of ordinates is the logarithm of the mean ion activity coefficient $\log_{10}\gamma_\pm$, multiplied by the product, z_+z_-, of the valence or charge on the positive ion, z_+, into the valence or charge on the negative ion, z_-. The data are from Randall and Vietti (*9*).

13. Activity coefficient of strong electrolytes in aqueous solution.

It was found by Lewis and Randall (*2*) that the study and correlation of the values of the activity coefficient of strong electrolytes are greatly simplified by comparing values for different types of electrolytes at equal values of the ionic strength, μ, which is defined as one-half the sum of the product of the stoichiometrical molality of each ion into the square of its charge or valence, summed for all the ions in the solution:

$$\mu = \tfrac{1}{2}\sum m_i z_i^2. \tag{166}$$

Figure 4 illustrates the pattern of behavior of the change in activity coefficient with ionic strength for different electrolytes in dilute aqueous solution. It is to be noted that in the limit of infinite dilution these data agree with the finding of Lewis and Randall (*2*) that for all strong electrolytes in aqueous solution

$$\ln \gamma_{\pm} = -g(z_{+}z_{-})\mu^{1/2}; \qquad \text{as } m \rightarrow 0. \tag{167}$$

In Equation 167, g is a constant for all strong electrolytes, z_{+} and z_{-} are the charges on the positive and negative ions, respectively, and μ is the ionic strength defined by Equation 166.

14. Collateral reading. For further details regarding the topics covered in this chapter, and data related thereto, the reader is referred to Lewis and Randall (*1*), Latimer (*3*), Harned and Owen (*4*), Glasstone (*5*), Spencer (*6*), Scatchard (*7*), Young (*8*), Adams (*10*), and Robinson and Stokes (*11*).

REFERENCES

1. G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill Book Company, New York, 1923.
2. G. N. Lewis and M. Randall, *J. Am. Chem. Soc.* **43**, 1112 (1921).
3. W. M. Latimer, *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, Prentice-Hall, New York, 1938.
4. H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold Publishing Corporation, New York, 1950.
5. S. Glasstone, *Thermodynamics for Chemists*, D. Van Nostrand Company, New York, 1947.
6. H. M. Spencer, *J. Am. Chem. Soc.* **54**, 4490 (1932).
7. G. Scatchard, *Chem. Revs.* **8**, 321 (1931).
8. T. F. Young, *Chem. Revs.* **13**, 103 (1933).
9. M. Randall and W. V. Vietti, *J. Am. Chem. Soc.* **50**, 1526 (1928).
10. L. H. Adams, *Chem. Revs.* **19**, 1 (1936).
11. R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.* **45**, 612 (1949).

PROBLEMS

1. What is the activity of H_2O in a solution from which the partial pressure of water vapor is 20 mm at 25°C?

2. What is the activity of the gas, Y_2, at 50°C and 100 atm, if its ratio of fugacity to pressure is 0.965?

3. Two liquids, MX and NY, of molecular weights 110 and 140, respectively, form an ideal solution at 25°C. The vapor pressure of pure MX at 25°C is 220 mm Hg, and that of pure NY is 400 mm Hg. A solution is made

up, using 100 g each of the two components. Assuming the gases ideal, calculate the activity of each component in the given solution.

4. For aqueous solutions of n-propanol, the following data are given in *International Critical Tables* for the mole per cent of n-propanol and the partial pressures, in millimeters of mercury, of the water and alcohol, respectively, at 49.9°C: 0, 92.0, 0; 9.04, 87.2, 49.2; 15.97, 87.0, 51.7; 30.47, 84.5, 54.6; 41.14, 83.0, 57.4; 55.5, 78.2, 60.2; 73.9, 60.9, 68.4; 82.0, 49.2, 72.1; 100, 0, 90.0. Taking the pure liquid as the standard state for each component, calculate a_1, a_2, $\bar{\mathrm{F}}_1 - \bar{\mathrm{F}}_1^{\circ}$, and $\bar{\mathrm{F}}_2 - \bar{\mathrm{F}}_2^{\circ}$ for mole fractions of n-propanol equal to 0, 0.2, 0.5, 0.8, and 1.0.

5. For aqueous solutions of sucrose, $C_{12}H_{22}O_{11}$, the following data are given in the *International Critical Tables* for the molality, m, of solute and for the percentage lowering of the vapor pressure of the solvent, respectively, at 30°C: 1.0, 1.94; 1.7, 3.49; 3.0, 6.75; 4.0, 9.44; 5.0, 12.30; 6.5, 16.58. Calculate the activity of the solvent and solute in these solutions for values of $m = 1,2,4$, and 6.

6. At 25°C and 1 atm, the following data are given:

NaCl (aq, $m = 6.14$), $\mathrm{V}_2 = 24.30\ \mathrm{cm^3/mole}$;

NaCl (c), density $= 2.163\ \mathrm{g/cm^3}$;

NaCl (c) is in equilibrium with NaCl (aq, $m = 6.14$).

Calculate the change, in calories per mole, in the partial molal free energy of the aqueous sodium chloride at the given molality as the pressure is increased from 1 to 2 atm. As the pressure is increased, with maintenance of equilibrium, does the molality increase or decrease?

7. At 18°C and 1 atm, the following data are given:

KCl (c) is in equilibrium with KCl (aq, $m = 4.42$);

KCl (c) = KCl (aq, $m = 4.42$), $\bar{\mathrm{H}}_2 - \mathrm{H}_2\,(\mathrm{c}) = 3.830$ kcal/mole;

KCl (c), $\displaystyle\int_0^{291.16} C_P\,d \ln T = 19.46$ cal/deg mole.

How is the equilibrium shifted with increase in temperature? Calculate the value of $\bar{\mathrm{S}}_2$ for KCl (aq, $m = 4.42$), at 18°C.

8. The following data are given for the range 18°C to 28°C:

KCl (c), $C_P = 12.10$ cal/deg mole;

KCl (aq, $m = 4.42$), $\bar{C}_{P_2} = 6.94$ cal/deg mole.

Utilizing data from the preceding problem, calculate the value of $\Delta F_{301.16}$ for the process KCl (c) = KCl (aq, $m = 4.42$).

9. For aqueous solutions of n-propanol, the *International Critical Tables* give the following data for the molality and the freezing point, in °C, respectively: 0, 0.000; 0.01, −0.0186; 0.05, −0.092; 0.10, −0.183; 0.60, −1.08; 1.00, −1.79; 1.50, −2.67; 2.00, −3.58; 3.00, −5.46; 4.00, −7.28; 5.00, −8.80; 6.00, −9.84; 7.00, −10.43; 8.00, −10.56. Calculate values of a_1 and a_2 for values of molality equal to 0.01, 0.10, 0.5, 1.0, 2.0, and 4.0.

10. For liquid solutions of bromine (component 2) in CCl_4 (carbon tetrachloride, component 1), at 25°C, Lewis and Storch found, for mole fractions of bromine up to $N_2 = 0.025$, the partial pressure of gaseous bromine over the solution to be, in atmospheres, 0.539 times the mole fraction of bromine in the liquid solution. Taking this as a dilute real solution, and the vapor pressure of pure liquid bromine to be 0.280 atm, and assuming the gaseous phase to be ideal, give an expression for a_2 over the range $N_2 = 0$ to $N_2 = 0.025$. What is the ratio $f_2{}^{\circ}/f_2{}^{*}$?

11. Lewis and Storch found that, when a very small amount of bromine is shaken up with carbon tetrachloride and water (slightly acidulated to prevent the hydrolysis of the bromine), the molality of the bromine in the aqueous phase is 0.371 times the mole fraction of bromine in the phase in which carbon tetrachloride is the solvent. Using the data of the preceding problem, give an expression for the fugacity and activity of the bromine as a function of its molality in the aqueous solution.

12. At 25°C, the solubility of carbon dioxide in water is 0.0338 molal when the partial pressure of gaseous carbon dioxide is 1 atm. Assuming the gas to be ideal and the solution to be a dilute real solution, calculate $\Delta F^{\circ}_{298.16}$ for the process CO_2 (g) = CO_2 (aq), naming the standard states used.

28

Equilibrium Constant and the Standard Change in Free Energy

1. Standard change in free energy. In studying the change in free energy accompanying any reaction or process, it is convenient to evaluate such a change with each reactant and product in its thermodynamic standard reference state. That is to say, for any reaction at any given temperature and pressure,

$$b\mathrm{B} + c\mathrm{C} = m\mathrm{M} + n\mathrm{N}, \tag{1}$$

the change in free energy for any given set of states of the reactants and products is

$$\Delta F = mF_{\mathrm{M}} + nF_{\mathrm{N}} - bF_{\mathrm{B}} - cF_{\mathrm{C}}, \tag{2}$$

and the standard change in free energy, with each reactant and product in its thermodynamic standard reference state, is

$$\Delta F^\circ = mF_{\mathrm{M}}^\circ + nF_{\mathrm{N}}^\circ - bF_{\mathrm{B}}^\circ - cF_{\mathrm{C}}^\circ. \tag{3}$$

The difference in the change in free energy for the given set of states and for the standard states is given by Equation 2 less Equation 3, or

$$\begin{aligned}\Delta F - \Delta F^\circ = m(F - F^\circ)_{\mathrm{M}} + n(F - F^\circ)_{\mathrm{N}} - b(F - F^\circ)_{\mathrm{B}} \\ - c(F - F^\circ)_{\mathrm{C}}.\end{aligned} \tag{4}$$

But, for any substance in any state,

$$F_i - F_i^\circ = RT \ln a_i, \tag{5}$$

where F_i and a_i refer to the same given state for substance i and F_i° refers to the standard state. Equation 4 then becomes

$$\Delta F - \Delta F^\circ = RT \ln \frac{(a_{\mathrm{M}})^m (a_{\mathrm{N}})^n}{(a_{\mathrm{B}})^b (a_{\mathrm{C}})^c}. \tag{6}$$

2. Definition of the proper quotient of activities and the equilibrium constant. The proper quotient of activities for any reaction such as that given by Equation 1 is defined as

$$Q_a = \frac{(a_{\mathrm{M}})^m (a_{\mathrm{N}})^n}{(a_{\mathrm{B}})^b (a_{\mathrm{C}})^c}. \tag{7}$$

That is, in the proper quotient of activities, the numerator is the product of the activity of each of the products of the reaction, each raised to a power equal to the number of moles of the given product, and the denominator is the corresponding product for the reactants of the reaction. The proper quotient of activities is thus identical with the fraction on the right side of Equation 6.

The equilibrium constant is defined as the proper quotient of activities when each reactant and product is in its equilibrium state for the given reaction, as

$$Q_a{}^e = K = \frac{(a_{\mathrm{M}}{}^e)^m (a_{\mathrm{N}}{}^e)^n}{(a_{\mathrm{B}}{}^e)^b (a_{\mathrm{C}}{}^e)^c}. \tag{8}$$

3. Relation between the standard change in free energy and the equilibrium constant. When the given reaction takes place with each reactant and product in its standard state, the change in free energy is the standard change in free energy, $\Delta F°$, and is equal to the value given by Equation 3. When the given reaction takes place with each reactant and product in its equilibrium concentration or pressure for the given conditions, then

$$\Delta F \text{ (equilibrium)} = \Delta F^e = mF_{\mathrm{M}}{}^e + nF_{\mathrm{N}}{}^e - bF_{\mathrm{B}}{}^e - cF_{\mathrm{C}}{}^e. \tag{9}$$

The difference in the change in free energy for the two sets of conditions, standard states and equilibrium states, is given by Equation 9 less Equation 3, or

$$\begin{aligned} \Delta F^e - \Delta F° = m(F^e - F°)_{\mathrm{M}} + n(F^e - F°)_{\mathrm{N}} - b(F^e - F°)_{\mathrm{B}} \\ - c(F^e - F°)_{\mathrm{C}}. \end{aligned} \tag{10}$$

Since, for any substance in its equilibrium state,

$$F_i^e - F_i^° = RT \ln a_i^e, \tag{11}$$

Equation 10 becomes

$$\Delta F^e - \Delta F° = RT \ln \frac{(a_{\mathrm{M}}{}^e)^m (a_{\mathrm{N}}{}^e)^n}{(a_{\mathrm{B}}{}^e)^b (a_{\mathrm{C}}{}^e)^c}. \tag{12}$$

But at constant temperature and pressure, the change in free energy at equilibrium is zero, so that

$$\Delta F^e = 0. \tag{13}$$

Substituting K for the proper quotient of activities at equilibrium, Equation 12 becomes

$$\Delta F^\circ = -RT \ln K. \tag{14}$$

Equation 14 is an important equation relating the standard change in free energy and the equilibrium constant.

4. Variation, with temperature, of the standard change in free energy and of the equilibrium constant. Differentiation of F/T at constant pressure gives

$$\frac{\mathrm{d}\left(\frac{F}{T}\right)}{\mathrm{d}T} = \frac{T\frac{\mathrm{d}F}{\mathrm{d}T} + F}{T^2}. \tag{15}$$

But, at constant pressure,

$$\frac{\mathrm{d}F}{\mathrm{d}T} = -S. \tag{16}$$

Therefore, at constant pressure,

$$\frac{\mathrm{d}\left(\frac{F}{T}\right)}{\mathrm{d}T} = \frac{-TS + F}{T^2} = -\frac{H}{T^2}. \tag{17}$$

Equation 17 holds for each reactant and product of the given reaction, so that for the reaction, at constant pressure,

$$\mathrm{d}\left(\frac{\Delta F}{T}\right) = -\frac{\Delta H}{T^2}\,\mathrm{d}T. \tag{18}$$

Applied to the reaction with each substance in its standard state, Equation 18 is written

$$\mathrm{d}\left(\frac{\Delta F^\circ}{T}\right) = -\frac{\Delta H^\circ}{T^2}\,\mathrm{d}T. \tag{19}$$

In an earlier chapter, we derived an expression for the change in heat content, ΔH, for a reaction, as a function of temperature. Indicating by means of the appropriate superscripts that this expression is to be applied to the reaction with each substance in its standard state, we have (Chapter 28)

$$\Delta H^\circ = \Delta H_*^\circ + (\Delta a)T + \tfrac{1}{2}(\Delta b)T^2 + \tfrac{1}{3}(\Delta c)T^3 + \cdots. \tag{20}$$

It is to be recalled that Equation 20 is valid only over the range of temperature for which the original expressions for heat capacity as a function of temperature were valid and that ΔH_*° is not the value of ΔH° at 0°K. When Equation 20 is substituted into Equation 19 and the latter is integrated, we obtain

$$\frac{\Delta F^\circ}{T} = \frac{\Delta H_*^\circ}{T} - (\Delta a)\ln T - \tfrac{1}{2}(\Delta b)T - \tfrac{1}{6}(\Delta c)T^2 + \cdots + I. \tag{21}$$

In Equation 21, I is the constant of integration. Equation 21 may also be written as

$$\Delta F^\circ = \Delta H_*^\circ - (\Delta a)T\ln T - \tfrac{1}{2}(\Delta b)T^2 - \tfrac{1}{6}(\Delta c)T^3 + \cdots + IT. \tag{22}$$

It is to be emphasized that, just as is the case for Equation 20, Equations 21 and 22 are valid only over the range of temperature for which the original expressions for the heat capacities of the reactants and products are valid. Furthermore, the constant of integration, I, must be evaluated from one value of ΔF° within the given range of temperature. If the change in heat content were by chance constant with temperature, the factors (Δa), (Δb), and (Δc) would be zero, and Equations 21 and 22 would reduce to

$$\Delta F^\circ = \Delta H^\circ + IT. \tag{23}$$

By comparison with the relation

$$\Delta F^\circ = \Delta H^\circ - T\,\Delta S^\circ, \tag{24}$$

it is seen that the constant of integration, I, has the nature of the negative of the standard change in entropy for the reaction.

The evaluation of the standard change in free energy by Equations 21 and 22 is subject to the disadvantage that, for a given set of constants, the range is limited and, further, the form of the equations may not be such as to reproduce the experimental observations at different temperatures within their limits of uncertainty.

A much more direct and more accurate way of evaluating $\Delta F°$ at different temperatures is by using the values of the free energy function of the reactants and products which may be available, tabulated at different temperatures. Values of $\Delta F°/T$ for a series of temperatures in the range of interest are calculated, and the value for any particular temperature may be obtained by suitable interpolation. The procedure is as follows:

For the given reaction, the value of $\Delta H_0°$ is obtained from the reference value of $\Delta H^\circ_{298.16}$ and the values of the heat content at 298.16°K, relative to 0°K, of each of the reactants and products, in accordance with Chapter 28:

$$\Delta H_0° = H^\circ_{298.16} - \Delta(H^\circ_{298.16} - H_0°). \tag{25}$$

But

$$\Delta\left(\frac{F° - H_0°}{T}\right) = \frac{\Delta F° - \Delta H_0°}{T} \tag{26}$$

or

$$\frac{\Delta F°}{T} = \frac{\Delta H_0°}{T} + \Delta\left(\frac{F° - H_0°}{T}\right). \tag{27}$$

That is to say, the value of $\Delta F°/T$ for the given reaction at the temperature T is equal to the change in heat content at 0°K, $\Delta H_0°$, divided by the temperature T, plus the increment, for the given reaction, of the free energy function, $\Delta(F° - H_0°)/T$. The last-named term is, of course,

$$\Delta\left(\frac{F° - H_0°}{T}\right) = \sum\left(\frac{F° - H_0°}{T}\right)\text{(products)} - \sum\left(\frac{F° - H_0°}{T}\right)\text{(reactants)}. \tag{28}$$

Since

$$\frac{\Delta F°}{T} = -R\ln K, \tag{29}$$

it follows that

$$\ln K = -\frac{1}{R}\left[\frac{\Delta H_0°}{T} + \Delta\left(\frac{F° - H_0°}{T}\right)\right]. \tag{30}$$

Substitution of $-R$ ln K in Equation 19 gives

$$\mathrm{d}\ln K = \frac{\Delta H°}{RT^2}\,\mathrm{d}T, \tag{31}$$

or

$$\frac{d \ln K}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H^\circ}{R}. \tag{32}$$

5. Equilibrium constant independent of pressure. It is important to note that, for any given temperature, the equilibrium constant is directly related to the standard change in free energy. Since, at any given temperature, the free energy in the standard state for each reactant and product, F_i°, is independent of the pressure, it follows that the standard change in free energy for the reaction, ΔF°, is independent of the pressure. Therefore, at constant temperature, the equilibrium constant K, as defined by Equation 8 and related to ΔF° by Equation 14, is also independent of the pressure. That is,

$$\left(\frac{\partial K}{\partial P}\right)_T = 0. \tag{33}$$

6. Effect of pressure on the concentrations of the components of a chemical reaction at equilibrium. The fact that, as shown above, the equilibrium constant does not change in value with pressure does not necessarily mean that the concentrations of the components of a chemical reaction at equilibrium remain constant as the pressure is increased.

Consider the following reaction at equilibrium at some temperature T, with each component being in the gaseous phase:

$$b\text{B (g)} + c\text{C (g)} = m\text{M (g)} + n\text{N (g)}. \tag{34}$$

In accordance with Equation 8, the equilibrium constant for this reaction is

$$K = \frac{(a_{\text{M}}{}^e)^m (a_{\text{N}}{}^e)^n}{(a_{\text{B}}{}^e)^b (a_{\text{C}}{}^e)^c}. \tag{35}$$

For gases, the activity is equal to the fugacity (Chapter 27), so that the equilibrium constant is

$$K = \frac{(f_{\text{M}}{}^e)^m (f_{\text{N}}{}^e)^n}{(f_{\text{B}}{}^e)^b (f_{\text{C}}{}^e)^c}. \tag{36}$$

The activity coefficient of each gas is defined as

$$\gamma_i = \frac{f_i}{P_i}, \tag{37}$$

and the partial pressure is

$$P_i = \mathrm{N}_i P, \tag{38}$$

where N_i is the mole fraction of the given component, and P is the total pressure.

Then

$$f_i = \gamma_i \mathrm{N}_i P. \tag{39}$$

Substituting Equation 39 into Equation 36 for each of the components, we obtain

$$K = \left[\frac{(\gamma_{\mathrm{M}}{}^e)^m(\gamma_{\mathrm{N}}{}^e)^n}{(\gamma_{\mathrm{B}}{}^e)^b(\gamma_{\mathrm{C}}{}^e)^c}\right]\left[\frac{(\mathrm{N}_{\mathrm{M}}{}^e)^m(\mathrm{N}_{\mathrm{N}}{}^e)^n}{(\mathrm{N}_{\mathrm{B}}{}^e)^b(\mathrm{N}_{\mathrm{C}}{}^e)^c}\right]P^{(m+n-b-c)}. \tag{40}$$

Letting $Q_\gamma{}^e$ and $Q_{\mathrm{N}}{}^e$ denote the proper quotient of activity coefficients (the first bracketed term) and the proper quotient of mole fractions (the second bracketed term), respectively, Equation 40 may be shortened to

$$K = Q_\gamma{}^e Q_{\mathrm{N}}{}^e P^{(m+n-b-c)}. \tag{41}$$

Written explicitly in terms of the proper quotient of mole fractions, Equation 41 becomes

$$Q_{\mathrm{N}}{}^e = K\left(\frac{1}{Q_\gamma{}^e}\right)P^{-(m+n-b-c)}. \tag{42}$$

Equation 42 shows that the proper quotient of mole fractions at equilibrium is equal to the equilibrium constant, K, multiplied by the reciprocal of the proper quotient of the activity coefficients at equilibrium, multiplied by the total pressure raised to the power $-(m + n - b - c)$. The quantity $-(m + n - b - c)$ represents the decrease in the stoichiometrical number of moles of gaseous components for reaction 34 as written.

When the gases involved in the reaction are ideal, the activity coefficient is unity for each gas, so that

$$Q_\gamma{}^e = 1, \tag{43}$$

$$K = Q_{\mathrm{N}}{}^e P^{(m+n-b-c)}, \tag{44}$$

and

$$Q_{\mathrm{N}}{}^e = KP^{-(m+n-b-c)}. \tag{45}$$

Equation 45 shows that, for the reaction of ideal gases, the proper quotient of mole fractions at equilibrium is independent of the pressure only when

$$m + n = b + c. \tag{46}$$

When the quantity $-(m + n - b - c)$ differs from zero, the proper quotient of mole fractions at equilibrium will vary with the total pressure raised to the power $-(m + n - b - c)$.

It is to be noted that the introduction of an inert gas into the system will have no effect on the foregoing relations, except to change the activity coefficients a little in the case of non-ideal gases, provided the partial pressure of the inert gas is not included in the value of the total pressure P. That is, the total pressure P given above must be counted as the sum of the partial pressures of the gaseous components participating in the given reaction.

If the number of moles of gaseous products is less than the number of moles of gaseous reactants, then $-(m + n - b - c)$ is positive, the proper quotient of mole fractions will increase with the pressure, and the mole fractions of the products will increase at the expense of the mole fractions of the reactants. That is, with increase in pressure, the equilibrium is shifted in favor of the products. Conversely, if the number of moles of gaseous products is greater than the number of moles of gaseous reactants, the equilibrium is shifted in favor of the reactants with increase in pressure. For real gases, the effect of pressure on the concentrations of the components of a chemical reaction at equilibrium will also include the change of the activity coefficient with pressure, as indicated in Equation 42. This effect may be very large. For example, in the equilibrium involving the synthesis of ammonia at 450°C according to the reaction,

$$\tfrac{1}{2}N_2\ (g) + \tfrac{3}{2}H_2\ (g) = NH_3\ (g), \tag{47}$$

the proper quotient of activity coefficients at equilibrium changes by a factor of 4 in going from a total pressure of 10 atmospheres to a total pressure of 1000 atmospheres.

7. Equilibrium in a chemical reaction at constant volume. It is occasionally necessary to make calculations of the equilibrium concentrations of the components of a chemical reaction at equilibrium in a vessel at constant volume.

In lieu of the pressures, there will be known the volume of the space available to the gaseous components and the number of moles of the substances at the beginning. Suppose that the temperature is high enough and the volume is large enough, in relation to the number of moles of gaseous reacting substances, for the gases to be assumed ideal. Usually, in such problems, the concentration is given in moles per liter, as c_i. Consider the reaction given by Equation 34, for which the equilibrium constant is given by Equation 36, in terms of fugacities. Since the gases are assumed ideal, the equilibrium constant is the proper quotient of pressures at equilibrium,

$$K = \frac{(P_{\mathrm{M}}{}^e)^m (P_{\mathrm{N}}{}^e)^n}{(P_{\mathrm{B}}{}^e)^b (P_{\mathrm{C}}{}^e)^c} = Q_P{}^e. \tag{48}$$

But, for ideal gases, the concentration in moles per liter is related to the pressure by the following relations, where n_i is the number of moles of component i, and V is the volume of the space available to the gaseous components:

$$c_i = \frac{n_i}{V}, \tag{49}$$

$$P_i = n_i \frac{RT}{V} = c_i RT. \tag{50}$$

Substituting into Equation 48 gives*

$$K = \left[\frac{(c_{\mathrm{M}}{}^e)^m (c_{\mathrm{N}}{}^e)^n}{(c_{\mathrm{B}}{}^e)^b (c_{\mathrm{C}}{}^e)^c}\right] (RT)^{(m+n-b-c)}. \tag{51}$$

Defining the proper quotient of concentrations in the usual manner, Equation 51 becomes

$$K = Q_c{}^e (RT)^{(m+n-b-c)}, \tag{52}$$

or

$$Q_c{}^e = K(RT)^{-(m+n-b-c)}. \tag{53}$$

Equation 53 permits the evaluation, for a reaction involving gases assumed ideal, of the proper quotient of concentrations at equilibrium from the value of the equilibrium constant and the stoichiometrical change in the number of moles of gaseous components between reactants and products. If the stoichiometrical

---

* Equation 51 has c representing two different quantities, namely, concentration and the stoichiometrical number of moles of component C. Since this duplication is transient and not ambiguous, it is preferred to the introduction of a new symbol.

number of moles of gaseous products is the same as the number of moles of gaseous reactants, that is,

$$m + n = b - c, \tag{54}$$

then

$$Q_c{}^e = K. \tag{55}$$

It is important to note that with the concentration in liters, and the equilibrium constant K defined in terms of atmospheres, the value of R in Equations 52 and 53 must be given in liter-atmospheres per degree mole.

REFERENCE

1. G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill Book Company, New York, 1923.

PROBLEMS

1. A mixture of 1 mole of CO_2 (g) and 1 mole of H_2 (g) is permitted to come to equilibrium at 25°C and a final total pressure of 0.1 atm, in the reaction

$$CO_2\ (g) + H_2\ (g) = CO\ (g) + H_2O\ (g).$$

Analysis of the equilibrium mixture shows the presence of 0.0032 mole of CO (g). Assuming the gases to be ideal, calculate the value of $\Delta F^\circ_{298.16}$ and $K_{298.16}$ for the given reaction.

2. Given the reaction

$$\tfrac{1}{2}N_2\ (g) + \tfrac{1}{2}O_2\ (g) = NO\ (g).$$

Assume $\Delta H^\circ_{300} = 21.6$ kcal/mole, $\Delta S^\circ_{300} = 3.0$ cal/deg mole, and $\Delta C_P{}^\circ = 0$ over the range 300° to 4000°K. Derive the equation for ΔF° as a function of T for the given range of temperature.

3. At equilibrium at 1000°K, the concentrations of M_2 (g) and M (g) are 0.10 and 0.20 mole/liter, respectively. Assuming the gases to be ideal, calculate ΔF°_{1000} and K_{1000} for the reaction

$$M_2\ (g) = 2M\ (g).$$

4. For the reaction

$$Ag_2O\ (c) = 2Ag\ (c) + \tfrac{1}{2}O_2\ (g),$$

take $\Delta H^\circ_{300} = 6.94$ kcal/mole and $\Delta C_P{}^\circ = -1.0$ cal/deg mole, over the range 300° to 600°K. At 600°K, it is found that the pressure of gaseous oxygen in equilibrium with solid silver and silver oxide is 33.9 atmospheres. Assuming the gas phase to be ideal, calculate the value of ΔF°_{300} and K_{300} for the given reaction.

5. Over the range 800°K to 1500°K,

$$\frac{\Delta F^\circ}{T} = \frac{34{,}300}{T} - 2.6 \ln T + 0.0005T - 5.44,$$

for the reaction X_2 (g) = 2X (g). Taking 1 mole of X_2 (g) and permitting it to come to equilibrium at 1000°K in accordance with the given reaction, and assuming the gas phase to be ideal, calculate the mole fractions of X_2 (g) and X (g) present at equilibrium at 1000°K, when the total pressure is (*a*) 1 atm and (*b*) 0.001 atm.

6. At 1000°K, equilibrium exists for the reaction

$$\mathrm{CO\ (g) + H_2O\ (g) = CO_2\ (g) + H_2\ (g)},$$

in the gaseous phase when the respective partial pressures of the components, as written, are 0.2275, 0.21, 0.3125, 0.21 atm. Assuming the gaseous phase to be ideal, calculate the value of ΔF°_{1000} and K_{1000} for the given reaction.

7. Lewis and Randall (*1*) give for the reaction

$$\mathrm{SO_2\ (g) + \tfrac{1}{2}O_2\ (g) = SO_3\ (g)},$$

$\Delta F^\circ = -22{,}600 + 21.36T$, over the range 800° to 1200°K. One mole of SO_3 (g) is placed in a closed bomb having a volume of 50 liters, and is permitted to come to equilibrium at 1000°K in accordance with the given reaction. Assuming the gases to be ideal, calculate the mole fractions of SO_2, O_2, and SO_3 in the equilibrium mixture.

8. At 25°C and a pressure of 1 atm, the vapor pressure of water is 23.76 mm Hg. Calculate the value of $\Delta F^\circ_{298.16}$ for the reaction

$$\mathrm{H_2O\ (liq) = H_2O\ (g)},$$

assuming the gaseous phase to be ideal.

9. For H_2 (g) and H (g), the values of the free energy function at 3000°K are, respectively, −40.719 and −33.894 cal/deg mole. For the reaction

$$\mathrm{H_2\ (g) = 2H\ (g)},$$

$\Delta H_0{}^\circ = 103.240$ kcal/mole. If 1 mole of H_2 (g) is introduced into a vessel at 3000°K and permitted to come to equilibrium with respect to H (g), at a total pressure of 1 atm, calculate the mole fraction of H (g) at equilibrium.

10. For gaseous cyclohexane and gaseous methylcyclopentane, the following data are given, respectively:

$$\Delta Hf^\circ_{298.16},\ -29.43,\ -25.50,\ \text{kcal/mole};$$

$$H^\circ_{298.16} - H_0{}^\circ,\ 4.237,\ 4.774,\ \text{kcal/mole};$$

$$\left[\frac{F^\circ - H_0{}^\circ}{T}\right]_{298.16},\ -57.07,\ -65.23,\ \text{cal/deg mole};$$

$$\left[\frac{F_0{}^\circ - H_0{}^\circ}{T}\right]_{600},\ -70.96,\ -80.07,\ \text{cal/deg mole}.$$

Assuming the gases ideal, calculate the relative amounts of gaseous cyclohexane and gaseous methylcyclopentane in equilibrium with one another through the reaction of isomerization at 298.16°K and at 600°K.

11. For gaseous methane and hydrogen and solid carbon (graphite), respectively, the following data are given:

$S^\circ_{298.16}$, 44.50, 31.211, 1.361, cal/deg mole;
$\Delta Hf^\circ_{298.16}$, −17.889, 0, 0, kcal/mole;
$\left[\frac{F^\circ - H_0{}^\circ}{T}\right]_{1500}$, −52.84, −35.590, −4.181, cal/deg mole;
$H^\circ_{298.16} - H_0{}^\circ$, 2.397, 2.0238, 0.2516, kcal/mole.

Calculate the value of $\Delta F^\circ_{298.16}$ and ΔF°_{1500}. Assuming ideal gases, calculate the partial pressure of H_2 (g) present at equilibrium with CH_4 (g) and C (c, graphite) at 1500°K, if the partial pressure of methane is 1 atm.

12. The following data are given:

H_2O (g), $\Delta Hf^\circ_{298.16} = -57.7979$ kcal/mole, $S^\circ_{298.16} = 45.106$ cal/deg mole;
HCl (g), $\Delta Hf^\circ_{298.16} = -22.063$ kcal/mole, $S^\circ_{298.16} = 44.617$ cal/deg mole;
Cl_2 (g), $S^\circ_{298.16} = 53.286$ cal/deg mole;
O_2 (g), $S^\circ_{298.16} = 49.003$ cal/deg mole.

Calculate $\Delta F^\circ_{298.16}$ and $K_{298.16}$ for the reaction, H_2O (g) + Cl_2 (g) = 2HCl (g) + $\frac{1}{2}O_2$ (g). The values of the free energy function, $(F^\circ - H_0{}^\circ)/T$, at 298.16° and 1000°K, respectively, are as follows, in calories per degree mole:

H_2O (g), −37.165, −47.010; Cl_2 (g), −45.928, −55.426;
HCl (g), −37.692, −46.127; O_2 (g), −42.061, −50.697.

Calculate the value of ΔF°_{1000}, K_{1000}, and $\Delta H_0{}^\circ$ for the given reaction.

13. For a solution of aqueous hydrogen chloride at 25°C, the partial pressure of HCl (g) in equilibrium with a 4 molal solution is 2.7×10^{-5} atm. If for HCl (aq) in this solution, $a_\pm = 7.36$, calculate $\Delta F^\circ_{298.16}$ for the process

$$\text{HCl (g)} = \text{HCl (aq)}.$$

29

Electromotive Force and Free Energy; Galvanic Cells and Standard Electrode Potentials

1. Galvanic cell. As regards thermodynamics, the galvanic cell is a system in which a chemical reaction or process is utilized to generate an electric current. Every change which occurs in the system as a result of the occurrence of the reaction or process is subject to the same scrutiny of thermodynamics as other reactions; that is, the change in energy and entropy, the heat energy evolved or absorbed, and the useful energy produced or consumed by the system must conform to the laws of thermodynamics. For the present purposes, it is desirable to limit our study to those galvanic cells in which a known chemical reaction occurs, and to those which may be operated reversibly.

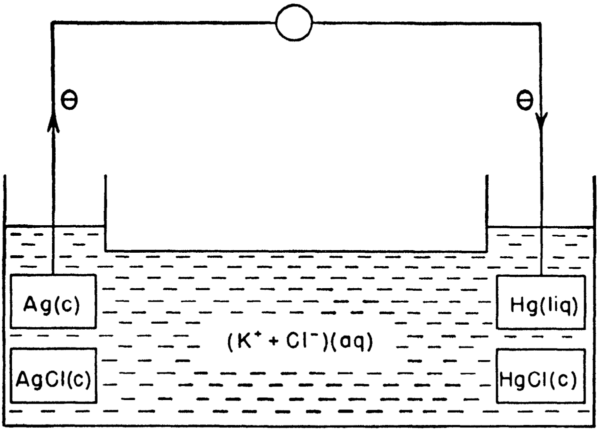


FIGURE 1. Schematic diagram of a galvanic cell for the reaction: Ag (c) + HgCl (c) = AgCl (c) + Hg (liq).

Figure 1 is a schematic diagram of a galvanic cell in which occurs the following reaction:

$$\mathrm{Ag\ (c) + HgCl\ (c) = AgCl\ (c) + Hg\ (liq).} \tag{1}$$

In accordance with the convention used by Lewis and Randall (*1*), the movement of electrons, θ, is indicated as from left to right in the external circuit and right to left in the cell, or in a clockwise direction for the complete circuit when the external path is drawn above the internal path as in Figure 1. On this basis, the reaction at the left electrode may be written as

$$\mathrm{Ag\ (c) + Cl^-\ (aq) = AgCl\ (c)} + \theta, \tag{2}$$

and that at the right electrode as

$$\mathrm{HgCl\ (c)} + \theta = \mathrm{Hg\ (liq) + Cl^-\ (aq).} \tag{3}$$

The sum of the two single electrode reactions is the complete reaction as in Equation 1.

The convention regarding the sign, positive or negative, of the electromotive force is that the value of the electromotive force represents the tendency for the reaction to proceed with the electrons moving clockwise in the system as drawn, left to right in the external circuit above and right to left through the solution below. That is, the electromotive force measures the tendency for that reaction to take place which evolves electrons at the left electrode and consumes electrons at the right electrode.

Unless it is possible to specify the reaction or process occurring in the galvanic cell with the same accuracy with which the thermodynamic properties can be evaluated, it is obvious that the thermodynamic study of the galvanic cell will have little use beyond the particular "unknown" system. In the specification of the reaction, it is important that the thermodynamic state of each of the substances involved be known with reference to the accepted standard state for that substance.

In order to be useful thermodynamically, the galvanic cell must be reversible and its electromotive force must be constant and reproducible. The latter two requirements are checked easily by observation. The galvanic cell is considered reversible when, with a very small current flowing, change in the direction of flow of the current produces a corresponding reversal in the direction of the reaction, with no significant change in the electromotive force of the cell.

It is important to note that, when the galvanic cell operates reversibly, the reaction or process that occurs is also proceeding reversibly, so that the reaction or process has the same thermodynamic characteristics as the reversible processes previously discussed.

2. Relation between electromotive force and free energy. Consider the galvanic cell shown in Figure 1 and the corresponding reaction given by Equation 1, at constant temperature and pressure. An electric motor is placed in the external circuit so that any useful energy produced by the given process may be measured. The following relation holds for the given system, represented by the galvanic cell:

$$\mathrm{d}E = \delta q + \delta w + \delta u. \tag{4}$$

Since the process is operating reversibly,

$$\delta q = T\,\mathrm{d}S, \tag{5}$$

$$\delta w = -P\,\mathrm{d}V, \tag{6}$$

and the useful energy absorbed by the system is the negative of the electrical work done by the electric motor on the surroundings,

$$\delta u = -\delta\text{ (electrical work)}. \tag{7}$$

For the passage of n moles of electrons, corresponding to the occurrence of one mole of the given reaction as written, the foregoing relations become, at constant temperature and pressure,

$$\Delta E = T\,\Delta S - P\,\Delta V - n\mathfrak{F}\mathfrak{E}. \tag{8}$$

Here $n\mathfrak{F}\mathfrak{E}$ is the electrical work performed by the electric motor on the surroundings, being measured as the quantity of electricity, $n\mathfrak{F}$, which is the number of moles of electrons, n, multiplied by quantity of electricity represented by one mole of electrons, $\mathfrak{F}$, into the difference in potential through which the quantity of electricity is taken, which is the electromotive force, $\mathfrak{E}$.

But, at constant temperature and pressure,

$$\Delta F = \Delta E + P\,\Delta V - T\,\Delta S, \tag{9}$$

so that, finally, per mole of reaction,

$$\Delta F = -n\mathfrak{F}\mathfrak{E}. \tag{10}$$

That is to say, with the galvanic cell operating reversibly at constant temperature and pressure, the electromotive force, $\mathcal{E}$, multiplied by the quantity of electricity per mole of reaction, $n\mathfrak{F}$, is equal to the decrease in the free energy for the system, per mole of reaction. If each of the substances participating in the given process is in its thermodynamic standard reference state, Equation 10 becomes

$$\Delta F^\circ = -n\mathfrak{F}\mathcal{E}^\circ. \tag{11}$$

3. Variation of electromotive force with pressure and temperature. At constant temperature, the change of the electromotive force of a cell with pressure may be derived from the relation,

$$\left(\frac{\partial F}{\partial P}\right)_T = V. \tag{12}$$

For an entire reaction or process, we can write, at constant temperature,

$$\frac{\mathrm{d}(\Delta F)}{\mathrm{d}P} = \Delta V, \tag{13}$$

or, substituting from Equation 10,

$$\frac{\mathrm{d}\mathcal{E}}{\mathrm{d}P} = -\frac{\Delta V}{n\mathfrak{F}}. \tag{14}$$

If, for the given reaction, ΔV may be taken as constant from a pressure P_A to a pressure P_B, then the difference in electromotive force of the cell at the two pressures, at constant temperature, is

$$\mathcal{E}_{P_B} - \mathcal{E}_{P_A} = -\frac{\Delta V(P_B - P_A)}{n\mathfrak{F}}. \tag{15}$$

Similarly, at constant pressure, the change of the electromotive force of a cell with temperature may be obtained from the relation,

$$\left(\frac{\partial F}{\partial T}\right)_P = -S. \tag{16}$$

For an entire reaction, we can write, at constant pressure,

$$\frac{\mathrm{d}(\Delta F)}{\mathrm{d}T} = -\Delta S, \tag{17}$$

or, from Equation 10,

$$\frac{d\mathfrak{E}}{dT} = \frac{\Delta S}{n\mathfrak{F}}. \tag{18}$$

But

$$\Delta F = \Delta H - T\,\Delta S. \tag{19}$$

Appropriate combination of the foregoing equations gives, for constant pressure,

$$\Delta H = -n\mathfrak{F}\left(\mathfrak{E} - T\frac{d\mathfrak{E}}{dT}\right), \tag{20}$$

with

$$\Delta S = n\mathfrak{F}\frac{d\mathfrak{E}}{dT}. \tag{21}$$

From the foregoing it is seen that the electromotive force of the cell, together with its temperature coefficient, permits calculation of ΔF, ΔH, and ΔS for the reaction occurring in the galvanic cell.

4. Electromotive force and activity. For any given reaction, as

$$b\mathrm{B} + c\mathrm{C} = m\mathrm{M} + n\mathrm{N}, \tag{22}$$

we have seen (Chapter 28) that, if the reaction is performed under two sets of conditions, one of which has each substance in its standard state, we can write

$$\Delta F - \Delta F^\circ = RT \ln \frac{(a_\mathrm{M})^m (a_\mathrm{N})^n}{(a_\mathrm{B})^b (a_\mathrm{C})^c}. \tag{23}$$

Substituting from Equations 10 and 11, we have

$$\mathfrak{E} - \mathfrak{E}^\circ = \frac{RT}{n\mathfrak{F}} \ln \frac{(a_\mathrm{M})^m (a_\mathrm{N})^n}{(a_\mathrm{B})^b (a_\mathrm{C})^c}. \tag{24}$$

Equation 24 is an important relation from which one may obtain significant information from measurements of the electromotive force, $\mathfrak{E}$, of a cell, for various combinations of activity of the components of the reaction. If the measurement of the electromotive force can be made with each substance at or approaching its standard state, then

$$\mathfrak{E} = \mathfrak{E}^\circ, \tag{25}$$

because the proper quotient of activities will be unity and its logarithm zero. Once $\mathfrak{E}^\circ$ is evaluated, measurement of $\mathfrak{E}$ for other conditions serves to evaluate the proper quotient of activities for these other conditions.

5. Electromotive force and the equilibrium constant. The standard electromotive force for a given cell reaction is related to the equilibrium constant for that reaction at the same temperature, as follows:

$$\Delta F^\circ = -RT \ln K = -n\mathcal{F}\mathcal{E}^\circ. \tag{26}$$

Therefore, we may write

$$\ln K = \frac{n\mathcal{F}}{RT}\,\mathcal{E}^\circ, \tag{27}$$

or

$$\mathcal{E}^\circ = \frac{RT}{n\mathcal{F}} \ln K. \tag{28}$$

The foregoing relations permit evaluation of $\mathcal{E}^\circ$ when K is known or of K when $\mathcal{E}^\circ$ is known, for any given cell reaction.

6. Standard single electrode potentials. For convenience in thermodynamic calculations, it is helpful to divide the complete reaction in a galvanic cell into the two half reactions occurring at the electrodes, and to assign to each single electrode reaction its appropriate portion of the value of the electromotive force of the cell. In order to do this, a value of zero electromotive force is assigned to the single electrode reaction involving gaseous hydrogen and aqueous hydrogen ion, as follows:

$$\tfrac{1}{2}H_2\ (g) = H^+\ (aq) + \theta; \qquad \mathcal{E}^\circ = 0. \tag{29}$$

The value of the standard potential is determined for the reaction

$$\tfrac{1}{2}H_2\ (g) + AgCl\ (c) = HCl\ (aq) + Ag\ (c); \qquad \mathcal{E}^\circ = a. \tag{30}$$

The single electrode reactions constituting this reaction are

$$\tfrac{1}{2}H_2\ (g) = H^+\ (aq) + \theta, \tag{31}$$

and

$$AgCl\ (c) + \theta = Cl^-\ (aq) + Ag\ (c). \tag{32}$$

Subtraction of Equations 30 and 29 then gives Equation 32, for which the value of the standard potential is $\mathcal{E}^\circ = a$.

Then $\mathcal{E}^\circ$ is evaluated for another complete reaction of which one of the half reactions is given by Equations 31 and 32. This produces a value of $\mathcal{E}^\circ$ for a new half reaction. Proceeding in this way, the value of $\mathcal{E}^\circ$ for each new complete reaction can be made to yield a value of $\mathcal{E}^\circ$ for a new half reaction. Thus, a complete tabulation of values of standard single electrode potentials can be compiled.

It is important to note that electrode potentials may be evaluated for reactions that can not actually be carried out in a galvanic cell, by calculating the value of $\mathcal{E}^\circ$ from the value of ΔF° determined in other ways. In this manner, single electrode potentials may be obtained for many half reactions that are not components of any real galvanic cell.

With regard to combination of half reactions and the evaluation of the corresponding potential, the following points are to be noted:

Whenever two half reactions with given single electrode potentials are added or subtracted to give a complete reaction, the algebraic addition or subtraction of the single potentials gives the electromotive force for the complete reaction. For example, consider the two half reactions,

$$\text{Ag (c)} + \text{Cl}^- \text{(aq)} = \text{AgCl (c)} + \theta; \qquad \mathcal{E}^\circ = b; \tag{33}$$

$$\text{Hg (liq)} + \text{Cl}^- \text{(aq)} = \text{HgCl (c)} + \theta; \qquad \mathcal{E}^\circ = c. \tag{34}$$

Subtraction of Equation 34 from Equation 33 gives

$$\text{Ag (c)} + \text{HgCl (c)} = \text{AgCl (c)} + \text{Hg (liq)}; \qquad \mathcal{E}^\circ = b - c. \tag{35}$$

But when two half reactions with given single electrode potentials are added or subtracted to give a third half reaction, the potential of the third half reaction must be derived by the addition or subtraction of the corresponding values of free energy. For example, consider the two half reactions,

$$\text{Fe (c)} = \text{Fe}^{++} \text{(aq)} + 2\theta; \qquad \mathcal{E}^\circ = d; \ \Delta F^\circ = -2\mathfrak{F}d; \tag{36}$$

$$\text{Fe}^{++} \text{(aq)} = \text{Fe}^{+++} \text{(aq)} + \theta; \qquad \mathcal{E}^\circ = e; \ \Delta F^\circ = -\mathfrak{F}e. \tag{37}$$

Addition of Equations 36 and 37 gives

$$\text{Fe (c)} = \text{Fe}^{+++} \text{(aq)} + 3\theta; \qquad \Delta F^\circ = -\mathfrak{F}(2d + e), \tag{38}$$

whence the standard potential for Equation 38 becomes

$$\mathcal{E}^\circ = \frac{-\Delta F^\circ}{n\mathfrak{F}} = \frac{\mathfrak{F}(2d + e)}{3\mathfrak{F}} = \frac{(2d + e)}{3}. \tag{39}$$

7. Collateral reading. For detailed discussions of the topics covered in this chapter, the reader is referred to the following: Lewis and Randall (*1*), Latimer (*2*), Dole (*3*), MacInnes (*4*), Harned and Owen (*5*), and Glasstone (*6*).

REFERENCES

1. G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill Book Company, New York, 1923.

2. W. M. Latimer, *The Oxidation States of the Elements and Their Potentials in Aqueous Solution*, Prentice-Hall, New York, 1938.

3. M. Dole, *Principles of Experimental and Theoretical Electrochemistry*, McGraw-Hill Book Company, New York, 1935.

4. D. A. MacInnes, *The Principles of Electrochemistry*, Reinhold Publishing Corporation, New York, 1935.

5. H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold Publishing Corporation, New York, 1943.

6. S. Glasstone, *An Introduction to Electrochemistry*, D. Van Nostrand Company, New York, 1942.

PROBLEMS

1. A galvanic cell has one electrode of platinum with hydrogen at a partial pressure of 0.9 atm, another electrode of mercury with solid mercurous chloride, and an aqueous electrolyte over which the pressure of gaseous hydrogen chloride is 0.01 atm. The electromotive force of this cell is 0.0110 volt at 25°C. Assuming the gases to be ideal and the cell reaction to be

$$\tfrac{1}{2}H_2\ (g) + HgCl\ (c) = Hg\ (liq) + HCl\ (g),$$

calculate the value of ΔF, $\mathcal{E}^\circ$, and ΔF° for the given reaction.

2. MX is a salt in which M and X each have a valence of one. The following thermodynamic data are available:

$$MX\ (c),\ \Delta Hf^\circ_{298.16} = a\ \text{kcal/mole},\ H^\circ_{298.16} - H_0^\circ = b\ \text{kcal/mole},$$

$$\left[\frac{F^\circ - H_0^\circ}{T}\right]_{500} = c\ \text{cal/deg mole};$$

$$M\ (c),\ H^\circ_{298.16} - H_0^\circ = d\ \text{kcal/mole},\ \left[\frac{F^\circ - H_0^\circ}{T}\right]_{500} = e\ \text{cal/deg mole};$$

$$X\ (c),\ H^\circ_{298.16} - H_0^\circ = f\ \text{kcal/mole},\ \left[\frac{F^\circ - H_0^\circ}{T}\right]_{500} = g\ \text{cal/deg mole}.$$

Calculate the standard electromotive force of a galvanic cell in which occurs, at 500°K, the reaction:

$$M\ (c) + X\ (c) = MX\ (c).$$

3. For the galvanic cell in which the reaction is

$$Ag\ (c) + HgCl\ (c) = AgCl\ (c) + Hg\ (liq),$$

it is found that

$$\mathcal{E}_{298.16} = 0.0455 \text{ volt, and } \frac{d\mathcal{E}^\circ}{dT} = 0.000338 \text{ volt/deg.}$$

Calculate the values of ΔF°, ΔS°, and ΔH°, at 25°C, for the given reaction.

4. For the galvanic cell in which the reaction is

$$\text{Ag (c)} + \tfrac{1}{2}\text{Cl}_2 \text{ (g)} = \text{AgCl (c)},$$

Gerke found that

$$\mathcal{E}^\circ_{298.16} = 1.1360 \text{ volts, and } \frac{d\mathcal{E}^\circ}{dT} = -0.000595 \text{ volt/deg.}$$

For the given reaction, calculate ΔF°, ΔS°, and ΔH°, at 25°C.

5. From the data of the two preceding problems, calculate the standard electromotive force at 25°C of the galvanic cell in which the following reaction occurs:

$$\text{Hg (liq)} + \tfrac{1}{2}\text{Cl}_2 \text{ (g)} = \text{HgCl (c)}.$$

6. Given the following two half reactions:

$$\text{Cu (c)} = \text{Cu}^+ \text{ (aq)} + \theta; \qquad \mathcal{E}^\circ = a;$$

$$\text{Cu}^+ \text{ (aq)} = \text{Cu}^{++} \text{ (aq)} + \theta; \qquad \mathcal{E}^\circ = b.$$

Evaluate $\mathcal{E}^\circ$ for the half reaction,

$$\text{Cu (c)} = \text{Cu}^{++} \text{ (aq)} + 2\theta.$$

7. Given the following two half reactions:

$$\text{Fe (c)} = \text{Fe}^{++} \text{ (aq)} + 2\theta; \qquad \mathcal{E}^\circ = d;$$

$$\text{Fe}^{++} \text{ (aq)} = \text{Fe}^{+++} \text{ (aq)} + \theta; \qquad \mathcal{E}^\circ = e.$$

Evaluate $\mathcal{E}^\circ$ for the reaction,

$$\text{Fe (c)} + 2\text{Fe}^{+++} \text{ (aq)} = 3\text{Fe}^{++} \text{ (aq)}.$$

8. From the data of the preceding problems, evaluate $\mathcal{E}^\circ$ for the reaction

$$\text{Cu}^+ \text{ (aq)} + \text{Fe}^{+++} \text{ (aq)} = \text{Cu}^{++} \text{ (aq)} + \text{Fe}^{++} \text{ (aq)}.$$

9. Given the following data:

$$\text{H}_2 \text{ (g)} + \tfrac{1}{2}\text{O}_2 \text{ (g)} = \text{H}_2\text{O (liq)}; \qquad \Delta F^\circ_{298.16} = -56.6899 \text{ kcal/mole};$$

$$\tfrac{1}{2}\text{H}_2 \text{ (g)} = \text{H}^+ \text{ (aq)} + \theta; \qquad \mathcal{E}^\circ_{298.16} = 0.$$

Calculate the value of the standard single electrode potential for the half reaction,

$$\text{H}_2\text{O (liq)} = \tfrac{1}{2}\text{O}_2 \text{ (g)} + 2\text{H}^+ \text{ (aq)} + 2\theta.$$

10. Given, for the reaction, at 1 atm,

$$\text{Ag (c)} + \text{HCl (aq)} = \text{AgCl (c)} + \tfrac{1}{2}\text{H}_2 \text{ (g)}; \qquad \Delta F^\circ_{298.16} = 5.126 \text{ kcal/mole.}$$

Calculate the electromotive force of the cell in which the foregoing reaction takes place when the partial pressure of the hydrogen gas is 0.65 atm and the aqueous solution of HCl is 1.0 molal. Assume the gaseous phase ideal and take for HCl (aq), at 1.0 molal, $\gamma_\pm = 0.809$.

11. Given the following half reactions:

$$\text{Cr (c)} = \text{Cr}^{+++}\text{ (aq)} + 3\theta; \qquad \mathcal{E}^\circ = a;$$

$$\text{Cr (c)} = \text{Cr}^{++}\text{ (aq)} + 2\theta; \qquad \mathcal{E}^\circ = b.$$

Evaluate $\mathcal{E}^\circ$ for the half reaction,

$$\text{Cr}^{++}\text{ (aq)} = \text{Cr}^{+++}\text{ (aq)} + \theta.$$

30

Thermodynamic Properties of Aqueous Ions of Strong Electrolytes

1. General statement. The value of a given property of an electrolyte at infinite dilution in aqueous solution is the sum of the values of the corresponding property for the several ions comprising the given electrolyte. Experimental measurements serve to give the value of a given property for one mole of a strong electrolyte, as MX, or $M^+ + X^-$. By selecting an arbitrary value of the given property for one of the ions, as M^+, the value for the other ion, X^-, is fixed. Experimental values for another strong electrolyte, as MY, or $M^+ + Y^-$, serves to give the value of the property for the ion Y^-. If, then, experimental data are obtained on the strong electrolyte, NY or $N^+ + Y^-$, there is obtained a value for the ion N^+. Now experimental data need not be obtained for the strong electrolyte, NX, or $N^+ + X^-$, since the value for it may be calculated from the values already obtained separately for N^+ and X^-.

By such a procedure, data obtained on one strong electrolyte actually serve to yield values for a number of other strong electrolytes without experimental measurements on them. Further, it is possible in this way to calculate values for certain electrolytes that could not actually be subjected to experimental measurement.

2. Conventions as to reference states. In order to conform to the convention already established in the preceding chapter with regard to standard single electrode potentials, it is desirable to select the hydrogen ion to have arbitrary values for its thermodynamic properties in aqueous solutions of strong electrolytes. Usually, it is convenient to let the arbitrary value of each of the thermodynamic properties of H^+ (aq) be zero in its thermodynamic standard state. The selection of zero as the arbitrary value for the standard single electrode potential for the hydrogen electrode gives zero as the standard free energy of formation of the aqueous hydrogen ion:

$$\tfrac{1}{2}H_2\ (g) = H^+\ (aq); \qquad \mathcal{E}^\circ = 0; \qquad \Delta F^\circ = 0. \tag{1}$$

It is also to be noted that the convention adopted in Chapter 27 for the relation between the activity of a strong electrolyte and of its ions at infinite dilution in water, namely,

$$a_2 = a_+a_-, \tag{2}$$

actually leads to

$$\mathrm{F}_2^\circ = \mathrm{F}_+^\circ + \mathrm{F}_-^\circ, \tag{3}$$

because

$$MX\ (aq) = M^+\ (aq) + X^-\ (aq); \quad K = \frac{a_+a_-}{a_2} = 1, \tag{4}$$

and, therefore,

$$\Delta F^\circ = \mathrm{F}_+^\circ + \mathrm{F}_-^\circ - \mathrm{F}_2^\circ = -RT \ln K = 0, \tag{5}$$

so that Equation 3 holds.

In the case of the strong electrolyte MX in aqueous solution, for example,

$$\mathrm{F}^\circ\,[MX\ (aq)] = \mathrm{F}^\circ\,[M^+\ (aq)] + \mathrm{F}^\circ\,[X^-\ (aq)]. \tag{6}$$

For the thermodynamic standard state in aqueous solution, we have selected (Chapter 27) the hypothetical one molal solution, which has all the properties of the same solution at infinite dilution except the property of concentration. That is, all properties that are not primarily a function of concentration, such as volume, heat content, and heat capacity, are ones for which the values for the real solute at infinite dilution are the values for the given solute in its thermodynamic standard state. That is, for a strong electrolyte at infinite dilution in aqueous solution,

$$\bar{V}_2^0 = \bar{V}_2^\circ; \quad \bar{H}_2^0 = \bar{H}_2^\circ; \quad \bar{C}_{P_2}^0 = \bar{C}_{P_2}^\circ. \tag{7}$$

Values of the foregoing properties for ions of strong electrolytes at infinite dilution in water are additive, irrespective of the strong electrolyte from which the ions originate. If values of $\bar{H}_2^0$ are additive, it follows that values of $\bar{H}_2^\circ$ are additive, and similarly for the volume and heat capacity. That is, the values of these properties are additive for aqueous ions of strong electrolytes in their thermodynamic standard states, so that we may write

$$\bar{\mathrm{V}}_2{}^\circ = \bar{\mathrm{V}}_+{}^\circ + \bar{\mathrm{V}}_-{}^\circ, \tag{8}$$

$$\bar{\mathrm{H}}_2{}^\circ = \bar{\mathrm{H}}_+{}^\circ + \bar{\mathrm{H}}_-{}^\circ, \tag{9}$$

and

$$\bar{\mathrm{C}}_{P_2}{}^\circ = \bar{\mathrm{C}}_{P+}{}^\circ + \bar{\mathrm{C}}_{P-}{}^\circ. \tag{10}$$

Since the values of $\mathrm{F}_i{}^\circ$ and $\bar{\mathrm{H}}_i{}^\circ$ for aqueous ions of strong electrolytes are additive, it follows that values of the partial molal entropy in the standard state are also additive for the same ions.

For convenience, the compilations are usually made for a selected temperature, such as 25°C.

3. Standard heat of formation. The evaluation of standard heats of formation for aqueous ions of strong electrolytes may be illustrated by the case of HCl (aq) (*2*).

Data are obtained for the heat of reaction of gaseous chlorine with gaseous hydrogen to form gaseous hydrogen chloride, and a value is calculated for the reaction with each substance in its standard state:

$$\tfrac{1}{2}\mathrm{H}_2\ (\mathrm{g}) + \tfrac{1}{2}\mathrm{Cl}_2\ (\mathrm{g}) = \mathrm{HCl}\ (\mathrm{g}); \tag{11}$$

$$\Delta H^\circ_{298.16} = -22.063\ \mathrm{kcal/mole}. \tag{12}$$

Data are obtained on the heat of solution of gaseous hydrogen chloride in water to form a given solution of aqueous hydrogen chloride, with the value being corrected, if necessary, to give the gaseous hydrogen chloride in its standard state:

$$\mathrm{HCl}\ (\mathrm{g}) = \mathrm{HCl}\ (\mathrm{aq},\ m = 0.2775); \tag{13}$$

$$[\Phi\mathrm{H}_2\ (m = 0.2775) - \mathrm{H}_2\ (\mathrm{g})]_{298.16} = -17.735\ \mathrm{kcal/mole} \tag{14}$$

Data are obtained on the heat of dilution of aqueous hydrogen chloride from $m = 0.2775$ to $m = 0$:

$$\mathrm{HCl}\ (\mathrm{aq},\ m = 0.2775) = \mathrm{HCl}\ (\mathrm{aq},\ m = 0); \tag{15}$$

$$[\Phi\mathrm{H}_2\ (m = 0) - \Phi\mathrm{H}_2\ (m = 0.2775)]_{298\ 16} = -0.225\ \mathrm{kcal/mole}. \tag{16}$$

Noting that

$$\Phi\mathrm{H}_2\ (m = 0) = \Phi\mathrm{H}_2{}^0 = \bar{\mathrm{H}}_2{}^0 = \bar{\mathrm{H}}_2{}^\circ, \tag{17}$$

we may write Equation 16 as

$$[\bar{H}_2^\circ - \Phi H_2\ (m = 0.2775)]_{298.16} = -0.225 \text{ kcal/mole.} \qquad (18)$$

Appropriately combining Equations 11, 12, 13, 14, 15, and 18, and noting that

$$\begin{aligned} \text{HCl (aq, } m = 0) &= \text{HCl (aq, std. hyp. } m = 1) \\ &= (\text{H}^+ + \text{Cl}^-)(\text{aq, std. hyp. } m = 1), \end{aligned} \qquad (19)$$

we obtain

$$\tfrac{1}{2}H_2\ (g) + \tfrac{1}{2}Cl_2\ (g) = (H^+ + Cl^-)(\text{aq, std. hyp. } m = 1); \qquad (20)$$

$$\Delta H^\circ_{298.16} = -40.023 \text{ kcal/mole.} \qquad (21)$$

But, by our convention, we have

$$\tfrac{1}{2}H_2\ (g) = H^+\ (aq); \qquad (22)$$

$$\Delta H^\circ_{298.16} = 0. \qquad (23)$$

Therefore, we may write,

$$\tfrac{1}{2}Cl_2\ (g) = Cl^-\ (aq); \qquad (24)$$

$$\Delta H^\circ_{298.16} = -40.023 \text{ kcal/mole.} \qquad (25)$$

Similarly, data on the following experimentally determinable reactions yield a value for the standard heat of formation of aqueous hydroxyl ion, OH^- (aq):

$$\begin{aligned} &(HCl\cdot 100H_2O)(liq) + (NaOH\cdot 100H_2O)(liq) \\ &\qquad = (NaCl\cdot 201H_2O)(liq); \end{aligned} \qquad (26)$$

$$\begin{aligned} &(HCl\cdot 100H_2O)(liq) + (\infty - 100)H_2O\ (liq) \\ &\qquad = (HCl\cdot \infty H_2O)(liq); \end{aligned} \qquad (27)$$

$$\begin{aligned} &(NaOH\cdot 100H_2O)(liq) + (\infty - 100)H_2O\ (liq) \\ &\qquad = (NaOH\cdot \infty H_2O)(liq); \end{aligned} \qquad (28)$$

$$\begin{aligned} &(NaCl\cdot 201H_2O)(liq) + (\infty - 201)H_2O\ (liq) \\ &\qquad = (NaCl\cdot \infty H_2O)(liq). \end{aligned} \qquad (29)$$

Appropriate combination of the foregoing equations yields

$$\begin{aligned} &(HCl\cdot \infty H_2O)(liq) + (NaOH\cdot \infty H_2O)(liq) \\ &\qquad = (NaCl\cdot \infty H_2O)(liq) + H_2O\ (liq); \end{aligned} \qquad (30)$$

or

$$\mathrm{HCl\ (aq,}\ m = 0) + \mathrm{NaOH\ (aq,}\ m = 0) \\ = \mathrm{NaCl\ (aq,}\ m = 0) + \mathrm{H_2O\ (liq)}; \qquad (31)$$

or

$$\mathrm{H^+\ (aq,}\ m = 0) + \mathrm{OH^-\ (aq,}\ m = 0) = \mathrm{H_2O\ (liq)}; \qquad (32)$$

or

$$\mathrm{H^+\ (aq,\ std.\ hyp.}\ m = 1) + \mathrm{OH^-\ (aq,\ std.\ hyp.}\ m = 1) \\ = \mathrm{H_2O\ (liq)}. \qquad (33)$$

Combination of this with the reaction

$$\mathrm{H_2\ (g)} + \tfrac{1}{2}\mathrm{O_2\ (g)} = \mathrm{H_2O\ (liq)}, \qquad (34)$$

gives

$$\mathrm{H_2\ (g)} + \tfrac{1}{2}\mathrm{O_2\ (g)} = \mathrm{OH^-\ (aq,\ std.\ hyp.}\ m = 1) \\ + \mathrm{H^+\ (aq,\ std.\ hyp.}\ m = 1). \qquad (35)$$

Combination with Equation 22 yields, finally, the standard heat of formation of aqueous hydroxyl ion:

$$\tfrac{1}{2}\mathrm{H_2\ (g)} + \tfrac{1}{2}\mathrm{O_2\ (g)} = \mathrm{OH^-\ (aq)}; \qquad \Delta H^\circ_{298.16}. \qquad (36)$$

In a similar way, data on the following reaction may be used with some of the foregoing reactions to obtain a value for the standard heat of formation of aqueous sodium ion:

$$\mathrm{Na\ (c)} + 101\mathrm{H_2O\ (liq)} = (\mathrm{NaOH\cdot 100H_2O})\mathrm{(liq)} + \tfrac{1}{2}\mathrm{H_2\ (g)}. \qquad (37)$$

Then, without any further measurements, the value for the standard heat of formation of aqueous sodium chloride is known, from the sum of the values for $\mathrm{Na^+}$ (aq) and $\mathrm{Cl^-}$ (aq).

In the foregoing manner, a complete table can be assembled of values of the standard heat of formation of aqueous ions of strong electrolytes.

4. Standard free energy of formation. From the values of the standard single electrode potentials discussed in the preceding chapter, values of the standard free energy of formation for many aqueous ions of strong electrolytes may be obtained directly from the relation:

$$\Delta F^\circ = -n\mathcal{F}\mathcal{E}^\circ. \qquad (38)$$

Since for

$$\tfrac{1}{2}\mathrm{H_2\ (g)} = \mathrm{H^+\ (aq)}; \qquad \Delta F^\circ = 0, \qquad (39)$$

the value of the standard free energy of formation of HCl (aq) gives immediately the value for

$$\tfrac{1}{2}Cl_2\ (g) = Cl^-\ (aq); \qquad \Delta F^\circ. \tag{40}$$

Similarly one can proceed as before and assemble a complete table of values of the standard free energy of formation for aqueous ions of strong electrolytes.

5. Standard entropy. For the standard heat of formation and the standard free energy of formation, the reference values were taken as zero for the process of forming aqueous hydrogen ion in its standard state from gaseous hydrogen in its standard state. In the case of the standard entropy, however, the reference state has been taken (*1*) as the aqueous hydrogen ion itself, in its standard state, as

$$H^+\ (aq); \qquad S^\circ = 0. \tag{41}$$

With this convention, values of S° for HCl (aq) would give the value for Cl^- (aq). And, similarly, values for the ions constituting other strong electrolytes may be obtained by appropriate combination of pairs, as was done for the standard heat of formation and the standard free energy of formation.

Whenever values are known for both the standard heat of formation and the standard free energy of formation for the sum of the ions constituting any given strong electrolyte in aqueous solution, the value of the standard entropy for the same ions may be calculated, utilizing the relation:

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta F^\circ}{T}. \tag{42}$$

The procedure may be illustrated as follows: Given the following data for 25°C:

$$\tfrac{1}{2}H_2\ (g) + \tfrac{1}{2}Cl_2\ (g) = HCl\ (aq); \tag{43}$$

$$\Delta H^\circ = -40.023\ \text{kcal/mole}; \tag{44}$$

$$\Delta F^\circ = -31.350\ \text{kcal/mole}. \tag{45}$$

Then, for the process given by Equation 43,

$$\begin{aligned}\Delta S^\circ &= S^\circ[HCl\ (aq)] - \tfrac{1}{2}S^\circ[H_2\ (g)] - \tfrac{1}{2}S^\circ[Cl_2\ (g)]\\ &= \frac{\Delta H^\circ - \Delta F^\circ}{T} = -29.088\ \text{cal/deg mole}.\end{aligned} \tag{46}$$

Taking, at 25°C,

$$S°[H_2\ (g)] = 31.211 \text{ cal/deg mole,} \tag{47}$$

and

$$S°[Cl_2\ (g)] = 53.286 \text{ cal/deg mole,} \tag{48}$$

we obtain

$$S°[HCl\ (aq)] = \frac{1}{2} S°[H_2(g)] + \frac{1}{2} S°[Cl_2\ (g)] + \frac{\Delta H° - \Delta F°}{T}$$

$$= 15.606 + 26.643 - 29.088 = 13.16 \text{ cal/deg mole.} \tag{49}$$

But

$$S°[HCl\ (aq)] = S°[H^+\ (aq)] + S°[Cl^-\ (aq)], \tag{50}$$

and

$$S°[H^+\ (aq)] = 0, \tag{51}$$

so that

$$S°[Cl^-(aq)] = 13.16 \text{ cal/deg mole.} \tag{52}$$

In the foregoing calculations, it must be noted that Equation 42 may not be applied to a half reaction but to the complete reaction, involving both positive and negative ions. Application of Equation 42 directly to the process

$$\tfrac{1}{2}Cl_2\ (g) = Cl^-\ (aq), \tag{53}$$

with the values of $\Delta H°$ and $\Delta F°$ taken as the conventional ones, would lead to a value for the standard entropy of aqueous chloride ion in error by one-half the standard molal entropy of gaseous hydrogen. The reason is the fact that, for the process,

$$\tfrac{1}{2}H_2\ (g) = H^+\ (aq), \tag{54}$$

the values for the standard change in heat content and standard change in free energy were taken as zero, but the value for the standard change in entropy was not taken as zero. That is, for Equation 54, by this convention,

$$\Delta H° = 0; \quad \Delta F° = 0; \quad \Delta S° \neq 0. \tag{55}$$

If the convention is followed that $\Delta S°$ should also be zero for Equation 54, then Equation 42 could be applied to both half reactions and complete reactions, and the value for the standard entropy of aqueous hydrogen ion would be, not zero, but the same as the standard entropy of one-half mole of gaseous hydrogen, or 15.606 cal/deg mole. Actually, it would appear to be simpler to follow this latter procedure and have symmetrical conventions regarding the heat of formation, free energy of formation, and entropy of formation of aqueous ions, in which case, for Equation 54,

$$\Delta H^\circ = 0; \quad \Delta F^\circ = 0; \quad \Delta S^\circ = 0. \tag{56}$$

No confusion need result in making calculations on this newer basis, provided that proper conversion is made of the values of the entropies of aqueous ions previously computed on the basis of the older convention that the standard entropy of aqueous hydrogen ion is zero.

In accordance with Equations 42 to 52, values may be calculated in the foregoing way for the standard entropy of all aqueous ions of strong electrolytes for which are known the values of both the standard heat of formation and the standard free energy of formation.

However, it frequently happens that for many ions there will be available either the standard heat of formation or the free energy of formation, but not both. In many such cases, it is possible to determine the standard entropy of the aqueous ions independently. Then the combination of the value of ΔS° with the value of ΔH° will yield the missing value of ΔF°:

$$\Delta F^\circ = \Delta H^\circ - T\,\Delta S^\circ. \tag{57}$$

And, in the other case, the combination of the value of ΔS° with the value of ΔF° will yield the missing value of ΔH°:

$$\Delta H^\circ = \Delta F^\circ + T\,\Delta S^\circ. \tag{58}$$

Where experimental values are available independently for all three quantities, ΔF°, ΔH°, and ΔS°, the values must conform to Equation 57.

Following is illustrated the procedure for determining the standard entropy of aqueous ions of strong electrolytes independently of the standard heat of formation and the standard free energy of formation of the given ions:

Given the following data at 25°C: From statistical calculations,

$$\text{HCl (g)}; \quad S^\circ = 44.617 \text{ cal/deg mole.} \tag{59}$$

For the process,

$$\text{HCl (g)} = \text{HCl (aq)}, \tag{60}$$

calorimetric data yield the value for the standard change in heat content, at 25°C,

$$\Delta H^\circ = -17.960 \text{ kcal/mole.} \tag{61}$$

Measurements of the partial pressure of gaseous hydrogen chloride over its aqueous solution at various concentrations serve to evaluate the activity of aqueous hydrogen chloride, and, hence, with the corresponding values of the partial pressure, assuming the gaseous phase to be ideal, give the equilibrium constant for the process given by Equation 60,

$$K = \frac{a[\text{HCl (aq)}]}{a[\text{HCl (g)}]} = \frac{a_2}{P_{\text{HCl}}}, \tag{62}$$

and hence the value of the standard change in free energy from the relation

$$\Delta F^\circ = -RT \ln K = -RT \ln \frac{a_2}{P_{\text{HCl}}} \cdot \tag{63}$$

With values of both ΔH° and ΔF° known for the process given by Equation 60, the value of ΔS° may be calculated from the relation

$$\Delta S^\circ = S^\circ[\text{HCl (aq)}] - S^\circ[\text{HCl (g)}] = \frac{\Delta H^\circ - \Delta F^\circ}{T} \cdot \tag{64}$$

Therefore, we have

$$S^\circ[\text{HCl (aq)}] = S^\circ[\text{HCl (g)}] + \Delta S^\circ. \tag{65}$$

In a similar way, the following experimental data would serve to yield a value for the standard entropy of aqueous sodium chloride.

Measurements of the heat capacity down to low temperatures yield the value of the standard entropy of solid sodium chloride, at 25°C, in accordance with the third law:

$$\text{NaCl (c)};\ S^\circ = \int_0^{298.16} \frac{\delta q}{T} = \int_0^{298.16} C_P \, d \ln T. \tag{66}$$

For the process,

$$\text{NaCl (c)} = \text{NaCl (aq)}, \tag{67}$$

calorimetric data at 25°C yield a value for the standard change in heat content, evaluated as the heat of solution of solid sodium chloride to infinite dilution:

$$\Delta H^\circ = a \text{ kcal/mole.} \tag{68}$$

It is found that NaCl (c) is in equilibrium with NaCl (aq, m = 6.14) at 25°C,

$$\text{NaCl (c)} = \text{NaCl (aq, } m = 6.14\text{),} \tag{69}$$

for which

$$\Delta F = 0, \tag{70}$$

and

$$K = \frac{a[\text{NaCl (aq, } m = 6.14)]}{a[\text{NaCl (c)}]}. \tag{71}$$

Since

$$a[\text{NaCl (c)}] = 1, \tag{72}$$

$$K = a[\text{NaCl (aq, } m = 6.14)]. \tag{73}$$

Therefore, for the process given by Equation 67,

$$\Delta F^\circ = -RT \ln K = -RT \ln a[\text{NaCl (aq, } m = 6.14)]. \tag{74}$$

The activity of sodium chloride in aqueous solution of molality 6.14 at 25°C is evaluated by one of the regular methods, lowering of the freezing point, lowering of the vapor pressure of the water, osmotic pressure, etc. Then the value of ΔF° is known. With values for both ΔF° and ΔH° known, the value of ΔS° for the process given by Equation 67 is calculated, and

$$S^\circ[\text{NaCl (aq)}] = S^\circ[\text{NaCl (c)}] + \Delta S^\circ. \tag{75}$$

It is to be noted that the foregoing two examples involve evaluation of the entropy of a given pure substance, gas, liquid, or solid, at 25°C, and then evaluation of the entropy of solution to the hypothetical one molal solution.

To obtain a value for the standard entropy of aqueous hydroxyl ion, all that is needed is to make appropriate experimental observation on a reaction or series of reactions leading to a value for the dissociation constant of water or the standard change in free energy for the process

$$H_2O \text{ (liq)} = H^+ \text{ (aq)} + OH^- \text{ (aq).} \tag{76}$$

For equation 76,

$$K = a[\mathrm{H}^+ \text{ (aq)}] \cdot a[\mathrm{OH}^- \text{ (aq)}], \tag{77}$$

and

$$\Delta F^\circ = -RT \ln K. \tag{78}$$

From Equation 33, a value is known for the standard change in heat content for Equation 76, so that, for the dissociation of water,

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta F^\circ}{T}. \tag{79}$$

Hence, since

$$S^\circ[\mathrm{H}^+ \text{ (aq)}] = 0, \tag{80}$$

$$S^\circ[\mathrm{OH}^- \text{ (aq)}] = S^\circ[\mathrm{H_2O} \text{ (liq)}] + \Delta S^\circ. \tag{81}$$

6. Illustrative problem. The usefulness of the concepts discussed in this and preceding chapters may be illustrated in a simple way by the following problem:

Given the following information:

$$\text{Na (c)},\ S^\circ_{298.16} = 12.2 \text{ cal/deg mole}; \tag{82}$$

$$\text{NaF (c)},\ S^\circ_{298.16} = 13.1 \text{ cal/deg mole}; \tag{83}$$

$$\mathrm{F_2} \text{ (g)},\ S^\circ_{298.16} = 48.6 \text{ cal/deg mole}; \tag{84}$$

$$\text{NaF (c)} = \text{NaF (aq)};$$

$$\Delta H^\circ_{298.16} = 0.19 \text{ kcal/mole}; \tag{85}$$

$$\text{Na (c)} + \tfrac{1}{2}\mathrm{F_2} \text{ (g)} = \text{NaF (aq)};$$

$$\Delta H^\circ_{298.16} = -136.14 \text{ kcal/mole}; \tag{86}$$

$$\text{NaF (c)} = \text{NaF (aq, } m = 1); \quad \Delta F_{298.16} = 0; \tag{87}$$

$$\text{NaF (aq, } m = 1); \quad \gamma_\pm (\text{at } 298.16^\circ\text{K}) = 0.60; \tag{88}$$

$$\text{Na (c)} = \mathrm{Na}^+ \text{ (aq)} + \theta; \quad \mathcal{E}^\circ = 2.713 \text{ volts}. \tag{89}$$

From the foregoing information, we desire to calculate the standard single electrode potential for $\frac{1}{2}\mathrm{F_2}$ (g), F^- (aq):

$$\tfrac{1}{2}\mathrm{F_2} \text{ (g)} = \mathrm{F}^- \text{ (aq)}; \quad \mathcal{E}^\circ = ? \tag{90}$$

For the process

$$\text{NaF (c)} = \text{NaF (aq)}, \tag{91}$$

we can calculate ΔF° by the relation

$$\begin{aligned}\Delta F^\circ_{298.16} &= -RT\ln K = -RT\ln a_2 = -RT\ln (a_\pm)^2\\ &= -RT\ln(\gamma_\pm m)^2 = -RT\ln(0.60)^2\\ &= +0.605\text{ kcal/mole.}\end{aligned} \tag{92}$$

But for reaction 91 the value of ΔH° is given by Equation 85. Therefore, we may calculate the value of ΔS° for reaction 91 by means of the relation

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta F^\circ}{T}, \tag{93}$$

where the values of ΔH° and ΔF° are given by Equations 85 and 92. Hence

$$\text{NaF (c)} = \text{NaF (aq)};\quad \Delta S^\circ = -1.39\text{ cal/deg mole.} \tag{94}$$

Hence, since S° for NaF (c) is known,

$$\text{NaF (aq)};\quad S^\circ_{298.16} = 11.7\text{ cal/deg mole.} \tag{95}$$

For the reaction given in Equation 86, the value of ΔF° is obtained from the relation

$$\Delta F^\circ = \Delta H^\circ - T\,\Delta S^\circ, \tag{96}$$

where ΔH° is given in Equation 86, and

$$\begin{aligned}\Delta S^\circ &= S^\circ[\text{NaF (aq)}] - S^\circ[\text{Na (c)}] - \tfrac{1}{2}S^\circ[\text{F}_2\text{ (g)}]\\ &= -\,24.8\text{ cal/deg mole.}\end{aligned} \tag{97}$$

Therefore,

$$\begin{aligned}&\text{Na (c)} + \tfrac{1}{2}\text{F}_2\text{ (g)} = \text{NaF (aq)};\\ &\qquad \Delta F^\circ_{298.16} = -128.75\text{ kcal/mole;}\\ &\qquad\qquad \mathcal{E}^\circ = 5.581\text{ volts.}\end{aligned} \tag{98}$$

Appropriate combination of Equations 89 and 98 gives

$$\tfrac{1}{2}\text{F}_2\text{ (g)} = \text{F}^-\text{ (aq)} + \theta;\quad \mathcal{E}^\circ = 2.87\text{ volts,} \tag{99}$$

which is the desired result.

7. Collateral reading. For further details concerning the thermodynamic properties of aqueous ions of strong electrolytes, the reader is referred to Latimer (*1*).

REFERENCES

1. W. M. Latimer, *The Oxidation States of the Elements and Their Potentials in Aqueous Solution*, Prentice-Hall, New York, 1938.

2. F. D. Rossini, *J. Research Natl. Bur. Standards* **9**, 679 (1932).

PROBLEMS

1. Outline a series of reactions or processes and the appropriate measurements needed to evaluate the standard free energy of formation, and the corresponding standard single electrode potential, for

$$\text{Mg (c)} = \text{Mg}^{++}\ \text{(aq)} + 2\theta.$$

2. Latimer gives the following data at 25°C: solubility of sodium chloride in water, 6.14 molal; for NaCl (aq, $m = 6.14$), $\gamma_\pm = 1.013$;

$$\text{NaCl (c)} = \text{NaCl (aq, } m = 0\text{)},\ \Delta H = 0.905\ \text{kcal/mole;}$$

$$\text{NaCl (c)},\ \int_0^{298.16} C_p d \ln T = 17.30\ \text{cal/deg mole.}$$

Calculate the standard entropy of NaCl (aq).

3. Latimer reports that, at 25°C, the solubility of sodium nitrate is 10.83 molal, the activity coefficient of the solute in this solution is $\gamma_\pm = 0.355$, and the value of $\int_0^{298.16} \delta q/T$ for $NaNO_3$ (c) is 27.87 cal/deg mole. If for

$$NaNO_3\ \text{(c)} = NaNO_3\ \text{(aq)},$$

$\Delta H°$ at 25°C is 4.844 kcal/mole, calculate the standard entropy of $NaNO_3$ (aq). Using the value given in the text for HCl (aq) and the data of the preceding problem, calculate the standard entropy of HNO_3 (aq).

4. Give a series of reactions or processes, and the appropriate measurements, that may be used to evaluate the standard free energy of formation of Al^{+++} (aq).

5. Given the following values of the standard entropies at 25°C, in calories per degree mole: HCl (aq), 13.16; H_2 (g), 31.211; Cl_2 (g), 53.286. Calculate the temperature coefficient of the electromotive force of the cell in which the following reaction occurs, with each substance in its standard state:

$$\tfrac{1}{2}H_2\ \text{(g)} + \tfrac{1}{2}Cl_2\ \text{(g)} = \text{HCl (aq).}$$

6. Given values of the standard free energy of formation at 25°C for MX (c), M^+ (aq), and X^- (aq). If the solubility of MX in water at 25°C is known, show how one may evaluate the activity coefficient of MX (aq) in the saturated solution.

7. Values of $S^\circ_{298.16}$, in calories per degree mole, are: HCl (g), 44.617; Cl^- (aq), 13.16. For HCl (g) = HCl (aq, $m = 0$), $\Delta H = -17.960$ kcal/mole at 25°C. The activity coefficient of HCl in a 3 molal aqueous solution is $\gamma_\pm = 1.32$. Calculate the partial pressure of gaseous hydrogen chloride in equilibrium with its 3 molal aqueous solution.

31

Thermodynamic Application of the Debye-Hückel Theory of Strong Electrolytes in Dilute Solution

1. Theory. From the standpoint of chemical thermodynamics, the development of the Debye-Hückel theory of strong electrolytes in dilute solution was an important advance because the theory provided an improved and reliable method of extrapolating to infinite dilution the thermodynamic properties of these solutions. As we have seen, our selection of the hypothetical one molal solution as the thermodynamic standard state for aqueous solutions necessitates extrapolation of the properties of the real solution to infinite dilution to evaluate the properties of the solute in the standard state. For the purposes of this text, the Debye-Hückel theory of strong electrolytes in very dilute solution is summarized in its simplest form, as follows (*1,2*):

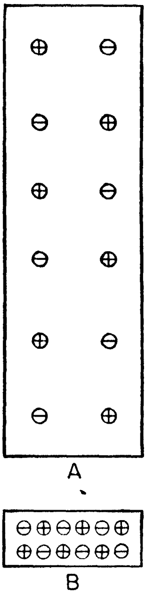


Figure 1. Schematic representation of ions of a strong electrolyte at infinite dilution, *A*, and at a finite concentration, *B*.

Consider the ions comprising a given electrolyte, first at infinite dilution and second at some finite molality, *m*. In Figure 1, *A* represents the ions at infinite dilution with the distances between the ions so great that they have no influence upon one another, and *B* represents the ions at some finite molality *m*, with the distances between the ions such that the interionic effects are significant. The fact which makes the strong electrolyte depart from the simple law of the ideal solution (Chapter 25) as the concentration is increased from infinite dilution to a finite value is the existence of the charge on each ion and the interaction between the charges as the ions approach one another with increasing concentration.

The problem is solved by calculating the contribution to the change in the partial molal free energy of one mole of the ions arising from the presence of the charges on the ions as the concentration is increased, as from A to B in Figure 1. This contribution may be evaluated by going from state A to state B in three steps, as follows: (1) Discharging the ions at infinite dilution in state A; (2) compressing the uncharged ions from infinite dilution at state A to the given molality at state B; and (3) charging the ions at the given molality in state B. The second step is calculated simply from the laws of the ideal solution. The contribution to the change in the partial molal free energy arising from the existence of the charges on the ions is equal to the sum of the work in the first and third steps, W_A, of discharging the ions at infinite dilution, and W_B, of charging the ions at the given molality, m.

In the infinitely dilute solution, the potential, Ψ_{i_A}, at the surface of each ion is equal to the number, z_i, of unit charges, e, on the ion, divided by the product of the radius, r, of the ion, and the dielectric constant, D, of the solvent:

$$\Psi_{i_A} = \frac{z_i e}{rD}. \tag{1}$$

In the solution of finite concentration, Debye and Hückel calculated the potential at the surface of each ion to be

$$\Psi_{i_B} = \Psi_{i_A} + \Psi_{i_{\text{elec}}}, \tag{2}$$

where Ψ_{i_A} is the same as the potential at infinite dilution, as given by Equation 1, and $\Psi_{i_{\text{elec}}}$ is the added potential due to the ionic atmosphere and has the value,

$$\Psi_{i_{\text{elec}}} = -\frac{z_i e \kappa}{D}, \tag{3}$$

where

$$\kappa = 2e\left(\frac{\pi}{DkT}\right)^{1/2} (\sum n_i z_i^2)^{1/2}. \tag{4}$$

In Equation 4, which is the heart of the Debye-Hückel theory in dilute solution, k is the Boltzmann constant, T is the absolute temperature, and n_i is the number of ions of the kind i per cubic centimeter.

The work of discharging one mole of ions of the kind i at infinite dilution is equal to one-half the product of the potential and the charge for each ion multiplied by the Avogadro constant:

$$W_A = -N\left(\frac{z_i e}{rD}\right)\left(\frac{z_i e}{2}\right) = -N\frac{z_i^2 e^2}{2rD}. \tag{5}$$

This work of discharging the ions at infinite dilution is, per mole, both the total electrical work or the partial molal electrical work, since at infinite dilution the two quantities are identical, in the same way that a given apparent molal property and the corresponding partial molal property are identical at infinite dilution.

At the finite concentration, we will consider the given one mole of ions to be surrounded by an extremely large amount of the same solution, so that the work of charging one mole of ions of the kind i at this concentration may be taken as the partial molal electrical work. This work, as before, is given by the product of the potential and the charge, so that the electrical work of charging one mole of ions of the kind i at the finite concentration is

$$W_B = N\frac{z_i^2 e^2}{2rD} - N\frac{z_i^2 e^2 \kappa}{2D}. \tag{6}$$

Then the algebraic sum of the work of discharging the ions at infinite dilution and of charging them at the finite concentration is given by

$$W_A + W_B = -\frac{N(z_i e)^2 \kappa}{2D}. \tag{7}$$

Now we may write the partial molal free energy of one mole of ions of the kind i, referred to the partial molal free energy in the standard state, as equal to the sum of two terms, one the ideal part, and the other the electrical part:

$$\mathrm{F}_i - \mathrm{F}_i^\circ = (\mathrm{F}_i - \mathrm{F}_i^\circ)_{\text{ideal}} + (\mathrm{F}_i - \mathrm{F}_i^\circ)_{\text{elec}}. \tag{8}$$

But

$$(\mathrm{F}_i - \mathrm{F}_i^\circ)_{\text{ideal}} = RT \ln m_i, \tag{9}$$

and

$$(\mathrm{F}_i - \mathrm{F}_i^\circ)_{\text{elec}} = -\frac{N(z_i e)^2 \kappa}{2D}. \tag{10}$$

For one mole of the ions constituting a given electrolyte, the relation corresponding to Equation 8 is

$$F_2 - F_2^\circ = (F_2 - F_2^\circ)_{\text{ideal}} + (F_2 - F_2^\circ)_{\text{elec}}. \tag{11}$$

Now,

$$(F_2 - F_2^\circ)_{\text{ideal}} = RT \ln m, \tag{12}$$

and

$$(F_2 - F_2^\circ)_{\text{elec}} = \nu_+(F_+ - F_+^\circ)_{\text{elec}} + \nu(F_- - F_-^\circ)_{\text{elec}}. \tag{13}$$

Substitution of Equation 10 into Equation 13 yields

$$(F_2 - F_2^\circ)_{\text{elec}} = -\frac{Ne^2\kappa}{2D}(\nu_+ z_+^2 + \nu z_-^2), \tag{14}$$

or

$$(F_2 - F_2^\circ)_{\text{elec}} = -\frac{Ne^2\kappa}{2D}(\sum \nu_i z_i^2). \tag{15}$$

The value of κ from Equation 4 may be rewritten in terms of the molarity, c_i, in moles per liter, utilizing the relation

$$n_i = \frac{Nc_i}{1000}. \tag{16}$$

Then

$$\sum n_i z_i^2 = \frac{N}{1000}\sum c_i z_i^2. \tag{17}$$

But

$$\sum c_i z_i^2 = (\sum \nu_i z_i^2)c. \tag{18}$$

But, in the limit of the very dilute solution,

$$c = \frac{mM_1}{V_1}, \tag{19}$$

where M_1 and V_1 represent the molecular weight and molal volume of the solvent, respectively, and we can pass to the molality, m. Hence, in Equation 4,

$$\sum n_i z_i^2 = \frac{N}{1000}(\sum \nu_i z_i^2)m\frac{M_1}{V_1}, \tag{20}$$

and

$$\kappa = (2e)\left(\frac{\pi N}{1000k}\right)^{1/2}(D^{-1/2}T^{-1/2})\left(\frac{M_1}{V_1}\right)^{1/2}(\sum \nu_i z_i^2)^{1/2}m^{1/2}. \tag{21}$$

Combination of Equations 15 and 21 gives

$$(\bar{F}_2 - \bar{F}_2^{\circ})_{\text{elec}} = -N^{3/2}e^3\left(\frac{\pi}{1000k}\right)^{1/2}(D^{-3/2}T^{-1/2})\left(\frac{M_1}{V_1}\right)^{1/2}(\sum\nu_i z_i^2)^{3/2}m^{1/2}, \quad (22)$$

or

$$(\bar{F}_2 - \bar{F}_2^{\circ})_{\text{elec}} = -AM_1^{1/2}(D^{-3/2}T^{-1/2}V_1^{-1/2})(\sum\nu_i z_i^2)^{3/2}m^{1/2}, \quad (23)$$

where, in cgs units,

$$A = \left(\frac{N^3e^6\pi}{1000k}\right)^{1/2} = 2.4697 \times 10^{14}. \quad (24)$$

2. Thermodynamic relations. From Chapter 27, we write

$$\bar{F}_2 - \bar{F}_2^{\circ} = RT\ln a_2 = RT\ln(a_{\pm})^{\nu} = RT\ln(\gamma_{\pm}m_{\pm})^{\nu}$$
$$= RT\ln(m_{\pm})^{\nu} + RT\ln(\gamma_{\pm})^{\nu}. \quad (25)$$

But

$$\bar{F}_2 - \bar{F}_2^{\circ} = (\bar{F}_2 - \bar{F}_2^{\circ})_{\text{ideal}} + (\bar{F}_2 - \bar{F}_2^{\circ})_{\text{elec}}, \quad (26)$$

and

$$(\bar{F}_2 - \bar{F}_2^{\circ})_{\text{ideal}} = RT\ln(m_{\pm})^{\nu}. \quad (27)$$

Therefore, on combining these equations, one finds

$$\ln\gamma_{\pm} = \frac{1}{\nu RT}(\bar{F}_2 - \bar{F}_2^{\circ})_{\text{elec}}. \quad (28)$$

Substituting the value of $(\bar{F}_2 - \bar{F}_2^{\circ})_{\text{elec}}$ from Equation 23, we obtain

$$\ln\gamma_{\pm} = -\left(\frac{A}{\nu RD^{3/2}T^{3/2}}\right)\left(\frac{M_1}{V_1}\right)^{1/2}(\sum\nu_i z_i^2)^{3/2}m^{1/2}. \quad (29)$$

Since

$$\bar{F}_2 - \bar{F}_2^{\circ} = (\bar{F}_2 - \bar{F}_2^{\circ})_{\text{ideal}} + (\bar{F}_2 - \bar{F}_2^{\circ})_{\text{elec}}, \quad (30)$$

it follows that

$$\bar{H}_2 - \bar{H}_2^{\circ} = (\bar{H}_2 - \bar{H}_2^{\circ})_{\text{ideal}} + (\bar{H}_2 - \bar{H}_2^{\circ})_{\text{elec}}, \quad (31)$$

$$\bar{C}_{P_2} - \bar{C}_{P_2}^{\circ} = (\bar{C}_{P_2} - \bar{C}_{P_2}^{\circ})_{\text{ideal}} + (\bar{C}_{P_2} - \bar{C}_{P_2}^{\circ})_{\text{elec}}, \quad (32)$$

and

$$\bar{V}_2 - \bar{V}_2^{\circ} = (\bar{V}_2 - \bar{V}_2^{\circ})_{\text{ideal}} + (\bar{V}_2 - \bar{V}_2^{\circ})_{\text{elec}}. \quad (33)$$

But

$$(\bar{H}_2 - \bar{H}_2^\circ)_{\text{ideal}} = 0; \quad (\bar{C}_{P_2} - \bar{C}_{P_2}^\circ)_{\text{ideal}} = 0; \quad (\bar{V}_2 - \bar{V}_2^\circ)_{\text{ideal}} = 0. \tag{34}$$

Therefore,

$$\bar{H}_2 - \bar{H}_2^\circ = (\bar{H}_2 - \bar{H}_2^\circ)_{\text{elec}}, \tag{35}$$

$$\bar{C}_{P_2} - \bar{C}_{P_2}^\circ = (\bar{C}_{P_2} - \bar{C}_{P_2}^\circ)_{\text{elec}}, \tag{36}$$

and

$$\bar{V}_2 - \bar{V}_2^\circ = (\bar{V}_2 - \bar{V}_2^\circ)_{\text{elec}}. \tag{37}$$

Since $(F_2 - F_2^\circ)_{\text{elec}}$ is known as a function of the temperature, the values of $(\bar{H}_2 - \bar{H}_2^\circ)_{\text{elec}}$ and $(\bar{C}_{P_2} - \bar{C}_{P_2}^\circ)_{\text{elec}}$ may be obtained by appropriate differentiation with temperature at constant pressure, using the regular thermodynamic relations (Chapter 27).

Thus, at constant pressure,

$$\bar{H}_2 - \bar{H}_2^\circ = (\bar{H}_2 - \bar{H}_2^\circ)_{\text{elec}} = -T^2 \frac{\mathrm{d}\left[\dfrac{F_2 - F_2^\circ}{T}\right]_{\text{elec}}}{\mathrm{d}T}. \tag{38}$$

Substituting the value of $[(F_2 - F_2^\circ)/T]_{\text{elec}}$ from Equation 23 and performing the differentiation, one obtains, for the strong electrolyte in the limiting case of extreme dilution,

$$\bar{H}_2 - \bar{H}_2^\circ = -\left(\frac{3}{2}\right)\left(\frac{AT^{1/2}}{D^{3/2}}\right)\left(\frac{M_1}{V_1}\right)^{1/2} \left[\frac{1}{T} + \frac{\mathrm{d}\ln D}{\mathrm{d}T} + \left(\frac{1}{3}\right)\left(\frac{\mathrm{d}\ln V}{\mathrm{d}T}\right)\right] (\textstyle\sum \nu_i z_i^2)^{3/2} m^{1/2}. \tag{39}$$

For this differentiation, it is to be noted that all the factors giving the value of $(F_2 - F_2^\circ)_{\text{elec}}$ are constant except the variables D, T, and V, all of which are within the first parenthesis on the right side of Equation 23.

Similarly, at constant pressure,

$$\bar{C}_{P_2} - \bar{C}_{P_2}^\circ = (\bar{C}_{P_2} - \bar{C}_{P_2}^\circ)_{\text{elec}} = \frac{\mathrm{d}(\bar{H}_2 - \bar{H}_2^\circ)_{\text{elec}}}{\mathrm{d}T}, \tag{40}$$

or, more directly,

$$\bar{C}_{P_2} - \bar{C}_{P_2}^\circ = (\bar{C}_{P_2} - \bar{C}_{P_2}^\circ)_{\text{elec}} = -T\frac{\mathrm{d}^2(F_2 - F_2^\circ)_{\text{elec}}}{\mathrm{d}T^2}. \tag{41}$$

Substituting the value of $(F_2 - F_2^\circ)_{\text{elec}}$ from Equation 23 and performing the double differentiation, one obtains

$$\bar{C}_{P_2} - \bar{C}_{P_2}{}^{\circ} = -\left(\frac{3}{4}\right)\left(\frac{A}{D^{3/2}T^{1/2}}\right)\left(\frac{M_1}{V_1}\right)^{1/2} \left[\frac{1}{T} + 2\frac{\mathrm{d}\ln D}{\mathrm{d}T} + 5T\left(\frac{\mathrm{d}\ln D}{\mathrm{d}T}\right)^2 + 2T\left(\frac{\mathrm{d}\ln D}{\mathrm{d}T}\right)\left(\frac{\mathrm{d}\ln V}{\mathrm{d}T}\right) + \left(\frac{2}{3}\right)\frac{\mathrm{d}\ln V}{\mathrm{d}T} + T\left(\frac{\mathrm{d}\ln V}{\mathrm{d}T}\right)^2 - 2\left(\frac{T}{D}\right)\left(\frac{\mathrm{d}^2D}{\mathrm{d}T^2}\right) - \left(\frac{2}{3}\right)\left(\frac{T}{V}\right)\left(\frac{\mathrm{d}^2V}{\mathrm{d}T^2}\right)\right] (\Sigma\nu_i z_i{}^2)^{3/2} m^{1/2}. \qquad (42)$$

Here again it is to be noted that, for this differentiation, all the factors giving the value of $(\text{F}_2 - \text{F}_2{}^{\circ})_{\text{elec}}$ are constant except the variables D, T, and V, which are within the first parenthesis on the right side of Equation 23.

In a similar way, at constant temperature,

$$\bar{V}_2 - \bar{V}_2{}^{\circ} = (\bar{V}_2 - \bar{V}_2{}^{\circ})_{\text{elec}} = \frac{\mathrm{d}(\text{F}_2 - \text{F}_2{}^{\circ})_{\text{elec}}}{\mathrm{d}P}. \qquad (43)$$

Substituting the value of $(\text{F}_2 - \text{F}_2{}^{\circ})_{\text{elec}}$ from Equation 23 and performing the differentiation with pressure at constant temperature, noting that the only variables are D and V, one obtains

$$\bar{V}_2 - \bar{V}_2{}^{\circ} = \left(\frac{1}{2}\right)\left(\frac{A}{D^{3/2}T^{1/2}}\right)\left(\frac{M_1}{V_1}\right)^{1/2} \left(3\frac{\mathrm{d}\ln D}{\mathrm{d}P} + \frac{\mathrm{d}\ln V}{\mathrm{d}P}\right) (\Sigma\nu_i z_i{}^2)^{3/2} m^{1/2}. \qquad (44)$$

Defining the partial molal compressibility at constant temperature as

$$\bar{K}_2 = \frac{\partial(\partial V/\partial P)}{\partial n_2} = \frac{\partial^2 V}{\partial P\,\partial n_2} = \frac{\partial(\partial V/\partial n_2)}{\partial P} = \frac{\partial \bar{V}_2}{\partial P}, \qquad (45)$$

we may utilize the relations, at constant temperature and composition,

$$\bar{K}_2 - \bar{K}_2{}^{\circ} = \frac{\mathrm{d}(\bar{V}_2 - \bar{V}_2{}^{\circ})}{\mathrm{d}P} = \frac{\partial^2(\text{F}_2 - \text{F}_2{}^{\circ})_{\text{elec}}}{\partial P^2}, \qquad (46)$$

to evaluate the relative partial molal compressibility. Substituting the value of $(\bar{\mathrm{F}}_2 - \bar{\mathrm{F}}_2^\circ)_{\mathrm{elec}}$ from Equation 23 and performing the double differentiation, noting that the only variables are D and V, we obtain

$$\bar{\mathrm{K}}_2 - \bar{\mathrm{K}}_2^\circ = -\left(\frac{1}{4}\right)\left(\frac{A}{D^{3/2}T^{1/2}}\right)\left(\frac{M_1}{V_1}\right)^{1/2}\left[\left(\frac{\mathrm{d}\ln V}{\mathrm{d}P}\right)^2 - 2\frac{\mathrm{d}^2\ln V}{\mathrm{d}P^2}\right.$$
$$\left. + 6\left(\frac{\mathrm{d}\ln V}{\mathrm{d}P}\right)\left(\frac{\mathrm{d}\ln D}{\mathrm{d}P}\right) + 15\left(\frac{\mathrm{d}\ln D}{\mathrm{d}P}\right)^2 - \frac{6}{D}\frac{\mathrm{d}^2D}{\mathrm{d}P^2}\right]$$
$$(\textstyle\sum\nu_i z_i^2)^{3/2} m^{1/2}. \qquad (47)$$

Defining the partial molal expansibility at constant pressure as

$$\bar{\mathrm{U}}_2 = \frac{\partial(\partial V/\partial T)}{\partial n_2} = \frac{\partial^2 V}{\partial T\,\partial n_2} = \frac{\partial(\partial V/\partial n_2)}{\partial T} = \frac{\partial\bar{\mathrm{V}}_2}{\partial T}, \qquad (48)$$

we may utilize the relation, at constant pressure and composition,

$$\bar{\mathrm{U}}_2 - \bar{\mathrm{U}}_2^\circ = \frac{\mathrm{d}(\bar{\mathrm{V}}_2 - \bar{\mathrm{V}}_2^\circ)}{\mathrm{d}T} = \frac{\partial^2(\bar{\mathrm{F}}_2 - \bar{\mathrm{F}}_2^\circ)_{\mathrm{elec}}}{\partial T\,\partial P}, \qquad (49)$$

to evaluate the relative partial molal expansibility. Substituting the value of $\bar{\mathrm{F}}_2 - \bar{\mathrm{F}}_2^\circ$ from Equation 23, and performing the successive differentiations, we obtain

$$\bar{\mathrm{U}}_2 - \bar{\mathrm{U}}_2^\circ = -\left(\frac{1}{4}\right)\left(\frac{A}{D^{3/2}T^{1/2}}\right)\left(\frac{M_1}{V_1}\right)^{1/2}$$
$$\left[\left(3\frac{\mathrm{d}\ln D}{\mathrm{d}P} + \frac{\mathrm{d}\ln V}{\mathrm{d}P}\right)\left(3\frac{\mathrm{d}\ln D}{\mathrm{d}T} + \frac{1}{T} + \frac{\mathrm{d}\ln V}{\mathrm{d}T}\right)\right.$$
$$\left. + 2\left(3\frac{\partial^2\ln D}{\partial P\,\partial T} + \frac{\partial^2\ln V}{\partial P\,\partial T}\right)\right](\textstyle\sum\nu_i z_i^2)^{3/2} m^{1/2}. \qquad (50)$$

Following are values of the important Debye-Hückel valence factor, $(\sum\nu_i z_i^2)^{3/2}$, occurring in the foregoing equations, for strong electrolytes of several valence types: 1-1, 2.8284; 2-1 or 1-2, 14.697; 2-2, 22.627; 3-1 or 1-3, 41.569; 3-2 or 2-3, 164.32; 3-3, 76.368.

From the foregoing, it is seen that, taking the value of $(\bar{\mathrm{F}}_2 - \bar{\mathrm{F}}_2^\circ)_{\mathrm{elec}}$ provided by the Debye-Hückel theory and utilizing the regular relations of thermodynamics, it is possible to evaluate for the strong electrolyte in very dilute solution the following properties: activity coefficient, relative partial molal heat content, relative partial molal heat capacity, relative partial molal volume, relative partial molal compressibility, and relative partial molal expansibility.

3. Free energy, activity, and activity coefficient. In accordance with the relations presented in the foregoing section, we may write for the relative partial molal free energy of any strong electrolyte in very dilute solution,

$$\mathrm{F}_2 - \mathrm{F}_2^\circ = RT \ln (m_\pm)^\nu - \left(\frac{A}{D^{3/2}T^{1/2}}\right)\left(\frac{M_1}{V_1}\right)^{1/2} (\textstyle\sum \nu_i z_i^2)^{3/2} m^{1/2}. \tag{51}$$

The value of A in cgs units is given by Equation 24. For water as the solvent, we may take

$$M_1 = 18.016 \text{ g/mole}; \quad V_1 = 18.069 \text{ cm}^3\text{/mole}; \quad D = 78.54. \tag{52}$$

Then, for very dilute aqueous solutions of strong electrolytes at 25°C, converting to calories per mole, we have

$$\mathrm{F}_2 - \mathrm{F}_2^\circ = RT \ln (m_\pm)^\nu - 490.40 (\textstyle\sum \nu_i z_i^2)^{3/2} m^{1/2} \text{ cal/mole}. \tag{53}$$

From the foregoing expression, one may readily calculate the activity from the relation

$$\ln a_2 = \frac{\mathrm{F}_2 - \mathrm{F}_2^\circ}{RT}. \tag{54}$$

Both the relative partial molal free energy and the activity are adequately specified by the activity coefficient as given by Equation 29. Evalution of the constants for water as the solvent at 25°C, and converting to logarithms to the base 10, one obtains the following quantitative expression for the activity coefficient of any strong electrolyte in very dilute aqueous solution at 25°C:

$$\log \gamma_\pm = -0.360 \frac{1}{\nu} (\textstyle\sum \nu_i z_i^2)^{3/2} m^{1/2}. \tag{55}$$

As may be readily shown, Equation 55, based on the Debye-Hückel theory, is equivalent to Equation 167 of Chapter 27, which was discovered earlier by Lewis and Randall (*4*) from a study of the then available data. We have already noted that the experimental data in the limiting region approaching infinite dilution are in excellent accord with Equation 167 of Chapter 27 and hence also with the above Equation 55. Figure 2 gives a simple comparison of the experimental values of the activity coefficients of several strong electrolytes of different valence types in dilute aqueous solution, the data being taken from the summaries of Latimer (*27*) and of Harned and Owen (*21*).

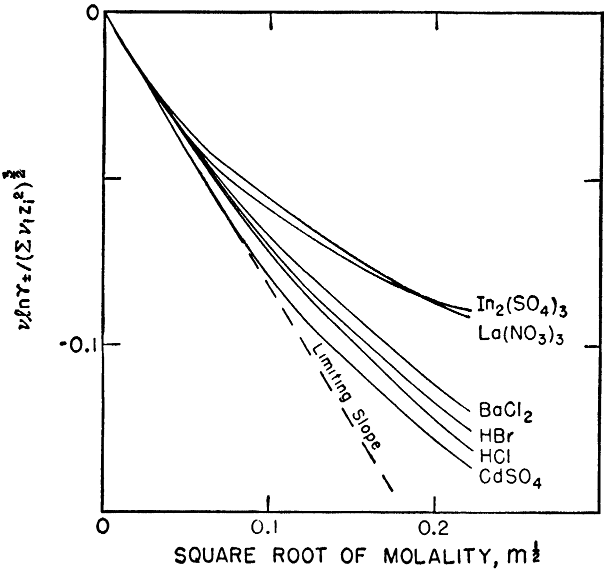


FIGURE 2. Values of the mean ion activity coefficient of several strong electrolytes of different types in dilute aqueous solution plotted to show the common limiting slope called for by the Debye-Hückel theory. The data are from Latimer (*27*) and Harned and Owen (*21*).

4. Relative partial molal heat content. In order to evaluate the relative partial molal heat content of the solute in a particular solvent, it is necessary to have values for the change with temperature of the dielectric constant and of the volume. For water at 25°C, we may take (*22*)

$$\frac{d \ln V}{dT} = \left(\frac{1}{V}\right)\left(\frac{dV}{dT}\right) = 0.00025674/\text{deg}. \tag{56}$$

For the dielectric constant of water, we may take (*3,26*), at constant pressure,

$$D = 78.54[1 - 0.004617(t - 25) + 0.0000122(t - 25)^2 - 2.7 \times 10^{-8}(t - 25)^3], \tag{57}$$

where t is the temperature in degrees centigrade (Celsius). Hence we have for water at 25°C,

$$\frac{\mathrm{d}\ln D}{\mathrm{d}T} = \left(\frac{1}{D}\right)\left(\frac{\mathrm{d}D}{\mathrm{d}T}\right) = -0.004617. \qquad (58)$$

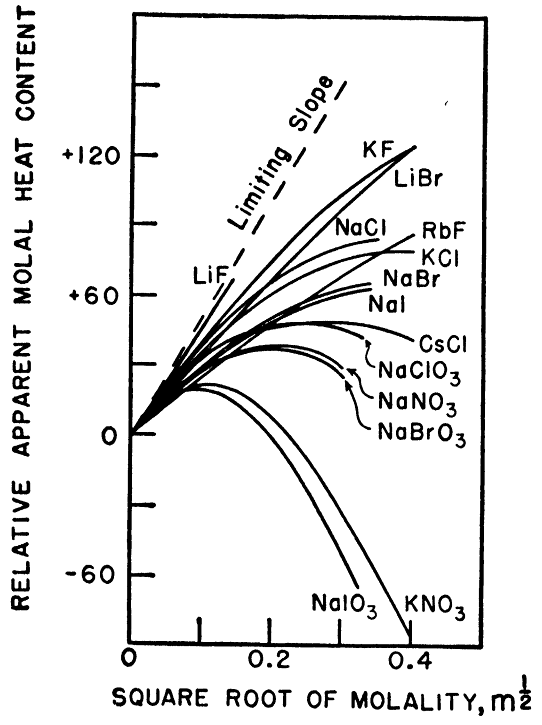


FIGURE 3. Plot of the relative apparent molal heat content of several strong electrolytes, of valence type 1–1, in dilute aqueous solution, showing the limiting slope called for by the Debye-Hückel theory. From Lange and Robinson (*11*).

Substituting the appropriate values of the constants into Equation 39, we obtain the following quantitative expression for the relative partial molal heat content of a strong electrolyte in the limiting range near infinite dilution in water at 25°C:

$$\bar{H}_2 - \bar{H}_2^{\circ} = 258.2(\textstyle\sum \nu_i z_i^2)^{3/2} m^{1/2} \text{ cal/mole.} \qquad (59)$$

Figures 3, 4, and 5, for which the data are taken from the review of Lange and Robinson (*11*), show how, in the limit near infinite dilution, the values of the relative apparent molal heat content for various types of strong electrolytes conform to the requirements of the Debye-Hückel theory. It is to be noted, from the equations derived in Chapter 24, that, if the relative partial molal heat content is linear with $m^{1/2}$, the following simple relation results:

$$\Phi H_2 - \Phi H_2^{\circ} = \tfrac{2}{3}(\bar{H}_2 - \bar{H}_2^{\circ}). \tag{60}$$

Mazhar

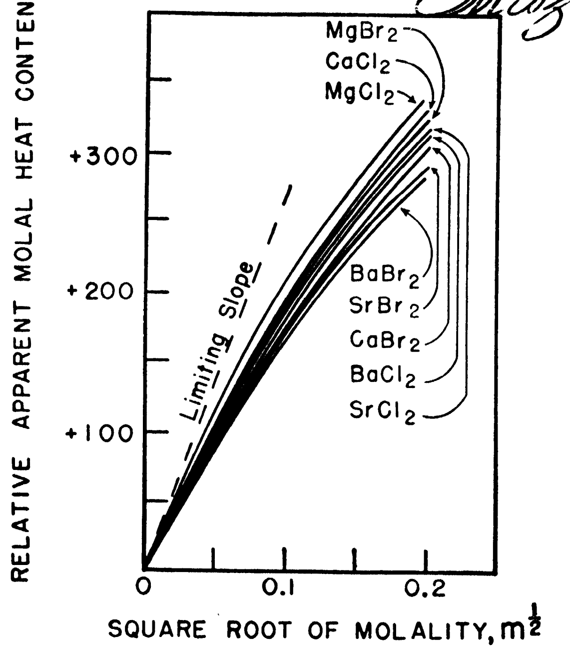


Figure 4. Plot of the relative apparent molal heat content of several strong electrolytes, of valence type 2–1, in dilute aqueous solution, showing the limiting slope called for by the Debye-Hückel theory. From Lange and Robinson (*11*).

5. Relative partial molal heat capacity. In order to evaluate the relative partial molal heat capacity in accordance with the Debye-Hückel theory in the limiting region, it is necessary to have also values for the second derivative, with temperature, of the dielectric constant and the volume of the solvent. For water at 25°C, we may take

$$\frac{d^2V}{dT^2} = 0.000180 \text{ cm}^3/\text{deg}^2\text{mole}. \tag{61}$$

From Equation 53, we calculate for 25°C,

$$\frac{d^2D}{dT^2} = 0.001916/\text{deg}^2. \tag{62}$$

Substituting the appropriate values of the constants into Equation 42, we obtain the following quantitative expression for the

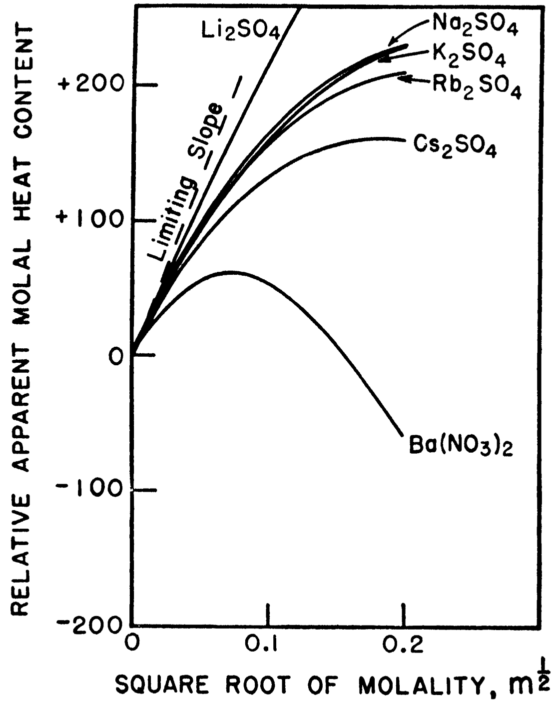


FIGURE 5. Plot of the relative apparent molal heat content of several strong electrolytes, of valence types 1–2 and 2–1, showing the limiting slope called for by the Debye-Hückel theory. From Lange and Robinson (*11*).

relative partial molal heat capacity of a strong electrolyte in the limiting range near infinite dilution in water at 25°C:

$$\bar{c}_{P_2} - \bar{c}_{P_2}^{\circ} = 3.26(\textstyle\sum \nu_i z_i^2)^{3/2} m^{1/2} \text{ cal/deg mole.} \tag{63}$$

Figure 7 of Chapter 24 shows that the limiting slopes called for by Equation 63 can be placed on the extension to infinite dilution of the curves of the experimental values. It is to be noted that the nearly linear relation existing between $m^{1/2}$ and the apparent and partial molal heat capacity of these strong electrolytes, in a range of concentration far greater than that at which the experimental values of the relative apparent and partial molal heat content depart greatly from the limiting values called for by the Debye-Hückel theory, has no relation to the simple limiting form of the Debye-Hückel theory. Rather, the limiting slopes called for by Equation 63, and the corresponding equation for the relative apparent molal heat capacity, are to be applied to the experimental curves as they pass from the very dilute range to infinite dilution. In any case, the experimental data on apparent and partial molal heat capacities of strong electrolytes in aqueous solution are not in discord with the limiting form of the Debye-Hückel theory.

6. Relative partial molal volume. In order to evaluate the relative partial molal volume in the very dilute region in accordance with the Debye-Hückel theory, it is necessary to know the change of the dielectric constant and volume with pressure at constant temperature. For water at 25°C, we may take (*22*)

$$V = 18.0697 - 8.3036 \times 10^{-4}P + 1.2310 \times 10^{-7}P^2 \quad \text{cm}^3/\text{mole}, \tag{64}$$

with P expressed in atmospheres, whence

$$\frac{\mathrm{d} \ln V}{\mathrm{d}P} = -4.593 \times 10^{-5}/\text{atm}. \tag{65}$$

For water at 25°C, the change of the dielectric constant with pressure at constant temperature may be taken (*15,22,23,24,25,28*), with some uncertainty, as

$$\frac{\mathrm{d} \ln D}{\mathrm{d}P} = 6.03 \times 10^{-5}/\text{atm}. \tag{66}$$

Substituting the appropriate values of the constants into Equation 44, we obtain the following quantitative expression for the relative partial molal volume of a strong electrolyte in the limiting range near infinite dilution in water at 25°C:

$$\bar{\mathrm{v}}_2 - \bar{\mathrm{v}}_2{}^\circ = 1.37(\textstyle\sum \nu_i z_i{}^2)^{3/2} m^{1/2} \text{ cm}^3/\text{mole}. \tag{67}$$

Plots of some experimental data on apparent molal volumes of strong electrolytes in dilute aqueous solution are given in Figure 6 of Chapter 24. As was stated above in connection with the relative partial molal heat capacity, the slope of $\bar{\mathrm{v}}_2 - \bar{\mathrm{v}}_2{}^\circ$ against $m^{1/2}$

provided by Equation 67 is to be applied only from the extremely dilute region to infinite dilution (*29*,*30*).

7. Relative partial molal compressibility. In order to evaluate the relative partial molal compressibility in the very dilute region in accordance with the Debye-Hückel theory, it is necessary to know the second derivative, with pressure at constant temperature, of the dielectric constant and volume of the solvent. For water at 25°C, we may take the rather uncertain value of (*15*,*22*,*23*,*24*,*25*,*28*)

$$\frac{d^2D}{dP^2} = -1 \times 10^{-6}/\text{atm}^2, \tag{68}$$

and the reliable value (*22*) of

$$\frac{d^2 \ln V}{dP^2} = 1.1515 \times 10^{-8}/\text{atm}^2. \tag{69}$$

Substituting the appropriate values of the constants into Equation 47, we obtain the following approximate quantitative expression for the relative partial molal compressibility of a strong electrolyte in the limiting range near infinite dilution in water at 25°C:

$$\bar{K}_2 - \bar{K}_2{}^\circ = 4.7 \times 10^{-4}(\textstyle\sum \nu_i z_i{}^2)^{3/2} m^{1/2} \text{ cm}^3/\text{atm mole.} \tag{70}$$

Gucker's review (*15*) indicates that the experimental data on the compressibility of strong electrolytes in very dilute aqueous solution are not in discord with the requirements of Equation 70.

8. Relative partial molal expansibility. In order to evaluate the relative partial molal expansibility in the very dilute region in accordance with the Debye-Hückel theory, it is necessary to know not only all the preceding changes of dielectric constant and volume with pressure and with temperature but also the variation of the pressure coefficients with temperature. The existing data for the latter, which are identified in Equation 50, are extremely meager. Gucker (*17*) has estimated the values of the constants to be such that, approximately,

$$\bar{U}_2 - \bar{U}_2{}^\circ = 4 \times 10^{-13}(\textstyle\sum \nu_i z_i{}^2)^{3/2} m^{1/2} \text{ cm}^3/\text{deg mole.} \tag{71}$$

The available experimental data on the apparent and partial molal expansibility do not go to sufficiently low concentrations to permit any positive comparison with the limiting Equation 71. In the region in which measurements have been made, the apparent and partial molal expansibility decreases with increase in concentration (*17*), whereas according to Equation 71 the values should increase with increase in concentration. It is possible that the range of applicability of the limiting law to this property lies only in the extremely dilute region where no experimental data yet exist, and that the curvature there may change sign on the way to infinite dilution, in the same way as does the property of the relative apparent and partial molal heat content of aqueous solutions of strong electrolytes of salts like the sodium and potassium chlorides and nitrates. The alternative is to assume that the existing data on the first and second derivatives of the dielectric constant as a function of pressure are so poorly known as to yield the wrong sign for the factor in Equation 71.

9. Collateral reading. For more detailed discussions relating to the Debye-Hückel theory of strong electrolytes, including its extension into less dilute solutions, the reader is referred to Debye and Hückel (*1*), Debye (*2*), Gross and Halpern (*5*), Bjerrum (*6*), Gross (*7*), Randall and Rossini (*8*), Gronwall, LaMer, and Sandved (*9*), LaMer, Gronwall, and Greiff (*10*), Lange and Robinson (*11*), Scatchard (*12*), Redlich (*13*), Redlich and Rosenfeld (*14*), Gucker (*15,17*), LaMer and Cowperthwaite (*16*), Dole (*18*), Young and Seligmann (*19*), MacInnes (*20*), Harned and Owen (*21*), and Redlich and Bigeleisen (*28,29,30*).

REFERENCES

1. P. Debye and E. Hückel, *Physik. Z.* **24**, 185 (1923).
2. P. Debye, *Physik. Z.* **25**, 97 (1924).
3. J. Wyman, Jr., *Phys. Revs.* **35**, 623 (1930).
4. G. N. Lewis and M. Randall, *J. Am. Chem. Soc.* **43**, 1112 (1921).
5. P. Gross and O. Halpern, *Physik. Z.* **26**, 403 (1925).
6. N. Bjerrum, *Z. physik. Chem.* **119**, 156 (1926).
7. P. Gross, *Monatsh.* **48**, 243 (1927).
8. M. Randall and F. D. Rossini, *J. Am. Chem. Soc.* **51**, 323 (1929).
9. T. H. Gronwall, V. K. LaMer, and K. Sandved, *Physik. Z.* **29**, 358 (1929).
10. V. K. LaMer, T. H. Gronwall, and L. J. Greiff, *J. Phys. Chem.* **35**, 2245 (1931).
11. E. Lange and A. L. Robinson, *Chem. Revs.* **9**, 89 (1931).
12. G. Scatchard, *J. Am. Chem. Soc.* **53**, 2037 (1931).
13. O. Redlich, *Naturwissenschaften* **19**, 251 (1931).
14. O. Redlich and P. Rosenfeld, *Z. physik. Chem.* **A155**, 65 (1931).
15. F. T. Gucker, Jr., *Chem. Revs.* **13**, 111 (1933).

16. V. K. LaMer and I. A. Cowperthwaite, *J. Am. Chem. Soc.* **55**, 1004 (1933).

17. F. T. Gucker, Jr., *J. Am. Chem. Soc.* **56**, 1017 (1934).

18. M. Dole, *Experimental and Theoretical Electrochemistry*, McGraw-Hill Book Company, New York, 1935.

19. T. F. Young and P. Seligmann, *J. Am. Chem. Soc.* **60**, 2379 (1939).

20. D. A. MacInnes, *The Principles of Electrochemistry*, Reinhold Publishing Corporation, New York, 1939.

21. H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold Publishing Corporation, New York, 1943.

22. *International Critical Tables*, Volume III, McGraw-Hill Book Company, New York, 1926.

23. G. Falckenberg, *Ann. Physik* **61**, 145 (1920).

24. S. Kyropoulos, *Z. Physik* **40**, 517 (1926).

25. B. B. Owen and S. R. Brinkley, Jr., *Phys. Revs.* **64**, 32 (1943).

26. J. Wyman, Jr., and E. N. Ingalls, *J. Am. Chem. Soc.* **60**, 1182 (1938).

27. W. M. Latimer, *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, Prentice-Hall, New York, 1938.

28. O. Redlich, *J. Phys. Chem.* **44**, 619 (1940).

29. O. Redlich and J. Bigeleisen, *Chem. Revs.* **30**, 171 (1942).

30. O. Redlich and J. Bigeleisen, *J. Am. Chem. Soc.* **64**, 758 (1942).

PROBLEMS

1. Show that, if a strong electrolyte dissociates into only two kinds of ions,

$$\Sigma \nu_i z_i^2 = (\nu_+ + \nu_-)|z_+ z_-|.$$

2. Calculate, to five significant figures, the values of the Debye-Hückel valence factor, $(\Sigma \nu_i z_i^2)^{3/2}$, for strong electrolytes of the following valence types: 4-1 or 1-4; 4-2; 4-3.

3. Derive the quantitative relations for the relative apparent molal heat content, the relative apparent molal heat capacity, and the relative apparent molal volume, for a strong electrolyte in the limiting range near infinite dilution in water at 25°C, starting with the relations already derived for the corresponding relative partial molal property, based on the Debye-Hückel theory.

4. Calculate the activity coefficient of aqueous silver sulfate in a 0.01 molal solution at 25°C, assuming the Debye-Hückel limiting equation.

5. Calculate the value of the relative apparent molal volume of any strong electrolyte, of valence type 2-2, in an aqueous solution of 0.005 molality at 25°C, assuming the Debye-Hückel limiting equation.

6. Calculate the value of the relative apparent molal heat content of any strong electrolyte, of valence type 1-2, in an aqueous solution of 0.008 molality at 25°C, assuming the Debye-Hückel limiting equation.

7. Calculate the value of the relative apparent molal heat capacity of any strong electrolyte, of valence type 3-1, in an aqueous solution of 0.004 molality at 25°C, assuming the Debye-Hückel limiting equation.

8. If the solubility of the strong electrolyte, MX, in water at 25°C is 0.01

molal, calculate the value of $F^\circ_{298.16}$ for this process:

$$\text{MX (c)} = \text{MX (aq)},$$

assuming the Debye-Hückel limiting equations as needed and the electrolyte to be of the 1-1 type.

9. What percentage error is made in the numerical factor of the limiting Debye-Hückel equation for the relative partial molal heat content of a strong electrolyte in dilute aqueous solution at 25°C if dV/dT for the water is taken as zero? Similarly, what percentage error is made in the numerical factor of the limiting Debye-Hückel equation for the relative partial molal heat capacity?

32

Equilibrium between Different Phases of Two or More Components

1. Free energy of components in different phases. If a system is composed of c components each present in p different phases, we can say that at equilibrium at constant pressure and temperature the partial molal free energy of a given component must be the same in all phases, and similarly for each of the other components. That is, if the phases are lettered a, b, $d, \cdots, p$, and the components are numbered $1, 2, 3, \cdots, c$, we may write

$$(\mathrm{F}_1)_a = (\mathrm{F}_1)_b = (\mathrm{F}_1)_d = \cdots = (\mathrm{F}_1)_p; \tag{1}$$

$$(\mathrm{F}_2)_a = (\mathrm{F}_2)_b = (\mathrm{F}_2)_d = \cdots = (\mathrm{F}_2)_p; \tag{2}$$

$$(\mathrm{F}_3)_a = (\mathrm{F}_3)_b = (\mathrm{F}_3)_d = \cdots = (\mathrm{F}_3)_p; \tag{3}$$

$$\begin{array}{ccccc} \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot \end{array}$$

$$(\mathrm{F}_c)_a = (\mathrm{F}_c)_b = (\mathrm{F}_c)_d = \cdots = (\mathrm{F}_c)_p. \tag{4}$$

The foregoing set of equations constitute $c(p - 1)$ independent equations which must be satisfied when thermodynamic equilibrium exists. If one or more of the components are absent from one or more phases, there is a corresponding reduction in the number of independent equations.

2. Phase rule. In Chapter 22, we discussed the phase rule in relation to the equilibrium between different phases of one pure substance. We now turn our attention to the phase rule in relation to the equilibrium between different phases of two or more components. As before we let f be the number of degrees of freedom of the given system, which is composed of c components in p phases, with r being the number of external variables, such as pressure, temperature, gravitational field, and magnetic field, needed to fix the state of the system as a whole.

The number of variables required to fix the composition of each phase is one less than the number of components in that phase, or $c - 1$. If each phase contains the same number of components, the number of variables required to fix the composition of p phases is $p(c - 1)$. Therefore, since we have, by Equations 1 to 4, $c(p - 1)$ independent equations, the number of degrees of freedom is

$$f = p(c - 1) + r - c(p - 1), \tag{5}$$

or

$$f = c - p + r. \tag{6}$$

That is, the number of degrees of freedom of any system is equal to the number of components less the number of phases plus the number of external variables required to fix the external state of the system. If one or more of the components are absent from one or more phases, the relation given by Equation 2 remains unchanged, since there is a corresponding and equal reduction in the number of composition variables for all the different phases and in the number of independent equations.

If the external variables such as the gravitational field, magnetic field, and electric field are constant, the external variables are reduced to pressure and temperature, so that $r = 2$. In such case

$$f = c - p + 2. \tag{7}$$

3. Binary systems involving the gaseous and liquid phases. In Chapter 25, we discussed the equilibrium between the gaseous and liquid phases where, in each phase, the components form an ideal solution. It was pointed out that, for a binary ideal solution at a constant temperature, the fugacity, or approximately the partial pressure, of each component, as well as the total fugacity, or approximately the total pressure, is proportional to the mole fraction, as shown in Chapter 25. In many cases, it is practically of much greater importance to examine such a system at constant pressure.

Figure 1 shows the diagram of temperature and composition for the liquid and gaseous phases for a binary ideal solution at constant pressure. It is possible to calculate the liquid line, which gives the composition of the liquid phase, for such a diagram for an ideal binary solution from the fact that at each temperature the sum of the partial pressures of the two components is equal to the constant pressure, P, imposed on the system. That is,

$$P_1 = N_1{}^l P_1{}^*; \quad P_2 = N_2{}^l P_2{}^*; \quad P_1 + P_2 = P. \tag{8}$$

But the pressure of each pure component can be expressed quite accurately over a short range of temperature by means of the

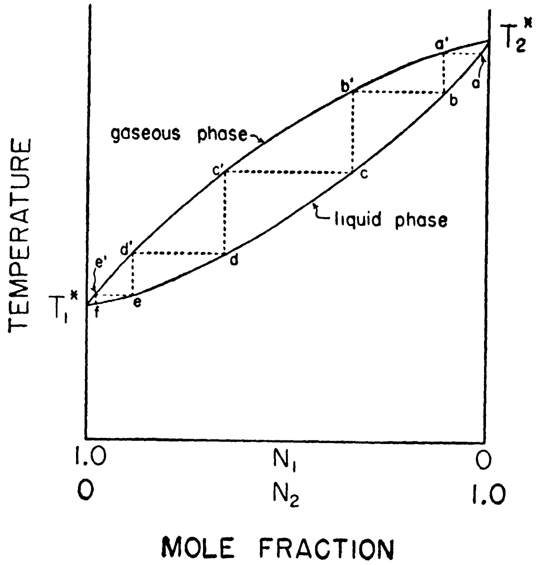


FIGURE 1. Diagram of temperature and composition, at constant pressure, for a substantially ideal binary system involving the gaseous and liquid phases.

Antoine equation for vapor pressures, which involves three constants, as

$$\log P_1{}^* = A_1 + \frac{B_1}{C_1 + T}, \tag{9}$$

and

$$\log P_2{}^* = A_2 + \frac{B_2}{C_2 + T}. \tag{10}$$

Then

$$P_1{}^* = e^{A_1'} e^{B_1'/(C_1'+T)}, \tag{11}$$

and

$$P_2{}^* = e^{A_2'} e^{B_2'/(C_2'+T)}. \tag{12}$$

Therefore, the total pressure, P, on the system, which will most frequently be the prevailing barometric pressure near 1 atmosphere, is

$$P = \mathrm{N}_1{}^l e^{A_1'} e^{B_1'/(C_1'+T)} + (1 - \mathrm{N}_1{}^l) e^{A_2'} e^{B_2'/(C_2'+T)}. \tag{13}$$

Here $\mathrm{N}_1{}^l$ is the mole fraction of component 1 in the liquid phase. For given values of the temperature and the pressure, and with known values of the constants of the equations for vapor pressure, one can evaluate the corresponding mole fraction. At $T_1{}^*$ and $T_2{}^*$, of course, $\mathrm{N}_1{}^l$ has the values 1.0 and 0, respectively. By making the calculation at several temperatures between $T_1{}^*$ and $T_2{}^*$, the entire liquid line can be located. Once the liquid line is fixed, the gaseous line, which gives the composition of the gaseous phase, is located from the fact that, at each temperature, the mole fraction of component 1 in the gaseous phase is equal to the partial pressure of component 1 divided by the sum of the partial pressures or the total pressure. That is,

$$\mathrm{N}_1{}^g = \frac{P_1}{P_1 + P_2} = \frac{P_1}{P}. \tag{14}$$

In the particular diagram shown in Figure 1, it may be noted that the liquid having the composition at a is in equilibrium with the gaseous phase of composition a', the gaseous phase at a' may be condensed to give a liquid of the same composition b, but at a lower temperature, the liquid at b is in equilibrium with vapors at b', etc. In this way, for this particular system, one may pass from a composition near 0.98 in component 2 to a composition near 0.98 in component 1 in five or six theoretical stages of separation. When the liquid and gaseous lines are closer together, as they are for substances for which $T_1{}^*$ and $T_2{}^*$ are nearer one another, the number of theoretical stages required to pass from nearly pure component 2 to nearly pure component 1 increases greatly.

Figure 2 shows the diagram of temperature and composition for a binary system which is non-ideal, and for which there is a composition at which the temperature of boiling, T_3, at the given pressure, is greater than $T_2{}^*$. This produces a maximum-boiling azeotropic mixture for which the liquid and gaseous phases are identical in composition. It is to be noted that to the left of the maximum-boiling mixture the gaseous phase is richer in component 1, whereas to the right of the maximum-boiling mixture the gaseous phase is richer in component 2. In such solutions, the non-ideality is manifested by an abnormal decrease in the escaping tendency of the components. The dashed lines within the zones bounded by the liquid and gaseous lines show, on the one side, the stepwise change from near the constant-boiling mixture toward pure component 1, and, on the other side, from near the constant-boiling mixture toward pure component 2.

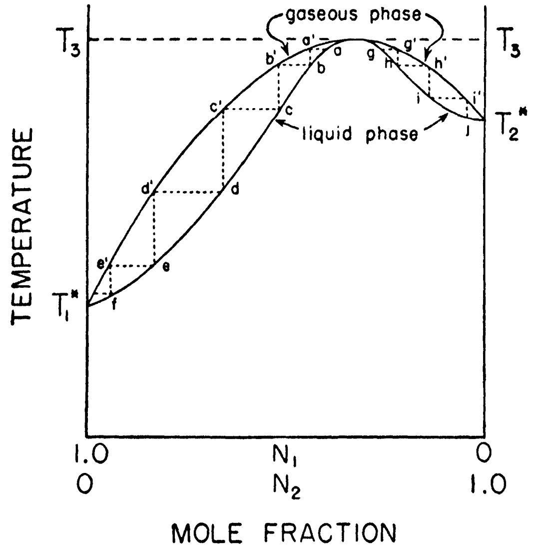


FIGURE 2. Diagram of temperature and composition, at constant pressure, for a binary system involving the gaseous and liquid phases, with a maximum-boiling azeotropic mixture.

Figure 3 shows the diagram of temperature and composition for a binary solution which is non-ideal, and for which there is a composition at which the temperature of boiling, T_3, at the given pressure, is below T_1^*. This produces a minimum-boiling azeotropic mixture for which the liquid and gaseous phases are identical in composition. It is to be noted that to the left of the minimum-boiling mixture the gaseous phase is richer in component 2, whereas to the right of the minimum-boiling mixture the gaseous phase is richer in component 1. In such solutions, the non-ideality is manifested by an abnormal increase in the escaping tendency of the components. The dashed lines within the zones bounded by the liquid and gaseous lines show, on the one side, the stepwise change from pure component 1 toward the constant-boiling mixture and, on the other side, from near pure component 2 toward the same constant-boiling mixture.

Whenever two components are dissimilar in molecular structure and properties, the non-ideality of a mixture of the two components may be great enough that the two liquids will not be soluble in one another over the entire range of composition. This results in the existence of two liquid phases over a certain range of composition, as illustrated schematically in Figure 4. The oblique dashed lines *ac* and *bd* below the temperature T_3 show the increasing solubility of the two components in one another with increasing temperature. At the temperature and overall composition represented by the point *x*, the system consists of two liquid phases in equilibrium with one another, the two phases having the compositions represented by x' and x'', respectively, and being present in the relative amounts required to give the overall composition represented by *x*. At any temperature, *T*, between T_3 and $T_1{}^*$, when the system has an overall composition such that N_1 is greater than its value at *y*, the liquid phase having a composition called for by the point *g* is in equilibrium with the gaseous phase

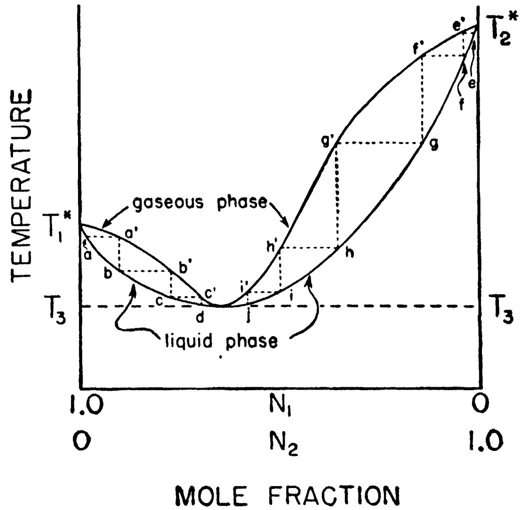


FIGURE 3. Diagram of temperature and composition, at constant pressure, for a binary system involving the gaseous and liquid phases, with a minimum-boiling azeotropic mixture.

having the composition corresponding to g'. Similarly, when the overall composition is such that N_1 is less than that corresponding to the point y, the equilibrium is one between a liquid phase having a composition corresponding to the point h and a gaseous phase having a composition corresponding to the point h'.

Whenever two components are extremely dissimilar, they may, at a given pressure and temperature, be substantially completely immiscible in one another. For such a mixture, at a given temperature, the total pressure is independent of the relative amounts of the two components present, and hence the boiling point is independent of the composition of the mixture. At a given temperature, the total pressure is the sum of the pressures of the two pure substances:

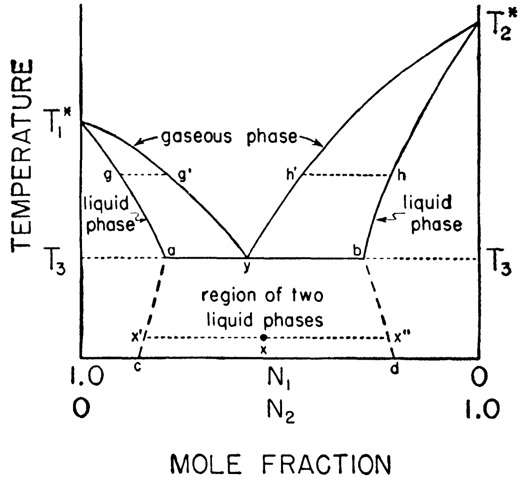


FIGURE 4. Diagram of temperature and composition, at constant pressure, for a binary system involving the gaseous and liquid phases, with the two components in the liquid phase being soluble only over a limited range of composition.

$$P = P_1^* + P_2^*. \tag{15}$$

The foregoing illustrations have been discussed in terms of the diagram of temperature and composition at constant pressure. Corresponding diagrams of pressure and composition at constant temperature may be constructed for the same systems.

4. Binary systems involving the liquid and solid phases. We have seen (Chapter 25) the nature of the diagram of temperature and composition for the equilibrium between an ideal binary liquid solution and a pure solid phase of one of the components, at a given pressure. Figure 5 is a representation of such a system, in which the curved lines represent the composition of the liquid solution in equilibrium with component 1 or component 2 as the case may be. Point *y* represents the eutectic mixture. The liquid solution of composition corresponding to *a* is in equilibrium with pure solid component 1 at *a*′. Similarly, the liquid solution of composition *b* is in equilibrium with pure solid component 2 at *b*′. The liquid solution of the composition corresponding to *y* is in equilibrium with both pure solid component 1 and pure solid component 2. Below T_3, the entire system is solid. From the previous discussion in Chapter 25, we have seen that, when the liquid solution is ideal and when the solid phase is pure component 1 or pure component 2, as the case may be, the curved liquid-phase line from $T_1{}^*$ to T_3 at *y* is dependent only on the properties of component 1, not on component 2; and, similarly, the curved liquid-phase line from $T_2{}^*$ to T_3 at *y* is dependent only on the properties of component 2, not on component 1.

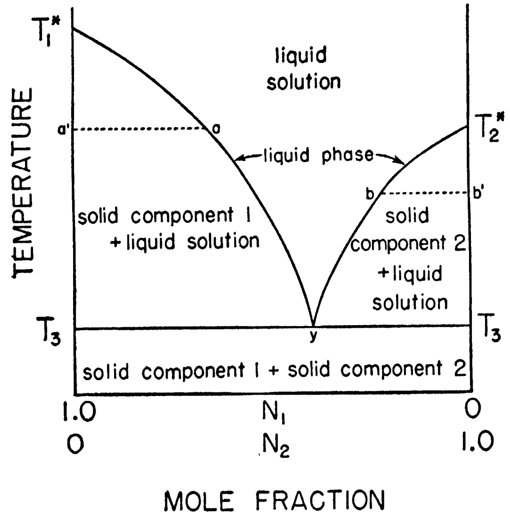


FIGURE 5. Diagram of temperature and composition, at constant pressure, for a substantially ideal binary system involving the liquid and solid phases, with the two compounds being insoluble in one another in the solid phase.

If the two components are such that they form a solid solution over the entire range of composition, that is, both components occur in both the liquid and solid phases over the entire range of composition, then three different kinds of diagrams are possible, depending upon the nature of the two components. These three different diagrams are analogous to those shown in Figures 1, 2, and 3 for the temperature and composition, at a given pressure, for a binary system involving the gaseous and liquid phases, with the two liquid components being completely soluble.

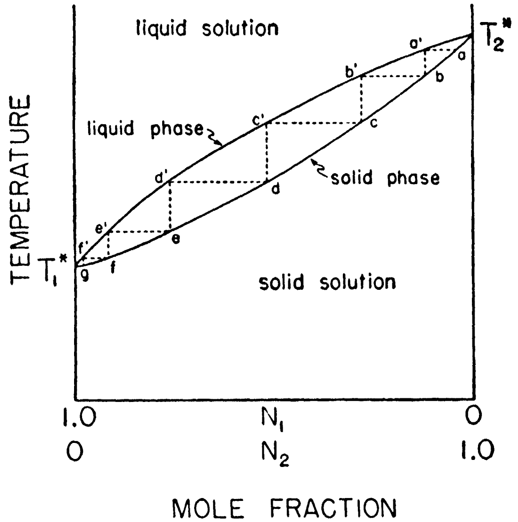


FIGURE 6. Diagram of temperature and composition, at constant pressure, for a substantially ideal binary system involving the liquid and solid phases, with the two components being soluble in the solid phase over the entire range of composition.

Figure 6 shows the diagram, at a given pressure, of the temperature and composition for a binary system involving equilibrium between the liquid and solid phases, with each phase being a solution of the two components, and with both curves lying between the freezing points of the two pure components. In such a system, the solid phase of composition corresponding to *a* would be in equilibrium with the liquid phase of composition corresponding to *a′*, and similarly for *b* and *b′*, *c* and *c′*, *d* and *d′*, etc.

Figure 7 shows the diagram, at a given pressure, of the temperature and composition for a binary system involving equilibrium between the liquid and solid phases, with each phase being a solution of the two components, and with the curves for both the liquid and solid phases passing through a minimum. This binary system of liquid and solid phases having a minimum freezing point is analogous to the binary system of liquid and gaseous phases having a minimum boiling point.

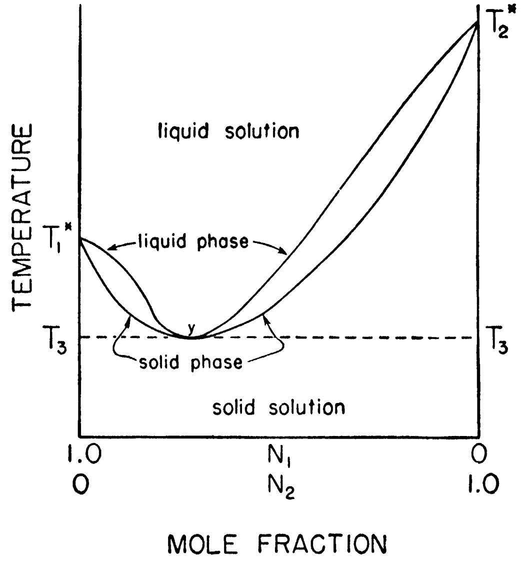


FIGURE 7. Diagram of temperature and composition, at constant pressure, for a binary system involving the liquid and solid phases, with the two components being soluble in the solid phase over the entire range of composition, with a minimum-freezing mixture.

Figure 8 shows the diagram, at a given pressure, of the temperature and composition for a binary system involving equilibrium between the liquid and solid phases, with each phase being a solution of the two components, and with the curves for both the liquid and solid phases passing through a maximum. This binary system of liquid and solid phases having a maximum freezing point is analogous to the binary system of liquid and gaseous phases having a maximum boiling point.

In connection with solid solutions of non-polar substances, it is to be noted that the tendency for components to dissolve in the solid state is more favorable when the solute molecules have nearly the same size and shape as do the molecules of the major component, permitting some of the latter molecules in the crystalline lattice to be replaced by solute molecules without fusion of the crystal. This replacement of molecules of the major component in the crystalline lattice by appropriate solute molecules without fusion of the crystal is further made much more favorable where the particular crystalline form of the major component has resulted from a transition involving the absorption of an amount of energy comparable to the energy of fusion. In such case, the crystal,

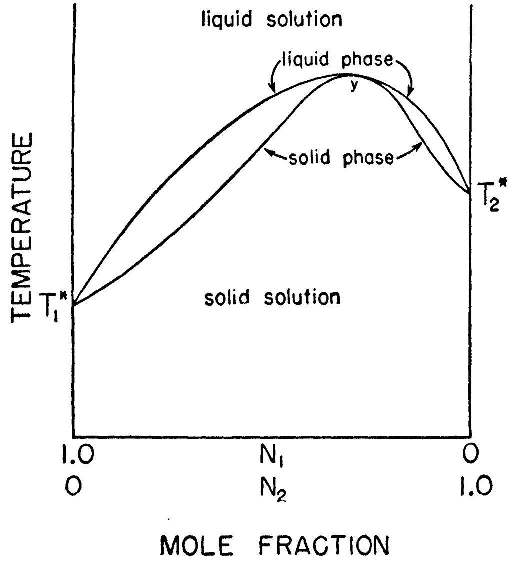


FIGURE 8. Diagram of temperature and composition, at constant pressure, for a binary system involving the liquid and solid phases, with the two components being soluble in the solid phase over the entire range of composition, with a maximum-freezing mixture.

which has a small heat of fusion, is not far removed from the liquid state and possesses considerable mobility of structure, thus permitting greater latitude in the size and shape of the solute molecules that may enter the crystalline lattice of the major component without its actual fusion.

When the two components of a binary mixture in the solid phase form a solid solution over only a limited range of composition, the resulting diagram of the temperature and composition for the equilibrium between the liquid and solid phases is of the form shown in Figure 9, when the system exhibits a eutectic. This diagram is analogous to the one shown in Figure 4 for the equilibrium between the liquid and gaseous phases.

The foregoing systems have been described in terms of the diagram of temperature and composition at constant pressure. As in the systems involving the gaseous and liquid phases, corresponding diagrams of pressure and composition at constant temperature may be constructed for the foregoing systems involving the liquid and solid phases.

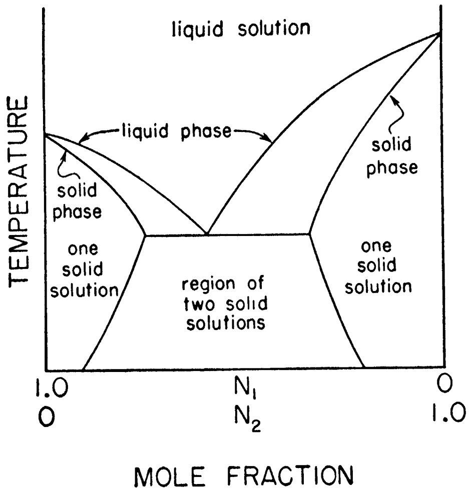


FIGURE 9. Diagram of temperature and composition at constant pressure, for a binary system involving the liquid and solid phases, with the two components exhibiting a eutectic mixture and having a limited range of solubility in the solid phase.

5. Systems of more than two components. The diagrams that must be employed to represent the phase relations in systems of three or more components become rather complex, both in the equilibria involving the gaseous and liquid phases of the several components and in the equilibria involving the liquid and solid phases. Since it is beyond the scope of this book to cover such systems, readers who wish to pursue this subject further are referred to the references given in the next section, with the reminder that all systems that are in thermodynamic equilibrium are subject to the laws and relations of chemical thermodynamics previously presented or derived.

6. Collateral reading. For further details regarding thermodynamics and the phase rule, and the study of systems of two, three, or more components, the reader is referred to Gibbs (*1*), Roozeboom (*2*), Findlay and Campbell (*3*), Washburn (*4*), Eastman and Rollefson (*5*), Young (*6*), Lecat (*7*), Ewell and Welch (*8*), and Bowden (*9*).

REFERENCES

1. J. W. Gibbs, *Collected Works*, Longmans, Green, and Company, New York, 1928.
2. H. W. B. Roozeboom, *Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre*, Vieweg, Braunschweig, Germany, 1901–1913.
3. A. Findlay and A. N. Campbell, *The Phase Rule and its Applications*, Longmans, Green, and Company, New York, 1938.
4. E. W. Washburn, *An Introduction to the Principles of Physical Chemistry*, McGraw-Hill Book Company, New York, 1921.
5. E. D. Eastman and G. K. Rollefson, *Physical Chemistry*, McGraw-Hill Book Company, New York, 1947.
6. S. Young, *Fractional Distillation*, Macmillan & Company, London, 1903.
7. M. Lecat, *L'azeotropisme*, Lamertin, Brussels, 1918.
8. R. H. Ewell and L. M. Welch, *Ind. Eng. Chem.* **37**, 1224 (1945).
9. S. T. Bowden, *The Phase Rule and Phase Reactions, Theoretical and Practical*, Macmillan & Company, London, 1938.

PROBLEMS

1. The following data are given for *o*-xylene and *m*-xylene, respectively, at 1 atm: freezing point, −25.187°, −47.872°C; heat of fusion at the freezing point, 3.250, 2.765, kcal/mole; C_P (liq) − C_P (c), at the freezing point, 6.80, 9.50, cal/deg mole. Assuming an ideal liquid solution, no solid solution, and constancy of the difference in heat capacity of the two phases, construct the diagram of temperature and composition, at a constant pressure of 1 atm, for the equilibrium between the liquid and solid phases, and calculate the eutectic composition and temperature. Compare with the observations of Pitzer and Scott, *J. Am. Chem. Soc.* **65**, 803 (1943).

2. Construct the diagram of temperature and composition, at a constant pressure of 1 atm, for the equilibrium between the gaseous and liquid phases of *o*-xylene and *m*-xylene, assuming an ideal liquid solution and an ideal gaseous phase, and taking the following equations for the vapor pressure of the two pure compounds, respectively:

$$\log P = 6.99891 - 1474.679\ (213.686 + t);$$
$$\log P = 7.00908 - 1462.266\ (215.105 + t).$$

Here P is in millimeters of mercury and t is in degrees Centigrade.

3. Construct diagrams of pressure and composition at constant temperature for the binary systems shown in Figures 1, 2, and 3, involving the liquid and gaseous phases.

33

Special Applications of Thermodynamics

1. Principles. Special applications of thermodynamics not discussed in the earlier chapters may include the examination of systems participating in processes involving changes in conditions which are normally constant, such as the gravitational field, magnetic field, electric field, surfaces and surface tension, centrifugal force, and elastic condition. In any process involving variables of this kind, the regular laws of thermodynamics suffice to provide the desired thermodynamic scrutiny.

The process, whatever its nature, must conform to the requirements of the first law in that, covering all the participating systems, the sum of all the changes in energy is zero,

$$\sum \mathrm{d}E = 0. \tag{1}$$

Or, if attention is focused upon some one particular system, its increase in energy is equal to the sum of all the different kinds of energy absorbed by the system less the sum of all the different kinds of energy given up by the system to the surroundings,

$$\mathrm{d}E = \delta q + \delta w + \delta u. \tag{2}$$

In Equation 2, q, w, and u are as defined in Chapter 6, representing, respectively, heat energy, PV work energy, and all other energy absorbed by the system.

If the process is a reversible one, it must also conform to the requirement of the second law in that, covering all the participating systems, the sum of the changes in entropy is zero,

$$\sum \mathrm{d}S = 0. \tag{3}$$

Or, for a specified system, the increase in entropy is equal to the heat absorbed divided by the absolute temperature,

$$\mathrm{d}S = \frac{\delta q}{T}\cdot \tag{4}$$

It is clear from the foregoing that the special variables will enter the calculations only in the term δu of Equation 2, which term includes all energy other than the heat energy, δq, or the PV work energy, δw, absorbed by the system during the process.

2. Gravitational field. Consider the process in which a system, consisting of one mole of any substance of molecular weight M is moved in a reversible manner at constant temperature and pressure from an initial position A in the gravitational field of the earth to a final position B in the same gravitational field, position B being at a height h vertically above position A. By the first law,

$$\mathrm{d}E = \delta q + \delta w + \delta u, \tag{5}$$

and, by the second law,

$$\mathrm{d}S = \frac{\delta q}{T}. \tag{6}$$

But

$$\delta w = -P\,\mathrm{d}V, \tag{7}$$

so that, with T and P constant, we have (see Chapter 16)

$$\delta u = \mathrm{d}(E + PV - TS) = \mathrm{d}F. \tag{8}$$

But the energy, δu, which is all the energy, other than heat energy and PV work energy, absorbed by the given system in the process, is the mechanical potential energy measured as the mass of the system multiplied by the gravitational acceleration, g, multiplied by the increase in height, $\mathrm{d}h$. That is,

$$\delta u = \mathrm{d}F = Mg\,\mathrm{d}h. \tag{9}$$

Since the temperature and pressure are constant, Equation 9 may be written as

$$\left(\frac{\partial F}{\partial h}\right)_{P,T} = Mg. \tag{10}$$

Equation 10 shows that the rate of change of the free energy of a system with height of position in a given gravitational field, with pressure, temperature, and other variables constant, is equal to the product of the mass and the gravitational acceleration.

As pointed out by Lewis and Randall (*1*), an interesting application of the foregoing relation is the simple case of a vertical column, of height, h, of a pure liquid, in thermodynamic equilibrium at constant temperature and constant external pressure. Consider a horizontal segment of the pure liquid near the top of the column and a similar horizontal segment near the bottom of the column. If thermodynamic equilibrium exists, the free energy of unit mass of the liquid must be the same in the two segments. But the molal free energy, under the described conditions, is a function only of the position in the gravitational field and of the pressure within the liquid. The pressure, P, within the liquid at any height, h, measured from the top of the vertical column of liquid, is equal to the constant external pressure, P (external), plus the pressure due to the height, h, of the column of liquid. That is, at any height, h,

$$P = P(\text{external}) + gh\rho, \tag{11}$$

where ρ is the density of the liquid.

At constant temperature, the free energy, per mole, of the liquid under consideration will be a function of the total pressure, P, and the height, h, in the gravitational field. Therefore,

$$F = f(P,h), \tag{12}$$

and

$$\mathrm{d}F = \left(\frac{\partial F}{\partial P}\right)_h \mathrm{d}P + \left(\frac{\partial F}{\partial h}\right)_P \mathrm{d}h. \tag{13}$$

From Chapter 17, we may write

$$\left(\frac{\partial F}{\partial P}\right)_h = V. \tag{14}$$

Substituting Equations 10 and 14 into Equation 13, we have

$$\mathrm{d}F = V\,\mathrm{d}P + Mg\,\mathrm{d}h. \tag{15}$$

But at equilibrium, at constant temperature and constant external pressure,

$$\mathrm{d}F = 0, \tag{16}$$

so that

$$\left(\frac{\partial P}{\partial h}\right)_F = -\frac{Mg}{V} = -g\rho. \tag{17}$$

The result given by Equation 17 is identical with that obtained directly from Equation 11 by differentiation with h at constant F, since the external pressure, the density, and the gravitational acceleration are constant.

If the liquid discussed above were a solution instead of a pure liquid, the partial molal free energy of a given component would be a function of composition as well as the height in the gravitational field and the pressure within the liquid. For component 1, then, at constant temperature and constant external pressure, we may write

$$d\mathrm{F}_1 = \left(\frac{\partial \mathrm{F}}{\partial h}\right)_{P,\mathrm{N}_1} dh + \left(\frac{\partial \mathrm{F}}{\partial P}\right)_{h,\mathrm{N}_1} dP + \left(\frac{\partial \mathrm{F}}{\partial \mathrm{N}_1}\right)_{h,P} d\mathrm{N}_1. \tag{18}$$

At equilibrium, at constant temperature and constant external pressure, the partial molal free energy of component 1 has the same value throughout the solution, so that

$$d\mathrm{F}_1 = 0. \tag{19}$$

Noting, from Equation 17, that

$$dP = -g\rho\, dh, \tag{20}$$

and substituting from Equations 10 and 14, we obtain

$$0 = M_1 g\, dh + \bar{\mathrm{v}}_1(-g\rho)\, dh + \left(\frac{\partial \mathrm{F}_1}{\partial \mathrm{N}_1}\right)_{h,P} d\mathrm{N}_1, \tag{21}$$

or

$$\frac{d\mathrm{N}_1}{dh} = \left(\frac{g(\bar{\mathrm{v}}_1\rho - M_1)}{\partial \mathrm{F}_1/\partial \mathrm{N}_1}\right)_{h,P}. \tag{22}$$

If the rate of change of the partial molal free energy with mole fraction, at constant h, P, and T, is known, then Equation 22 permits the calculation of the change in composition of the solution with height in the gravitational field. If the solution is an ideal one, then, from Chapter 25, we have

$$\left(\frac{\partial \mathrm{F}_1}{\partial \mathrm{N}_1}\right)_{h,P,T} = \frac{RT}{\mathrm{N}_1}, \tag{23}$$

so that Equation 22 becomes

$$\frac{d\mathrm{N}_1}{dh} = \frac{g(\mathrm{v}_1{}^*\rho - M_1)\mathrm{N}_1}{RT}. \tag{24}$$

For further discussion of the thermodynamics of systems subjected to changes in the gravitational field, the reader is referred to Lewis and Randall (*1*), Gibbs (*8*), and Guggenheim (*13*).

3. Centrifugal force. If a solution is subjected to centrifugal force by rotation in a centrifugal machine in such a way that the solution is held as a column of liquid perpendicular to the axis of rotation, very appreciable changes in the composition of the solution, as a function of its distance from the center of rotation, may occur. In such a case, the centrifugal force per unit mass of liquid will replace the gravitational acceleration occurring in Equations 22 and 24, and the distance h is measured from the axis of rotation. For a given distance h from the center of rotation, the centrifugal force per unit mass, g', is

$$g' = 4\pi^2 s^2 h, \tag{25}$$

where s is the speed of rotation in revolutions per second, and h is the distance from the center of rotation.

Substitution of g' from Equation 25 for g in Equation 22 gives

$$\frac{d\mathrm{N}_1}{dh} = 4\pi^2 s^2 h(\bar{\mathrm{v}}_1\rho - M_1)\frac{1}{\left(\dfrac{\partial \mathrm{F}_1}{\partial \mathrm{N}_1}\right)_{h,P}}\cdot \tag{26}$$

It may be seen from Equation 26 that the change of composition with distance from the center of rotation may become very considerable for large values of the speed of rotation, since the effect increases with the square of the speed of rotation. It should be pointed out that modern commercial apparatus is available for such experiments in which the speeds of rotation are of the order of 1000 to 2000 revolutions per second.

If the solution is an ideal one, Equation 26 becomes

$$\frac{d\mathrm{N}_1}{dh} = 4\pi^2 s^2 h(\mathrm{v}_1{}^*\rho - M_1)\frac{\mathrm{N}_1}{RT}, \tag{27}$$

or

$$\frac{d\ln \mathrm{N}_1}{dh} = 4\pi^2 s^2 h(\mathrm{v}_1{}^*\rho - M_1)\frac{1}{RT}\cdot \tag{28}$$

For further discussion of the thermodynamics of systems subjected to a centrifugal force, the reader is referred to Tolman (*2*) and MacInnes (*11*).

4. Magnetic field. If a substance having a magnetic moment, $\mathfrak{M}$, per mole, is in a magnetic field, $\mathcal{H}$, and is subjected to a reversible process involving a change in the magnetic field as well as the usual variables, we may write from the first law:

$$dE = \delta q + \delta w + \delta u. \tag{29}$$

From the second law,

$$\delta q = T\,dS. \tag{30}$$

But the PV energy taken up by the system is

$$\delta w = -P\,dV, \tag{31}$$

and the magnetic energy absorbed by the system is

$$\delta u = \mathcal{H}\,d\mathcal{M}. \tag{32}$$

Substitution into Equation 29 gives the fundamental equation applicable to any reversible change,

$$dE = T\,dS - P\,dV + \mathcal{H}\,d\mathcal{M}. \tag{33}$$

Since, at constant temperature and pressure,

$$dE + P\,dV - T\,dS = d(E + PV - TS) = dF, \tag{34}$$

we have, at constant temperature and pressure,

$$dF = \mathcal{H}\,d\mathcal{M}, \tag{35}$$

or

$$\left(\frac{\partial F}{\partial \mathcal{M}}\right)_{P,T} = \mathcal{H}. \tag{36}$$

From the fundamental Equation 33, the following additional relations may be readily derived (see Chapter 17): At constant volume and temperature,

$$d(E - TS) = \mathcal{H}\,d\mathcal{M}, \tag{37}$$

or

$$\left[\frac{\partial(E - TS)}{\partial \mathcal{M}}\right]_{V,T} = \mathcal{H}. \tag{38}$$

At constant entropy and volume,

$$dE = \mathcal{H}\,d\mathcal{M}, \tag{39}$$

or

$$\left(\frac{\partial E}{\partial \mathcal{M}}\right)_{S,V} = \mathcal{H}. \tag{40}$$

At constant energy and volume,

$$dS = -\left(\frac{\mathcal{H}}{T}\right) d\mathcal{M}, \tag{41}$$

or

$$\left(\frac{\partial S}{\partial \mathcal{M}}\right)_{E,V} = -\frac{\mathcal{H}}{T}. \tag{42}$$

At constant entropy and pressure,

$$d(E + PV) = dH = \mathcal{H} d\mathcal{M}, \tag{43}$$

or

$$\left(\frac{\partial H}{\partial \mathcal{M}}\right)_{S,P} = \mathcal{H}. \tag{44}$$

Proceeding as in Chapter 17, one may obtain the following relations between the several variables, at constant volume:

$$\left(\frac{\partial T}{\partial \mathcal{M}}\right)_{S,V} = \left(\frac{\partial \mathcal{H}}{\partial S}\right)_{\mathcal{M},V}; \tag{45}$$

$$\left(\frac{\partial T}{\partial \mathcal{H}}\right)_{S,V} = -\left(\frac{\partial \mathcal{M}}{\partial S}\right)_{\mathcal{H},V}; \tag{46}$$

$$\left(\frac{\partial S}{\partial \mathcal{M}}\right)_{T,V} = -\left(\frac{\partial \mathcal{H}}{\partial T}\right)_{\mathcal{M},V}; \tag{47}$$

$$\left(\frac{\partial S}{\partial \mathcal{H}}\right)_{T,V} = \left(\frac{\partial \mathcal{M}}{\partial T}\right)_{\mathcal{H},V}. \tag{48}$$

With pressure constant, similar relations hold:

$$\left(\frac{\partial T}{\partial \mathcal{M}}\right)_{S,P} = \left(\frac{\partial \mathcal{H}}{\partial S}\right)_{\mathcal{M},P}; \tag{49}$$

$$\left(\frac{\partial T}{\partial \mathcal{H}}\right)_{S,P} = -\left(\frac{\partial \mathcal{M}}{\partial S}\right)_{\mathcal{H},P}; \tag{50}$$

$$\left(\frac{\partial S}{\partial \mathcal{M}}\right)_{T,P} = -\left(\frac{\partial \mathcal{H}}{\partial T}\right)_{\mathcal{M},P}; \tag{51}$$

$$\left(\frac{\partial S}{\partial \mathcal{H}}\right)_{T,P} = \left(\frac{\partial \mathcal{M}}{\partial T}\right)_{\mathcal{H},P}. \tag{52}$$

Additional details regarding thermodynamics and magnetization, including applications, may be found in articles by Stoner (*3*), Weiss and Forrer (*4,5*), Giauque (*6*), Debye (*7*), and Guggenheim (*13*).

5. Electric field. Consider a system composed of a dielectric fluid placed between the parallel plates of a condenser. If $\mathfrak{E}$ is the potential and $\mathfrak{Q}$ is the charge, the differential electrical work of charging the condenser is $\mathfrak{E}\,\mathrm{d}\mathfrak{Q}$. If the system participates in a reversible process involving a change in the potential, $\mathfrak{E}$, we may write from the first law,

$$\mathrm{d}E = \delta q + \delta w + \delta u. \tag{53}$$

But, from the second law, the heat energy is

$$\delta q = T\,\mathrm{d}S. \tag{54}$$

The PV work is

$$\delta w = -P\,\mathrm{d}V. \tag{55}$$

The remaining energy absorbed by the system during the process is the electrical work, so that

$$\delta u = \mathfrak{E}\,\mathrm{d}\mathfrak{Q}. \tag{56}$$

Combination of the foregoing gives the fundamental equation

$$\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V + \mathfrak{E}\,\mathrm{d}\mathfrak{Q}. \tag{57}$$

At constant temperature and pressure, Equation 57 becomes

$$d(E + PV - TS) = \mathrm{d}F = \mathfrak{E}\,\mathrm{d}\mathfrak{Q}, \tag{58}$$

or

$$\left(\frac{\partial F}{\partial \mathfrak{Q}}\right)_{T,P} = \mathfrak{E}. \tag{59}$$

From the fundamental equation, the following additional equations may be readily derived:

$$\left[\frac{\partial(E - TS)}{\partial \mathfrak{Q}}\right]_{V,T} = \mathfrak{E}; \tag{60}$$

$$\left(\frac{\partial E}{\partial \mathfrak{Q}}\right)_{S,V} = \mathfrak{E}; \tag{61}$$

$$\left(\frac{\partial S}{\partial \mathfrak{Q}}\right)_{E,V} = -\frac{\mathfrak{E}}{T}; \tag{62}$$

$$\left(\frac{\partial H}{\partial \mathfrak{Q}}\right)_{S,P} = \mathfrak{E}. \tag{63}$$

Proceeding as in the preceding section, and also as described by Lewis and Randall (*1*) and Guggenheim (*13*), many additional thermodynamic relations involving the variables for an electric field may be derived.

6. Surfaces and surface tension. The surface tension, γ, is defined as the work required per unit increase in surface area, $\mathfrak{S}$. When any substance participates in a reversible process involving a significant change in the surface area per unit mass, it is necessary to take account of the energy associated with the increase in surface. For the given reversible process, we write from the first law,

$$\mathrm{d}E = \delta q + \delta w + \delta u. \tag{64}$$

From the second law,

$$\delta q = T\,\mathrm{d}S. \tag{65}$$

But

$$\delta w = -P\,\mathrm{d}V. \tag{66}$$

and

$$\delta u = \gamma\,\mathrm{d}\mathfrak{S}. \tag{67}$$

Combination of the foregoing equations yields the fundamental relation

$$\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V + \gamma\,\mathrm{d}\mathfrak{S}. \tag{68}$$

At constant temperature and pressure, Equation 68 becomes

$$\mathrm{d}\,(E + PV - TS) = \mathrm{d}F = \gamma\,\mathrm{d}\mathfrak{S}, \tag{69}$$

or

$$\left(\frac{\partial F}{\partial \mathfrak{S}}\right)_{P,T} = \gamma. \tag{70}$$

From the fundamental equation, the following additional equations may be readily derived:

$$\left[\frac{\partial (E - TS)}{\partial \mathfrak{S}}\right]_{V,T} = \gamma; \tag{71}$$

$$\left(\frac{\partial E}{\partial \mathfrak{S}}\right)_{S,V} = \gamma; \tag{72}$$

$$\left(\frac{\partial S}{\partial \mathfrak{S}}\right)_{E,V} = -\frac{\gamma}{T}; \tag{73}$$

$$\left(\frac{\partial H}{\partial \mathfrak{S}}\right)_{S,P} = \gamma. \tag{74}$$

Proceeding as in the preceding sections, one may derive many additional relations involving surface, surface tension, and the regular thermodynamic variables (*1*). For example, at constant temperature, we have, by simple calculus,

$$\frac{\partial^2 F}{\partial P\,\partial \mathcal{S}} = \left[\frac{\partial\left(\frac{\partial F}{\partial \mathcal{S}}\right)_P}{\partial P}\right]_{\mathcal{S},T} = \left[\frac{\partial\left(\frac{\partial F}{\partial P}\right)_{\mathcal{S}}}{\partial \mathcal{S}}\right]_{P,T}. \qquad (75)$$

But

$$\left(\frac{\partial F}{\partial \mathcal{S}}\right)_{P,T} = \gamma, \qquad (76)$$

and

$$\left(\frac{\partial F}{\partial P}\right)_{\mathcal{S},T} = V. \qquad (77)$$

Substitution into Equation 75 yields

$$\left(\frac{\partial \gamma}{\partial P}\right)_{\mathcal{S},T} = \left(\frac{\partial V}{\partial \mathcal{S}}\right)_{P,T}. \qquad (78)$$

Similarly, at constant pressure,

$$\frac{\partial^2 F}{\partial T\,\partial \mathcal{S}} = \left[\frac{\partial\left(\frac{\partial F}{\partial \mathcal{S}}\right)_T}{\partial T}\right]_{\mathcal{S},P} = \left[\frac{\partial\left(\frac{\partial F}{\partial T}\right)_{\mathcal{S}}}{\partial \mathcal{S}}\right]_{T,P}. \qquad (79)$$

But

$$\left(\frac{\partial F}{\partial \mathcal{S}}\right)_{P,T} = \gamma, \qquad (80)$$

and

$$\left(\frac{\partial F}{\partial T}\right)_{\mathcal{S},P} = -S, \qquad (81)$$

so that

$$\left(\frac{\partial \gamma}{\partial T}\right)_{\mathcal{S},P} = -\left(\frac{\partial S}{\partial \mathcal{S}}\right)_{T,P}. \qquad (82)$$

But

$$S = \frac{H - F}{T}, \qquad (83)$$

and, by differentiation

$$\left(\frac{\partial S}{\partial \mathcal{S}}\right)_{T,P} = \frac{\left(\frac{\partial H}{\partial \mathcal{S}}\right)_{T,P} - \left(\frac{\partial F}{\partial \mathcal{S}}\right)_{T,P}}{T}. \qquad (84)$$

Appropriate combination of the foregoing equations yields the relation

$$\gamma = T\left(\frac{\partial \gamma}{\partial T}\right)_{\mathcal{S}} + \left(\frac{\partial H}{\partial \mathcal{S}}\right)_T . \tag{85}$$

Equation 85 provides an important relation involving the surface tension, the temperature coefficient of surface tension, and the change of heat content with surface area.

In the foregoing, the composition of the system under investigation has remained constant. Consider now the system at constant pressure and temperature, with the composition as an additional variable. We may write, then, as above,

$$\frac{\partial^2 F}{\partial n_2\, \partial \mathcal{S}} = \left[\frac{\partial \left(\dfrac{\partial F}{\partial \mathcal{S}}\right)_{n_2}}{\partial n_2}\right]_{\mathcal{S},P,T} = \left[\frac{\partial \left(\dfrac{\partial F}{\partial n_2}\right)_{\mathcal{S}}}{\partial \mathcal{S}}\right]_{n_2,P,T} . \tag{86}$$

But

$$\left(\frac{\partial F}{\partial \mathcal{S}}\right)_{n_2,P,T} = \gamma, \tag{87}$$

and

$$\left(\frac{\partial F}{\partial n_2}\right)_{\mathcal{S},P,T} = \mathrm{F}_2 . \tag{88}$$

Hence

$$\left(\frac{\partial \gamma}{\partial n_2}\right)_{\mathcal{S},P,T} = \left(\frac{\partial \mathrm{F}_2}{\partial \mathcal{S}}\right)_{n_2,P,T} . \tag{89}$$

This equation may be converted to the form of Gibbs's adsorption theorem by remembering that

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial x}{\partial z}\right)_y . \tag{90}$$

Hence

$$\left(\frac{\partial \mathrm{F}_2}{\partial \mathcal{S}}\right)_{n_2} = -\left(\frac{\partial \mathrm{F}_2}{\partial n_2}\right)_{\mathcal{S}} \left(\frac{\partial n_2}{\partial \mathcal{S}}\right)_{\bar{\mathrm{F}}_2}, \tag{91}$$

and

$$\left(\frac{\partial n_2}{\partial \mathcal{S}}\right)_{\bar{\mathrm{F}}_2} = -\frac{\left(\dfrac{\partial \gamma}{\partial n_2}\right)_{\mathcal{S}}}{\left(\dfrac{\partial \mathrm{F}_2}{\partial n_2}\right)_{\mathcal{S}}} . \tag{92}$$

Equation 92 gives the value of the coefficient of adsorption, $(\partial n_2/\partial \mathfrak{S})_{\bar{F}_2}$, in terms of the change of surface tension with composition and the change of the partial molal free energy with composition.

It is interesting to apply Equation 69 to the evaluation of the change in escaping tendency of a drop of liquid with its size, at constant temperature and pressure. If the drop contains n moles of the given substance, of molal volume, V, the total volume of the drop is

$$nV = \frac{4\pi r^3}{3}, \tag{93}$$

where r is the radius of the drop. Differentiation gives

$$dn = \frac{4\pi r^2}{V}\, dr. \tag{94}$$

The surface area of the drop is

$$\mathfrak{S} = 4\pi r^2. \tag{95}$$

Differentiation gives

$$d\mathfrak{S} = 8\pi r\, dr. \tag{96}$$

For the process of transferring dn moles of the given substance, at constant temperature and pressure, from a large body of the substance, where its molal free energy is F°, to the given drop, where its molal free energy is F, we may write

$$dF = (F - F^\circ)\, dn. \tag{97}$$

But by Equation 69

$$dF = \gamma\, d\mathfrak{S}. \tag{98}$$

Appropriate combination of the foregoing equations yields

$$F - F^\circ = \frac{2\gamma V}{r}. \tag{99}$$

Also

$$F - F^\circ = \frac{RT \ln f}{f^\circ} \doteq \frac{RT \ln P}{P^\circ}, \tag{100}$$

so that

$$\frac{\ln P}{P^\circ} \doteq \frac{\ln f}{f^\circ} = \frac{2\gamma V}{rRT}. \tag{101}$$

Equation 101 shows how the fugacity, and approximately the vapor pressure, change with the size of the drop at constant temperature and pressure.

For more details concerning the thermodynamics of surfaces, the reader is referred to Gibbs (*8*), Lewis and Randall (*1*), Tolman (*9*), and Harkins, Young, and Boyd (*12*).

7. Elasticity. In connection with the study of elastic substances of very high molecular weight, such as rubber, a number of interesting applications of thermodynamics have been made. For example, consider a sample of rubber participating in a reversible process in which it passes from its unstretched state A to a stretched state B. According to the first law,

$$\mathrm{d}E = \delta q + \delta w + \delta u. \tag{102}$$

By the second law,

$$\delta q = T\,\mathrm{d}S. \tag{103}$$

The PV work energy is

$$\delta w = -P\,\mathrm{d}V. \tag{104}$$

The remaining energy absorbed by the system is the mechanical energy of stretching the rubber, so that

$$\delta u = f_e\,\mathrm{d}l, \tag{105}$$

where l is the length and f_e is the elastic force constant. Substitution into Equation 102 gives the fundamental relation

$$\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V + f_e\,\mathrm{d}l. \tag{106}$$

At constant external pressure and temperature, Equation 104 becomes

$$\mathrm{d}(E + PV - TS) = \mathrm{d}F = f_e\,\mathrm{d}l, \tag{107}$$

or

$$\left(\frac{\partial F}{\partial l}\right)_{P,T} = f_e. \tag{108}$$

Now, by definition,

$$F = H - TS. \tag{109}$$

Differentiation of Equation 109 with l at constant P and T gives

$$\left(\frac{\partial F}{\partial l}\right)_{P,T} = \left(\frac{\partial H}{\partial l}\right)_{P,T} - T\left(\frac{\partial S}{\partial l}\right)_{P,T}. \tag{110}$$

Combination of Equations 108 and 110 gives

$$f_e = \left(\frac{\partial H}{\partial l}\right)_{P,T} - T\left(\frac{\partial S}{\partial l}\right)_{P,T}. \tag{111}$$

Equation 111 permits the evaluation of the change of entropy with length when the elastic constant and the heat content change on stretching are known.

From Equation 106, the following additional equations may be derived:

$$\left[\partial \frac{(E - TS)}{\partial l}\right]_{V,T} = f_e; \tag{112}$$

$$\left(\frac{\partial E}{\partial l}\right)_{S,V} = f_e; \tag{113}$$

$$\left(\frac{\partial S}{\partial l}\right)_{E,V} = -\frac{f_e}{T}; \tag{114}$$

$$\left(\frac{\partial H}{\partial l}\right)_{S,P} = f_e. \tag{115}$$

As in the case of the other special applications considered in the preceding sections, many additional thermodynamic relations involving elasticity may be derived in the usual manner. For some additional discussions of the application of thermodynamics to elasticity in polymers, the reader is referred to Flory (*10*) and the additional references given therein.

8. Collateral reading. For further details and extensions regarding the special applications of thermodynamics discussed in this chapter, the reader is referred to the publications cited in the relevant sections, together with appropriate references given in the cited papers or books.

REFERENCES

1. G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill Book Company, New York, 1923.
2. R. C. Tolman, *J. Am. Chem. Soc.* **33**, 121 (1911).
3. E. C. Stoner, *Phil. Mag.* **19**, 565 (1935).
4. P. Weiss, *Ann. phys.* **17**, 97 (1932).
5. P. Weiss and R. Forrer, *Ann. phys.* **5**, 153 (1926).
6. W. F. Giauque, *J. Am. Chem. Soc.* **49**, 1864 (1927).
7. P. Debye, *Ann. Physik* **81**, 1154 (1926).

8. J. W. Gibbs, *Collected Works*, Longmans, Green, and Company, New York, 1928.

9. R. C. Tolman, *J. Chem. Phys.* **16**, 758 (1948).

10. P. J. Flory, *J. Chem. Phys.* **15**, 397 (1947).

11. D. A. MacInnes, *Ann. N.Y. Acad. Sci.* **43**, 243 (1942).

12. W. D. Harkins, T. F. Young, and E. Boyd, *J. Chem. Phys.* **8**, 954 (1940).

13. E. A. Guggenheim, *Thermodynamics. An Advanced Treatment for Chemists and Physicists*, Interscience Publishers, New York, 1949.

34

Thermodynamic Calculations

1. Modern compilations of selected values of thermodynamic properties. In the modern compilations of selected values of thermodynamic properties, as in the tables of *Selected Values of Properties of Hydrocarbons* (*1*), there may be found values of the following thermodynamic properties given for the thermodynamic standard state from the absolute zero to high temperatures:

$(F^\circ - H_0^\circ)/T$, free energy function;
$(H^\circ - H_0^\circ)/T$, heat content function;
S°, entropy;
$H^\circ - H_0^\circ$, heat content (referred to 0°K);
C_P°, heat capacity;
ΔHf°, heat of formation (from the elements);
ΔFf°, free energy of formation (from the elements);
$\log_{10} Kf$, logarithm of the equilibrium constant of formation (from the elements).

In making up such a compilation, the basic values used are the following:

$\Delta Hf^\circ_{298.16}$, the standard heat of formation (from the elements) at 25°C;
$(H^\circ - H_0^\circ)/T$, for each temperature for which the thermodynamic values are to be tabulated;
$(F^\circ - H_0^\circ)/T$, for each temperature for which the thermodynamic values are to be tabulated;
C_P°, for each temperature for which the thermodynamic values are to be tabulated.

From the foregoing basic values, the entire table is made up as follows:

From the heat content function, values of $H^\circ - H_0^\circ$, the heat content at the given temperature referred to the absolute zero, are obtained by simple multiplication of the heat content function by the temperature, as

$$H^\circ - H_0^\circ = (T)\left(\frac{H^\circ - H_0^\circ}{T}\right). \qquad (1)$$

Values of the standard entropy, S°, are obtained as the value of the heat content function less the value of the free energy function, as

$$S^\circ = \left(\frac{H^\circ - H_0^\circ}{T}\right) - \left(\frac{F^\circ - H_0^\circ}{T}\right). \qquad (2)$$

The value of ΔHf_0° is obtained from the relation

$$\Delta Hf_0^\circ = \Delta Hf^\circ_{298.16} - \Delta(H^\circ_{298.16} - H_0^\circ), \qquad (3)$$

where

$$\Delta(H^\circ_{298.16} - H_0^\circ) = (H^\circ_{298.16} - H_0^\circ)(\text{compound} \\ - \sum(H^\circ_{298.16} - H_0^\circ)(\text{elements}). \qquad (4)$$

When the value of ΔHf_0° is obtained, the values of ΔHf° at all other temperatures are obtained from the relation

$$\Delta Hf^\circ = \Delta Hf_0^\circ + \Delta(H^\circ - H_0^\circ), \qquad (5)$$

where

$$\Delta(H^\circ - H_0^\circ) = (H^\circ - H_0^\circ)(\text{compound}) \\ - \sum(H^\circ - H_0^\circ)(\text{elements}). \qquad (6)$$

Values of ΔFf° at each temperature are obtained from the relation

$$\Delta Ff^\circ = \Delta Hf_0^\circ + T\Delta\left(\frac{F^\circ - H_0^\circ}{T}\right), \qquad (7)$$

where

$$\Delta\left(\frac{F^\circ - H_0^\circ}{T}\right) = \left(\frac{F^\circ - H_0^\circ}{T}\right)(\text{compound}) \\ - \sum\left(\frac{F^\circ - H_0^\circ}{T}\right)(\text{elements}). \qquad (8)$$

Values of $\log_{10} Kf$ are obtained at each temperature from the values of ΔFf° from the relation

$$\Delta Ff^\circ = -RT \ln Kf, \qquad (9)$$

or

$$\log_{10} Kf = -\frac{\Delta Ff^\circ}{2.302585RT}. \qquad (10)$$

The same tables of *Selected Values of Properties of Hydrocarbons* also give values for the following properties:

Heat of formation, free energy of formation, and entropy, for the liquid state, at 25°C;
Heat and entropy of fusion;
Heat and entropy of vaporization;
Standard heat, entropy, and free energy of vaporization, at 25°C;
Heat of combustion, for the gaseous and liquid states, at 25°C;
Vapor pressures, from 10 mm to 1500 mm Hg.

The tables of *Selected Values of Chemical Thermodynamic Properties* (*2*) list the following thermodynamic properties for all substances for which thermodynamic data are available, except carbon compounds containing more than two carbon atoms per molecule:

Series I: Heat of formation, free energy of formation, logarithm of the equilibrium constant of formation, entropy, and heat capacity, each at 25°C, for solid, liquid, and gaseous states, as appropriate and known; also, where calculable, the heat of formation at 0°K.

Series II: Heat, temperature, and entropy of transition, fusion, and vaporization, including values of pressure as appropriate and known.

2. Standard order of arrangement of compounds. The substances listed in the foregoing tables are arranged in a manner similar to that used by Bichowsky and Rossini (*3*), with some modification. The chemical elements are arranged in the order shown in Figure 1. If the elements are taken to be arranged in the order *a, b, c, d, e,* etc., the compounds are in the order *a, b, ba, c, ca, cb, cba, d, da, db, dba, dc, dca, dcb, dcba*; etc.

With regard to the carbon compounds, the following arrangement holds: All the compounds containing carbon with one or more of the elements preceding it in the standard order of arrangement (given in Figure 1) but including none of the elements following carbon in the standard order of arrangement, are placed in the group of carbon compounds. Within this group, the compounds of carbon, having the empirical formula $C_aO_bH_cX_dY_e \cdots$, all the compounds containing one carbon atom per molecule are listed first, in the order O,H, etc., of the standard arrangement. Then follow the compounds containing two carbon atoms per molecule, etc.

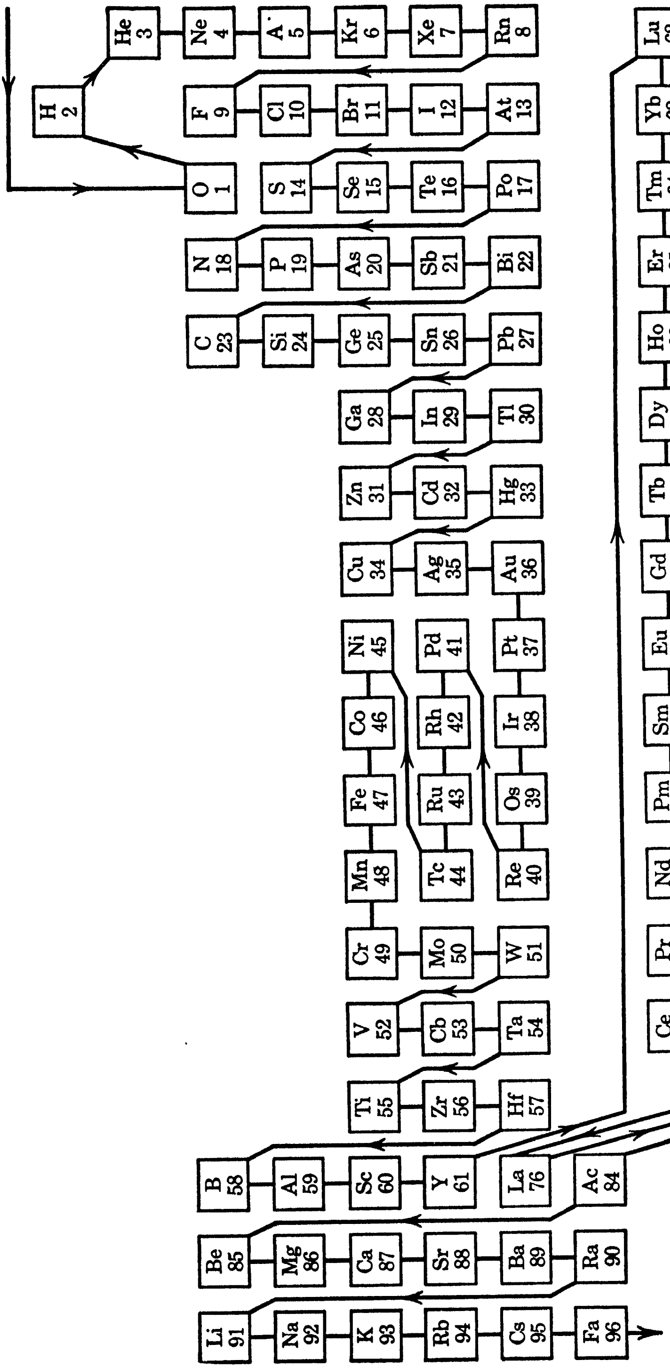


FIGURE 1. Standard order of arrangement of the chemical elements.

3. Equilibrium constants for chemical reactions. Whenever values of $\log_{10} Kf$ are available for the temperature or temperatures of interest for each of the reactants and products in a given chemical reaction, the calculation of $\log_{10} K$ or the equilibrium constant for the given reaction may be made very simply. Consider the reaction

$$b\mathrm{B} + c\mathrm{C} = m\mathrm{M} + n\mathrm{N}. \tag{11}$$

Then, for this reaction,

$$\log_{10} K = \sum \log_{10} Kf\ (\text{products}) - \sum \log_{10} Kf\ (\text{reactants})$$

$$= m \log_{10} Kf_{\mathrm{M}} + n \log_{10} Kf_{\mathrm{N}} - b \log_{10} Kf_{\mathrm{B}} - c \log_{10} Kf_{\mathrm{C}}. \tag{12}$$

For each reactant or product that is an element in the standard state, the value of $\log_{10} Kf$ is of course given in the table as zero since ΔFf° is zero.

In the foregoing manner, values of the logarithm of the equilibrium constant as a function of temperature for a number of reactions involving O_2, H_2, H_2O, C (graphite), CO, CO_2, and CH_4 were calculated and plotted by Wagman, Kilpatrick, Taylor, Pitzer, and Rossini (*4*), as shown in Figure 2.

4. Evaluation of thermodynamic properties for real conditions at high pressures. In most of the foregoing calculations, the various properties dealt with have usually applied to the thermodynamic reference state (Chapter 27), which for gases is the ideal condition of unit fugacity (1 atmosphere, unless otherwise specified) and for pure liquids and solids is the real condition at actual unit pressure (1 atmosphere, unless otherwise specified).

We have seen that a simple framework can be assembled to give values for all the important thermodynamic properties as a function of temperature for the thermodynamic standard state. In the solution of a given problem involving real states at some high pressure P, at some elevated temperature T, the procedure is to calculate the results for the standard states at the given temperature, and then to compute, at that constant temperature, the change in the values of the given properties in going from the standard states to the given real conditions at the pressure P.

This means that, for example, a complete description and evaluation of the thermodynamic properties of a substance can be provided by means of (*a*) a tabulation giving values of the several

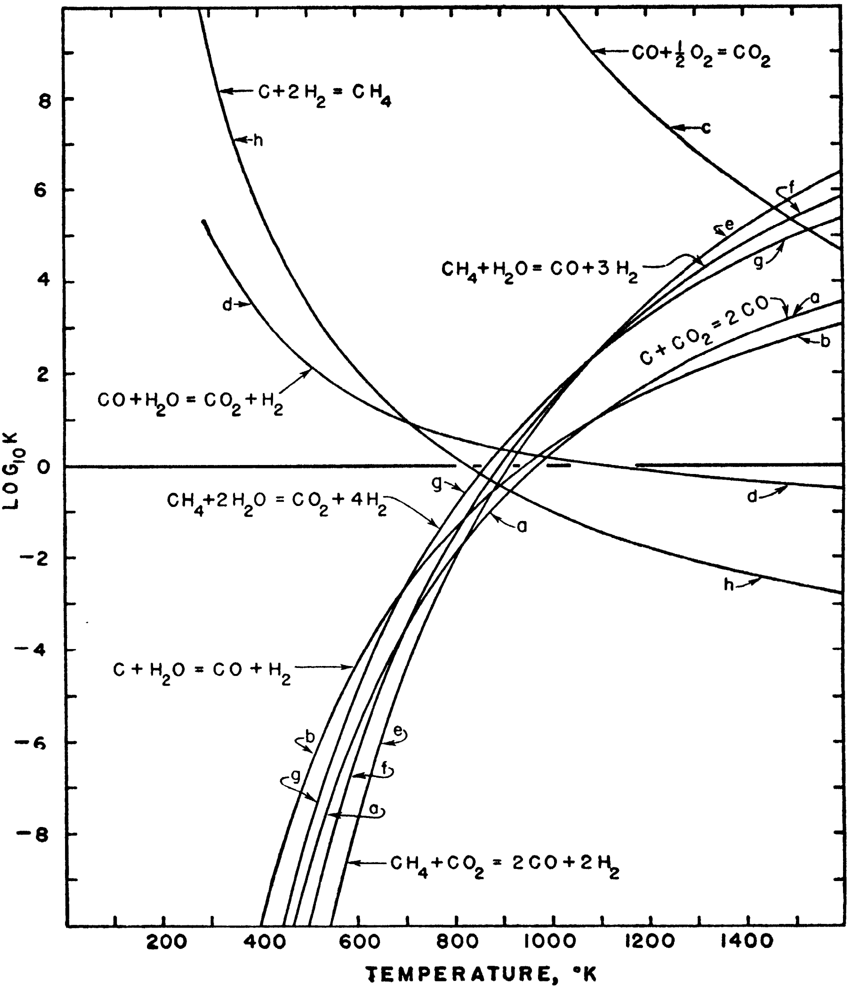


FIGURE 2. Plot of the logarithm of the equilibrium constant for eight reactions involving O_2, H_2, H_2O, C (graphite), CO, CO_2, and CH_4.

The scale of ordinates gives the logarithm (to the base 10) of the equilibrium constant, $\log_{10} K$, for the given reaction. The scale of abscissas gives the temperature in degrees Kelvin. The curves apply to the following reactions:

(*a*) C (solid, graphite) + CO_2 (g) = 2CO (g).
(*b*) C (solid, graphite) + H_2O (g) = CO (g) + H_2 (g).
(*c*) CO (g) + $\frac{1}{2}O_2$ (g) = CO_2 (g).
(*d*) CO (g) + H_2O (g) = CO_2 (g) + H_2 (g).
(*e*) CH_4 (g) + CO_2 (g) = 2CO (g) + $2H_2$ (g).
(*f*) CH_4 (g) + H_2O (g) = CO (g) + $3H_2$ (g).
(*g*) CH_4 (g) + $2H_2O$ (g) = CO_2 (g) + $4H_2$ (g).
(*h*) C (solid, graphite) + $2H_2$ (g) = CH_4 (g).

From D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer, and F. D. Rossini (*4*).

thermodynamic properties for the standard state at each temperature of interest, and (*b*) a tabulation giving, for the same temperatures, values of the difference in the given thermodynamic property between various pressures and the standard state, covering each pressure of interest.

In preceding sections and chapters, we have seen how values of the several thermodynamic properties may be assembled for the standard state at various temperatures. The next step is to evaluate, as mentioned above, the change of the given thermodynamic property with pressure at the given temperature.

If, at the given temperature, we know how the energy, entropy, and volume change with the pressure, the picture is complete. That is to say, if we know

$$\left(\frac{\partial E}{\partial P}\right)_T, \quad \left(\frac{\partial S}{\partial P}\right)_T, \quad \text{and} \quad \left[\frac{\partial (PV)}{\partial P}\right]_T, \tag{13}$$

as a function of pressure, all the other defined thermodynamic properties become known as a function of pressure at the given temperature. Chapters 13, 14, and 17 summarize the equations required for the calculations, including those for

$$\left(\frac{\partial H}{\partial P}\right)_T, \quad \text{and} \quad \left(\frac{\partial F}{\partial P}\right)_T. \tag{14}$$

Changes of the defined functions of fugacity and activity with pressure are given by the equations derived in Chapters 23 and 27, as

$$\left(\frac{\partial \ln f}{\partial P}\right)_T, \quad \text{and} \quad \left(\frac{\partial \ln a}{\partial P}\right)_T. \tag{15}$$

It is to be noted from the various relations involved that a knowledge of the P-V-T relations for the given substance, over the range of temperature and pressure to be covered, would serve to give a complete evaluation of the difference in the given thermodynamic property between the standard state and the real state at each pressure of interest, at each temperature. Similarly, it would suffice to have, at each temperature, values of

$$PV = f(P), \tag{16}$$

together with values, at the given temperature, of

$$\left[\frac{\partial(PV)}{\partial T}\right]_P, \tag{17}$$

at the various pressures involved.

5. Equations for vapor pressures. For many calculations in thermodynamics it is convenient to have mathematical equations that give the vapor pressure of condensed substances, liquid or solid, as a function of the temperature. Of the many different equations for vapor pressures that have been developed, ranging from one with two constants to those with six to ten constants, the most generally useful equation appears to be the Antoine equation of three constants (*5,6,7*):

$$\log P = A - \frac{B}{C + t}. \tag{18}$$

Equation 18 may also be expressed in terms of the absolute temperature by writing

$$\log P = A - \frac{B}{C' + T}, \tag{19}$$

where

$$C' = C - 273.16. \tag{20}$$

The Antoine equation may also be expressed explicitly in terms of temperature, as

$$t = \frac{B}{A - \log P} - C, \tag{21}$$

or

$$T = \frac{B}{A - \log P} - C'. \tag{22}$$

The advantages of the Antoine equation are that, over not too large ranges of temperature, it reproduces the best experimental observations with great accuracy, that it can be extrapolated reasonable distances beyond the range of the experimental observations with good accuracy, and that it can be extrapolated great distances beyond the range of the experimental observations without too large uncertainties. It is to be noted that some equations that contain five or six constants, the values of which have been juggled to fit the experimental observations accurately over a small range of temperature, may be quite useless beyond the range of measurement. For a review of the Antoine equation for vapor pressures the reader is referred to Thomson (*6*), and for its application to precise measurements to Willingham, Taylor, Pignocco, and Rossini (*7*).

6. Evaluation of heats of vaporization from data on vapor pressures and compressibilities. The problem of calculating a reliable value of the heat of vaporization of a given substance under its own vapor pressure at a given temperature resolves itself into one of obtaining an accurate value for the change of vapor pressure with temperature for the given substance at the given temperature and, with the same percentage accuracy, a value for the difference in the molal volumes of the substance in the gaseous and liquid phases.

The change of vapor pressure with temperature is obtained from the experimental observations of vapor pressure at various temperatures, or by calculation from an equation, such as the Antoine equation, which has been set up to represent the experimental observations of vapor pressure as a function of temperature.

The value for the difference in the molal volumes of the substance in the gaseous and liquid phases is calculated from values of the compressibility factor for the gas at the given temperature and pressure, and the density of the liquid at the given temperature and pressure.

The accurate calculation of the heat of vaporization in this way may be illustrated as follows: Given, for a given substance, the following equation representing the vapor pressure of the liquid over the required range of temperature:

$$\log P = A - \frac{B}{C' + T}\cdot \tag{23}$$

From Chapter 22, we have found that, for the process,

$$\text{MX (liq)} = \text{MX (g)}, \tag{24}$$

the heat of vaporization at equilibrium is given by the relation

$$\Delta Hv = T[V\text{ (g)} - V\text{ (liq)}]\frac{dP}{dT}\cdot \tag{25}$$

Now

$$\text{V (g)} - V\text{ (liq)} = V\text{ (g)}\left[1 - \frac{V\text{ (liq)}}{V\text{ (g)}}\right]. \tag{26}$$

From Equation 23,

$$\frac{dP}{dT} = 2.30259\frac{BP}{(C' + T)^2}. \tag{27}$$

Therefore

$$\Delta Hv = 2.30259\left[1 - \frac{V\text{ (liq)}}{V\text{ (g)}}\right]\frac{BPTV\text{ (g)}}{(C' + T)^2}, \tag{28}$$

or

$$\Delta Hv = 2.30259\left[1 - \frac{V\text{ (liq)}}{V\text{ (g)}}\right]\frac{BRT^2}{(C' + T)^2}\frac{PV\text{ (g)}}{RT}. \tag{29}$$

Using the abbreviation for the compressibility factor,

$$z = \frac{PV\text{ (g)}}{RT}, \tag{30}$$

Equation 29 becomes

$$\Delta Hv = 2.30259\left[1 - \frac{PV\text{ (liq)}}{zRT}\right]\frac{zBRT^2}{(C' + T)^2}. \tag{31}$$

Equation 31 shows that the heat of vaporization at a temperature T may be calculated if there are known for the given temperature and pressure the compressibility factor z and the molal volume of the liquid, together with the constants B and C' of the Antoine equation. In making such calculations it is important that the constants, including the gas constant, be expressed in consistent units.

7. Equilibria in chemical reactions at constant volume. The procedure for calculating mole fractions of the components present at equilibrium in a reaction proceeding at constant volume in the gaseous phase may be illustrated in a simple way for the case where the concentrations are small enough and the temperatures high enough for the gases to be assumed ideal. For the reaction

$$\text{CO (g)} + \tfrac{1}{2}\text{O}_2\text{ (g)} = \text{CO}_2\text{ (g)}, \tag{32}$$

the value of the standard change in free energy at 3000°K is

$$\Delta F^\circ_{3000} = -6.44\text{ kcal/mole}, \tag{33}$$

and

$$\log_{10} K_{3000} = 0.4691; \qquad K_{3000} = 2.945. \tag{34}$$

One mole of carbon monoxide and one-half mole of oxygen are placed in a vessel having a volume of 50 liters. Assume that the gases are ideal and that equilibrium is established at 3000°K with respect to the reaction given by Equation 32. It is desired to calculate the mole fractions of the three gases at equilibrium at 3000°K. Now

$$K = \frac{(a_{CO_2})}{(a_{CO})(a_{O_2})^{1/2}}. \tag{35}$$

For gases, the activity is equal to the fugacity, and, if the gases are ideal, the fugacity may be replaced by the pressure. Accordingly, with this approximation,

$$K = \frac{P_{CO_2}}{P_{CO}P_{O_2}^{1/2}}. \tag{36}$$

If x is the number of moles of CO_2 present at equilibrium, then the number of moles of CO and O_2 at equilibrium are $1 - x$ and $(1 - x)/2$, respectively, as calculated from the stoichiometry. The relations are summarized in the following table:

Gas	Number of Moles, n			Mole Fraction at Equilibrium
	Initial	Change	At Equilibrium	
CO	1	$-x$	$1 - x$	$\frac{2(1-x)}{3-x}$
O_2	$\frac{1}{2}$	$-\frac{x}{2}$	$\frac{1-x}{2}$	$\frac{1-x}{3-x}$
CO_2	0	$+x$	x	$\frac{2x}{3-x}$
Total	$1\frac{1}{2}$	$-\frac{x}{2}$	$\frac{3-x}{2}$	

The pressure of each gas at equilibrium is equal to the number of moles of that gas at equilibrium multiplied by RT/V. That is, at equilibrium, for the given volume,

$$P_{CO} = (1 - x)\frac{RT}{V}. \tag{37}$$

For the given conditions, RT/V is a constant, with the value

$$\frac{RT}{V} = \frac{(0.0820544)(3000)}{50} = 4.923. \tag{38}$$

It is important to note that, if the volume is in liters and we wish the pressure to be in atmospheres, the value of the gas constant must be given in liter-atmospheres per degree mole. Similarly,

$$P_{O_2} = \left(\frac{1-x}{2}\right)\left(\frac{RT}{V}\right), \tag{39}$$

and

$$P_{CO_2} = x\frac{RT}{V}. \tag{40}$$

Then, substituting Equations 37, 39, and 40 into Equation 36, we obtain

$$K = \left[\frac{x}{(1-x)^{1/2}}\right]\left(\frac{2V}{RT}\right)^{1/2}. \tag{41}$$

Substituting the values of K and RT/V from Equations 34 and 38, Equation 41 becomes

$$\frac{x}{(1-x)^{1/2}} = (2.945)(2.462)^{1/2}. \tag{42}$$

The value of x in Equation 42 may be determined by the usual method of squaring both sides and solving the resulting cubic equation for the value of x lying between 0 and 1. Then the values of the mole fractions of the components at equilibrium may be calculated in accordance with the fourth column of the table given above.

8. Equilibria in reactions of isomerization. When values of $\log_{10} Kf$ are available for each of a given group of isomers, the relative amounts of each isomer at equilibrium may be readily calculated. Consider, for example, the equilibrium in the gaseous phase among the four C_8 alkyl benzenes, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene, labeled a, b, c, and d, respectively. For the reaction,

$$\text{ethylbenzene (g)} = o\text{-xylene (g)}, \tag{43}$$

the value of $\log_{10} K$ is given by the difference in $\log_{10} Kf$ for the two isomers, as

$$\log_{10} K_{b/a} = \log_{10} Kf_b - \log_{10} Kf_a. \tag{44}$$

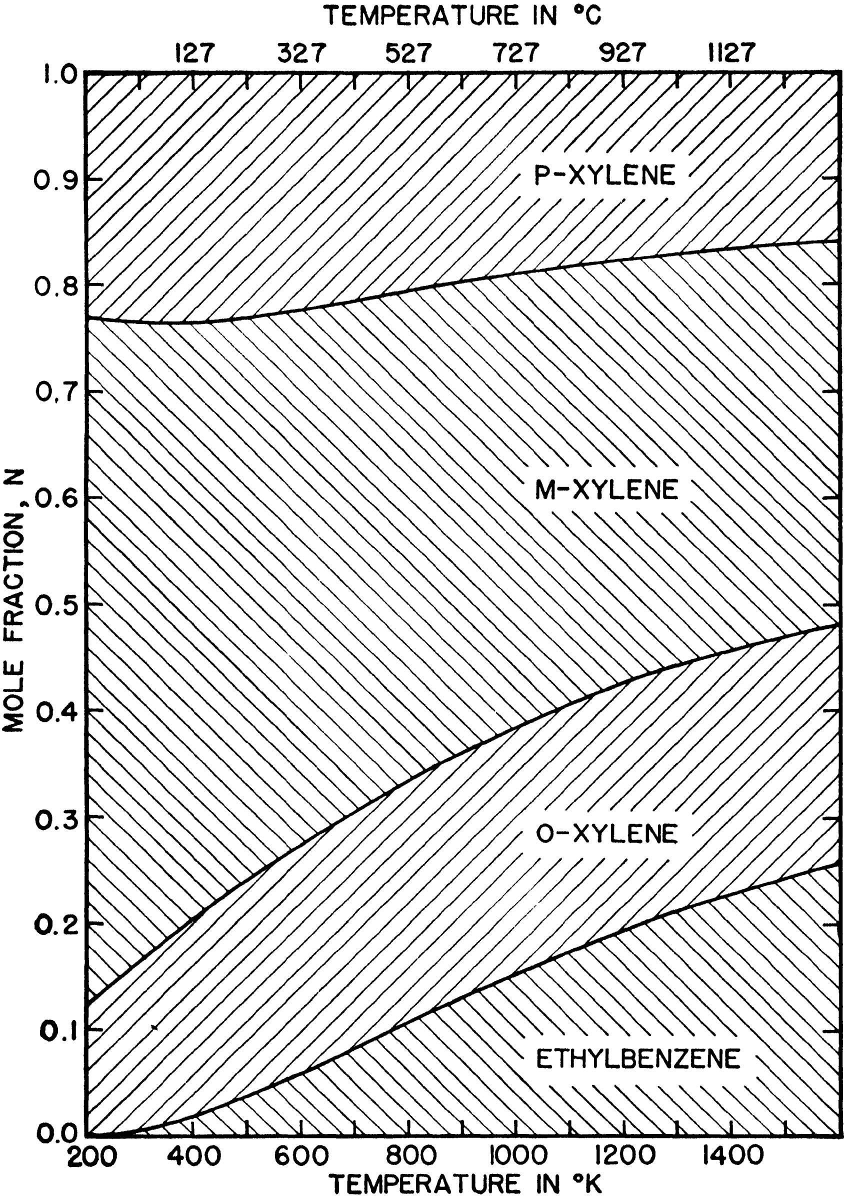


FIGURE 3. Equilibrium concentrations of the C_8H_{10} alkyl benzenes.

The scale of ordinates measures the amount in mole fraction, and the scale of abscissas gives the temperature in degrees Kelvin and degrees centigrade. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present when in equilibrium with all its other isomers, in the gas phase. From W. J. Taylor, D. D. Wagman, M. G. Williams, K. S. Pitzer, and F. D. Rossini (*8*).

From this value of $\log_{10} K_{b/a}$, the value of $K_{b/a}$ is calculated. But

$$K_{b/a} = \frac{N_b}{N_a}. \qquad (45)$$

Similarly, values are calculated for the ratios of the mole fractions of c to a, and d to a, as N_c/N_a and N_d/N_a. But

$$\frac{N_a}{N_a} + \frac{N_b}{N_a} + \frac{N_c}{N_a} + \frac{N_d}{N_a} = \frac{N_a + N_b + N_c + N_d}{N_a} = \frac{1}{N_a}. \qquad (46)$$

With the value of N_a thus known, the values of N_b, N_c, and N_d become known from the ratios previously calculated. In this manner, the results shown in Figure 3 were obtained (*8*).

An extension of this problem is to calculate the mole fraction of each of the four isomers present in the liquid state at thermodynamic equilibrium at a given temperature, as for example 100°C. From the vapor-pressure equations (*1*), one may calculate the vapor pressure of each compound in the pure state at the given temperature to be P_a^*, P_b^*, P_c^*, and P_d^*, respectively. A liquid mixture of these four isomers may be assumed to be an ideal solution. Therefore, at the given temperature,

$$P_a = N_a^l P_a^*; \quad P_b = N_b^l P_b^*; \quad P_c = N_c^l P_c^*; \quad P_d = N_d^l P_d^*. \qquad (47)$$

But

$$P_a = N_a^g P; \quad P_b = N_b^g P; \quad P_c = N_c^g P; \quad P_d = N_d^g P. \qquad (48)$$

In these equations, N_i^l and N_i^g represent the mole fractions of the given component in the liquid and gaseous phases, respectively, and P is the sum of the partial pressures, as

$$P = \sum P_i. \qquad (49)$$

From Equations 47 and 48, we have the required mole fractions of the liquid phase as

$$N_a^l = \frac{N_a^g P}{P_a^*}; \quad N_b^l = \frac{N_b^g P}{P_b^*}; \quad N_c^l = \frac{N_c^g P}{P_c^*}; \quad N_d^l = \frac{N_d^g P}{P_d^*}. \qquad (50)$$

Since

$$\sum N_i^l = 1, \qquad (51)$$

it follows that

$$P\left(\frac{N_a^g}{P_a^*} + \frac{N_b^g}{P_b^*} + \frac{N_c^g}{P_c^*} + \frac{N_d^g}{P_d^*}\right) = 1. \qquad (52)$$

Equation 52 gives the value of P, which may then be used in Equation 50 to give the values of the mole fractions at equilibrium in the liquid phase.

9. Toluene for explosives. During World War II, the requirements for toluene for use in the manufacture of explosives were far beyond all that could be produced by the conventional method of recovery from coal tar. The petroleum industry in the United States brought two new processes for toluene into commercial use, achieving a production many times that available from coal tar.

Figure 4, from Rossini (*9*), gives a plot of $\log_{10} K$ as a function of temperature for the reactions used in producing toluene from petroleum by two different processes.

In the first process, advantage is taken of the fact that the light gasoline fraction of petroleum contains appreciable amounts of (*a*) toluene, (*b*) methylcyclohexane, which can be dehydrogenated to toluene, and (*c*) ethylcyclopentane and dimethylcyclopentanes, which can be isomerized to methylcyclohexane, which can then be dehydrogenated to toluene. All the toluene, including that originally present plus the additional amount formed, is then removed from the other hydrocarbons in the original stock by well-established methods of extraction, or azeotropic distillation, or extractive distillation. The reactions involved are as follows, in the sequence of actual operation:

$$C_7H_{14}\ (\text{g, ethylcyclopentane}) = C_7H_{14}\ (\text{g, methylcyclohexane}); \qquad (53)$$

$$C_7H_{14}\ (\text{g, methylcyclohexane}) = C_7H_8\ (\text{g, toluene}) + 3H_2\ (\text{g}). \qquad (54)$$

Curves A and B in Figure 4 give the logarithm of the equilibrium constant as a function of temperature for Reactions 53 and 54, respectively. Curve A shows that the reaction of isomerization is required to be carried out at low temperatures. Curve B shows that the reaction of dehydrogenation of methylcyclohexane to toluene is required to be performed at higher temperatures. In each case, of course, a suitable catalyst is required.

In the second method for producing toluene from petroleum stock, advantage is taken of the fact that, of the several types of hydrocarbons present in gasoline from a cracking process, the aromatic hydrocarbons (benzene, toluene, xylenes, etc.) are the most stable at high temperatures. The operation here is to pass the mixture of hydrocarbons (paraffins, cycloparaffins, olefins, and aromatics) through a catalytic reaction zone at high temperatures in the presence of hydrogen gas. The several general reactions involve the conversion to aromatics of cycloparaffins, paraffins,

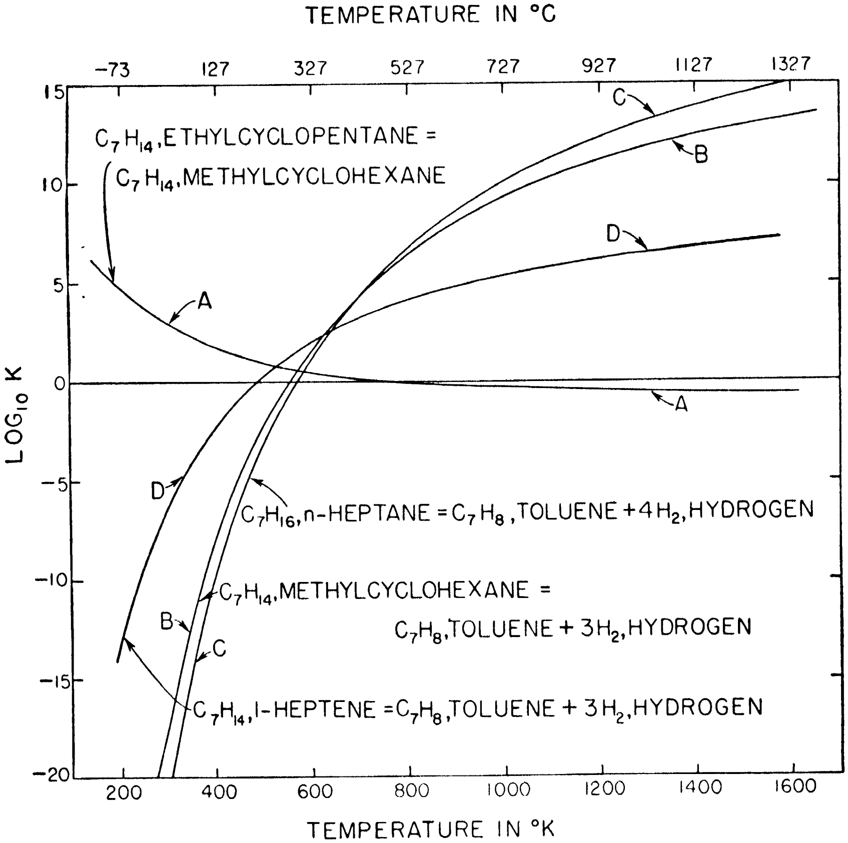


FIGURE 4. Equilibria in reactions involved in the production of toluene from petroleum.

The vertical scale gives the value of the logarithm of the equilibrium constant for the given reactions as written, in the gas phase. From Rossini (*9*).

and olefins, in accordance with the following representative reactions:

$$C_7H_{14}\text{ (g, methylcyclohexane)} = C_7H_8\text{ (g, toluene)} + 3H_2\text{ (g)}; \qquad (55)$$

$$C_7H_{16}\text{ (g, }n\text{-heptane)} = C_7H_8\text{ (g, toluene)} + 4H_2\text{ (g)}; \qquad (56)$$

$$C_7H_{14}\text{ (g, 1-heptene)} = C_7H_8\text{ (g, toluene)} + 3H_2\text{ (g)}. \qquad (57)$$

For each of these reactions, a plot of log K vs. T is given in Figure 4. It may be noted that for each of these reactions in the gas phase the equilibrium is most favorable at high temperatures for the production of toluene. One of the practical problems in such high-temperature operations is to reduce the amount of side reactions, particularly decomposition to carbon in the form of coke.

10. "Isooctane" for aviation fuel. The military need for enormous quantities of "high-octane" aviation fuel during World War II was met by the production of "alkylate" and of "hydrocodimer" materials. These materials were blended with regular aviation-fuel base stock to give larger quantities of material of sufficiently high quality when appropriately fortified with tetraethyl lead. The production of these materials, which are largely mixtures of branched-chain octanes, was made possible by the discovery of commercially usable catalysts (sulfuric acid and hydrofluoric acid) which were able to make hydrocarbons, previously considered quite inert, react rapidly at room temperature.

"Alkylate" material is the product obtained when isobutane is added to a mixture of butenes (preferably rich in isobutene) to form a mixture of branched-chain paraffins, largely octanes, but containing appreciable amounts of hexanes, heptanes, and lower-boiling nonanes. Usually the isobutene is obtained from the gases produced as a by-product of the cracking process. The amount of isobutane available in natural gasoline is augmented by the isomerization of the larger amount of nomal butane present in the natural gasoline. The reactions may be represented as follows:

$$C_4H_{10}\text{ (g, normal butane)} = C_4H_{10}\text{ (g, isobutane)}; \qquad (58)$$

$$C_4H_{10}\text{ (g, isobutane)} + C_4H_8\text{ (g, isobutene)} = C_8H_{18}\text{ (g, "isooctane")}. \qquad (59)$$

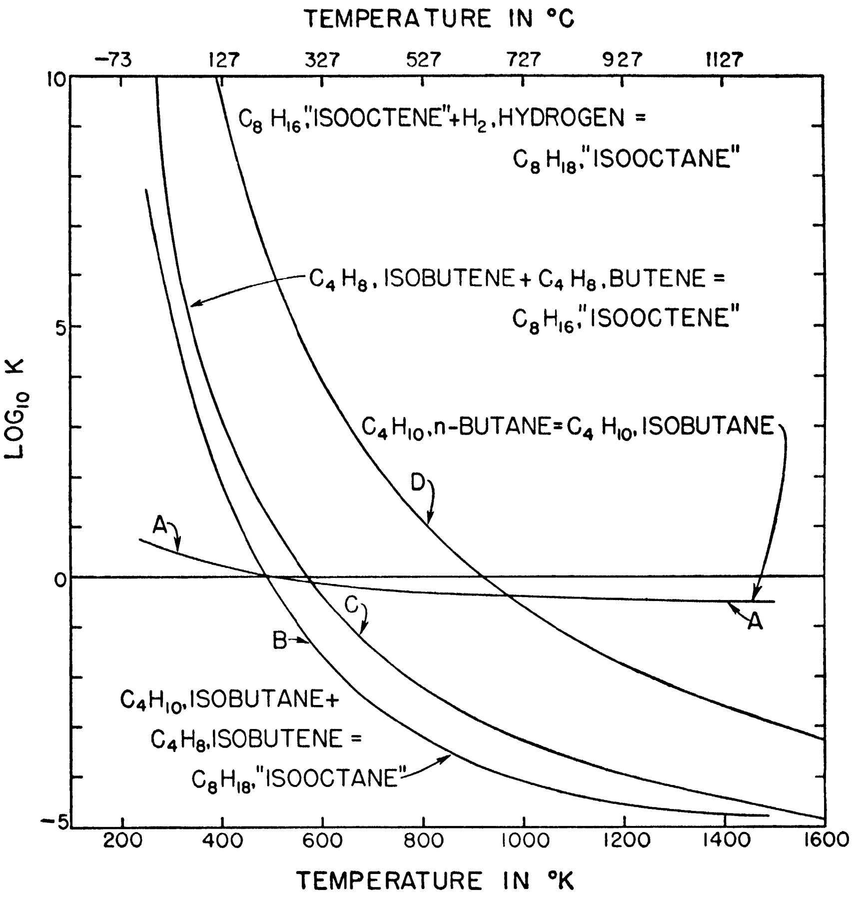


FIGURE 5. Equilibria in reactions involved in the production of "isooctane" for aviation fuel.

The vertical scale gives the value of the logarithm of the equilibrium constant for the given reactions as written, in the gas phase. From Rossini (*9*).

The logarithms of the equilibrium constant of these reactions are given as Curves *A* and *B*, respectively, in Figure 5, from Rossini (*9*). The importance of a suitable catalyst is readily seen from the fact that these reactions must be carried out near room temperature in order to have a favorable equilibrium.

"Hydrocodimer" material is the product obtained on the hydrogenation of codimers of the butenes. The product is similar to "alkylate" in consisting largely of branched-chain octanes and containing also branched-chain hexanes, heptanes, and lower-boiling nonanes, but differs in the relative amounts of the main components. The two reactions may be represented, in principle, as follows:

$$C_4H_8 \text{ (g, isobutene)} + C_4H_8 \text{ (g, 1-butene)} = C_8H_{16} \text{ (g, ``isooctene'')}; \quad (60)$$

$$C_8H_{16} \text{ (g, ``isooctene'')} + H_2 \text{ (g)} = C_8H_{18} \text{ (g, ``isooctane'')}. \quad (61)$$

In Figure 5, Curve *C* gives the logarithm of the equilibrium constant for Reaction 60, and Curve *D* gives that for Reaction 61. It may be seen that for both reactions the equilibrium is more favorable at low temperatures.

11. Butadiene and styrene for synthetic rubber. One of the most remarkable technological accomplishments in history was the creation in this country during World War II of a synthetic rubber industry, which was necessitated by the stoppage of the supply of natural rubber. Regular synthetic rubber today is produced largely from petroleum stock through the copolymerization of 1,3-butadiene and styrene.

The 1,3-butadiene is made by the dehydrogenation of butenes obtained from the cracking processes, and the reaction may be represented as follows:

$$C_4H_8 \text{ (g, 1-butene)} = C_4H_6 \text{ (g, 1,3-butadiene)} + H_2 \text{ (g)}. \quad (62)$$

Curve *A* in Figure 6 gives the values of the logarithm of the equilibrium constant for this reaction, which may be seen to have a more favorable equilibrium at high temperatures.

The styrene is made by adding ethylene to benzene to make ethylbenzene and then dehydrogenating ethylbenzene to styrene, as follows:

$$C_2H_4 \text{ (g, ethylene)} + C_6H_6 \text{ (g, benzene)} = C_8H_{10} \text{ (g, ethylbenzene)}; \quad (63)$$

$$C_8H_{10} \text{ (g, ethylbenzene)} = C_8H_8 \text{ (g, styrene)} + H_2 \text{ (g)}. \quad (64)$$

In Figure 6, Curve *C* gives the logarithm of the equilibrium constant for Reaction 63, and Curve *D* gives that for Reaction 64. It may be noted that the production of ethylbenzene by Reaction 63 must be carried out at relatively low temperatures, whereas the dehydrogenation of ethylbenzene to styrene must be carried out at higher temperatures.

The copolymerization of 1,3-butadiene and styrene to form "regular" synthetic rubber is performed near room temperature, with newer developments indicating a better product for lower temperatures of polymerization.

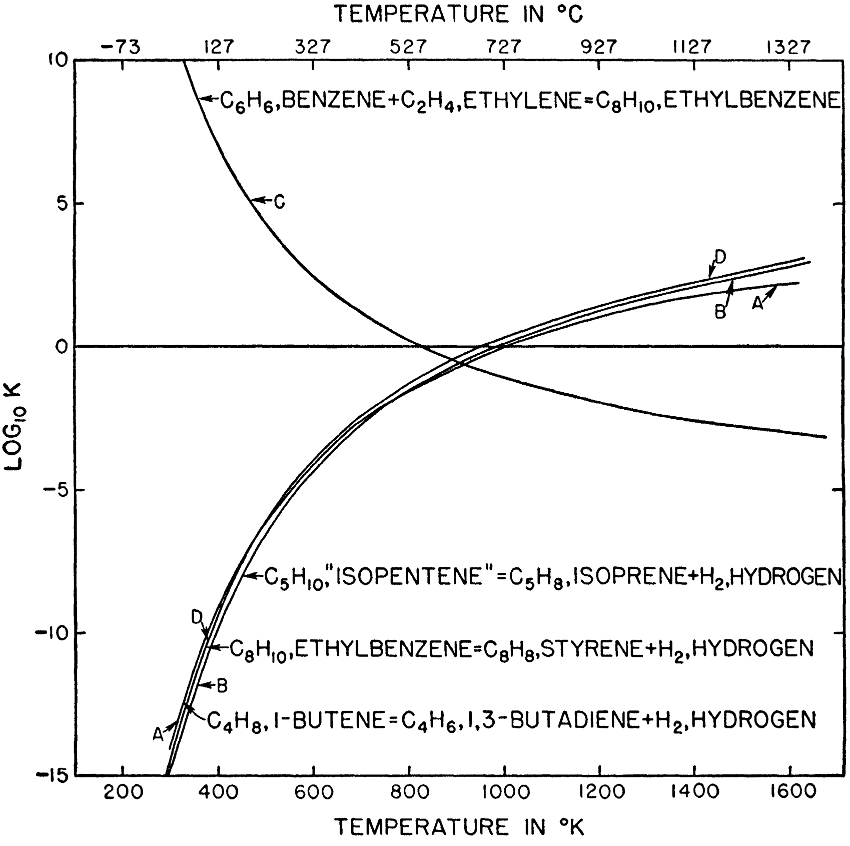


FIGURE 6. Equilibria in reactions involved in the production of components for synthetic rubber.

The vertical scale gives the value of the logarithm of the equilibrium constant for the given reactions as written, in the gas phase. From Rossini (*9*).

12. Isobutene and isoprene for special synthetic rubber. Isobutene, C_4H_8, with which is mixed a small amount of isoprene, C_5H_8, is commercially polymerized at low temperatures to form "butyl" rubber.

The isobutene is obtained from the gases of the cracking process, in which occur appreciable amounts of all four butenes (C_4 monoolefins).

Curve *B* in Figure 6 gives the logarithm of the equilibrium constant as a function of temperature for the reaction of dehydrogenation to isoprene of isopentene, C_5H_{10}, which is also obtained from the gases of the cracking process:

$$C_5H_{10} \text{ (g, isopentene)} = C_5H_8 \text{ (g, isoprene)} + H_2 \text{ (g)}. \qquad (65)$$

As is usual with reactions of dehydrogenation, the equilibrium for Reaction 65 is more favorable at higher temperatures.

13. Synthetic fuels. The reactions for the direct synthesis of gaseous and liquid fuels from carbon and hydrogen have equilibria which are more favorable at low temperatures, and suitable catalysts for the commercial operation of such synthesis at low temperatures are being sought. Curves *C* and *D* in Figure 7 give the logarithm of the equilibrium constant as a function of temperature for the direct synthesis, from carbon and hydrogen, of methane, CH_4, and octane, C_8H_{18}, respectively:

$$C \text{ (c, graphite)} + 2H_2 \text{ (g)} = CH_4 \text{ (g)}; \qquad (66)$$

$$8C \text{ (c, graphite)} + 9H_2 \text{ (g)} = C_8H_{18} \text{ (g, octane)}. \qquad (67)$$

However, it should be pointed out that it is possible to increase the concentration of the wanted hydrocarbon at the higher temperatures by utilizing high pressures of hydrogen. For the reaction given by Equation 67, the equilibrium constant is

$$K = \frac{a_{C_8H_{18}}}{(a_{H_2})^9(a_C)^8}. \qquad (68)$$

The activity of each gas is equal to its fugacity, and the activity of the solid may be taken as unity. As an approximation, the fugacity may be taken as equal to the partial pressure, so that

$$K = \frac{P_{C_8H_{18}}}{(P_{H_2})^9}. \qquad (69)$$

At each temperature, *K* is a constant, and the pressure of the octane may be expressed as the product of the equilibrium constant and the pressure of hydrogen raised to the ninth power:

$$P_{C_8H_{18}} = (P_{H_2})^9K. \qquad (70)$$

The mole ratio of octane to hydrogen in the gaseous phase is approximately $P_{C_8H_{18}}/P_{H_2}$. Then

$$\frac{P_{C_8H_{18}}}{P_{H_2}} = (P_{H_2})^8 K. \tag{71}$$

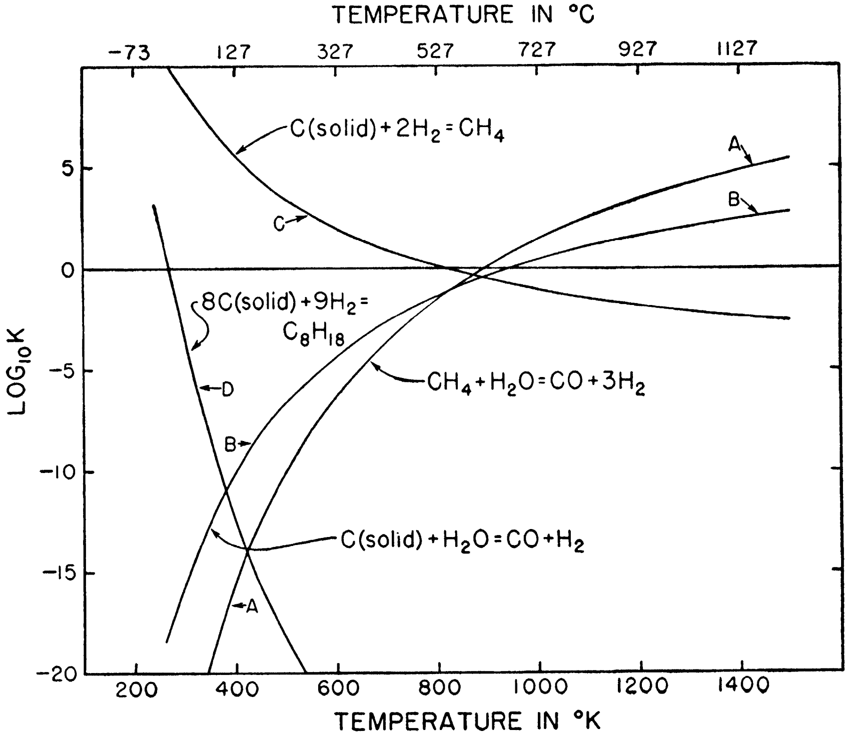


FIGURE 7. Equilibria in reactions involved in the direct synthesis of hydrocarbons and in the production of "synthesis gas" (carbon monoxide plus hydrogen).

The vertical scale gives the value of the logarithm of the equilibrium constant for the given reactions as written, in the gas phase except for the solid carbon. From Rossini (*9*).

Equation 71 shows that, as an approximation, the mole ratio of octane to hydrogen varies directly with the eighth power of the pressure of hydrogen.

At 600°K, for Reaction 67,

$$\log_{10} K = -22.594. \tag{72}$$

If the pressure of hydrogen is 1 atmosphere, the mole ratio of octane to hydrogen at equilibrium at 600°K is almost infinitesimal, being

$$\frac{P_{C_8H_{18}}}{P_{H_2}} = 2.5 \times 10^{-23}. \qquad (73)$$

But, if the pressure of hydrogen is 500 atmospheres, then at equilibrium at 600°K, the mole ratio of octane to hydrogen is

$$\frac{P_{C_8H_{18}}}{P_{H_2}} = (500)^8(10^{-22.594}) = 0.1. \qquad (74)$$

Equation 74 shows that, approximately, the mole ratio of octane to hydrogen is about one-tenth at equilibrium at 600°K, with a pressure of hydrogen of 500 atmospheres.

The foregoing shows that it is extremely advantageous to use a high pressure of hydrogen, as well as low temperatures, to synthesize hydrocarbons directly from carbon and hydrogen.

However, the synthesis of hydrocarbons can be brought about in two steps, one step involving the formation of "synthesis gas" (carbon monoxide plus hydrogen) from solid carbon and steam, and the other step involving the reaction of carbon monoxide and hydrogen to form the hydrocarbon and steam. The formation of the "synthesis gas" may be illustrated by the following reaction:

$$\text{C (c, graphite)} + H_2O\ \text{(g)} = \text{CO (g)} + H_2\ \text{(g)}. \qquad (75)$$

Curve *B* in Figure 7 gives the logarithm of the equilibrium constant for this reaction as a function of the temperature and shows that the equilibrium is more favorable at high temperatures.

With an abundance of natural gas, which is largely methane, synthesis gas may also be produced as follows:

$$CH_4\ \text{(g)} + H_2O\ \text{(g)} = \text{CO (g)} + 3H_2\ \text{(g)}. \qquad (76)$$

Curve *A* in Figure 7 applies to the reaction given by Equation 76.

Hydrocarbon fuels may be made from the synthesis gas by operation at lower temperatures and with suitable catalysts to guide the reaction along the desired path. The following are illustrative reactions:

$$4\text{CO (g)} + 9H_2\ \text{(g)} = C_4H_{10}\ \text{(g, butane)} + 4H_2O\ \text{(g)}; \qquad (77)$$

$$8\text{CO (g)} + 17H_2\ \text{(g)} = C_8H_{18}\ \text{(g, octane)} + 8H_2O\ \text{(g)}. \qquad (78)$$

Curves *A* and *B* in Figure 8 give the logarithm of the equilibrium constant as a function of the temperature for Reactions 77 and 78, respectively. It is seen that the equilibria are more favorable at the lower temperatures for these reactions.

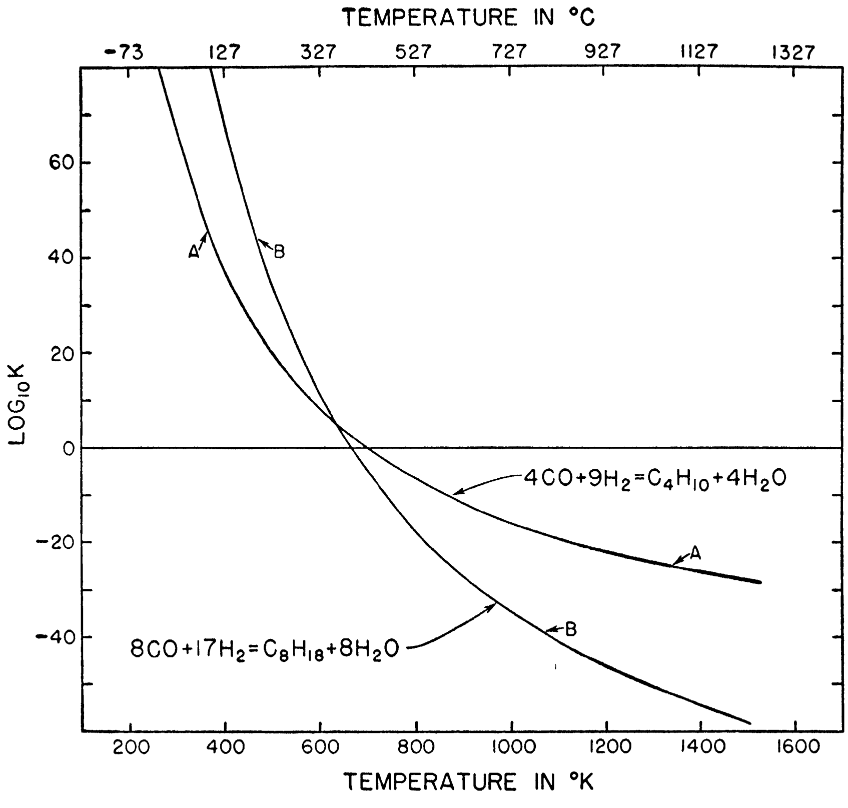


FIGURE 8. Equilibria in reactions involved in the production of synthetic fuels.

The vertical scale gives the value of the logarithm of the equilibrium constant for the given reactions as written, in the gas phase. From Rossini (*9*).

In the reactions given by Equations 77 and 78, it is seen that the stoichiometrical volume of the gaseous reactants is appreciably greater than the stoichiometrical volume of the gaseous products. Therefore, it will be advantageous to carry out such reactions at high pressures of the reactant gases.

14. Synthetic alcohols. By operation with appropriate different catalysts, the same synthesis gas may be used to produce alcohols, as illustrated by the following reaction:

$$2CO\ (g) + 4H_2\ (g) = C_2H_5OH\ (g,\ \text{ethyl alcohol}) + H_2O\ (g). \quad (79)$$

Curve *A* in Figure 9 gives the logarithm of the equilibrium constant as a function of temperature for this reaction, and indicates a more favorable equilibrium at lower temperatures.

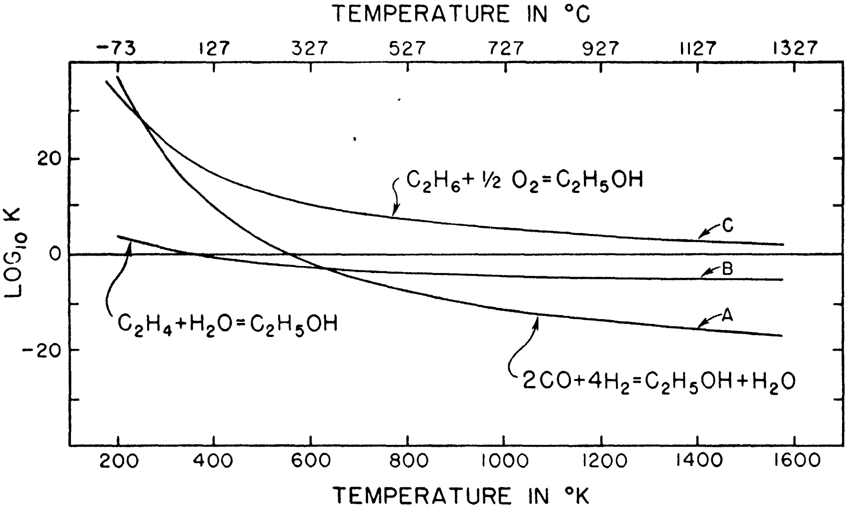


FIGURE 9. Equilibria in reactions involved in the production of synthetic alcohols.

The vertical scale gives the value of the logarithm of the equilibrium constant for the given reactions as written, in the gas phase. From Rossini (*9*).

With special catalysts, it is possible to add water directly to ethylene to form ethyl alcohol:

$$C_2H_4\ (\text{ethylene}) + H_2O\ (g) = C_2H_5OH\ (g,\ \text{ethyl alcohol}). \quad (80)$$

Curve *B* in Figure 9 applies to this reaction and shows a favorable equilibrium at lower temperatures.

Theoretically, ethane may be oxidized directly to form ethyl alcohol:

$$C_2H_6\ (g,\ \text{ethane}) + \tfrac{1}{2}O_2\ (g) = C_2H_5OH\ (g,\ \text{ethyl alcohol}). \quad (81)$$

Curve *C* in Figure 9 applies to this reaction and shows a more favorable equilibrium at low temperatures, although the equilibrium constant is still favorable even at the higher temperatures. It is likely that the successful control of this reaction will require the development of a special catalyst for operation not far from room temperature.

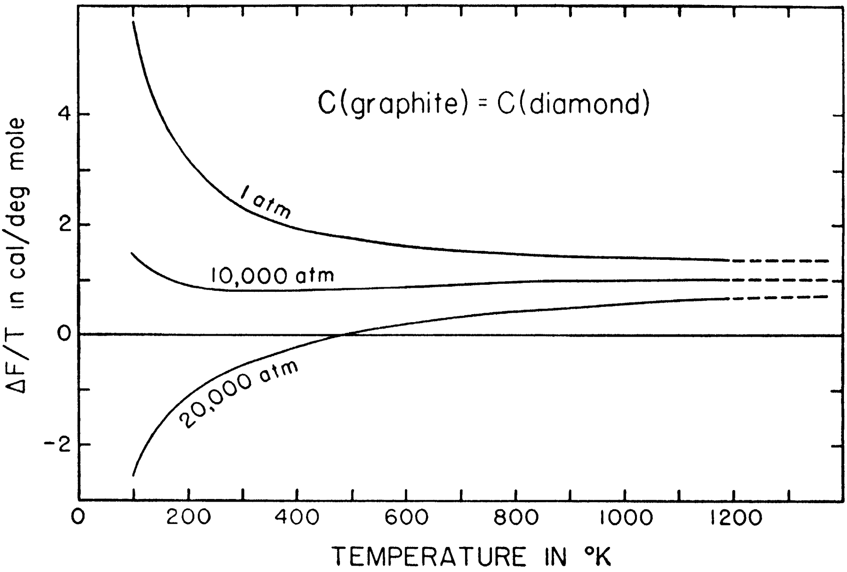


FIGURE 10. Values of $\Delta F/T$ for the conversion of graphite to diamond. The reaction will have a thermodynamic tendency to proceed as written when the value of $\Delta F/T$ is negative. The three curves apply to pressures of 1, 10,000, and 20,000 atmospheres, respectively. From Rossini (*9*).

15. Transition of graphite to diamond.

Figure 10 shows the results of some thermodynamic calculations on the transition of graphite into diamond (*4*). Negative values of $\Delta F/T$ for the transition,

$$C\ (c,\ \text{graphite}) = C\ (c,\ \text{diamond}), \tag{82}$$

correspond to conditions under which the conversion of graphite to diamond would be thermodynamically possible. Of course, for such conditions, a suitable catalyst to make the reaction proceed at a suitable rate must still be found. As may be noted from the plot, the conversion of graphite to diamond is favored by low temperatures and high pressures. At room temperature, a pressure of about 15,000 atmospheres is calculated to be necessary to make the conversion thermodynamically possible. As a result of some work in his laboratory, Bridgman (*10*) has concluded that at temperatures beyond those shown in Figure 10 it is possible that the values of $\Delta F/T$ may tend to become negative rather than continuing to increase to greater positive values. If this is true, it is possible that the pressures necessary for the conversion at high temperatures (where the rate of reaction will be adequate) may not be out of the range of attainment.

16. Evaluation of purity from measurements of freezing points. One of the most important applications of the thermodynamic relations describing the behavior of dilute real solutions, as well as ideal solutions, is in the evaluation of the purity of a substance from experimental observations of the temperature of the equilibrium between the liquid and solid phases of the given substance.

The applicable thermodynamic relations are those given in Chapters 25 and 26 for the equilibrium between a liquid phase consisting of a major component and one or more other components and a solid crystalline phase of the major component alone. The thermodynamic relation to be used is

$$\begin{aligned}\ln \mathrm{N}_1 &= \ln (1 - \mathrm{N}_2)\\ &= -A(T_1{}^* - T)[1 + B(T_1{}^* - T) + \cdots], \qquad (83)\end{aligned}$$

where the constants A and B are defined in Chapter 25, T is the temperature of equilibrium, and $T_1{}^*$ is the value of the temperature when $\mathrm{N}_1 = 1$ or $\mathrm{N}_2 = 0$. When T approaches $T_1{}^*$ in value, as for values of N_1 near unity, or of N_2 near zero, Equation 83 reduces to

$$\mathrm{N}_2 = A(T_1{}^* - T). \qquad (84)$$

For the present purpose, one may imagine a suitable sample of a given liquid substance gradually lowered in temperature. At that temperature at which an infinitesimal amount of crystals of the major component appears and is at equilibrium with the liquid phase, we have a temperature that we may call the freezing point of the given substance. This temperature will be identical with that temperature at which, on the gradual raising of the temperature of the solidified sample, an infinitesimal amount of crystals remains in equilibrium with the liquid phase. Since the quantity of the crystalline phase in each case is negligible, the temperature is that corresponding to the temperature of the liquid-solid equilibrium when the composition of the liquid phase is identical with the composition of the original sample. If the original sample is absolutely pure component 1 (though this is never the situation, since every substance contains some amount of impurity, however small) the temperature of the freezing point so defined is identical with T_1^*. As the amount of impurity in the original sample increases, the freezing point differs more and more from T_1^*, in accordance with Equations 83 and 84.

If the value of T_1^* is known in terms of the same thermometric system as is used to determine the freezing point, then a determination of the freezing point of the actual sample T^s will serve to evaluate the amount of impurity in the sample, in accordance with Equations 83 and 84. That is, for nearly pure substances, the mole fraction of impurity in the original sample, N_2^s, is given by the relation

$$N_2^s = A(T_1^* - T^s), \tag{85}$$

where T^s is the freezing point of the actual sample, and T_1^* is the freezing point of the pure major component. It is to be noted that T^s is, for the original sample, the temperature at which an infinitesimal amount of crystals of the major component is in equilibrium with the liquid phase of the original sample.

The foregoing procedure is satisfactory for the evaluation of purity, for the qualifying systems, when T_1^* is known and when the value of $T_1^* - T^s$ is large in comparison with the uncertainty in the value of T_1^* itself.

When T_1^* is not known, its value may be determined from observations of the temperature of the liquid-solid equilibrium as a function of the fraction of the major component of the original sample which is in the liquid phase. If N_2^s is the mole fraction of impurity in the original sample, then the mole fraction, N_2, of impurity in the liquid phase, for different fractions of the original amount of the major component in the liquid phase, is given by the following relation:

$$N_2 = N_2^s \frac{1}{r}. \tag{86}$$

Here r is the fraction of the original amount of the major component that is in the liquid phase. The fraction of the original amount of the major component that is in the solid phase is, of course, $1 - r$. It is to be remembered that we are dealing with a system in which only the major component appears in the solid phase.

Combination of Equations 84 and 86 gives

$$T = T_1^* - \left(\frac{N_2^s}{A}\right)\left(\frac{1}{r}\right). \tag{87}$$

If experimental observations of the equilibrium temperature T are made as a function of r, which is approximately the fraction

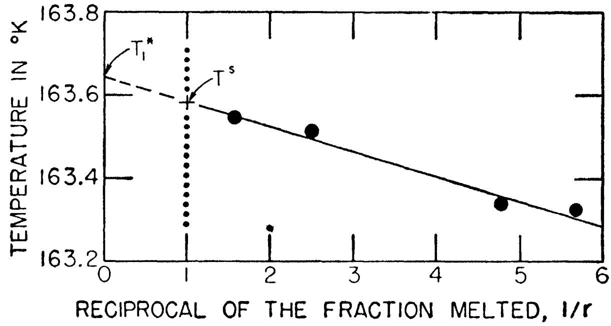


FIGURE 11. Plot of the temperature of the liquid-solid equilibrium for a sample of 2,3,4-trimethylpentane as a function of the reciprocal of the fraction of sample melted. The data are from Pitzer and Scott (*11*).

T^s is the freezing point of the actual sample, and T_1^* is the freezing point of an absolutely pure sample.

of the sample melted, then the values of T may be plotted against $1/r$, as in Figure 11, which is from the data of Pitzer and Scott (*11*). Since T_1^* and N_2^s/A are constant, the data should yield a straight line, as given by Equation 87, at least in the region of small values of N_2.

From Equation 87, it may be noted that, when $1/r = 1$, T is equal to T^s, the freezing point of the actual sample having N_2^s mole fraction of impurity; and when $1/r = 0$, T is equal to T_1^*, the value of the freezing point for the absolutely pure material, with $N_2 = 0$. When $1/r = 2$, only half of the major component is in the liquid phase, and since all the impurity remains in the liquid phase, the mole fraction of impurity in the liquid phase when $1/r = 2$ is $2N_2^s$, that is, twice that in the original sample. The difference in temperature between the points corresponding to $1/r$ equal to 1 and 2, is, of course, the same as the difference in temperature between the points corresponding to $1/r$ equal to 0 and 1. That is to say, there is thus determined the freezing point of the absolutely pure major component without the necessity of ever actually preparing such a sample. Further, it is to be noted from Equation 87 that the slope of the line in Figure 11 gives the value of the constant $\text{N}_2{}^s/A$. Thus, this type of experiment serves to determine not only $T_1{}^*$ but also the value of $\text{N}_2{}^s$. It is to be remembered that the value of $\text{N}_2{}^s$ so determined is not dependent upon the absolute accuracy of $T_1{}^*$ or of T^s.

It is to be emphasized that the foregoing relations between the temperature and the composition of the liquid phase in the solid-liquid equilibrium require that all the solute (impurity) remain in the liquid phase during crystallization and form with the major component an ideal solution (Chapter 25) or a dilute real solution (Chapter 26). In order for all the solute to remain in the liquid phase, no solid solution must be formed. The tendency to form a solid solution is more favorable when the solute molecules have nearly the same size and shape as the solvent molecules (major component), permitting some of the latter molecules to be replaced by solute molecules without fusion of the crystal. This replacement of molecules of the major component in the crystalline lattice by appropriate solute molecules without fusion of the crystal is further made much more favorable where the crystalline form of the major component is obtained, below the freezing point, as the product of a transition with absorption of a quantity of energy comparable with the energy of fusion. That is, this transition corresponds somewhat to a process in which the crystal has almost, but not quite, melted. In such case, the crystal at the melting point, which has a small heat of fusion, is not far removed from the liquid state and possesses considerable mobility of structure, thus permitting greater latitude in the size and shape of the solute molecules which may enter the crystalline lattice without its actual fusion. Thus, the formation of some solid solution may be suspected in any system in which the major component has a small heat of fusion.

From extensive experience in the field of hydrocarbons (*27*), it would appear that solid solutions occur only seldom between a given compound of low molecular weight and the related compounds which are likely to remain as impurity in the given compound after the latter has been subjected to a thorough fractionation, except in the above-mentioned case involving a major component having a small heat of fusion. Furthermore, it is apparent that, when a given compound of low molecular weight has been subjected to a logical system of purification, there will remain as impurity only those compounds which are similar in type to the major component. These latter compounds are, however, precisely those which are most likely to form with the major component the required ideal solution or dilute real solution.

Another method for evaluating the purity of substances involves observation of the amount of premelting, as described by Johnston and Giauque (*12*).

For further details regarding experimental apparatus and procedures for determining purity from measurements of freezing points, from time-temperature observations, and from calorimetric observations, as well as discussions of the kinds of substances amenable to such observations, the reader is referred to Johnston and Giauque (*12*), Taylor and Rossini (*13*), Mair, Glasgow, and Rossini (*14*), Glasgow, Streiff, and Rossini (*15*), Glasgow, Krouskop, Beadle, Axilrod, and Rossini (*16*), Aston, Fink, Tooke, and Cines (*17*), and Streiff, Murphy, Sedlak, Willingham, and Rossini (*18*).

17. Fractionating processes. Because many of the processes used to fractionate molecules involve the thermodynamic equilibrium between two or more phases, one of the most important applications of thermodynamics lies in the analysis of such fractionating processes.

In the simple case, one has a mixture of two kinds of molecules. The problem is to subject the mixture to the action of some appropriate fractionating process for the purpose of separating the two kinds of molecules as much as possible. The fractionating process usually involves the equilibrium between two phases, each containing a mixture of the two molecules, but in different proportions. The two phases may be solid and liquid, as in crystallization or adsorption, or liquid and gaseous, as in distillation, or liquid and liquid, as in extraction, or solid and gaseous, as in adsorption.

In the simple case, the fractionating process can be considered as equivalent to a succession of single stages of fractionation, each one involving the thermodynamic equilibrium between a mixture of the two molecules in one phase and a mixture of the two molecules in the other phase. Letting the two components be numbered 1 and 2 and the two phases be indicated by A and B, we may define the separation factor α as (*27*)

$$\alpha = \frac{\left(\dfrac{N_1}{N_2}\right)^A}{\left(\dfrac{N_1}{N_2}\right)^B}. \tag{88}$$

In the first stage of the given fractionating process, phase A is in equilibrium with phase B, and the composition of phase A may be expressed in terms of α and the composition of phase B:

$$\left(\frac{N_1}{N_2}\right)_1^A = \alpha\left(\frac{N_1}{N_2}\right)_1^B. \tag{89}$$

(In Equation 89 and following, the numeral in the subscript outside the parentheses denotes the number of the stage, as 1,2,3, etc.) In the given fractionating process, phase A of stage 1 is converted without change of composition to become phase B of stage 2, as for example in distillation, the condensation of the gaseous phase of stage 1 to become the liquid phase of stage 2. That is,

$$\left(\frac{N_1}{N_2}\right)_1^A = \left(\frac{N_1}{N_2}\right)_2^B. \tag{90}$$

Similarly, for succeeding stages, up to the number, n, in the process,

$$\left(\frac{N_1}{N_2}\right)_2^A = \left(\frac{N_1}{N_2}\right)_3^B; \tag{91}$$

$$\left(\frac{N_1}{N_2}\right)_3^A = \left(\frac{N_1}{N_2}\right)_4^B; \tag{92}$$

$$\left(\frac{N_1}{N_2}\right)_{n-1}^A = \left(\frac{N_1}{N_2}\right)_n^B; \tag{93}$$

and

$$\left(\frac{N_1}{N_2}\right)_n^A = \left(\frac{N_1}{N_2}\right)_{n+1}^B. \tag{94}$$

These relations are shown schematically in Figure 12. The equilibrium of the two phases in the second, third, and succeeding stages, up to the number, n, in the process, is specified by the following relations, in which, for simplicity, the separation factor α is assumed constant over the range of composition covered:

$$\left(\frac{N_1}{N_2}\right)_2^A = \alpha\left(\frac{N_1}{N_2}\right)_2^B; \tag{95}$$

$$\left(\frac{N_1}{N_2}\right)_3^A = \alpha\left(\frac{N_1}{N_2}\right)_3^B; \tag{96}$$

and

$$\left(\frac{N_1}{N_2}\right)_n^A = \alpha\left(\frac{N_1}{N_2}\right)_n^B. \tag{97}$$

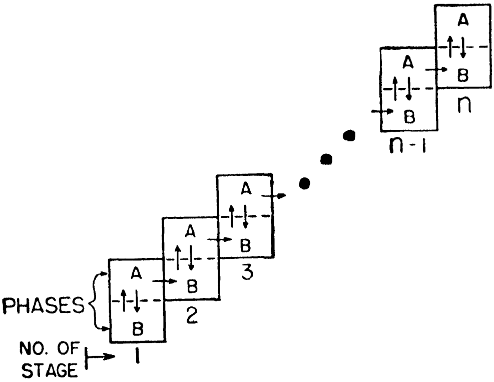


Figure 12. Schematic diagram of a simple fractionating process of n stages, involving thermodynamic equilibrium of two components in each of two phases.

Combination of Equations 89 and 90 gives

$$\left(\frac{N_1}{N_2}\right)_1^A = \alpha\left(\frac{N_1}{N_2}\right)_2^A. \tag{98}$$

Combination of Equations 91, 95, and 98 gives

$$\left(\frac{N_1}{N_2}\right)_1^A = \alpha^2\left(\frac{N_1}{N_2}\right)_3^A. \tag{99}$$

Proceeding in this way to the nth stage, we have

$$\left(\frac{N_1}{N_2}\right)_1^A = \alpha^{n-1}\left(\frac{N_1}{N_2}\right)_n^A. \tag{100}$$

When, as is assumed, the separation factor α is a constant over the given range of composition, Equation 100 provides a simple means of evaluating the number of stages in a given fractionating process if there can be measured the composition of the material in one phase in the first and the final stages of the process, and if the value of the separation factor for the given binary system is known. For this purpose, Equation 100 is rewritten as follows:

$$\alpha^{n-1} = \frac{\left(\frac{N_1}{N_2}\right)_1^A}{\left(\frac{N_1}{N_2}\right)_n^A}; \tag{101}$$

$$(n - 1) \log \alpha = \log \frac{\left(\frac{N_1}{N_2}\right)_1^A}{\left(\frac{N_1}{N_2}\right)_n^A}; \tag{102}$$

$$n - 1 = \frac{1}{\log \alpha} \log \frac{\left(\frac{N_1}{N_2}\right)_1^A}{\left(\frac{N_1}{N_2}\right)_n^A}. \tag{103}$$

The relations apply to any fractionating process, whether it be distillation, extraction, adsorption, or crystallization (in which the solid phase is a solution) if α is constant.

In processes involving thermodynamic equilibrium between the liquid and gaseous phases, the measurement of the composition of the two phases in equilibrium in one stage, for the purpose of evaluating the separation factor, is relatively simple, although high accuracy in the measurement of composition is required for those systems for which the value of α approaches unity. The simplicity of measurement of the composition in such cases lies in the fact that a true sample of the given phase can be withdrawn from the system for measurement of the composition, without the withdrawal changing the equilibrium composition of either phase. In general, a sample of any liquid phase can be so withdrawn for measurement, satisfactorily. However, for the solid phase, the procedure of sampling is not simple. If the equilibrium is between a liquid solution of two components and a solid solution of the same two components, a sample of the solid phase may be obtained without complication. However, if the equilibrium is one between a liquid phase and a "solid" phase adsorbed on a chemically inert solid adsorbent, it is difficult, if not impossible, to obtain a sample of the actual solid phase in direct contact with the liquid phase without significant contamination with the liquid phase. However, it is possible to interpose a gaseous phase between the adsorbed and liquid phases, and permit each of these two phases to come to equilibrium with the gaseous phases, after which the adsorbed and liquid phases will be in equilibrium with one another. A sample of the adsorbed phase in contact with the gaseous phase can then be obtained without significant contamination.

An interesting and important practical tie-in of the foregoing relations with what actually occurs in any fractionating process in which the fractionation in the rectifying section is continuous, rather than a succession of ideal single stages as pictured in Figure 12, is provided by the theory developed for distillation by Westhaver (*19,20*) and for adsorption by Mair, Westhaver, and Rossini (*21*). The same theory may be applied to any fractionating process operating by reason of differences of composition between two phases in thermodynamic equilibrium. The phases may be any combination of two phases, as crystalline solid and liquid, crystalline solid and gaseous, liquid and liquid, liquid and gaseous, "adsorbed solid" and liquid, and "adsorbed solid" and gaseous. The property determining the separation may be volatility, solubility, crystallizability, or adsorbability. In each case, of course, the difference in composition of the two phases is caused by the fact that for the same composition a difference in the relative escaping tendency of the two components from the two phases exists, and a change in the relative concentrations in the two phases is required to equalize the escaping tendencies to bring the two phases into equilibrium.

Consider an equimolal mixture of components 1 and 2 which are to be separated by reason of differences in volatility in a vertical distilling column in which both components are present in each of two phases, gas and liquid, with the entire charge of material being in the rectifying section. At the moment of starting, the average composition of the gas and liquid phases in the rectifying section is everywhere 50 mole percent. Before the molecules can be separated it is necessary to provide for their transport through the system from one end to the other and to provide for their interchange from one phase to another. These requirements are met by providing a heater at the bottom end of the rectifying section and a condenser at the top end. By this means, the molecules in the liquid phase at the bottom are vaporized, and the gas travels upward through the length of the column. On reaching the condenser at the top, the gas is condensed to the liquid phase and the liquid material flows by gravity down the rectifying section to the bottom end. As the gas passes upward and the liquid phase flows downward, a continual interchange of molecules between the two phases occurs. Finally, after a certain time, a state of equilibrium in the given system will be substantially attained, with a higher concentration of the more volatile molecules of component 1 at the top of the column and a higher concentration of the less volatile molecules of component 2 at the bottom.

In the fractionation of liquids by adsorption, a similar picture may be developed. Consider an equimolal mixture of components 1 and 2 which are to be separated by reason of differences in adsorbability in a vertical column packed with a suitable adsorbent. In this column, both components are present in each of two phases, liquid and "adsorbed solid," and the entire charge of material is in the fractionating section. At the moment of starting, the average composition of the adsorbed and liquid phases in the adsorption column is everywhere 50 mole percent. Before the molecules can be fractionated, it is necessary to provide for their transport through the system and for their interchange from one phase to another. This may be accomplished by introducing fresh adsorbent at the bottom of the column and letting it pass upward through the column, and placing a suitable desorbent at the top of the column in order to keep the charge of material in the column. In this way, the molecules in the liquid phase at the bottom of the column pass to the "adsorbed solid" state as fresh adsorbent is introduced at the bottom, and the molecules in the "adsorbed solid" phase at the top of the column are returned to the liquid phase as the desorbent meets the adsorbent as the latter is on its way out of the column.

In actual laboratory practice, the adsorption experiment is more easily performed by using a long column of adsorbent and having the zone of molecules move downward over fresh adsorbent with a suitable desorbent following. The length of column of adsorbent required is that corresponding to the volume of fresh adsorbent which is required to be introduced at the bottom of the stationary zone of material being separated in order to reach equilibrium. The volume of fresh adsorbent required is that volume which will convert, from the liquid to the adsorbed state, a volume of material which corresponds in principle to the volume of material which, in the distillation process, is converted from the liquid to the gaseous state in the boiler.

Similar considerations hold for other methods of fractionation, as by extraction with two liquid solvent phases, or for fractionation by crystallization with a crystalline solid phase and a liquid phase, the solid phase being a solid solution of the two components, etc. (It is to be noted, in connection with crystallization, that, when only the major component appears in the solid phase and the solid phase is therefore pure component 1, fractionation by crystallization theoretically produces in one stage a separation complete as to composition.) In Table 1 are summarized the phases, manner of conversion of the phases, manner of producing transport, etc., for the various fractionating processes. The general picture is illustrated in Figure 13.

TABLE 1. GENERALIZED SUMMARY OF FRACTIONATING PROCESSES CORRESPONDING TO FIGURE 13

Process	Phase *A*	Phase *B*	Transport Provided in		At bottom, Phase *B* is converted to Phase *A* by	At top, Phase *A* is converted to Phase *B* by
			Phase *A* by	Phase *B* by		
Distillation	g	liq	difference in pressure	flow by gravity	adding heat in the boiler	removing heat, in the condenser
Adsorption	solid adsorbed	liq	mechanical movement of solid	flow by gravity	contact with fresh adsorbent	desorption from the adsorbent
Extraction	liq solvent	liq solvent	mechanical pumping or flow by gravity	mechanical pumping or flow by gravity	removing solvent *B* and adding solvent *A*	removing solvent *A* and adding solvent *B*
Crystallization	c (solid soln.)	liq	mechanical movement of solid	flow by gravity	removing heat, to crystallize	adding heat, to melt

Consider a mixture of two components, 1 and 2, which is to be fractionated by the scheme illustrated in Figure 13, with the entire charge placed in the rectifying section. The separation factor α is

$$\alpha = \frac{\left(\frac{N_1}{N_2}\right)^A}{\left(\frac{N_1}{N_2}\right)^B}, \tag{104}$$

so that the ratio of the mole fractions of 1 to 2 is greater in phase A than in phase B. For simplicity in subsequently relating mole fractions to volume fractions, the partial molal volume of each component in each of the phases is taken constant, independent of the mole fraction. At the beginning of the experiment, the average composition of the two phases is uniform throughout the length of the fractionating section and is the same as that of the original mixture, in which the mole fractions of components 1 and 2 are $N_1{}^i$ and $N_2{}^i$, respectively. At a horizontal cross-section near the middle of the fractionating section, equilibrium is established in accordance with Equation 104. The mole fractions of components 1 and 2 in the two phases are

$N_1{}^i + \Delta N_1{}^A$ and $N_2{}^i - \Delta N_2{}^A$ for phase A,

and

$N_1{}^i + \Delta N_1{}^B$ and $N_2{}^i + \Delta N_2{}^B$ for phase B.

Since the sum of the mole fractions in each phase, as well as in the original material, is unity, it follows that

$$\Delta N_1{}^A = -\Delta N_2{}^A; \quad \Delta N_1{}^B = -\Delta N_2{}^B. \tag{105}$$

Therefore,

$$N_1{}^A - N_1{}^B = \Delta N_1; \quad N_2{}^A - N_2{}^B = \Delta N_2; \quad \Delta N_1 = -\Delta N_2. \tag{106}$$

Similar relations hold for the volume fractions.

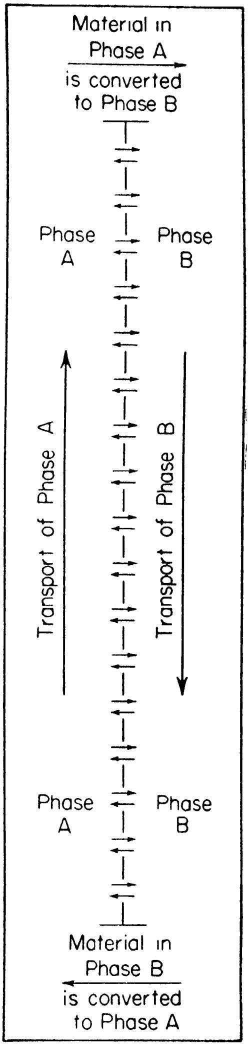


FIGURE 13. Schematic diagram of the generalized fractionating process involving transport and thermodynamic equilibrium between two phases.

See text and Table 1.

Provision is suitably made for the transport of the molecules from one end of the fractionating section to the other as shown in Figure 13. Components 1 and 2 travel in phase A from the bottom to the top, and in phase B from the top to the bottom. At the bottom, the material in phase B is converted to phase A, and at the top the material in phase A is converted to phase B.

At the given cross-sectional level, the two phases are moving in opposite directions, with equilibrium being maintained.

The flow of molecules in the two phases, upward in phase A and downward in phase B, is such that across any cross-section of either phase the volume of material flowing in unit time is the same throughout the system. If the flow of material in any given time is Q units of volume,* then the volume of component 1 transported upward in phase A across the given cross-section is equal to the volume fraction of component 1 in phase A, v_1^A or $v_1^i + \Delta v_1^A$, multiplied by Q. Similarly the volume of component 1 transported downward in phase B is the volume fraction in phase B, v_1^B, or $v_1^i + \Delta v_1^B$, multiplied by Q. Then the net volume of component 1 transported upward across the given cross-section is the difference between the two amounts, or the net transport of component 1 upward is

$$\begin{aligned}\Delta Q_1 &= (v_1^i + \Delta v_1^A)Q - (v_1^i + \Delta v_1^B)Q \\ &= Q(\Delta v_1^A - \Delta v_1^B) = Q(\Delta v_1). \qquad (107)\end{aligned}$$

In the same way, one finds that the net transport of component 2 downward is

$$\begin{aligned}\Delta Q_2 &= (v_2^i + \Delta v_2^B)Q - (v_2^i + \Delta v_2^A)Q \\ &= Q(-\Delta v_2^A + \Delta v_2^B) = -Q(\Delta v_2). \qquad (108)\end{aligned}$$

Since

$$\Delta v_1 = -\Delta v_2, \qquad (109)$$

it follows that the net amount of component 1 transported upward is equal to the net amount of component 2 transported downward, in unit time, and

$$\Delta Q_1 = \Delta Q_2. \qquad (110)$$

---

* Here the unit of volume is taken not as the actual volume of the given component in the given phase but as the volume of the pure component measured at a selected temperature.

If the molecular volumes of the two components, measured pure at the reference temperature, are equal, then, across the given cross-section in unit time, the net number of moles of component 1 transported upward is equal to the net number of moles of component 2 transported downward.

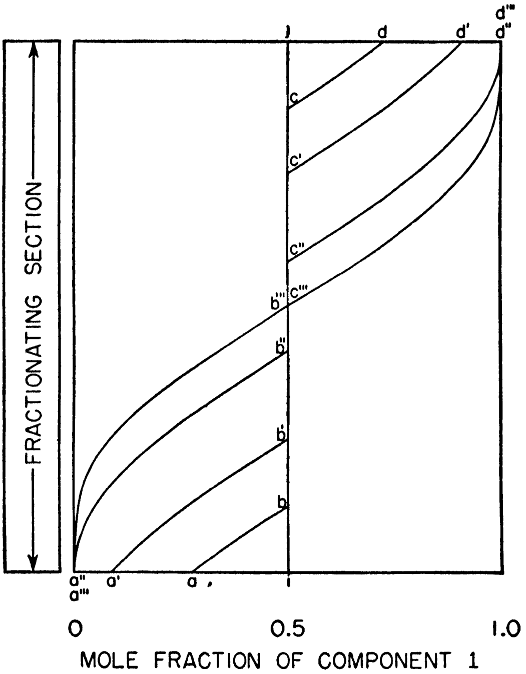


FIGURE 14. Schematic diagram of the progressive changes in composition occurring during the fractionation of an equimolal mixture of two components, for the generalized fractionating process involving transport and thermodynamic equilibrium between two phases.

Figure 14 gives a schematic diagram of the composition of a mixture of the two components along the length of the fractionating section at various stages of the process of fractionation. It is assumed that the molal volumes of the two components are equal and that the initial composition of the system is equimolal. The average composition of the two phases in the system at the start is given by the vertical straight line, *ij*, at $N_1 = 0.5$. After flow of material through the system has started, and fractionation and transport of material occur according to the picture previously given, there will be a net amount of component 1 transported upward and an equal net amount of component 2 transported downward. After fractionation has been under way for some time, with a certain quantity of material having circulated through the system, the composition of the material may be represented by the lines *a,b,c,d*. At this stage, the areas of the triangles *cdj* and *abi* are proportional, respectively, to the net amounts of component 1 transported upward and to the net amount of component 2 transported downward. It is to be noted that, at this stage, the bulk of the material, represented by the line *bc*, has the same composition as the original mixture.

At successive later stages of the fractionation, the composition may be represented by the lines $a'b'c'd'$ and $a''b''c''d''$. It may be noted that the corresponding areas at the ends, $c'd'j$, $a'b'i$, and $c''d''j$, $a''b''i$, are becoming larger and that the quantity of material in the middle having the initial composition, represented by the lines $b'c'$ and $b''c''$, is becoming smaller and smaller.

Finally, a stage will be reached when the quantity of material at the middle having the initial composition becomes infinitesimal and the points b''' and c''' coincide. The resulting curve of composition is represented by $a'''b'''c'''d'''$. At this final stage, the areas $d'''c'''j$ and $a'''b'''i$ are proportional to the total net amounts of 1 transported upward and 2 transported downward, respectively.

Equations 107 and 108 are valid only so long as some material with the initial composition remains at the middle of the fractionating section.

The separation factor is

$$\alpha = \frac{\dfrac{N_1{}^A}{N_2{}^A}}{\dfrac{N_1{}^B}{N_2{}^B}}. \tag{111}$$

Subtracting unity from both sides and simplifying, one obtains the relation

$$\alpha - 1 = \frac{N_1{}^A N_2{}^B - N_2{}^A N_1{}^B}{N_1{}^B N_2{}^A}. \tag{112}$$

Substituting

$$N_2 = 1 - N_1, \tag{113}$$

and noting that

$$\mathrm{N}_1{}^A - \mathrm{N}_1{}^B = \Delta\mathrm{N}_1, \tag{114}$$

Equation 112 becomes

$$\alpha - 1 = \frac{\Delta\mathrm{N}_1{}^B}{\mathrm{N}_1{}^B\mathrm{N}_2{}^A}. \tag{115}$$

It can be shown that the ratio of the ratios of the volume fractions of the two components in the two phases is equal to the corresponding ratio of the ratios of the mole fractions, as in the separation factor. Therefore, we may write

$$\alpha = \frac{\left(\frac{v_1}{v_2}\right)^A}{\left(\frac{v_1}{v_2}\right)^B}. \tag{116}$$

Proceeding as above, in the case of mole fractions, we obtain from Equation 116 the relation

$$\alpha - 1 = \frac{\Delta v_1}{v_1{}^B v_2{}^A}. \tag{117}$$

Equations 115 and 117 are the fundamental equations expressing the separation factor in terms of the difference in mole fraction (or volume fraction) of one component in the two phases being transported and the composition of the two phases.

In order to express Equation 117 in terms of the initial composition, $N_1{}^i$, it is necessary to introduce the factor giving the ratio of the amount of the material in the two phases. If r is the ratio of the quantity of material in phase A to the total quantity of material in both phases, and the quantity being measured is the volume of the liquid at the reference temperature, then

$$v_1{}^i = rv_1{}^A + (1 - r)v_1{}^B. \tag{118}$$

Equation 118 may be rewritten as

$$v_1{}^i = v_1{}^B + r(v_1{}^A - v_1{}^B) = v_1{}^B + r(\Delta v_1), \tag{119}$$

so that

$$v_1{}^B = v_1 - r(\Delta v_1), \tag{120}$$

and

$$v_1{}^A = v_1{}^i + (1 - r)(\Delta v_1). \tag{121}$$

Similarly,

$$v_2^B = v_2^i + r(\Delta v_1), \tag{122}$$

and

$$v_2^A = v_2^i - (1 - r)(\Delta v_1). \tag{123}$$

In terms of the difference in volume fraction of one component in the two phases and the composition of the original material, Equation 117 becomes

$$\alpha - 1 = \frac{\Delta v_1}{[v_1^i - r(\Delta v_1)][v_2^i - (1 - r)(\Delta v_1)]}. \tag{124}$$

Equations 108 and 124 permit evaluation of the separation factor α from the initial composition, the fraction, r, the total flow through the system, Q, and the quantity of component 1 (or the equal quantity of component 2) transported.

18. Collateral reading. The thermodynamic applications discussed in the several sections of this chapter are illustrative of many more and varied problems that may be solved by means of thermodynamics. For many additional applications of thermodynamics, the reader is referred to Lewis and Randall (*22*), Wenner (*23*), Perry *et al.* (*24*), Hougen and Watson (*25*), and Edmister (*26*).

REFERENCES

1. F. D. Rossini, K. S. Pitzer, W. J. Taylor, J. P. Ebert, J. E. Kilpatrick, C. W. Beckett, M. G. Williams, and H. G. Werner, *Selected Values of Properties of Hydrocarbons*, American Petroleum Institute Research Project 44, *Natl. Bur. Standards Circ.* 461, U.S. Government Printing Office, Washington, 1947.
2. F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, *Selected Values of Chemical Thermodynamic Properties*, Natl. Bur. Standards Circ. 500, U.S. Government Printing Office, Washington, 1950.
3. F. R. Bichowsky and F. D. Rossini, *Thermochemistry of the Chemical Substances*, Reinhold Publishing Corporation, New York, 1936.
4. D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer, and F. D. Rossini, *J. Research Natl. Bur. Standards* **34**, 143 (1945).
5. C. Antoine, *Compt. rend.* **107**, 681, 836, 1143 (1888).
6. G. W. Thomson, *Chem. Revs.* **38**, 1 (1946).
7. C. B. Willingham, W. J. Taylor, J. M. Pignocco, and F. D. Rossini, *J. Research Natl. Bur. Standards* **35**, 219 (1945).
8. W. J. Taylor, D. D. Wagman, M. G. Williams, K. S. Pitzer, and F. D. Rossini, *J. Research Natl. Bur. Standards* **37**, 95 (1946).
9. F. D. Rossini, *J. Wash. Acad. Sci.* **39**, 249 (1949).
10. P. W. Bridgman, *J. Chem. Phys.* **15**, 92 (1947).

11. K. S. Pitzer and D. W. Scott, *J. Am. Chem. Soc.* **63**, 2419 (1941).

12. H. L. Johnston and W. F. Giauque, *J. Am. Chem. Soc.* **51**, 3194 (1929).

13. W. J. Taylor and F. D. Rossini, *J. Research Natl. Bur. Standards* **32**, 197 (1944).

14. B. J. Mair, A. R. Glasgow, Jr., and F. D. Rossini, *J. Research Natl. Bur. Standards* **26**, 591 (1941).

15. A. R. Glasgow, Jr., A. J. Streiff, and F. D. Rossini, *J. Research Natl. Bur. Standards* **35**, 355 (1945).

16. A. R. Glasgow, Jr., N. C. Krouskop, J. Beadle, G. D. Axilrod, and F. D. Rossini, *Anal. Chem.* **20**, 410 (1948).

17. J. G. Aston, H. L. Fink, J. W. Tooke, and M. R. Cines, *Anal. Chem.* **19**, 218 (1947).

18. A. J. Streiff, E. T. Murply, V. A. Sedlak, C. B. Willingham, and F. D. Rossini, *J. Research Natl. Bur. Standards* **37**, 331 (1946).

19. J. W. Westhaver, *Ind. Eng. Chem.* **34**, 126 (1942).

20. J. W. Westhaver, *J. Research Natl. Bur. Standards* **38**, 169 (1947).

21. B. J. Mair, J. W. Westhaver, and F. D. Rossini, *Ind. Eng. Chem.* **42**, 1279 (1950).

22. G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill Book Company, New York, 1923.

23. R. R. Wenner, *Thermochemical Calculations*, McGraw-Hill Book Company, New York, 1941.

24. J. H. Perry, F. D. Rossini, W. M. D. Bryant, J. C. Elgin, and J. C. Whitwell, "Physical and chemical principles," Section 4 in *Chemical Engineers Handbook*, McGraw-Hill Book Company, New York, 1950.

25. O. A. Hougen and K. M. Watson, *Chemical Process Principles*, Volumes I–III, John Wiley & Sons, New York, 1943–1947.

26. W. C. Edmister, *Petroleum Refiner*, **26**, Nos. 7–12 (1947), **27**, Nos. 1–12 (1948); **28**, Nos. 1–12 (1949).

27. M. R. Fenske, *Ind. Eng. Chem.* **24**, 482 (1932).

35

The Data of Chemical Thermodynamics

1. Sources of data needed for thermodynamic calculations. The purpose of this chapter is to discuss briefly the places where may be found the data required for calculations in chemical thermodynamics. In general, the sources will include original journal articles, abstracts of original journal articles, articles summarizing or reviewing a particular area, and various compilations of values of thermodynamic properties.

2. Original articles in journals. The foundation for all compilations and assemblies of values of thermodynamic properties comes from original data appearing in articles published in the various chemical, physical, and engineering journals. Among the journals in which are constantly appearing new data that are useful in thermodynamic calculations are the following:*

PUBLISHED IN THE UNITED STATES

Journal of the American Chemical Society (*J. Am. Chem. Soc.*).
Industrial and Engineering Chemistry (*Ind. Eng. Chem.*).
Journal of Chemical Physics (*J. Chem. Phys.*).
Physical Review (*Phys. Rev.*).
Journal of Physical & Colloid Chemistry (*J. Phys. & Colloid Chem.*).

PUBLISHED IN GREAT BRITAIN

Journal of the Chemical Society (*London*) (*J. Chem. Soc.*).
Philosophical Magazine (*Phil. Mag.*).
Proceedings of the Royal Society (*London*) [*Proc. Roy. Soc.* (*London*)].
Nature (*Nature*).

PUBLISHED IN FRANCE

Annales de chimie (*Ann. chim.*).
Annales de physique (*Ann. phys.*).
Bulletin de la société chimique de France (*Bull. soc. chim. France*).

---

* The abbreviation following the name of each serial publication is the designation used by *Chemical Abstracts* to refer to the given publication.

Comptes rendus hebdomadaires des séances de l'académie des sciences (*Compt. rend.*).

Journal de chimie physique et de physico-chimie biologique (*J. chim. phys.*).

PUBLISHED IN THE NETHERLANDS

Proceedings Koninklijke Nederlandsche Akademie von Wetenschappen (*Proc. Koninkl. Nederland. Akad. Wetenschap.*).

Recueil des travaux chimiques des Pays-Bas (*Rec. trav. chim.*).

PUBLISHED IN BELGIUM

Bulletin de la société chimique de Belges (*Bull. soc. chim. Belg.*).

PUBLISHED IN SWITZERLAND

Helvetica Chimica Acta (*Helv. Chim. Acta*).

Helvetica Physica Acta (*Helv. Phys. Acta*).

PUBLISHED IN ITALY

Gazzetta chimica italiana (*Gazz. chim. ital.*).

Nuovo cimento (*Nuovo cimento*).

Atti della accademia nazionale dei Lincei. Rendiconti, Classe di scienze fisiche, matematiche e naturali (*Atti accad. nazl. Lincei. Classe sci. fis. mat. e nat.*).

PUBLISHED IN GERMANY

Annalen der Physik (*Ann. Physik*).

Chemisches Berichte (*Chem. Ber.*).

Monatshafte für Chemie und verwandte Teile anderer Wissenschaften (*Monatsh.*).

Physikalische Zeitschrift vereinigt mit dem Jahrbuch der Radioaktivität und Elektronik (*Physik. Z.*).

Journal für praktische Chemie (*J. prakt. Chem.*).

Angewandte Chemie (*Angew. Chem.*).

Zeitschrift für anorganische Chemie (*Z. anorg. Chem.*).

Zeitschrift für Elektrochemie und angewandte physikalische Chemie (*Z. Elektrochem.*).

Zeitschrift für Naturforschung (*Z. Naturforsch.*).

Zeitschrift für Physik (*Z. Physik*).

Zeitschrift für physikalische Chemie (*Z. physik. Chem.*).

PUBLISHED IN JAPAN

Science Reports of the Tôhoku Imperial University (*Science Repts. Tôhoku Imp. Univ.*).

Scientific Papers of the Institute of Physical and Chemical Research (*Tokyo*) [*Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*)].

Journal of the Chemical Society of Japan (*J. Chem. Soc. Japan*).

PUBLISHED IN RUSSIA

Acta Physicochimica U.R.S.S. (*Acta Physicochim. U.R.S.S.*).
Journal of General Chemistry (*U.S.S.R.*) [*J. Gen. Chem.* (*U.S.S.R.*)].
Journal of Physical Chemistry (*U.S.S.R.*) [*J. Phys. Chem.* (*U.S.S.R.*)].

3. Abstracts. The journals which carry abstracts of the original articles appearing in the various scientific and technical journals listed above include the following:

PUBLISHED IN THE UNITED STATES

Chemical Abstracts (*C.A.*).

PUBLISHED IN GREAT BRITAIN

British Abstracts (*Brit. Abstracts*).

PUBLISHED IN FRANCE

Bulletin de la société chimique de France (*Bull. soc. chim. France*).

PUBLISHED IN GERMANY

Chemische Zentralblatt (*Chem. Zentr.*).

4. Reviews. Publications giving reviews and summaries of the existing data on various particular properties of importance in thermodynamics appear at frequent intervals in a number of journals, including the following:

PUBLISHED IN THE UNITED STATES

Chemical Reviews (*Chem. Revs.*).

Transactions of the American Society of Mechanical Engineers (*Trans. Am. Soc. Mech. Engrs.*).

Transactions of the Electrochemical Society (*Trans. Electrochem. Soc.*).

Chemical Engineering Progress with Transactions of American Institute of Chemical Engineers (*Chem. Eng. Progress*).

PUBLISHED IN GREAT BRITAIN

Transactions of the Faraday Society (*Trans. Faraday Soc.*)

Science Progress (*Science Progress*).

Annual Reports on the Progress of Chemistry (*Chemical Society of London*) [*Ann. Repts. on Progress Chem.* (*Chem. Soc. London*)].

PUBLISHED IN FRANCE

Bulletin of the International Institute of Refrigeration (*Bull. Intern. Inst. Refrig.*).

PUBLISHED IN GERMANY

Chemiker-Zeitung mit dem Sonderteil, Die Chemische Praxis und der Beilage, Chemisch-technische Übersicht (*Chem. Ztg.*).

5. Books. A number of books written on certain specialized areas of thermodynamics contain appreciable numbers of data in the given field. Among these are included the following:

Molecular Spectra and Molecular Structure. I. *Spectra of Diatomic Molecules,* by G. Herzberg, D. Van Nostrand Company, New York, 1950.

Molecular Spectra and Molecular Structure. II. *Infrared and Raman Spectra of Polyatomic Molecules,* by G. Herzberg, D. Van Nostrand Company, New York, 1945.

Molecular Spectra and Their Application to Chemical Problems, by H. Sponer, Julius Springer, Berlin, 1936.

The Physical Chemistry of Electrolytic Solutions, by H. S. Harned and B. B. Owen, Reinhold Publishing Corporation, New York, 1950.

Dissociation Energies and Spectra of Diatomic Molecules, by A. G. Gaydon, John Wiley & Sons, New York, 1948.

Electrochemistry of Solutions, by S. Glasstone, Methuen and Company, London, 1930.

6. Compilations. Among the compilations in which may be found assemblies of values of thermodynamic properties, either critically selected or reproduced as originally published, are the following:

PUBLISHED IN THE UNITED STATES

Selected Values of Properties of Hydrocarbons, by F. D. Rossini, K. S. Pitzer, W. J. Taylor, J. P. Ebert, J. E. Kilpatrick, C. W. Beckett, M. G. Williams, and H. G. Werner, American Petroleum Institute Research Project 44, *Natl. Bur. Standards Circ.* 461, U.S. Government Printing Office, Washington, 1947. Also issued currently in loose-leaf form by the American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh (formerly at the National Bureau of Standards, Washington).

Selected Values of Chemical Thermodynamic Properties, by F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, *Natl. Bur. Standards Circ.* 500, U.S. Government Printing Office, Washington, 1950.

International Critical Tables, McGraw-Hill Book Company, New York, 1926–1933.

Thermochemistry of the Chemical Substances, by F. R. Bichowsky and F. D. Rossini, Reinhold Publishing Corporation, New York, 1936.

The Oxidation States of the Elements and Their Potentials in Aqueous Solutions, by W. M. Latimer, Prentice-Hall, New York, 1938.

Free Energies of Some Organic Compounds, by G. S. Parks and H. M. Huffman, Reinhold Publishing Corporation, New York, 1932.

"Contributions to the data on theoretical metallurgy. I–IX," by K. K. Kelley, *U.S. Bur. Mines Bulls.* 350, 371, 383, 384, 393, 394, 406, 407, 434, 476 (1932–1949).

Chemical Engineers Handbook, edited by J. H. Perry, McGraw-Hill Book Company, New York, 1950.

Solubilities of Inorganic and Metal Organic Compounds, by A. Seidell, 3rd Edition, D. Van Nostrand Company, New York, 1940.

Solubilities of Organic Compounds, A. Seidell, 3rd Edition, D. Van Nostrand Company, New York, 1950.

Handbook of Chemistry, by N. A. Lange, Handbook Publishers, Sandusky, Ohio, 1949.

Handbook of Chemistry and Physics, by C. D. Hodgman, Chemical Rubber Publishing Company, Cleveland, Ohio, 1949.

PUBLISHED IN FRANCE

Annual Tables of Constants and Numerical Data, Hermann and Company, Paris, 1910–1948.

PUBLISHED IN GERMANY

Landolt-Börnstein-Roth-Scheele Physikalisch-Chemische Tabellen, 5th Edition, Julius Springer, Berlin, 1923–1936.

Spezifische Wärme, Enthalpie, Entropie, und Dissoziation technischer Gase, by E. Justi, Julius Springer, Berlin, 1938.

Thermochemie der Legierungen, by F. Weibke and O. Kubaschewski, Julius Springer, Berlin, 1943.

Reine Metalle, by A. E. van Arkel, Julius Springer, Berlin, 1939.

Abhandlungen der Deutschen Bunsen-Gesellschaft, Verlag Chemie, Berlin, 1911–1929.

Appendix

TABLE 1. VALUES OF CONSTANTS*

* References are given in Chapter 4. The electrical units used in these tables are those in terms of which certification of standard cells, standard resistances, etc., is made by the National Bureau of Standards.

1 sec = 1.00273791 sidereal second	sec = mean solar second
g_0 = 980.665 cm/sec^2	Definition: g_0 = standard gravity
1 liter = 1000.028 ± 0.004 cm^3	
1 atm = 1,013,250 dynes/cm^2	Definition: atm = standard atmosphere
1 mm Hg (pressure) = (1/760) atm	Definition: mm Hg (pressure) = standard millimeter mercury
= 1333.2237 dynes/cm^2	
1 abs ohm = 0.999505 ± 0.000015 int ohm	abs = absolute; int = international
1 abs volt = 0.999670 ± 0.000029 int volt	
1 abs amp = 1.000165 ± 0.000025 int amp	amp = ampere
1 abs coul = 1.000165 ± 0.000025 int coul	coul = coulomb
1 abs watt = 0.999835 ± 0.000052 int watt	
1 abs joule = 0.999835 ± 0.000052 int joule	
1 cal = 4.1840 abs joules	Definition: cal = thermochemical calorie
= 4.1833 int joules	
= 41.2929 ± 0.0020 cm^3 atm	
= 0.0412917 ± 0.0000020 liter-atm	
T_0°C = 273.160 ± 0.010°K	Absolute temperature of the ice point, 0°C
$(PV)_{0°C}^{P=0} = (RT)_{0°C}$ = 2271.16 ± 0.04 abs joules/mole	PV product for ideal gas at 0°C
= 22414.6 ± 0.4 cm^3 atm/mole	
= 22.4140 ± 0.0004 liter-atm/mole	
$\boldsymbol{R}$ = 8.31439 ± 0.00034 abs joules/deg mole	R = gas constant per mole
= 1.98719 ± 0.00013 cal/deg mole	
= 82.0567 ± 0.0034 cm^3 atm/deg mole	
= 0.0820544 ± 0.0000034 liter-atm/deg mole	
ln 10 = 2.302585	ln = natural logarithm (base e)
$R \ln x$ = (19.14460 ± 0.00078) $\log_{10} x$ abs joules/deg mole	
= (4.57567 ± 0.00030) $\log_{10} x$ cal/deg mole	

TABLE 1. VALUES OF CONSTANTS* (*Continued*)

$N = (6.0235 \pm 0.0004) \times 10^{23}$ molecules/mole	N = Avogadro number
$\mathfrak{F} = 96{,}496 \pm 7$ abs coul/equiv, or	$\mathfrak{F}$ = Faraday constant
abs joules/abs volt equiv	
$= 96{,}512 \pm 7$ int coul/equiv, or	
int joules/int volt equiv	
$= 23{,}063.1 \pm 1.7$ cal/abs volt equiv	
$= 23{,}070.7 \pm 1.7$ cal/int volt equiv	
$(\mathfrak{F}/R \ln 10) = 5040.38 \pm 0.40$ deg/abs volt	
$= 5042.04 \pm 0.40$ deg/int volt	
$e = (1.60199 \pm 0.00016) \times 10^{-19}$ abs coul	e = electronic charge = $(\mathfrak{F}/N)$
$= (1.60199 \pm 0.00016) \times 10^{-20}$ abs emu	
$= (4.8024 \pm 0.0005) \times 10^{-10}$ abs esu	
1 abs electron-volt/molecule	
$= 96{,}496 \pm 7$ abs joules/mole	
$= 23{,}063.1 \pm 1.7$ cal/mole	
1 int electron-volt/molecule	
$= 96{,}528 \pm 7$ abs joule/mole	
$= 96{,}512 \pm 7$ int joule/mole	
$= 23{,}070.7 \pm 1.7$ cal/mole	
1 abs electron-volt $= (1.60199 \pm 0.00016) \times 10^{-12}$ erg	
1 int electron-volt $= (1.60252 \pm 0.00016) \times 10^{-12}$ erg	
$h = (6.6237 \pm 0.0008) \times 10^{-27}$ erg sec/molecule	h = Planck's constant
$c = (2.99776 \pm 0.00008) \times 10^{10}$ cm/sec	c = velocity of light
$k = (1.38032 \pm 0.00011) \times 10^{-16}$ erg/deg molecule	k = Boltzmann constant = (R/N)
$= (8.6163 \pm 0.0007) \times 10^{-5}$ abs electron-volt/deg	
$= (8.6134 \pm 0.0007) \times 10^{-5}$ int electron-volt/deg	
$hc = (1.23947 \pm 0.00019) \times 10^{-4}$ abs electron-volt cm	Constant relating wave number and energy per molecule
$= (1.23906 \pm 0.00019) \times 10^{-4}$ int electron-volt cm	
$(h^2/8\pi^2k) = (4.0256 \pm 0.0010) \times 10^{-39}$ g cm^2 deg	Constant in rotational partition function of gases

$(h/8\pi^2 c) = (2.7984 \pm 0.0003) \times 10^{-39}$ g cm	Constant relating wave number and moment of inertia
$Z = Nhc = 11.9604 \pm 0.0012$ abs joule cm/mole $= 11.9584 \pm 0.0012$ int joule cm/mole $= 2.85861 \pm 0.0003$ cal cm/mole	Z = constant relating wave number, ν, and energy per mole, E, in the relation: $(\Delta E) = Nhc\ (\Delta\nu) = Z(\Delta\nu)$
$(\boldsymbol{Z/R}) = (hc/k) = c_2 = 1.43852 \pm 0.00016$ cm deg	c_2 = second radiation constant
$Y = c^2 = (8.98656 \pm 0.00045) \times 10^{13}$ abs joule/g $= (2.14784 \pm 0.00011) \times 10^{13}$ cal/g	Y = Einstein constant relating energy, E, and mass, m, in the Einstein relation: $(\Delta E) = c^2\ (\Delta m) = Y\ (\Delta m)$
1 in. = (1/0.3937) = 2.54000508 cm	Definition: in. = U.S. inch
1 ft = 30.4800610 cm	ft = U.S. foot (1 ft = 12 in.)
1 lb = 453.5924277 g	Definition: lb = avoirdupois pound
1 gal = 231 cu in. = 0.133680555 cu ft = 3785.43449 cm^3 = 3.785329 liters	Definition: gal = U.S. gallon
1 I.T. cal = (1/860) = 0.00116279 int watt-hr = 4.18674 abs joules = 4.18605 int joules = 1.000654 cal	Definition: I.T. = International Steam Tables cal = thermochemical calorie
1 BTU/lb = (1/1.8) = 0.5555556 I.T. cal/g	Definition: BTU = I.T. British Thermal Unit
1 BTU = 251.996 I.T. cal = 1055.040 abs joules = 1054.866 int joules = 0.293018 int watt-hr = 252.161 cal	cal = thermochemical calorie
1 horsepower = 550 ft-lb(wt)/sec = 745.701 abs watts = 745.578 int watts	Definition: lb(wt) = weight of 1 lb at standard gravity

Table 2. Conversion Factors for Units of Length, Centimeter and Smaller

To convert the numerical value of a property expressed in one of the units in the left-hand column of the table to the numerical value of the same property 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.

Units → ↓	cm	μ	mμ	A
1 centimeter (cm) =	1	10^4	10^7	10^8
1 micron (μ) =	10^{-4}	1	10^3	10^4
1 millimicron (mμ) =	10^{-7}	10^{-3}	1	10
1 angstrom unit (A) =	10^{-8}	10^{-4}	10^{-1}	1

Table 3. Conversion Factors for Units of Length, Centimeter and Larger

To convert the numerical value of a property expressed in one of the units in the left-hand column of the table to the numerical value of the same property 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.

Units → ↓	cm	m	in.	ft	yd
1 cm =	1	0.01	0.3937	0.032808333	0.010936111
1 m =	100	1	39.37	3.2808333	1.0936111
1 in. =	2.5400051	0.025400051	1	0.083333333	0.027777778
1 ft =	30.480061	0.30480061	12	1	0.33333333
1 yd =	91.440183	0.91440183	36	3	1

TABLE 4. CONVERSION FACTORS FOR UNITS OF AREA

To convert the numerical value of a property expressed in one of the units in the left-hand column of the table to the numerical value of the same property 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.

Units → ↓	cm^2	m^2	sq in.	sq ft	sq yd
1 cm^2 =	1	10^{-4}	0.15499969	1.0763867×10^{-3}	1.1959853×10^{-4}
1 m^2 =	10^4	1	1549.9969	10.763867	1.1959853
1 sq in. =	6.4516258	6.4516258×10^{-4}	1	6.9444444×10^{-3}	7.7160494×10^{-4}
1 sq ft =	929.03412	0.092903412	144	1	0.11111111
1 sq yd =	8361.3070	0.83613070	1296	9	1

TABLE 5. CONVERSION FACTORS FOR UNITS OF VOLUME

To convert the numerical value of a property expressed in one of the units in the left-hand column of the table to the numerical value of the same property 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.

Units → ↓	cm^3	cu in.	cu ft	ml	liter	gal
1 cm^3 =	1	0.061023378	3.5314455×10^{-5}	0.9999720	0.9999720×10^{-3}	2.6417047×10^{-4}
1 cu in. =	16.387162	1	5.7870370×10^{-4}	16.38670	1.638670×10^{-2}	4.3290043×10^{-3}
1 cu ft =	28,317.017	1728	1	28,316.22	28.31622	7.4805195
1 ml =	1.000028	0.06102509	3.531544×10^{-5}	1	0.001	2.641779×10^{-4}
1 liter =	1000.028	61.02509	0.03531544	1000	1	0.2641779
1 gal =	3785.4345	231	0.13368056	3785.329	3.785329	1

TABLE 6. CONVERSION FACTORS FOR UNITS OF MASS

To convert the numerical value of a property expressed in one of the units in the left-hand column of the table to the numerical value of the same property 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.

Units → ↓	g	kg	lb	metric ton	ton
1 g =	1	10^{-3}	2.2046223×10^{-3}	10^{-6}	1.1023112×10^{-6}
1 kg =	10^{3}	1	2.2046223	10^{-3}	1.1023112×10^{-3}
1 lb =	453.59243	0.45359243	1	4.5359243×10^{-4}	0.0005
1 metric ton =	10^{6}	10^{3}	2204.6223	1	1.1023112
1 ton =	907,184.86	907.18486	2000	0.90718486	1

TABLE 7. CONVERSION FACTORS FOR UNITS OF DENSITY

To convert the numerical value of a property expressed in one of the units in the left-hand column of the table to the numerical value of the same property 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.

Units → ↓	g/cm^{3}	g/ml	lb/cu in.	lb/cu ft	lb/gal
1 g/cm =	1	1.000028	0.036127504	62.428327	8.3454535
1 g/ml =	0.9999720	1	0.03612649	62.42658	8.345220
1 lb/cu in. =	27.679742	27.68052	1	1728	231
1 lb/cu ft =	0.016018369	0.01601882	5.7870370×10^{-4}	1	0.13368056
1 lb/gal =	0.11982572	0.1198291	4.3290043×10^{-3}	7.4805195	1

Table 8. Conversion Factors for Units of Pressure

To convert the numerical value of a property expressed in one of the units in the left-hand column of the table to the numerical value of the same property 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.

Units ⟶ ↓	dyne/cm^2	bar	atm	kg (wt)/cm^2	mm Hg	in. Hg	lb (wt)/sq in.
1 dyne/cm^2 =	1	10^{-6}	0.9869233×10^{-6}	1.0197162×10^{-6}	7.500617×10^{-4}	2.952993×10^{-5}	1.4503830×10^{-5}
1 bar =	10^6	1	0.9869233	1.0197162	750.0617	29.52993	14.503830
1 atm =	1,013,250	1.013250	1	1.0332275	760	29.92120	14.696006
1 kg (wt)/cm^2 =	980,665	0.980665	0.9678411	1	735.5592	28.95897	14.223398
1 mm Hg =	1333.2237	1.3332237×10^{-3}	1.3157895×10^{-3}	1.3595098×10^{-3}	1	0.03937	0.019336850
1 in. Hg =	33,863.95	0.03386395	0.03342112	0.03453162	25.40005	1	0.4911570
1 lb(wt)/sq in. =	68,947.31	0.06894731	0.06804570	0.07030669	51.71473	2.036009	1

TABLE 9. CONVERSION FACTORS FOR UNITS OF ENERGY

To convert the numerical value of a property expressed in one of the units in the left-hand column of the table to the numerical value of the same property 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.

Units→ ↓	g mass (energy equiv)	abs joule	int joule	cal	I.T. cal	BTU	abs kw-hr	hp-hr	ft-lb (wt)	cu ft-lb (wt)/sq in.	liter-atm
1 g mass (energy equiv) =	1	8.98656 $\times 10^{13}$	8.98508 $\times 10^{13}$	2.14784 $\times 10^{13}$	2.14644 $\times 10^{13}$	8.51775 $\times 10^{10}$	2.49627 $\times 10^{7}$	3.34754 $\times 10^{7}$	6.62814 $\times 10^{13}$	4.60287 $\times 10^{11}$	8.86880 $\times 10^{11}$
1 abs joule =	1.112772 $\times 10^{-14}$	1	0.999835	0.239006	0.238849	0.947831 $\times 10^{-3}$	2.77778 $\times 10^{-7}$	3.72505 $\times 10^{-7}$	0.737561	5.12195 $\times 10^{-3}$	9.86896 $\times 10^{-3}$
1 int joule =	1.112956 $\times 10^{-14}$	1.000165	1	0.239045	0.238889	0.947988 $\times 10^{-3}$	2.77824 $\times 10^{-7}$	3.72567 $\times 10^{-7}$	0.737682	5.12279 $\times 10^{-3}$	9.87058 $\times 10^{-3}$
1 cal =	4.65584 $\times 10^{-14}$	4.1840	4.1833	1	0.999346	3.96573 $\times 10^{-3}$	1.162220 $\times 10^{-6}$	1.558562 $\times 10^{-6}$	3.08595	2.14302 $\times 10^{-2}$	4.12917 $\times 10^{-2}$
1 I.T. cal =	4.65888 $\times 10^{-14}$	4.18674	4.18605	1.000654	1	3.96832 $\times 10^{-3}$	1.162985 $\times 10^{-6}$	1.559582 $\times 10^{-6}$	3.08797	2.14443 $\times 10^{-2}$	4.13187 $\times 10^{-2}$
1 BTU =	1.174019 $\times 10^{-11}$	1055.040	1054.866	252.161	251.996	1	2.93067 $\times 10^{-4}$	3.93008 $\times 10^{-4}$	778 156	5.40386	10.41215
1 abs kw-hr =	4.00598 $\times 10^{-8}$	3,600,000	3,599,406	860,422	859,856	3412.19	1	1.341018	2,655,220	18439.02	35,528.2
1 hp-hr =	2.98727 $\times 10^{-8}$	2,684,525	2,684,082	641,617	641,197	2544.48	0.745702	1	1,980,000	13,750	26,493.5
1 ft-lb (wt) =	1.508720 $\times 10^{-14}$	1.355821	1.355597	0.324049	0.323837	1.285089 $\times 10^{-3}$	3.76617 $\times 10^{-7}$	5.05051 $\times 10^{-7}$	1	6.94444 $\times 10^{-3}$	1.338054 $\times 10^{-2}$
1 cu ft-lb (wt)/sq in. =	2.17256 $\times 10^{-12}$	195.2382	195 2060	46.6630	46.6325	0.1850529	5.42328 $\times 10^{-5}$	7.27273 $\times 10^{-5}$	144	1	1.926797
1 liter-atm =	1.127548 $\times 10^{-12}$	101.3278	101.3111	24.2179	24.2021	0.0960417	2.81467 $\times 10^{-5}$	3.77452 $\times 10^{-5}$	74.7354	5.18996	1

TABLE 10. CONVERSION FACTORS FOR UNITS OF MOLECULAR ENERGY

To convert the numerical value of a property expressed in one of the units in the left-hand column of the table to the numerical value of the same property 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.

Units ⟶ ↓	erg/molecule	abs joule/mole	int joule/mole	cal/mole	abs electron-volt/molecule	int electron-volt/molecule	wave no. (cm^{-1})
1 erg/molecule =	1	6.0235×10^{16}	6.0225×10^{16}	1.43965×10^{16}	6.2422×10^{11}	6.2402×10^{11}	5.0362×10^{15}
1 abs joule/mole =	1.66016×10^{-17}	1	0.999835	0.239006	1.03631×10^{-5}	1.03597×10^{-5}	8.3609×10^{-2}
1 int joule/mole =	1.66043×10^{-17}	1.000165	1	0.239046	1.03648×10^{-5}	1.03614×10^{-5}	8.3623×10^{-2}
1 cal/mole =	6.9461×10^{-17}	4.18400	4.1833	1	4.3359×10^{-5}	4.3345×10^{-5}	0.34982
1 abs electron-volt/molecule =	1.60199×10^{-12}	96,496	96,480	23,063.1	1	0.99967	8067.9
1 int electron-volt/molecule =	1.60252×10^{-12}	96,528	96,512	23,070.7	1.000330	1	8070.6
1 wave no. (cm^{-1}) =	1.98562×10^{-16}	11.9604	11.9584	2.85861	1.23947×10^{-4}	1.23906×10^{-4}	1

TABLE 11. CONVERSION FACTORS FOR UNITS OF SPECIFIC ENERGY

To convert the numerical value of a property expressed in one of the units in the left-hand column of the table to the numerical value of the same property 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.

Units → ↓	abs joule/g	int joule/g	cal/g	I.T. cal/g	BTU/lb
1 abs joule/g =	1	0.999835	0.239006	0.238849	0.429929
1 int joule/g =	1.000165	1	0.239045	0.238889	0.430000
1 cal/g =	4.1840	4.1833	1	0.999346	1.798823
1 I.T. cal/g =	4.18674	4.18605	1.000654	1	1.8
1 BTU/lb =	2.32597	2.32558	0.555919	0.555556	1

TABLE 12. CONVERSION FACTORS FOR UNITS OF SPECIFIC ENERGY PER DEGREE

To convert the numerical value of a property expressed in one of the units in the left-hand column of the table to the numerical value of the same property 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.

Units → ↓	abs joule/g deg C	int joule/g deg C	cal/g deg C	I.T. cal/g deg C	BTU/lb deg F
1 abs joule/g deg C =	1	0.999835	0.239006	0.238849	0.238849
1 int joule/g deg C =	1.000165	1	0.239045	0.238889	0.238889
1 cal/g deg C =	4.1840	4.1833	1	0.999346	0.999346
1 I.T. cal/g deg C =	4.18674	4.18605	1.000654	1	1
1 BTU/lb deg F =	4.18674	4.18605	1.000654	1	1

TABLE 13. UNITS IN WHICH VALUES OF THERMODYNAMIC PROPERTIES ARE DETERMINED

Property	Method of Determination	Relation Involved	Quantities Actually Measured, and Their Units	Constants Involved, and Their Units	Resultant Units for the Property
ΔE	Change in mass	$\Delta E = MY\,\Delta m/m$	m, mass, g Δm, change in mass, g	M, molecular weight, g/mole Y, Einstein constant, joules/g	joules/mole
ΔE	Spectroscopically	$\Delta E = Z/\lambda$	λ, wavelength, cm	Z, spectroscopic constant, joules cm/mole	joules/mole
ΔH	Calorimetrically	$\Delta H = q$ $= Mtv^2/mr$	m, mass, g t, time, sec v, voltage drop, volts r, resistance, ohms	M, molecular weight, g/mole	joules/mole
ΔS	Calorimetrically	$\Delta S = q/T$ $= Mtv^2/mrT$	m, mass, g t, time, sec v, voltage drop, volts r, resistance, ohms T, temperature, °K	M, molecular weight, g/mole	joules/deg mole
ΔS	Statistical calculations	$\Delta S = R \ln W/W'$	W, W' are independent of units	R, gas constant, joules/deg mole	joules/deg mole
ΔF	Equilibrium measurements	$\Delta F^\circ = -RT \ln K$	K is independent of units T, temperature, °K	R, gas constant, joules/deg mole	joules/mole
ΔF	Electromotive force of cells	$\Delta F = -n\mathfrak{F}\mathcal{E}$	n is independent of units $\mathcal{E}$, electromotive force, volts	$\mathfrak{F}$, Faraday constant, coul/equiv	joules/mole
C_P, C_V	Calorimetrically	$C = q/\Delta T$ $= Mtv^2/mr(\Delta T)$	m, mass, g t, time, sec v, voltage drop, volts r, resistance, ohms ΔT, increment in temperature, °K	M, molecular weight, g/mole	joules/deg mole

Table 14. Notation; Symbols and Abbreviations

Mathematical Signs

d	Differential sign
∂	Partial differential sign
δ	Infinitesimal quantity
$\int$	Integral sign
Δ	Increment in a given property for a given process of reaction, taken as the value for the final state (sum of products) less the value for the initial state (sum of reactants)
$\sum_{i}$	Summation over i terms
ln	Logarithm to the base e
log	Logarithm to the base 10
$\vert \quad \vert$	Absolute value of any quantity, irrespective of algebraic sign

Abbreviations for Units of Time

sec	Second
hr	Hour

Abbreviations for Units of Mass

g	Gram
kg	Kilogram, equal to 1000 g
lb	Pound

Abbreviations for Units of Length

m	Meter
cm	Centimeter, equal to 0.01 meter
mm	Millimeter, equal to 0.001 meter
μ	Micron, equal to 10^{-4} cm
mμ	Millimicron, equal to 10^{-7} cm
A	Angstrom unit, equal to 10^{-8} cm
in.	Inch
ft	Foot
yd	Yard

Abbreviations for Units of Volume

ml	Milliliter, equal to 0.001 liter
cu in.	Cubic inch
cu ft	Cubic foot
gal	Gallon

Abbreviations for Units of Pressure

atm	Atmosphere
mm Hg	Millimeter of mercury

TABLE 14. NOTATION; SYMBOLS AND ABBREVIATIONS (*Continued*)

Abbreviations for Units of Energy

j	Joule
cal	Calorie, thermochemical calorie
kcal	Kilocalorie, equal to 1000 cal
I.T. cal	International Steam Tables calorie
BTU	British thermal unit

Abbreviations for Physical States

c	Crystal (solid)
liq	Liquid
g	Gas
aq	Aqueous (in aqueous solution)
gls	Glass

Symbols for Fundamental Constants

c	Velocity of light
g_0	Standard gravity
e	Charge on the electron
h	Planck constant
k	Boltzmann constant
N	Avogadro constant
R	Gas constant, per mole
$\mathfrak{F}$	Faraday constant
Y	Einstein constant, relating energy and mass
Z	Spectroscopic constant, relating wave number and energy

Symbols for Units of Amount and Concentration

n_i	Number of moles of component i
N_i	Mole fraction of component i in a solution
m	Molality, concentration in moles per 1000 g solvent
c	Molarity, concentration in moles per liter of solution

Symbols Relating to Ions of Strong Electrolytes

ν_+, ν_-	Number of ions of positive sign, or negative sign, respectively, produced by one molecule of the given strong electrolyte
ν	Number of ions produced by one molecule of the given strong electrolyte, equal to $\nu_+ + \nu_-$
z_+, z_-	Valence of or charge on the positive ion, or negative ion, respectively
μ	Ionic strength

Subscripts Attached to Symbols for Thermodynamic Properties

0, 298.16, 1000	Numerals to represent the absolute temperature

TABLE 14. NOTATION; SYMBOLS AND ABBREVIATIONS (*Continued*)

1, 2, 3	Numerals, simple integers, beginning with 1, to represent the several components of a solution

Superscripts Attached to Symbols for Thermodynamic Properties

*	Asterisk, to represent the pure state of the given substance or component
^{0}	Zero, to represent the given component at infinite dilution in a solution
$^\circ$	Degree mark, or small circle, to represent the thermodynamic standard reference state, or briefly, standard state
^{e}	Letter *e* in lower case, to represent the equilibrium state

Symbols for Certain Quantities Related to Energy

q	Quantity of energy transferred in the form of heat
w	Quantity of energy transferred in the form of PV work
u	Quantity of energy, other than q or w, transferred
$\mathcal{E}$	Electromotive force

Fundamental Thermodynamic Properties

P	Pressure
V	Volume
T	Temperature (absolute)
E	Energy
S	Entropy

Characterization of Symbols for Thermodynamic Properties

G	Any thermodynamic property of any quantity of a system or substance
G	Any thermodynamic property, per mole
$\bar{\mathrm{G}}_i$	Partial molal property for component i
$\phi\mathrm{G}_i$	Apparent molal property for component i

Defined Thermodynamic Functions

H	Heat content or enthalpy, equal to $E + PV$
F	Free energy, equal to $E + PV - TS$ or $H - TS$
$(H^\circ - H_0^\circ)/T$	Heat content (or enthalpy) function
$(F^\circ - H_0^\circ)/T$	Free energy function
C_P	Heat capacity at constant pressure, equal to $(\partial H/\partial T)_P$
C_V	Heat capacity at constant volume, equal to $(\partial E/\partial T)_V$
μ	Joule-Thomson coefficient, equal to $(\partial T/\partial P)_H$
z	Compressibility factor, for a gas, equal to PV/RT
ΔH, ΔF, ΔS, ΔC_P, etc.	Increment in heat content, free energy, entropy, and heat capacity, etc., respectively, for the given process or reaction, with each substance in a specified thermodynamic state

TABLE 14. NOTATION; SYMBOLS AND ABBREVIATIONS (*Continued*)

$\Delta H°$, $\Delta F°$, $\Delta S°$, $\Delta C_P°$, etc.	Standard increment in heat content, free energy, entropy, and heat capacity, etc., respectively, for the given process or reaction, with each substance in its standard state
f	Fugacity
a_i	Activity of component i, equal to $f_i/f_i°$
γ_i	Activity coefficient of component i, equal to a_i/N_i, or a_i/m_i, or a_i/P_i
Q_a	Proper quotient of activities for the components of any reaction, as, for the reaction $$bB + cC = mM + nN,$$ $$Q_a = \frac{(a_M)^m(a_N)^n}{(a_B)^b(a_C)^c}$$
Q_P, Q_N, Q_c	Proper quotient of pressures, mole fractions, or concentrations in moles per liter, respectively, for the components of any reaction
Q_γ	Proper quotient of activity coefficients for the components of any reaction
K	Equilibrium constant for any reaction or process, equal to $Q_a{}^e$, the proper quotient of activities for the given reaction or process, with each component at equilibrium with respect to the given reaction or process, and also equal to $e^{-\Delta F°/RT}$ for the given reaction or process
$\Delta Hf°$	Standard heat of formation, which is the increment in heat content associated with the reaction of forming the given compound from its elements, with each substance in its standard state at the given temperature
$\Delta Ff°$	Standard free energy of formation, which is the increment in free energy associated with the reaction of forming the given compound from its elements, with each substance in its standard state at the given temperature
$\log_{10} Kf$	Logarithm (to the base 10) of the equilibrium constant of formation, for the reaction of forming one mole of the given compound from its elements, with each substance in its standard state at the given temperature. The equilibrium constant of formation is related to the standard free energy of formation, per mole, by the relation: $$\log_{10} Kf = -\frac{\Delta Ff°}{2.302585RT}\cdot$$

TABLE 14. NOTATION; SYMBOLS AND ABBREVIATIONS (*Continued*)

ΔHm, ΔSm	Increment in heat content and entropy, respectively, for the process of fusion, as B (c) = B (liq), with the crystal and liquid each in a specified thermodynamic state, as at saturation pressure. With superscripts indicating standard states, as ΔHm° and ΔSm°, the process refers to one in which the crystal and liquid are in their respective standard states, and the increments represent the standard heat of fusion and the standard entropy of fusion, respectively. For the process of fusion, the values of the standard heat and entropy of fusion usually do not differ significantly from the heat and entropy of fusion, respectively, at saturation pressure.
ΔHv, ΔSv	Increment in heat content and entropy, respectively, for the process of vaporization, as B (liq) = B (g), with the liquid and the gas in a specified thermodynamic state, as at saturation pressure. With superscripts indicating standard states, as ΔHv° and ΔSv°, the process refers to one in which the liquid and gas are in their respective standard states, and the increments represent the standard heat of vaporization and the standard entropy of vaporization, respectively. For the process of vaporization, the value of the standard heat of vaporization usually differs by only a small amount from the value of the heat of vaporization at saturation pressures of 1 atmosphere or less, whereas the value of the standard entropy of vaporization may differ considerably from the value of the entropy of vaporization at saturation pressure
ΔHc°	Increment in heat content for the reaction of combustion of the given substance (compound containing C, H, O, N) in gaseous oxygen to form gaseous carbon dioxide, gaseous or liquid water, and gaseous nitrogen, as indicated, with all the reactants and products in their appropriate standard states at the given temperature

TABLE 15. PUBLICATIONS OF THE AUTHOR AND COLLABORATORS

1. "Heat capacities in aqueous salt solutions," by M. Randall and F. D. Rossini, *J. Am. Chem. Soc.* **51**, 323 (1929).
2. "The heat of formation of sulfur dioxide," by J. R. Eckman and F. D. Rossini, *J. Research Natl. Bur. Standards* **3**, 597 (1929). RP 111.
3. "Heat capacities in some aqueous solutions," by F. D. Rossini, *J. Research Natl. Bur. Standards* **4**, 313 (1930). RP 151.

4. "The heat of formation of water," by F. D. Rossini, *Proc. Natl. Acad. Sci. U.S.* **16**, 694 (1930).

5. "The heat of formation of water," by F. D. Rossini, *J. Research Natl. Bur. Standards* **6**, 1 (1931). RP 259.

6. "The heats of combustion of methane and carbon monoxide," by F. D. Rossini, *J. Research Natl. Bur. Standards* **6**, 37 (1931). RP 260.

7. "Heat content values for aqueous solutions of the chlorides, nitrates, and hydroxides of hydrogen, lithium, sodium, and potassium at 18°C," by F. D. Rossini, *J. Research Natl. Bur. Standards* **6**, 791 (1931). RP 305.

8. "The heat of ionization of water," by F. D. Rossini, *J. Research Natl. Bur. Standards* **6**, 847 (1931). RP 309.

9. "The heat of combustion of methyl alcohol," by F. D. Rossini, *Proc. Natl. Acad. Sci. U.S.* **17**, 343 (1931).

10. "Review of thermodynamics and thermochemistry for 1930," by F. D. Rossini, Chapter IV in *Annual Survey of American Chemistry*, Volume 5, Chemical Catalog Company, New York, 1931.

11. "Apparent and partial molal heat capacities in aqueous solutions of 19 uni-univalent strong electrolytes," by F. D. Rossini, *J. Research Natl. Bur. Standards* **7**, 47 (1931). RP 331.

12. "The heat of formation of water and the heats of combustion of methane and carbon monoxide. A correction," by F. D. Rossini, *J. Research Natl. Bur. Standards* **7**, 329 (1931). RP 343.

13. "The heats of combustion of methyl and ethyl alcohols," by F. D. Rossini, *J. Research Natl. Bur. Standards* **8**, 119 (1932). RP 405.

14. "Review of thermodynamics and thermochemistry for 1931," by F. D. Rossini, Chapter IV in *Annual Survey of American Chemistry*, Volume 6, Chemical Catalog Company, New York, 1932.

15. "The heat of formation of hydrogen chloride and some related thermodynamic data," by F. D. Rossini, *J. Research Natl. Bur. Standards* **9**, 679 (1932). RP 499.

16. "The calorimetric determination of the intrinsic energy of gases as a function of the pressure. Data on oxygen and its mixtures with carbon dioxide to 40 atmospheres at 28°C," by F. D. Rossini and M. Frandsen, *J. Research Natl. Bur. Standards* **9**, 733 (1932). RP 503.

17. "Review of thermodynamics and thermochemistry for 1932," by F. D. Rossini, Chapter IV in *Annual Survey of American Chemistry*, Volume 7, Chemical Catalog Company, New York, 1933.

18. "A simple calorimeter for heats of fusion. Data on the fusion of pseudocumene, mesitylene (α and β), hemimellitene, *o*- and *m*-xylene, and on two transitions of hemimellitene," by F. D. Rossini, *J. Research Natl. Bur. Standards* **11**, 553 (1933). RP 607.

19. "The energies of the atomic linkages in methane, ethane, methanol, and ethanol," by F. D. Rossini, *J. Chem. Phys.* **2**, 145 (1934).

20. "The energies of the atomic linkages in the normal paraffin hydrocarbons," by F. D. Rossini, *Proc. Natl. Acad. Sci. U.S.* **20**, 323 (1934).

21. "Calorimetric determination of the heats of combustion of ethane, propane, normal butane, and normal pentane," by F. D. Rossini, *J. Research Natl. Bur. Standards* **12**, 735 (1934). RP 686.

22. "Heats of combustion and of formation of the normal paraffin hydrocarbons in the gaseous state, and the energies of their atomic linkages," by F. D. Rossini, *J. Research Natl. Bur. Standards* **13**, 21 (1934). RP 692.

23. "Heats of combustion and of formation of the normal aliphatic alcohols in the gaseous and liquid states, and the energies of their atomic linkages," by F. D. Rossini, *J. Research Natl. Bur. Standards* **13**, 189 (1934). RP 701.

24. "The chemical constitution of the gasoline fraction of petroleum," by F. D. Rossini, American Petroleum Institute Research Project 6; *Proc. Am. Petroleum Inst.* **16M** (III), 47 (1935); *Oil Gas J.* **33**, 61 (1935); *Refiner Natural Gasoline Mfr.* **14**, 255 (1935).

25. "Fundamental research on the chemical constitution of lubricating oil," by F. D. Rossini, American Petroleum Institute Research Project 6; *Proc. Am. Petroleum Inst.* **16M** (III), 63 (1935); *Oil Gas J.* **34**, 41 (1935); *Refiner Natural Gasoline Mfr.* **14**, 266 (1935).

26. "The difference in the heats of formation of the two isomers of butane. An estimate of the heat of formation of tetramethylmethane (neopentane)," by F. D. Rossini, *J. Chem. Phys.* **3**, 438 (1935).

27. "The development of thermochemistry," by F. D. Rossini, *J. Wash. Acad. Sci.* **25**, 399 (1935).

28. "Heat of combustion of isobutane," by F. D. Rossini, *J. Research Natl. Bur. Standards* **15**, 357 (1935). RP 833.

29. "Modern thermochemistry," by F. D. Rossini, *Chem. Revs.* **18**, 233 (1936).

30. "Heat of hydrogenation of ethylene," by F. D. Rossini, *J. Research Natl. Bur. Standards* **17**, 629 (1936). RP 933.

31. "The chemical constituents of lubricating oil," by F. D. Rossini, *Proc. Am. Petroleum Inst.* **17**, III (1936); *Oil Gas J.* **35**, 146 (1936); *Refiner Natural Gasoline Mfr.* **15**, 499 (1936).

32. *Thermochemistry of the Chemical Substances*, by F. R. Bichowsky and F. D. Rossini, Reinhold Publishing Corporation, New York, 1936.

33. "Calorimetric determination of the heats of combustion of ethylene and propylene," by F. D. Rossini and J. W. Knowlton, *J. Research Natl. Bur. Standards* **19**, 249 (1937). RP 1024.

34. "Heats of combustion and of formation of the normal olefins (alkene-1) hydrocarbons in the gaseous state," by F. D. Rossini and J. W. Knowlton, *J. Research Natl. Bur. Standards* **19**, 339 (1937). RP 1028.

35. "A decade of research on the chemical constitution of petroleum," by F. D. Rossini, *Proc. Am. Petroleum Inst.* **18**, III, 36 (1937); *Oil Gas J.* **36**, 193 (1937); *Refiner Natural Gasoline Mfr.* **16**, 545 (1937).

36. "Method and apparatus for the rapid conversion of deuterium oxide into deuterium," by J. W. Knowlton and F. D. Rossini, *J. Research Natl. Bur. Standards* **19**, 605 (1937). RP 1050.

37. "Heats of formation of the simple organic molecules," by F. D. Rossini, *Ind. Eng. Chem.* **29**, 1424 (1937).

38. "The energy of isomerization of normal pentane into tetramethylmethane," by F. D. Rossini and J. W. Knowlton, *J. Chem. Phys.* **6**, 168 (1938).

39. "The free energy of the producer-gas reaction, and the 'zero-point' entropy of graphite," by F. D. Rossini, *J. Chem. Phys.* **6**, 569 (1938).

40. "Heat and free energy of formation of carbon dioxide and of the transition between graphite and diamond," by F. D. Rossini and R. S. Jessup, *J. Research Natl. Bur. Standards* **21**, 491 (1938). RP 1141.

41. "Hydrocarbons in the lubricant fraction of petroleum," by F. D. Rossini, *Proc. Am. Petroleum Inst.* **19**, III, 99 (1938); *Oil Gas J.* **37**, 141 (1938); *Refiner Natural Gasoline Mfr.* **17**, 557 (1938).

42. "Heat and free energy of formation of water and of carbon monoxide," by F. D. Rossini, *J. Research Natl. Bur. Standards* **22**, 407 (1939). RP 1192.

43. "Heats of combustion of tetramethylmethane and 2-methylbutane," by J. W. Knowlton and F. D. Rossini, *J. Research Natl. Bur. Standards* **22**, 415 (1939). RP 1193.

44. "The assignment of uncertainties to the data of chemistry and physics, with specific recommendations for thermochemistry," by. F. D. Rossini and W. E. Deming, *J. Wash. Acad. Sci.* **29**, 416 (1939).

45. "Reflux regulator and head for laboratory rectifying column," by F. D. Rossini and A. R. Glasgow, Jr., *J. Research Natl. Bur. Standards* **23**, 509 (1939). RP 1249.

46. "Heats of formation of gaseous hydrocarbons," by F. D. Rossini, *Chem. Revs.* **27**, 1 (1940).

47. "Heat and free energy of formation of deuterium oxide," by F. D. Rossini, J. W. Knowlton, and H. L. Johnston, *J. Research Natl. Bur. Standards* **24**, 369 (1940). RP 1287.

48. "Energies of isomerization of the five hexanes," by F. D. Rossini and E. J. Prosen, *J. Am. Chem. Soc.* **62**, 2250 (1940).

49. "Use of azeotropic distillation in separating hydrocarbons from petroleum," by F. D. Rossini, B. J. Mair, and A. R. Glasgow, Jr., *Proc. Am. Petroleum Inst.* **21** (III), 43 (1940); *Refiner Natural Gasoline Mfr.* **19**, 116 (1940); *Oil Gas J.* **39**, 158 (1940).

50. "Determination of freezing points and amounts of impurity in hydrocarbons from freezing and melting curves," by B. J. Mair, A. R. Glasgow, Jr., and F. D. Rossini, *J. Research Natl. Bur. Standards* **26**, 591 (1941). RP 1397.

51. "Separation of hydrocarbons by azeotropic distillation," by B. J. Mair, A. R. Glasgow, Jr., and F. D. Rossini, *J. Research Natl. Bur. Standards* **27**, 39 (1941). RP 1402.

52. "Heats of isomerization of the five hexanes," by E. J. Prosen and F. D. Rossini, *J. Research Natl. Bur. Standards* **27**, 289 (1941). RP 1420.

53. "Heats of isomerization of the nine heptanes," by E. J. Prosen and F. D. Rossini, *J. Research Natl. Bur. Standards* **27**, 519 (1941). RP 1439.

54. "Free energies and equilibria of isomerization of the butanes, pentanes, hexanes, and heptanes," by F. D. Rossini, E. J. Prosen, and K. S. Pitzer, *J. Research Natl. Bur. Standards* **27**, 529 (1941). RP 1440.

55. "Progress report on the hydrocarbons in the kerosine fraction of petroleum," by F. D. Rossini and B. J. Mair, American Petroleum Institute Research Project 6; *Proc. Am. Petroleum Inst.* **22** (III), **7** (1941); *Oil Gas J.* **40**, 129 (1941); *Refiner Natural Gasoline Mfr.* **20**, 494 (1941).

56. "Thermodynamics, thermochemistry and chemical equilibrium," by F. D. Rossini, Section 5 in *Chemical Engineers Handbook*, 2nd Edition, 1941.

57. "Chemical thermodynamics of hydrocarbons," by F. D. Rossini,

chapter in *Chemical Background for Engine Research*, published for the Graduate School of Western Reserve University by Interscience Publishers, New York, 1942.

58. "Hydrocarbons in petroleum," by F. D. Rossini, *Record Chem. Progress* **3**, 53 (1942).

59. "Method for analyzing the gasoline fraction of petroleum, with preliminary results on East Texas and Oklahoma crudes," by F. D. Rossini, B. J. Mair, A. F. Forziati, A. R. Glasgow, Jr., and C. B. Willingham, *Proc. Am. Petroleum Inst.* **23**, III, 7 (1942); *Oil Gas J.* **41**, 106 (1942); *Petroleum Refiner* **21**, 73 (1942).

60. "Hydrocarbons in petroleum—some results of the API Research Project 6," by F. D. Rossini, *Petroleum Eng.* **14**, 223 (1943).

61. "Hydrocarbons in the gasoline fraction of seven representative crudes, including all the distillate to 102°C and the aromatics to 160°C," by A. F. Forziati, C. B. Willingham, B. J. Mair, and F. D. Rossini, *Proc. Am. Petroleum Inst.* **24** (III), 34 (1943); *J. Research Natl. Bur. Standards* **32**, 11 (1944). RP 1571.

62. "The calory and the joule in thermodynamics and thermochemistry," by E. F. Mueller and F. D. Rossini, *Am. J. Phys.* **12**, 1 (1944).

63. "Note on the macroanalysis of carbon and hydrogen by combustion," by D. D. Wagman and F. D. Rossini, *J. Research Natl. Bur. Standards* **32**, 95 (1944). RP 1577.

64. "Method for determining individual hydrocarbons in mixtures of hydrocarbons by measurement of freezing points," by A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards* **32**, 185 (1944). RP 1584.

65. "Theoretical analysis of certain time-temperature freezing and melting curves as applied to hydrocarbons," by W. J. Taylor and F. D. Rossini, *J. Research Natl. Bur. Standards* **32**, 197 (1944). RP 1585.

66. "Heats of combustion of eight normal paraffin hydrocarbons in the liquid state," by E. J. Prosen and F. D. Rossini, *J. Research Natl. Bur. Standards* **33**, 255 (1944). RP 1607.

67. "Improved reflux regulator and head for laboratory distilling columns," by C. B. Willingham and F. D. Rossini, *J. Research Natl. Bur. Standards* **33**, 383 (1944). RP 1615.

68. "Some experimental data on the heats of combustion of benzoic acid and carbon (graphite)," by E. J. Prosen and F. D. Rossini, *J. Research Natl. Bur. Standards* **33**, 439 (1944). RP 1619.

69. "Heat of formation of carbon dioxide and of the transition of graphite into diamond," by E. J. Prosen, R. S. Jessup, and F. D. Rossini, *J. Research Natl. Bur. Standards* **33**, 447 (1944). RP 1620.

70. "Heats of formation and combustion of 1,3-butadiene and styrene," by E. J. Prosen and F. D. Rossini, *J. Research Natl. Bur. Standards* **34**, 59 (1945). RP 1628.

71. "Heats of combustion of benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, *n*-propylbenzene, and styrene," by E. J. Prosen, R. Gilmont, and F. D. Rossini, *J. Research Natl. Bur. Standards* **34**, 65 (1945). RP 1629.

72. "Heats, free energies, and equilibrium constants of some reactions

involving O_2, H_2, H_2O, C, CO, CO_2, and CH_4," by D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer, and F. D. Rossini, *J. Research Natl. Bur. Standards* **34**, 143 (1945). RP 1634.

73. "Heats of isomerization of the 18 octanes," by E. J. Prosen and F. D. Rossini, *J. Research Natl. Bur. Standards* **34**, 163 (1945). RP 1635.

74. "Free energies and equilibria of isomerization of the 18 octanes," by E. J. Prosen, K. S. Pitzer, and F. D. Rossini, *J. Research Natl. Bur. Standards* **34**, 255 (1945). RP 1641.

75. "Heats of combustion and formation of the paraffin hydrocarbons at 25°C," by E. J. Prosen and F. D. Rossini, *J. Research Natl. Bur. Standards* **34**, 263 (1945). RP 1642.

76. "Heats and free energies of formation of the paraffin hydrocarbons in the gaseous state, to 1500°K," by E. J. Prosen, K. S. Pitzer, and F. D. Rossini, *J. Research Natl. Bur. Standards* **34**, 403 (1945). RP 1650.

77. "Method for calculating the properties of hydrocarbons and its application to the refractive indices, densities, and boiling points of the paraffin and monoolefin hydrocarbons," by W. J. Taylor, J. M. Pignocco, and F. D. Rossini, *J. Research Natl. Bur. Standards* **34**, 413 (1945). RP 1651.

78. "Heats of combustion and isomerization of the eight C_9H_{12} alkylbenzenes," by W. H. Johnson, E. J. Prosen, and F. D. Rossini, *J. Research Natl. Bur. Standards* **35**, 141 (1945). RP 1665.

79. "Vapor pressures and boiling points of some paraffin alkylcyclopentane, alkylcyclohexane, and alkylbenzene hydrocarbons," by C. B. Willingham, W. J. Taylor, J. M. Pignocco, and F. D. Rossini, *J. Research Natl. Bur. Standards* **35**, 219 (1945). RP 1670.

80. "Determination of the purity of hydrocarbons by measurement of freezing point," by A. R. Glasgow, Jr., A. J. Streiff, and F. D. Rossini, *J. Research Natl. Bur. Standards* **35**, 355 (1945). RP 1676.

81. "Heats, equilibrium constants, and free energies of formation of the acetylene hydrocarbons through the pentynes, to 1500°K," by D. D. Wagman, J. E. Kilpatrick, K. S. Pitzer, and F. D. Rossini, *J. Research Natl. Bur. Standards* **35**, 467 (1945). RP 1682.

82. "Assembly and calibration of a density balance for liquid hydrocarbons," by A. F. Forziati, B. J. Mair, and F. D. Rossini, *J. Research Natl. Bur. Standards* **35**, 513 (1945). RP 1685.

83. "Purification and properties of 29 paraffin, 4 alkylcyclopentane, 10 alkylcyclohexane, and 8 alklybenzene hydrocarbons," by A. F. Forziati, A. R. Glasgow, Jr., C. B. Willingham, and F. D. Rossini, *J. Research Natl. Bur. Standards* **36**, 129 (1946). RP 1695.

84. "Heats of formation, hydrogenation, and combustion of the monoolefin hydrocarbons through the hexenes, and of the higher 1-alkenes, in the gaseous state, at 25°C," by E. J. Prosen and F. D. Rossini, *J. Research Natl. Bur. Standards* **36**, 269 (1946). RP 1702.

85. "Heats of combustion and formation at 25°C of the alkylbenzenes through $C_{10}H_{14}$ and of the higher normal monoalkylbenzenes," by E. J. Prosen, W. H. Johnson, and F. D. Rossini, *J. Research Natl. Bur. Standards* **36**, 455 (1946). RP 1714.

86. "Heats of combustion of four cyclopentane and five cyclohexane hydro-

carbons," by W. H. Johnson, E. J. Prosen, and F. D. Rossini, *J. Research Natl. Bur. Standards* **36**, 463 (1946). RP 1715.

87. "Heats, equilibrium constants, and free energies of formation of the monoolefin hydrocarbons," by J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer, and F. D. Rossini, *J. Research Natl. Bur. Standards* **36**, 559 (1946). RP 1722.

88. "Assembly, testing, and operation of laboratory distilling columns of high efficiency," by C. B. Willingham and F. D. Rossini, *J. Research Natl. Bur. Standards* **37**, 15 (1946). RP 1724.

89. "Heats of formation and combustion of the normal alkylcyclopentanes and cyclohexanes, and the increments per CH_2 group for several homologous series of hydrocarbons," by E. J. Prosen, W. H. Johnson, and F. D. Rossini, *J. Research Natl. Bur. Standards* **37**, 51 (1946). RP 1728.

90. "Heats, equilibrium constants, and free energies of formation of the alkylbenzenes," by W. J. Taylor, D. D. Wagman, M. G. Williams, K. S Pitzer, and F. D. Rossini, *J. Research Natl. Bur. Standards* **37**, 95 (1946). RP 1732.

91. "Purification, purity, and freezing points of 31 hydrocarbons of the API-NBS series," by A. R. Glasgow, Jr., E. T. Murphy, C. B. Willingham, and F. D. Rossini, *J. Research Natl. Bur. Standards* **37**, 141 (1946). RP 1734.

92. "Purification and sealing 'in vacuum' of National Bureau of Standards standard samples of hydrocarbons," by B. J. Mair, D. J. Termini, C. B. Willingham, and F. D. Rossini, *J. Research Natl. Bur. Standards* **37**, 229 (1946). RP 1744.

93. "Laboratory distilling columns of high efficiency used in the work of the API Research Project 6," by C. B. Willingham and F. D. Rossini, *Proc. Am. Petroleum Inst.* **26** (III), 1 (1946).

94. "Purification, purity, and freezing points of 7 heptanes, 16 octanes, 6 pentenes, cyclopentene, and 7 C_9H_{12} alkylbenzenes of the API-Standard and API-NBS series," by A. J. Streiff, E. T. Murphy, V. A. Sedlak, C. B. Willingham, and F. D. Rossini, *J. Research Natl. Bur. Standards* **37**, 331 (1946). RP 1752.

95. "Proposed method of test for aromatic hydrocarbons in mixtures with naphthenes and paraffins by silica gel adsorption," by B. J. Mair and F. D. Rossini, *ASTM Standards on Petroleum Products, Committee D-2, Year Book*, 1946, p. 20; *ASTM Standards on Petroleum Products, Committee D-2, Year Book*, 1947, p. 486.

96. "Hydrocarbons in petroleum," by F. D. Rossini, *Chem. Eng. News* **25**, 230 (1947).

97. "Purification, purity, and freezing points of 8 nonanes, 11 alkylcyclopentanes, 6 alkylcyclohexanes, and 4 butylbenzenes of the API-Standard and API-NBS series," by A. J. Streiff, E. T. Murphy, J. C. Cahill, H. F. Flanagan, V. A. Sedlak, C. B. Willingham, and F. D. Rossini, *J. Research Natl. Bur. Standards* **38**, 53 (1947). RP 1760.

98. "Heats of combustion and isomerization of six nonanes," by W. H. Johnson, E. J. Prosen, and F. D. Rossini, *J. Research Natl. Bur. Standards* **38**, 419 (1947). RP 1783.

99. "Analysis of alkylates and hydrocodimers," by A. R. Glasgow, Jr., A. J. Streiff, C. B. Willingham, and F. D. Rossini, *Proc. Am. Petroleum Inst.*

26 (III), 127 (1946); *J. Research Natl. Bur. Standards* **38**, 537 (1947). RP 1795.

100. "Hydrocarbons in the 102° to 108°C fraction of petroleum," by A. R. Glasgow, Jr., C. B. Willingham, and F. D. Rossini, *J. Research Natl. Bur. Standards* **39**, 621 (1947). RP 1800.

101. "Relabeling of the *cis* and *trans* isomer of 1,3-dimethylcyclohexane," by F. D. Rossini and K. S. Pitzer, *Science* **105**, 647 (1947).

102. "Rotary concentric-tube distilling column," by C. B. Willingham, V. A. Sedlak, J. W. Westhaver, and F. D. Rossini, *Ind. Eng. Chem.* **39**, 706 (1947).

103. "Heats of combustion and isomerization of the 8 C_8H_{16} alkylcyclohexanes," by W. H. Johnson, E. J. Prosen, and F. D. Rossini, *J. Research Natl. Bur. Standards* **39**, 49 (1947). RP 1812.

104. "Heats of formation and isomerization of the 8 C_8H_{16} alkylcyclohexanes in the liquid and gaseous state," by E. J. Prosen, W. H. Johnson, and F. D. Rossini, *J. Research Natl. Bur. Standards* **39**, 173 (1947). RP 1821.

105. "Heat of combustion and formation of 1,3,5,7-cyclooctatetraene and its heat of isomerization to styrene," by E. J. Prosen, W. H. Johnson, and F. D. Rossini, *J. Am. Chem. Soc.* **69**, 2068 (1947).

106. "Assembly and testing of a 52-foot laboratory adsorption column. Separation of hydrocarbons by adsorption," by B. J. Mair, A. L. Gaboriault, and F. D. Rossini, *Ind. Eng. Chem.* **39**, 1072 (1947).

107. "Alkylbenzenes in the C_8 fraction from five different catalytic petroleum refining processes," by A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards* **39**, 303 (1947). RP 1830.

108. "Purification, purity, and freezing points of *n*-decane, 4 alkylcyclopentanes, 9 alkylcyclohexanes, 2 monoolefins, 1,2-butadiene, and 2-butyne of the API-Standard and API-NBS series," by A. J. Streiff, E. T. Murphy, J. C. Zimmerman, L. F. Soule, V. A. Sedlak, C. B. Willingham, and F. D. Rossini, *J. Research Natl. Bur. Standards* **39**, 321 (1947). RP 1833.

109. "Tentative method of test for determination of purity by measurement of freezing points," by A. R. Glasgow, Jr., A. J. Streiff, and F. D. Rossini, *ASTM Standards on Petroleum Products, Committee D-2, Year Book*, 1947, p. 510.

110. "Alkylbenzenes in the C_9 fraction of seven representative crude petroleums," by A. F. Forziati and F. D. Rossini, *J. Research Natl. Bur. Standards* **39**, 425 (1947). RP 1839.

111. "Heats, equilibrium constants, and free energies of formation of the alkylcyclopentanes and alkylcyclohexanes," by J. E. Kilpatrick, H. G. Werner, C. W. Beckett, K. S. Pitzer, and F. D. Rossini, *J. Research Natl. Bur. Standards* **39**, 523 (1947). RP 1845.

112. "Selected values of properties of hydrocarbons," by F. D. Rossini, K. S. Pitzer, W. J. Taylor, J. P. Ebert, J. E. Kilpatrick, C. W. Beckett, M. G. Williams, and H. G. Werner, *Natl. Bur. Standards Circ.* 461 (1947).

113. "Pure compounds from petroleum; purification and purity of hydrocarbons," by F. D. Rossini, *Anal. Chem.* **20**, 110 (1948).

114. "Determination of purity by measurement of freezing points of compounds involved in the production of synthetic rubber," by A. R. Glasgow, Jr.,

N. Krouskop, J. Beadle, G. D. Axilrod, and F. D. Rossini, *Anal. Chem.* **20**, 410 (1948).

115. "Heats of formation and chemical thermodynamic properties," by F. D. Rossini, *Trans. Am. Soc. Mech. Engrs.* **70**, 625 (1948).

116. "Naming of *cis* and *trans* isomers of hydrocarbons containing olefin double bonds," by M. B. Epstein and F. D. Rossini, *Chem. Eng. News* **26**, 2959 (1948).

117. "Purification, purity, and freezing points of 30 hydrocarbons of the API-Standard and API-NBS series," by A. J. Streiff, J. C. Zimmerman, L. F. Soule, M. T. Butt, V. A. Sedlak, C. B. Willingham, and F. D. Rossini, *J. Research Natl. Bur. Standards* **41**, 323 (1948). RP 1929.

118. "Separation of the 177° to 200°C fraction of petroleum and the isolation of normal undecane," by M. B. Epstein, B. J. Mair, C. B. Willingham, and F. D. Rossini, *J. Research Natl. Bur. Standards* **42**, 139 (1949). RP 1957.

119. "Heats, equilibrium constants, and free energies of formation of the C_3 to C_5 diolefins, styrene, and the methylstyrenes," by J. E. Kilpatrick, C. W. Beckett, E. J. Prosen, K. S. Pitzer, and F. D. Rossini, *J. Research Natl. Bur. Standards* **42**, 225 (1949). RP 1964.

120. "Heats of combustion and isomerization of the six C_7H_{14} alkylcyclopentanes," by W. H. Johnson, E. J. Prosen, and F. D. Rossini, *J. Research Natl. Bur. Standards* **42**, 251 (1949). RP 1966.

121. "Heat of isomerization of the two butadienes," by E. J. Prosen, F. W. Maron, and F. D. Rossini, *J. Research Natl. Bur. Standards* **42**, 269 (1949). RP 1968.

122. "Heats, equilibrium constants, and free energies of formation of cyclopentene and cyclohexene," by M. B. Epstein, K. S. Pitzer, and F. D. Rossini, *J. Research Natl. Bur. Standards* **42**, 379 (1949). RP 1976.

123. "Fractionation, analysis, and purification of hydrocarbons," in *Recent Advances in Analytical Chemistry*, by F. D. Rossini, Interscience Publishers, Inc., New York, 1949.

124. "Analysis of 'recycle' styrene," by A. R. Glasgow, Jr., N. C. Krouskop, V. A. Sedlak, C. B. Willingham, and F. D. Rossini, *Anal. Chem.* **21**, 688 (1949).

125. "Excursion in chemical thermodynamics," by F. D. Rossini, *J. Wash. Acad. Sci.* **39**, 249 (1949).

126. "Summary of the hydrocarbons isolated from one representative petroleum," by F. D. Rossini, B. J. Mair, and A. R. Glasgow, Jr., *Record Chem. Progress* **10**, 121 (1949).

127. "Heat of combustion and formation of cyclopropane," by J. W. Knowlton and F. D. Rossini, *J. Research Natl. Bur. Standards* **43**, 113 (1949). RP 2012.

128. "Purification of five hydrocarbons by adsorption," by A. J. Streiff, B. J. Mair, and F. D. Rossini, *Ind. Eng. Chem.* **41**, 2037 (1949).

129. "Heats, equilibrium constants, and free energies of formation of the five dimethylcyclopentanes," by M. B. Epstein, G. M. Barrow, K. S. Pitzer, and F. D. Rossini, *J. Research Natl. Bur. Standards* **43**, 245 (1949). RP 2026.

130. "Separation of the gas-oil and wax fractions of petroleum by adsorption," by B. J. Mair, A. J. Sweetman, and F. D. Rossini, *Ind. Eng. Chem.* **41**, 2224 (1949).

131. "Components of a gasoline produced by catalytic cracking," by A. R. Glasgow, Jr., C. B. Willingham, and F. D. Rossini, *Ind. Eng. Chem.* **41**, 2292 (1949).

132. "Physical properties of 60 API-NBS hydrocarbons," by A. F. Forziati and F. D. Rossini, *J. Research Natl. Bur. Standards* **43**, 473 (1949). RP 2038.

133. "Vapor pressures and boiling points of 60 API-NBS hydrocarbons," by A. F. Forziati, W. R. Norris, and F. D. Rossini, *J. Research Natl. Bur. Standards* **43**, 555 (1949). RP 2049.

134. "Chemical thermodynamic equilibria among hydrocarbons," by F. D. Rossini, Chapter 9 in *Physical Chemistry of Hydrocarbons*, Volume I, Academic Press, New York, 1950.

135. "Heat of combustion and formation of 1,3,5,7-cyclooctatetraene and its heat of isomerization to styrene," by E. J. Prosen, W. H. Johnson, and F. D. Rossini, *J. Am. Chem. Soc.* **72**, 626 (1950).

136. "Hydrocarbons in the 108° to 116°C fraction of petroleum," by A. R. Glasgow, Jr., C. B. Willingham, and F. D. Rossini, *J. Research Natl. Bur. Standards* **44**, 145 (1950).

137. "Separation of 2,3-dimethylpentane, 1,*cis*-3-dimethylcyclopentane, and 3-ethylpentane from petroleum," by A. R. Glasgow, Jr., C. B. Willingham, and F. D. Rossini, *J. Research Natl. Bur. Standards* **44**, 411 (1950). RP 2088.

138. "Note on the naming of geometric isomers of polyalkyl monocycloalkanes," by M. B. Epstein and F. D. Rossini, *Chem. Eng. News* **28**, 1910 (1950).

139. "Apparatus for determining freezing points at saturation pressure ('in vacuum') from time-temperature freezing and melting curves," by A. R. Glasgow, Jr., N. C. Krouskop, and F. D. Rossini, *J. Research Natl. Bur. Standards* **45** (1950).

140. "Purification, purity, and freezing points of 29 hydrocarbons of the API-Standard and API-NBS series," by A. J. Streiff, L. F. Soule, C. M. Kennedy, M. E. Janes, V. A. Sedlak, C. B. Willingham, and F. D. Rossini, *J. Research Natl. Bur. Standards* **45** (1950).

141. "Theoretical analysis of the fractionating process of adsorption," by B. J. Mair, J. W. Westhaver, and F. D. Rossini, *Ind. Eng. Chem.* **42**, 1279 (1950).

142. "Chemical thermodynamics; fractionating processes; hydrocarbons in petroleum," by F. D. Rossini, Reilly Lectures, University of Notre Dame, Notre Dame, Ind., 1950.

143. "Thermochemistry and the thermodynamic properties of substances," by F. D. Rossini, D. D. Wagman, W. H. Evans, and E. J. Prosen, in Volume I, *Annual Review of Physical Chemistry*, Annual Reviews, Inc., Stanford, 1950.

144. "Relation between energy and structure of paraffin hydrocarbon molecules," by E. J. Prosen and F. D. Rossini, *J. Research Natl. Bur. Standards* **45** (1950).

145. "Heats of combustion, formation, and isomerization of 10 C_4 hydrocarbons," by E. J. Prosen, F. W. Maron, and F. D. Rossini, *J. Research Natl. Bur. Standards* **45** (1950).

146. "Chemical thermodynamic properties of hydrocarbons," by F. D. Rossini, in Volume V, *Science of Petroleum*, Oxford University Press, New York.

147. "Fractionation, analysis, and isolation of hydrocarbons in petroleum," by B. J. Mair and F. D. Rossini, in Volume V, *Science of Petroleum*, Oxford University Press, New York.

148. "Densities, refractive indices, and vapor pressures and boiling points of 8 monoolefin (1-alkene), 6 pentadiene, and 2 cyclomonoolefin hydrocarbons," by A. F. Forziati, D. L. Camin, and F. D. Rossini, *J. Research Natl. Bur. Standards* **45** (1950).

149. "Heats of combustion and formation of 1-hexadecene, *n*-decylbenzene, *n*-decylcyclohexane, and *n*-decylcyclopentane, and the heats of formation and vaporization of homologous compounds of these series," by F. W. Maron, E. J. Prosen, and F. D. Rossini, *J. Research Natl. Bur. Standards* **45** (1950).

150. *Selected Values of Chemical Thermodynamic Properties*, by F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, *Natl. Bur. Standards Circ.* 500, U. S. Government Printing Office, Washington, 1950.

151. *Chemical Thermodynamics*, by F. D. Rossini, John Wiley & Sons, Inc., New York, 1950.

Author Index

Subject Index